11/7-3-91

CONF-8808320--

PROCEEDINGS OF THE OPPORTUNITIES IN THE SYNFUELS INDUSTRY

AUGUST 29-31, 1988

Energy &
Mineral
Research
Center

PROCEEDINGS PREPARED BY THE
ENERGY & MINERAL RESEARCH CENTER

DISCLAIMER

DISCLAIMER

SPONSORS

University of North Dakota
Energy and Mineral Research Center

U.S. Senator Kent Conrad

Bismarck Development Association
Bismarck, ND USA

IN COOPERATION WITH

Economic Development Administration
U.S. Department of Energy

ADDITIONAL CONTRIBUTORS

NORTH DAKOTA ECONOMIC DEVELOPMENT COMMISSION
NORTH DAKOTA LIGNITE RESEARCH COUNCIL
THE NORTH AMERICAN COAL CORPORATION
BURLINGTON NORTHERN RAILROAD
MDU RESOURCES GROUP, INC.
BASIN ELECTRIC POWER COOPERATIVE
NORTHERN STATES POWER COMPANY

TABLE OF CONTENTS

J. ALLEN WAMPLER

J. Allen Wampler is Assistant Secretary for Fossil Energy, U.S. Department of Energy. Mr. Wampler manages the department's coal, petroleum and natural gas research and development programs and oversees the nation's Strategic Petroleum Reserve and Naval Petroleum and Oil Shale Reserves. Prior to joining the Department of Energy, Mr. Wampler was a college administrator, served on the President's Commission on Coal and was Vice President of Training and Development for the Bituminous Coal Operators' Association.

FOSSIL ENERGY SPEECHES

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY

Synthetic Fuels

Perspectives on the Synfuels Industry

*Keynote Address
of
J. Allen Wampler
Assistant Secretary
for Fossil Energy
U.S. Department of
Energy
to the
"Opportunities in the
Synfuels Industry"
Symposium
in
Bismarck, North
Dakota
August 29, 1988*

On behalf of the Department of Energy, let me add my welcome to that of Senator Conrad's. It is indeed a pleasure to be back in North Dakota and to participate in this conference.

To many people in Washington and elsewhere today, the phrase "opportunities in the synfuels industry" is an oxymoron. They will tell you that synthetic fuels died in the early part of this decade—the victim of first the moderation in world oil prices and then their sudden drop. They will tell you that a synthetic fuels industry is a dream of the past—that we have no better chance of seeing synfuel plants in this country than seeing the return of the dinosaurs. They equate synfuel plants with an energy policy of last resort, with national energy shortages, and with high energy prices.

That's what they will say in Washington and elsewhere. But what I want to tell you today is that the picture they paint of synfuels is simply, and categorically, wrong.

We will be spending nearly $70 million in the coming fiscal year to develop the technology of synthetic fuels. We will have spent roughly the same amount this year. We will spend another $40 to $60 million on ways to use the liquids, gases and solids produced by synthetic fuel technologies. Since 1981, our cumulative funding for synthetic fuels development and use is approaching $1 billion.

To me, that doesn't sound like we've written synfuels off. It doesn't sound like we see synfuels as the energy option of last resort.

No, if anything, synfuels didn't die in the 1980s. If anything, they returned to the laboratory where the processes were refined and improved – where new and more advanced processes were developed and tested – where economics became better, product yields were increased, product qualities were enhanced.

And today, we stand at the threshold of a new decade and, perhaps, at the beginning of a new appreciation of the potential for synthetic fuels. We are seeing a new generation of synfuel processes emerge from the laboratory. These are new techniques that are more efficient, cleaner, targeted better to new markets, and with better prospects to compete economically in the 1990s and beyond.

...today, we stand at the threshold of a new decade and, perhaps, at the beginning of a new appreciation of the potential for synthetic fuels.

I want to set the stage for this conference by talking about some of the advances that have been made in the science and technology of synthetic fuels during the 1980s. But before I do that, let me spend just a minute talking about one project that didn't go back to the laboratory in the 1980s – a project that, as many of you know, spent most of the 1970s trying to get off the drawing board and most of this decade wondering – and worrying about – what was in store for it in the future.

The project is, of course, the Great Plains Coal Gasification Plant.

Three weeks ago, we announced our selection of Basin Electric as the preferred buyer of the Great Plains plant. Last week, Basin's membership voted unanimously to move ahead and acquire the plant. Let me tell you how we see the Great Plains project – and in particular, what we see in store for its future.

The Great Plains project was built in response to a critical energy situation. America faced a time in the 1970s when it saw an energy future it couldn't control. It was a future in which energy and economic choices were being made increasingly by overseas producers – many of them diametrically opposed to our best interests. One by one, our energy options seemed to be diminishing. The breeder reactor fell victim to concerns over the proliferation of nuclear materials that could be used for weapons. The nuclear industry itself felt the blows of public opinion in the aftermath of Three Mile Island. Solar power and geothermal and biomass all seemed promising but just over the horizon. Coal was abundant, but we were beginning to see the formation of a new environmental movement that voiced new concerns about acid rain and other environmental disorders.

The Great Plains plant was conceived in that era. The decisions made in those days were not so much driven by economics – after all, oil prices were going through the roof – but by a national movement to regain control of our energy future.

The Great Plains plant was conceived in [an] era [when] decisions...were not so much driven by economics...but by a national movement to regain control of our energy future.

Today, we have restored a measure of energy security. Yes, oil imports are rising again. But we have a Strategic Petroleum Reserve in Louisiana and Texas that exceeds 550 million barrels of emergency oil safely stored in the ground and is growing at a rate of 50,000 barrels per day.

Yes, the domestic oil industry has been hurt and production is down. But a measure of stability has been restored, and companies are running leaner and more efficiently, and beginning again to concentrate on the business of producing oil as effectively and economically as possible.

Yes, the prospects are there for a slow, sustained rise in energy prices over the next decade. But today, we have in place the knowledge that we can build and operate a plant that can convert our most abundant domestic fossil energy resource – coal – into a clean-burning, premium fuel.

We not only have the knowledge, we have the experience. And because of Great Plains, we have the actual working model.

That's what the plant means to this country. It tells us that a synfuels plant can be built. It tells us how much it is going to cost. It tells us how many people are needed – both to build it and to operate it. It gives us a baseline of production data, efficiencies, performances, reliability, maintenance. Most importantly, it tells us if the drawing board concepts developed in precise detail in years of laboratory research actually work in the field.

In the 1950s, South Africa decided to build a synthetic fuels plant—both as an energy producer and as the core of a commercial chemical industry. They built SASOL 1. It took them five years to design and build it and another five years to work out the technical bugs. In 1974, they responded to the threats of an energy shortage by breaking ground for their second SASOL plant—this one four times larger. They had it up and running in five years. In 1979, they saw an energy threat again—this time more real than before since their major supplier was Iran. They built SASOL III—almost a twin of SASOL II. It took them *less than three years*. They knew how to do it. They knew how to cut both time and expense. They knew where that was possible. They had built such a plant before.

For 40 years, in the post-war world, the South Africans were unique. They could lay claim to being the world's synfuel experts—not just laboratory experts, but construction experts and operational experts....Today, we can make the same claim.

For 40 years, in the post-war world, the South Africans were unique. They could lay claim to being the world's synfuel experts—not just laboratory experts, but construction experts and operational experts. They could make decisions on the basis of actual hardware, not just on blueprints. They knew how to do it. They had done it before.

Today, we can make the same claim. We have done it. We know how to build a major, commercial-scale synthetic fuel plant. We have our own experts. We know what it takes to plan, finance, build and operate a commercial-scale facility. We can replicate it, if necessary. But most importantly, we can build upon its technological foundation. We can improve the process. We can see the opportunities it presents—many of which will be described in this conference. We have a baseline upon which to build.

That is progress in my view. Yes, it was expensive progress. But Great Plains has helped return a measure of energy stability to this country. It gave us an energy option at a time when such options were hard to find. It showed that we had the national will to complete something we had begun. And now, we are writing the next chapter in this project's history. Note I said the *next* chapter, not the last.

Great Plains served a significant national purpose. Now it has the opportunity to serve as the core of new economic growth in North Dakota and the surrounding region. One of the major advantages in returning the plant to the private sector is that it opens up the potential for new market opportunities through the expansion of its by-product slate.

We already know that the plant can produce marketable quantities of argon. We know that krypton and xenon production is possible. We have a $1.5 million series of studies underway that will give us a more complete measure of the plant's by-product potential. Some of the studies are done; the rest will be completed by January. They will give us a better picture of the potential for everything from the sale of CO2 to wood preservatives to highway construction materials – all of which could add to the economic viability of the plant. And we will turn those studies over to Basin for their evaluation as soon as they are completed.

The development of [Great Plains] by-products will likely be 25 percent technology and 75 percent market savvy. The government has very little of the latter. But a private sector owner...can bring that advantage to the project.

We also have by-product work underway through the Air Force, which you will hear about later in this conference. Its principal purpose was to look at jet fuels, but the study is giving us some good information about the production of high value chemicals and motor gasoline blendstock.

The development of these by-products will likely be 25 percent technology and 75 percent market savvy. The government has very little of the latter. But a private sector owner, operating in the business community, looking for new business opportunities, and adapting to changes in the business climate can bring that advantage to the project. We think that Basin will do just that and do it as well as any of the prospective buyers.

New opportunities in synthetic fuels – they exist at Great Plains, and they are emerging in a number of other areas across the country.

Let me describe a few of them. First, coal gasification.

The Great Plains plant was built to produce a substitute for natural gas from coal. But coal gasification is perhaps the most versatile of synthetic fuel technologies.

At just about the time the first gas left the Great Plains plant in 1984, another gasification plant, much smaller in size but using commercial-scale components, began operating in the Mojave Desert in California. The Cool Water plant produces synthetic gas for use in a gas turbine configured in a combined-cycle, electric power generating arrangement.

If I had to make a prediction today, that's where I see the first widespread niche developing for synthetic fuel technology. Why? Because this nation will need new power generating equipment in the 1990s and well into the 21st Century.

Over the next two decades, the U.S. could add as much as 150 gigawatts of new capacity – more than the entire generating capacity of Japan, German or Great Britain. The problem is that nobody is building power plants today – not nuclear plants and very few coal plants.

If we are to meet the demand for electricity in the 1990s, we will need small, modular power options that can be fabricated quickly and installed in multiple increments as demand increases.

If we are to meet the demand for electricity in the 1990s, we will need small, modular power options that can be fabricated quickly and installed in multiple increments as demand increases.

For one thing, our regulatory process – particularly at the state level – is geared to this kind of approach. There is a built-in disincentive for large, multi-thousand megawatt baseload plants. And coal gasification technology lends itself quite well to the modular type of incremental capacity addition. The Cool Water project was the pioneer. Today, a similar project is starting operations in Louisiana. Back near Washington, a local utility has announced plans to use coal gasification for its next major capacity addition. And in our research and Clean Coal Technology demonstration programs, we are achieving major advances in coal-based, combined-cycle technology, and in turn, that is bringing down costs.

But the potential for coal gasification extends beyond just the SNG produced by Great Plains or the electric power generated at Cool Water. You will hear a discussion later today about *mild gasification*. Mild gasification is a new term for an old process. A few years ago, we would have called it coal pyrolysis.

It's a process that produces a range of products, from clean-burning gases to solids to liquids. The concept may be the same, but one reason the name has changed is because the technology is changing. We're becoming more sophisticated in the way we produce and use the products.

Today the concept of mild gasification opens the door to coal not just as a fuel for combustion but as a feedstock for a *coal refinery* – a plant producing different products for different markets, just as an oil refinery does today.

Much of the exploratory work in mild gasification is being done by the University of North Dakota Energy and Mineral Center. They are one of four major project teams that we have in place to develop the technology.

When the decade of the 1980s began, the best we could do was produce liquids from coal at a cost approaching $60 to $70 per barrel. Given the state of knowledge then, that looked good. But the times and technology have changed.

Look into the future of coal gasification and you might see other interesting applications.

Last week, we announced the award of a contract to the Caterpillar company in Illinois. Their project is to take coal gasification technology – the same basic chemistry applied in those 4-story high, 170 ton gasifiers at Great Plains – and reduce it to a size that can fit inside a railroad locomotive and produce gas that can be burned in a diesel engine. It's concept that won't be ready until the late 1990s, but we're starting today.

Or let's look at coal liquefaction.

When the decade of the 1980s began, the best we could do was produce liquids from coal at a cost approaching $60 to $70 per barrel. Given the state of knowledge then, that looked good. But the times and technology have changed. If synthetic fuels are going to compete in the foreseeable future, costs are going to have to come down.

For most of the 1980s, we have been funding a test facility at Wilsonville, Alabama, for the purpose of exploring new, high-risk, more economical liquefaction concepts. The facility was originally built for some of the early modern-day processes that attracted commercial interest in the 1970s.

In the 1980s, it was reconfigured to begin testing a new generation of liquefaction concepts. These were concepts that reflected a substantial jump forward in our understanding of the reactions that take place when coal liquefies. These were concepts that moved away from brute-force chemistry to a more sophisticated sequence of processes, each tailored to the ideal chemical reactions taking place at that point in the liquefaction process.

Today, the data from Wilsonville tells us we have coal liquefaction concepts that cut the earlier costs in half. We see the real potential today to reduce the cost of coal liquids to as low as $30 per barrel. And perhaps even more encouraging, the development of entirely new, multi-stage processes opens the door to further cost reductions, perhaps down to the $25 to $30 per barrel range.

The data from Wilsonville [test unit] tells us we have coal liquefaction concepts that cut the earlier costs in half. We see the real potential today to reduce the cost of coal liquids to as low as $30 per barrel.

Look into the future of coal liquefaction, and you may see the emergence of an entirely new class of technology. You may see, for example, the use of microorganisms to liquefy coal. It's being done on a small scale in today's laboratories.

There are other examples I could give you — and I haven't even mentioned such techniques as underground coal gasification, or new concepts for oil shale retorting both in the West and East, or tar sands or coal slurries...and the list goes on.

My point is — and my message to this conference is — that there are opportunities in the synfuels business. There are opportunities born from the ingenuity of scientists and engineers in places like the University of North Dakota, or Wilsonville, Alabama, or Peoria, Illinois. There are opportunities being supported by farsighted public officials like Senator McClure, Senator Johnston and Senator Conrad. There are opportunities being encouraged and pursued by industry leaders like Dick Lawson of the National Coal Association. And there are opportunities that will be realized by people with the same perserverance and dedication of those who built and operate the Great Plains Plant.

These are the people brought together in this conference -- people that you will hear over the next three days. And that is why I am pleased to be here today.

Thank you.

KEYNOTE SPEAKERS

U.S. SENATOR JAMES A McCLURE

U.S. Senator James A. McClure (R-Idaho) is his state's senior senator, elected to the U.S. Senate in 1972. He is the ranking Republican member of the Senate Energy and Natural Resources Committee, is a member of the Senate Appropriations Committee and is the ranking Republican on its Subcommittee on Interior and related agencies. In addition, he is a member of the Appropriations Subcommittees on defense, agriculture, energy and water development, labor, health and human services.

McClure serves as chairman of the Senate Steering Committee, an informal group of conservative senators who meet to review legislation and discuss ways to further the conservative agenda. He has received 12 consecutive "Watchdog of the Treasury" awards for his efforts to curb federal spending and eliminate waste in government.

NO PAPER SUBMITTED

U.S. SENATOR BENNETT JOHNSTON

U.S. Senator Bennett Johnston (D-Louisiana) is chairman of the Senate Committee on Energy and Natural Resources. He is also chairman of the Appropriations Subcommittee on Energy and Water Development and a member of the Budget Committee and Special Committee on Aging. Senator Johnston is a senior member of the Appropriations Panel and serves on the subcommittees on Defense, Foreign Operations, Interior, HUD, and Independent Agencies.

NO PAPER SUBMITTED

GENERAL (RET.) RICHARD L. LAWSON

General (ret.) Richard L. Lawson was named president of the National Coal Association in 1987 and also serves on NCA's board of directors and executive committee.

Lawson came to NCA after a distinguished military career spanning four decades. He retired from the Air Force as a four-star general in 1986 after serving as deputy commander-in-chief of the U.S. European Command in Stuttgart, Germany. From 1973 to 1975, Lawson served as military assistant to the President of the United States. His education background includes degrees in chemical engineering and public administration.

A NATIONAL POLICY OF ENERGY INDEPENDENCE:
COAL, ALTERNATE FUELS AND AMERICA'S SECURITY

A KEYNOTE ADDRESS
BY
RICHARD L. LAWSON
PRESIDENT
NATIONAL COAL ASSOCIATION

TO
SYNOPS '88
AN INTERNATIONAL SYMPOSIUM

SPONSORED BY
THE UNIVERSITY OF NORTH DAKOTA
ENERGY AND MINERAL RESEARCH CENTER
AND
U.S. SENATOR KENT CONRAD
AND
THE BISMARCK DEVELOPMENT ASSOCIATION
IN COOPERATION WITH
THE U.S. DEPARTMENT OF ENERGY
ECONOMIC DEVELOPMENT ADMINISTRATION

BISMARCK, NORTH DAKOTA
AUGUST 30, 1988

THANK YOU, JOHN DWYER, FOR A FINE INTRODUCTION. THE LIGNITE COUNCIL IS AN IMPORTANT PART OF THE TOTAL EFFORT TO KEEP THE COAL INDUSTRY MOVING FORWARD AGAINST POLITICAL AND ECONOMIC FRICTION.

SENATOR CONRAD, I ALSO WANT TO PUBLICLY COMMEND YOU AND THE OTHER SPONSORS OF SYNOPS '88 FOR THE HIGH QUALITY OF THIS INTENSIVE INTERNATIONAL SYMPOSIUM. IT IS THROUGH GATHERINGS SUCH AS THIS THAT WE BUILD CONSENSUS ABOUT OPPORTUNITIES AND BEGIN TO SET PRIORITIES.

AND I WANT TO EXTEND AN EARLY WORD OF THANKS TO YOU IN THE AUDIENCE, BOTH FOR YOUR ATTENTION TO MY REMARKS AND, MORE IMPORTANT, FOR THE DEDICATION SHOWN BY YOUR ATTENDANCE.

IF YOU'VE REMAINED INTERESTED IN HYDROCARBON FUEL ALTERNATIVES TO IMPORTED OIL AFTER THE FALL OF PRICES AND OF THE SYNTHETIC FUELS CORPORATION, IT IS CLEAR YOUR PRESENCE IS DRIVEN BY CONCERNS OTHER THAN IMMEDIATE PROFIT.

So is my presence, both at this conference and as president of the National Coal Association. This will be a subject of my remarks.

That you come from at least 14 states and five countries says that the need for reliable energy is not unrecognized, despite current market prices and conditions, which do not reflect the true cost of imported oil.

The prospects for commercial success in the rearrangement of the links between hydrocarbon molecules will consume much of your time here.

My remarks will concern links as well:

The link between energy and economic strength for the United States and the Free World she leads;

And the link between energy and peace.

IT ALL BEGINS WITH ENERGY.

THE LINKS ARE IN JEOPARDY TODAY BECAUSE SOUND POLICY AND SOUND STRATEGY HAVE BEEN OVERRULED BY PHILOSOPHIES THAT REFUSE TO RECOGNIZE THE TRUE COST OF IMPORTED OIL.

MY PURPOSE IS TO DRAW YOUR ATTENTION TO THE NON-MARKET DIMENSIONS OF OUR RISING IMPORTED-OIL DEPENDENCE, AND TO THE VERY HIGH COST OF FAILING TO DEVELOP ALTERNATIVES.

SINCE THE GREAT PLAINS COAL GASIFICATION PLANT IS AT BEULAH -- A NAME WITH CONNOTATIONS THAT ARE NOT FULLY APPRECIATED IN AN EFFORT WHOSE SUCCESSES HAVE NOT BEEN FULLY APPRECIATED -- I WILL TOUCH ON BOTH.

BEULAH -- IN THE CLASSIC NOVEL, PILGRIM'S PROGRESS -- WAS THE LAND THAT KNEW NO PROBLEMS: WHERE THERE WAS NOTHING THAT ANNOYED AND ALL SOUNDS WERE AGREEABLE.

Another location in Pilgrim's Progress was the Slough of Despond, a place where we still sometimes find ourselves; in the novel it was the Pilgrim's starting point. Characters he met on his journey included Mr. Ready-to-Halt, Mr. Fearing, Mr. Despondency's daughter and Giant Despair, among others.

A longer version of the title is The Pilgrim's Progress from This World to That Which Is to Come. The pioneers, whose westering movement made America a continental nation, took it as a metaphor for what they were about.

America still is about trying to make the day to come better than the present, and my remarks will touch on this and some current challenges -- not unlike the Pilgrim's -- as well.

WITH ALL OF THIS IN MIND, PERHAPS THE BEST PLACE TO BEGIN IS TO EXPLAIN WHY THERE IS A DIFFERENCE BETWEEN THE TRUE COST OF IMPORTED OIL AND THE MARKET PRICE.

I CAME TO UNDERSTAND THE TRUE COST IN MY FORMER PROFESSION: AS MILITARY ASSISTANT TO TWO PRESIDENTS; AS A GENERAL RESPONSIBLE FOR PLANS OF THE JOINT CHIEFS; AND AS DEPUTY COMMANDER-IN-CHIEF OF U.S. FORCES IN EUROPE.

THE LAST TIMES I HAD TO ORDER AMERICA'S SONS AND DAUGHTERS INTO HARM'S WAY, AN INFLEXIBLE AND GROWING DEPENDENCE ON IMPORTED OIL FIGURED IN THE REQUIREMENT TO DO SO. BUT THAT PORTION OF THE REQUIREMENT ALWAYS WAS OBSCURED BY OTHER EVENTS.

HOWEVER, IN THE PERSIAN GULF, FOR MORE THAN A YEAR, AMERICANS HAVE AN UNOBSCURED FORETASTE OF THE TRUE COST OF IMPORTED OIL.

We are somewhat dependent; Europe is more dependent; and both dependencies are rising. Japan is almost totally dependent.

Today the primary source of energy for the United States and the Free World is oil. In general, dependence is rising rather than falling.

The Mid-East holds almost two-thirds of the world's oil. The nations of the Persian Gulf are the world's dominant producers and reserve holders. What happens to them strongly influences the market.

The Oil Embargo of 1973 arose in the Mid-East. It saw the price of oil rise by five times. The 1979-80 crisis that followed the fall of the Shah saw the price rise to about nine times the pre-Embargo price. Economies shook, inflation raged and serious trade frictions began to appear.

ENERGY IS A STRATEGIC COMMODITY. AS THE DOMINANT SOURCE OF ENERGY, OIL IS A STRATEGIC COMMODITY. WITH A SHORT SUPPLY, A NATION IS CRIPPLED AND SUBJECT TO POLITICAL INTIMIDATION.

INTENSE STRUGGLES CAN BE WAGED ON ECONOMIC GROUNDS WITHOUT A SHOT BEING FIRED. THEY ARE SHORT OF WAR BUT WELL BEYOND THE WORKINGS OF THE FREE MARKET. THE EMBARGO WAS JUST SUCH A STRUGGLE; THAT IT FAILED MAKES IT NO LESS AN ATTEMPT.

THIS IS WHAT MAKES OIL MORE THAN JUST ANOTHER ITEM ON THE FREE MARKET. THE GEOGRAPHIC DISTRIBUTION OF THE WORLD'S OIL RESOURCES DOES NOT FAVOR OR FIT PHILOSOPHIES THAT DO NOT CONSIDER COSTS BEYOND THE MARKET PRICE.

UNDER THESE CONDITIONS, DEPENDENCE IS A WEAKNESS AND A VULNERABILITY. WEAKNESSES WILL BE EXPLOITED BY ANY WHO ARE ABLE -- OR SIMPLY WILLING -- TO TRY.

Because they are the world's dominant producers and reserve holders, the Gulf nations must remain in hands that will not try to manipulate oil as a weapon of policy.

The Strait of Hormuz carries much of the Gulf's oil to the world market it dominates. It must be kept open so the market will work and the oil flow: some to the United States and a lot to Europe, Japan and other nations.

This is a primary reason the United States has maintained a big-time presence in the Persian Gulf for more than a year. The Iran-Iraq war threatened to disrupt to flow.

We've come a long way from the time a World War One chief-of-state could say, "One drop of oil is worth one drop of soldier's blood."

But the father of free market economics, Adam Smith, said the true cost of anything is the toil and trouble of acquiring it.

And today the true cost of imported oil is high indeed -- much higher than the published market price.

For all Americans it includes keeping $8-billion aircraft carriers, $3-billion battleships, $1-billion cruisers and frigates and support ships at sea for a year, or for large portions of a year.

From the beginning of the third oil crisis last July through the present fitful cease-fire, our force in and around the Gulf has numbered as many as 49 ships and as few as the present 27. The cost above normal operating expenses for the 13 months on station may have run as high as half-a-billion dollars say nothing of the damage suffered by ships and aircraft; this may run another half billion.

But the true cost is higher than a simple billion dollars.

It includes keeping 25,000 souls in harm's way for more than year, and it requires courageous American captains to make in seconds decisions with ramifications that may be years in settling.

And foremost, it demands that Presidents twist and bend foreign, military and economic policy to compensate for our dependence and, prospectively, for the actions taken in compensation.

It looks like we've had a success in this third crisis.

However, one can forecast that there will be an oil-driven crisis of one kind or another with regularity until the weakness is mended and flexibility is gained. We've been shown that -- shown it not once, not twice, but three times.

UNLESS AND UNTIL WE ADDRESS THE WEAKNESS, MANY DECISIONS OF FOREIGN POLICY AND MUCH MILITARY PLANNING -- FOR THE TWO OFTEN CANNOT BE SEPARATED -- WILL BE DICTATED BY THE NEED TO KEEP THE OIL FLOWING.

ENERGY DRIVES NATIONAL SECURITY AND UPHOLDS THE ECONOMIC SECURITY OF THE FREE WORLD, OF ALL NATIONS OF THE WORLD.

YET WE CONTINUE TO PURSUE FREE MARKET PHILOSOPHIES THAT SEE BASIC ENERGY AS JUST ANOTHER MARKET ITEM DESPITE PERIODIC NOTICE TO THE CONTRARY.

THE TRUE COST OF OIL DEPENDENCE IS A PRICE TO BE PAID ONLY IF -- AND ONLY AS LONG AS -- THERE IS NO ALTERNATIVE.

NOT UNTIL THERE IS A STRATEGY TO MAKE OIL JUST ANOTHER MARKET ITEM IN FACT AS WELL AS IN ECONOMIC PHILOSOPHY WILL THE TRUE COST OF OIL BE IN BALANCE WITH THE MARKET PRICE -- NO MATTER WHAT THE MARKET PRICE.

I'VE BEEN PRESIDENT OF THE NATIONAL COAL ASSOCIATION FOR JUST OVER A YEAR. I'M STILL LEARNING THE FACTS AND THE DETAILS OF THE COAL BUSINESS.

BUT I KNOW SECURITY AND I UNDERSTAND STRATEGY AND STRENGTH. I SENSE THAT THE VULNERABILITY IS INCREASING. LET'S REVIEW THE TRENDS BEHIND THAT STATEMENT. AND THEN LET'S TALK ABOUT STRATEGY AND STRENGTH.

THE NEW OIL PRODUCTION THAT BROKE PRICES IS PEAKING AND GOING INTO DECLINE. AT HOME WE AREN'T REPLACING THE OIL THAT WE USE. CURRENT PRICES HAVE CAUSED A DECLINE IN EXPLORATION, DISCOVERY AND DEVELOPMENT. OLD OIL THAT AS BEEN DEEMED "TOO EXPENSIVE TO PUMP" IS BEING TAKEN OUT OF PRODUCTION. U.S. PRODUCTION IS DOWN BY OVER A MILLION BARRELS A DAY.

Meantime, demand is rising in the United States and the developed nations in general. OECD consumption was up 2 percent in the first quarter.

But estimates and assessments are that reserves will not rise. The only real growth in estimated reserves has been in the Mid-East and among OPEC nations. Reserves have declined in the United States and the communist world. The U.S. Geological Survey recently decided it had been 40 percent too high on domestic reserves of oil and natural gas.

Meantime, the energy news of last spring was that OPEC and seven non-OPEC producers are flirting with an alliance to cut production and raise prices; if they join, they will control 56 percent of the world's production outside the Soviet bloc.

No one can say whether peace in the Gulf will hasten or impede this movement. Some experts expect the price will be high enough to prosper, but low enough to stall the development of technologies such as those you are discussing.

Nevertheless, the U.S. Department of Energy has estimated that by 1995 the Mid-East producers and OPEC may control as much as 60 percent of the world market with the customary economic consequences. It estimated that by 1995 the U.S. could be spending $80 billion a year on imported oil.

The Economist magazine recently went so far as to assert that at current levels of exploration, discovery and production in the non-communist world "the oil companies have less than 10 years of reserves left."

It doesn't matter if these estimates are accurate or off by as much as 100 percent. It doesn't matter if the Economist is wrong by as much as 40 years, or more.

As James Morrison, the executive vice president of Atlantic Richfield, recently said, "The future of oil is very simple; we are going to run out of it. Any talk about oil's future has to do with how fast that day . . . is approaching."

The point is that reliable production is declining, reliable reserves are questionable at best, and the importance of Persian Gulf and OPEC reserves will grow.

We are importing more oil today than in 1973. Our oil imports were 35.5 percent of consumption in 1987 and increased by 25 percent between 1984 and 1987. Our imports from the Persian Gulf increased by 113.5 percent between 1984 and 1987, and our OPEC imports went up 49.8 percent.

THIS MEANS THE NON-MARKET POWER OF IMPORTED OIL OVER DEPENDENT NATIONS WILL GROW. AND THE POLICY FRICTIONS ENGENDERED BY DEPENDENCE WILL GROW.

EVERYTHING BEGINS WITH ENERGY, AND EVERYTHING ABOUT OIL SAYS IT IS NO FOUNDATION TO UNDERPIN PROGRESS OR EVEN THE HOPE OF PROGRESS.

THE UNITED STATES AND SOME OTHER NATIONS MAINTAIN WHAT WE CALL "STRATEGIC" PETROLEUM RESERVES AS A CUSHION AGAINST SHOCK. BUT NO RESERVE WILL LAST EVEN SIX MONTHS AGAINST FULL DEMAND, AND WHO CAN SAY WHAT PANIC MIGHT DO TO PRICES.

LIKE THE GULF FORCE, THE RESERVES ARE MERELY TACTICAL ANSWERS TO DELIVER TEMPORARY RELIEF. THEY BUY TIME. BUT THEY DO NOTHING TO CHANGE THE BALANCE.

Strategies build on strength, deliver flexibility and change the balance. Strategies deprive would-be exploiters of their strength and make their risk of failure high.

The only flexibility in our national energy forecasts is in American coal in partnership with domestic oil, gas, nuclear energy and alternate energy resources.

And the only dispute about America's coal reserves is how many centuries worth we have; whether the recoverable reserves are 250-billion tons or a little less.

Even at double today's rates of production we have proved recoverable reserves sufficient to break the strength of imported oil and to underwrite a break with oil for the remainder of this century; for all of the next; and for a significant portion of the one to follow.

This is a strategic reserve. And it is secure.

There'll never be a need for air cover to get a unit train to an electric generating station. The tows and towboats moving coal on the river system will never need a flotilla to sweep for mines or to prevent a machine-gun attack by fanatics in speedboats.

No foreign power can destabilize America's coalfields, and no force will ever have to stay at sea in harm's way for a year to keep the coal moving.

Coal -- in conjunction with domestic oil, natural gas, alternate sources of hydrocarbon energy, nuclear power and sound policies of conservation -- can provide complete energy flexibility.

The cost of not achieving it is far beyond the dollars that might be spent perfecting and deploying technologies to break the ever-tightening grip of relatively cheap imported oil.

Imported oil is a hand around our throat, the throats of our allies and of all nations. This hand is much stronger than the invisible hand of the free market. It's time to quit pretending the hand isn't there in the hope it will go away.

And it's well past time to quit treating energy as just another market item.

America must have an energy policy founded on a strategy and strength rather than a weakness and economic philosophies that assign no cost to some very important considerations.

There is no danger in importing oil when we have a choice of imported oil versus domestic energy. The concern today is that so many of us _must_ have access to imported oil in order to function. We must have it regardless of cost. And unless we change our energy plans and habits, we will require more, not less.

Our first objective must be to reverse the increase of oil imports into the United States, and to begin driving imported oil out of the economy until we are no longer dependent on that resource.

This means harnessing all of our domestic energy resources to achieve the goal of "Energy Independence," which also underwrites real independence of action.

A Policy for Energy Independence would rationalize all of our energy resources to ensure that we get the best efficiency and economy from each. It would balance short-term advantage at the bottom line with long-term stability and requirements. It would consider not only this year and this decade, but also this century and the next century of our Nation's survival.

Electric generation is the heaviest user of basic energy and coal is the most abundant resource, and the most suitable; therefore, a policy would remove impediments to coal use and guide coal into all replacement and new capacity that it can best serve. It would restore nuclear power as a long-term choice.

Transportation levies heavy demands for oil-based fuel. The requirements of commerce and the private automobile account for most of our oil imports. Methanol motor fuel from natural gas -- and processes discussed here -- could offer relief. But as an official of the Bechtel Group recently told me, current plant-gate prices of petroleum-derived gasoline seem to put it out of reach at the moment. There also is room to squeeze out imported oil in further electrification of rail transport. There is potential for more relief with deeper concentration on the work being done on diesel engines, turbines and fuel extenders and alternates.

Industry has major requirements. Coal can help American industry become more competitive and less subject to surprise and shock. Clean Coal Technology and things such as coal-water and other mixtures have potential here as well as in electric power. That potential must be investigated and deployed. Care must be taken to encourage a break with imported oil and not to preclude by environmental or other regulation the use of the most abundant fuel.

In my view, a Policy for Energy Independence for the United States would include the following objectives:

* To offer across-the-board conservation incentives for industry and commerce, for automobiles and for individuals; and,

- To STIMULATE EXPLORATION AND DEVELOPMENT OF DOMESTIC OIL AND NATURAL GAS RESERVES TO HELP PUSH OUT IMPORTED OIL; AND,

- To INCREASE COAL USE IN EVERY APPLICATION FOR WHICH IT IS SUITABLE, AND TO EXPAND RESEARCH AND DEVELOPMENT TO INCREASE THE APPLICATIONS FOR WHICH IT IS SUITABLE; AND,

- To DEVELOP AND DEPLOY THE FULL ARRAY OF FUEL MIXTURES, FUEL EXTENDERS AND ALTERNATE FUELS, INCLUDING SHALE OIL AND TAR SANDS AND THE USE OF NATURAL GAS TO PRODUCE METHANOL FOR TRANSPORTATION; AND,

- To FURTHER WRING IMPORT-OIL DEMAND OUT OF TRANSPORTATION BY FOSTERING GREATER USE OF ELECTRICITY IN PUBLIC AND PRIVATE TRANSPORTATION; AND,

- To support development and deployment of Clean Coal Technologies in the generation of electricity; and,
- To start now the work of untangling the layers of regulation and fear that have all but excluded additional nuclear power as a tool for pushing out imported oil in the next 15-to-20 years; and,
- To balance our export-import requirements in energy; that is, to modulate the tremendous dollar drain of oil imports with programs and policies to export to energy-dependent nations our coal and Clean Coal Technology.

Earlier I mentioned the Synthetic Fuels Corporation, an $88 billion crash program that lived up to its name in a peculiar way: it crashed.

The Synfuels Corporation failed for two reasons.

FIRST, IT WAS A HASTY RESPONSE TO SURPRISE. BUT THE TIME TO SET IN PLACE A COMPETENT RESPONSE TO SURPRISE IS BEFORE IT HAPPENS, NOT AFTER. SYNFUELS TRIED SIMULTANEOUSLY TO CREATE THE MEANS TO MOBILIZE AND TO MOBILIZE. IT IS AKIN TO ATTEMPTING TO SOLO ON YOUR FIRST RIDE IN AN AIRPLAINE. IT IS ALWAYS DIFFICULT.

AND SECOND, AS PEOPLE ADJUSTED TO THE AFTERSHOCKS OF THE SURPRISE -- AS THE GASOLINE LINES DWINDLED -- THE MARKET PRICE OF OIL OVERSHADOWED THE TRUE COST OF OIL AND THE REAL POINT OF THE EXERCISE: TO BREAK THE POWER OF OIL, NOT TO COMPETE HEAD-TO-HEAD WITH IT FROM DAY ONE. THAT TIME COMES LATER WHEN THE TECHNOLOGIES ARE PERFECTED AND WIDELY DEPLOYED.

SO AS THE PRICE OF OIL DROPPED, THE POLITICS OF THE MOMENT AND THE ECONOMICS OF THE NEXT QUARTER'S BOTTOM LINE TOOK HOLD.

Nevertheless, Synfuels established the Integrated Coal Gasification Combined Cycle test plant generating electricity at Daggett, California, and the Great Plains Plant near Beulah.

I think it's worth noting that despite the federal takeover of Great Plains, there was competition when the time to divest came: not one, not two, but three serious bidders. Moreover, the government got a good deal.

And from the wreckage of Synfuels some far-sighted political leaders also plucked the beginnings of the Clean Coal Technology Program.

All the products of Synfuels -- if we will treat them as points of beginning rather than destinations -- offer means to start countering the dangers of the journey to the world that is to come in the 21st Century.

All -- if the Pilgrim's companions of Mr. Ready-to-Halt, Mr. Fearing, Mr. Despondency's daughter and Giant Despair are not heeded in the extreme - give us a way to start dealing with other problems.

I refer to the political questions of acid rain and the recently advanced theory that the earth already has begun to warm according to a theory that CO_2 from fossil fuel combustion eventually will cause it to warm -- the so-called "greenhouse effect."

In 1981, there was a call for immediate legislation to curtail projected-to-rise SO_2 emissions to forestall prospective but projected-to-be-widespread damage from acid rain.

But the studies went forward. And we learned some things we didn't know: First, that SO_2 emissions actually are falling and will continue to fall absent new legislation; and, foremost, that acid rain presents no worsening environmental crisis.

Meantime, research and development went forward. And today we have at hand the Clean Coal Technologies, which offer increases in generating efficiency, lower capital costs and -- perhaps most important -- from 90-to-99 percent sulfur removal.

However, if investment in old-style controls is forced, deployment of the new technology will be delayed for lack of funds, or may not even take place. There will be economic losses rather than gains. And we'll run out of capital for time of need. Because electricity drives a modern economy, there will be consequences related to growth and international competitiveness.

This summer the so-called "greenhouse effect" was elevated from the status of scientific question to that of political issue by the heat and the drought and a Conference in Toronto.

One American scientist told a Senate committee that the warming has begun, and a few agreed.

But more agreed with Dr. Tom Karl of the National Climatic Data Center, who said, "You can get in a heap of trouble if you look at a climate time series and draw an inference; you can get swings that last for 10 or 20 years."

In short, there is nothing abnormal about hot years and dry years -- such as our Dust Bowl of the 1930s. Nor about cool years and wet years, which this decade caused the Great Lakes and the Salt Lake to rise to almost unprecedented levels.

Cycles notwithstanding, the call again is for "immediate" legislation to dramatically curtail the use of fossil fuels.

However -- and let's be very clear about this -- we do not believe the possibility that CO_2 will eventually affect the climate should be ignored; nor should anyone scorn the overall experience of mankind in finding and creating the path for the pilgrimage to the future, which is always in progress.

There's a lot we don't know about CO_2. And there's a lot we do know.

We know that CO_2 from the coal-fired generation of electricity in the U.S. is about 4 percent of what's going into the atmosphere around the world. We also know it has been estimated that fires from forest clearing in Brazil are responsible for as much as 10 percent.

And we know it will take a worldwide approach if anything the U.S. does is to have any meaning -- or any effect.

We also know that some of the Clean Coal Technologies emerging -- and others still in research -- offer through better combustion anywhere from 20-to-70 percent less CO_2.

We know that gasification at Great Plains produces carbon in the raw gas, and that the washing process used captures all but one-half of one percent of the CO_2 present at that stage.

We know that -- if only the market, or policy, were right -- up to 200 million cubic feet a day of CO_2 could be put in a pipeline and later injected in the recovery of old domestic oil.

And most important, we know that a future has never been won by withdrawing in fear to stagnate.

ALL OUR TECHNOLOGY IS IN ITS INFANCY. TO DRAW BACK WITH RESTRICTIONS THAT FREEZE EVERYTHING AS IT EXISTS TODAY IS TO KEEP IT -- AND US -- PRISONER TO THE PAST.

THE NATIONAL COAL ASSOCIATION IS WORKING WITH THE DEPARTMENT OF ENERGY TO ESTABLISH CO_2 RESEARCH IN PHASE THREE OF THE CLEAN COAL TECHNOLOGY PROGRAM, AND WE ARE PUSHING TO BRING ABOUT ORDERLY DEPLOYMENT OF THE COMMERCIALIZATION-READY TECHNOLOGIES.

AMERICA DOES NOT HAVE A LOT OF TIME BEFORE THE DEMAND FOR THE WORLD'S DOMINANT ENERGY -- OIL -- EXCEEDS THE FREELY AVAILABLE SUPPLY. WE'VE BEEN SURPRISED THREE TIMES. THE TIME TO PREPARE A RESPONSE TO SURPRISE IS BEFORE, NOT AFTER.

In Washington I sense that the time is getting ripe to assemble the pieces -- the vulnerabilities and the resources, the things we know and the opportunities -- and to get on with the building of an America strong enough to win a third century of independence.

We can start the journey from a position of weakness or with a strategy of strength. Which is better?

As the Chairman of the United States Senate Energy Committee, Bennett Johnston, said recently: "We will have an energy policy. The only question is whether it will be forced on us by . . . national travail. It will take political agitation."

If there is to be agitation -- and there must be -- let it arise from a consensus process that begins at gatherings such as this one here: among "we the people," the people most directly concerned and involved.

Let that consensus rally around broad objectives, and let those working to reach it save settlement of details until after the political system is committed to the objective.

In this regard, a maxim of Napoleon that I found in my reading as a young officer comes to mind now: "If you plan to take Vienna, then take Vienna."

It means set a goal and stick to it; those who cannot or will not will lose both the original goal and the things they abandoned it to chase.

Failing firmness, whatever we attempt will fall into the Synfuels trap: short-term trends and goals -- economic and otherwise -- will conflict; marketplace and other actions will tend to cancel one another and the effort.

We have no chance to solve our energy problems by following primary policies with exclusively or predominantly environmental goals.

But we can answer environmental concerns with an energy policy that advances technology that is more efficient and that respects the environment. We're doing that without legislation and we will continue to do it.

Everything does begin with energy, and the true cost of imported oil has never been more apparent.

Energy Independence won't be won tomorrow, or even next year. It will not be an easy trail. It will be at least as challenging as the pilgrimage west: to Beulah, North Dakota, and the territory beyond. To set the destination, to mark out the route and to clear the way are major efforts in themselves.

It may take until 1995 to get rolling, and even the year 2010 is not an unreasonable estimated time of arrival.

The important thing is to start and stick with it.

Let's not even think about learning to live with the full and true cost of imported-oil dependence: American lives in harm's way for as long as the oil lasts, and her choices forever limited, to cover a dependency in our power to break.

It's time we began making some moral choices along with our economic and political decisions.

If we band together and start now and win through to Energy Independence, the prize at the end of the trail is without equal and beyond value.

For it may well be nothing less than the rightful heritage of independence and "the American Way of Life" of generations now unborn.

Thank you, and may God bless you all. There is no work in the world more important than that you are about here.

DAVID ALLEN

David Allen is Assistant Professor of Business Administration at Penn State University, University Park. He teaches undergraduate and graduate classes in entrepreneurship. His research is on business incubators and commercialization of university research.

In addition to numerous articles and reports, David is the Senior Author of "Nurturing Advanced Technology Enerprises," (Praeger, 1986).

David is also a partner in the consulting firm, TEC-NEC.

NO PAPER SUBMITTED

SESSION 1: ALTERNATIVE SYNFUELS PRODUCTS

SESSION CHAIRS:

DON POLLOCK
ANG COAL GASIFICATION CO.
BEULAH, ND

EVERETT SONDREAL
ENERGY & MINERAL RESEARCH CENTER, UND
GRAND FORKS, ND

1. "The Development of a Synfuels Industry in South Africa Identifies Opportunities for Future Projects"

   by: Theo Van Der Pas
   General Manager
   SASOL Ltd
   Johannesburg, RSA

2. "Production of Aviation Fuel from Great Plains Gasification Plant By-Products"

   by: William E. Harrison III
   Wright Aeronautical Laboratory
   U.S. Air Force
   Wright Patterson AFB, Ohio

3. "Methanol Fuel: Converting North Dakota Lignite Into Liquid Transportation Fuel for the Nation"

   by: Galen Andersen and Ralph D. Bartz
   The Nokota Co.
   Bismarck, ND

4. "Synfuels Technologies What is Appropriate to China"

   by: Bao Han-Chen, Director
   Energy Research Committee, Chinese Academy of Science
   Beijing, People's Republic of China

"THE DEVELOPMENT OF A SYNFUELS INDUSTRY IN SOUTH AFRICA IDENTIFIES OPPORTUNITIES FOR FUTURE PROJECTS"

BY: THEO VAN DER PAS
GENERAL MANAGER
SASOL LTD
JOHANNESBURG, RSA

THE DEVELOPMENT OF A SYNFUELS INDUSTRY IN SOUTH AFRICA IDENTIFIES OPPORTUNITIES FOR FUTURE PROJECTS

Theo Van der Pas, General Manager
SASOL Ltd., Johannesburg, RSA

ABSTRACT

Under normal world trading conditions with crude oil freely available, synthetic automotive fuels may never be able to compete with products derived from crude oil unless we change our approach towards these projects.

It is generally accepted that we are still far away from a global crude oil shortage and for the foreseeable future crude oil prices will therefore remain relatively depressed. The massive research and development effort around the world and specifically in the USA which was started after the energy crisis has been disappointing. No breakthroughs have been achieved or are expected which will fundamentally change the economics of synfuel production.

The drawback of the indirect Fischer-Tropsch route in comparison with the direct route is its lack of selectivity, but this also provides an opportunity. Byproducts often considered a disadvantage can be turned into marketable products with considerably higher value than fuels. In South Africa, Sasol the only operator in the world of a number of synfuel plants, has capitalised on this fact and the paper provides examples and discusses opportunities in this area.

THE DEVELOPMENT OF A SYNFUELS INDUSTRY IN SOUTH AFRICA IDENTIFIES OPPORTUNITIES FOR FUTURE PROJECTS

The Dilemma

Under normal world trading conditions with crude oil freely available synthetic automotive fuels may never be able to compete with products derived from crude oil unless we change our approach towards these projects. It may seem a sweeping statement but I believe it to be true. Time and again one reads articles about synthetic fuels production and the price of crude oil required to make such a project viable. An increasing crude oil price is not likely to make synfuels production more competitive unless we are referring to an existing synfuels producer. Higher crude oil prices mean higher energy costs which results in turn in higher equipment cost, general inflation and thus higher capital as well as operating costs of a new synfuels complex. Having said that new synthetic fuels ventures are unlikely to be able to compete, the question is what will have to happen to render new synfuels ventures competitive? I could visualise three scenario's.

- Crude oil availability becoming limited,
- Significant improvement in synfuels production technology,
- A different approach towards the production of synthetic fuels.

A reduced availability of crude oil world wide will obviously result in crude oil price increases. These increases would continue until a new base has been established namely the cost of producing alternate energy. I am intentionally not using the name alternate fuels, because there are many alternatives to crude oil as a source of energy. Looking at the world today it is generally accepted that we are still far away from a global crude shortage. Regional shortages yes, global shortages no. The sudden increase in oil prices first in 1973/74 and again in 1979 made it attractive to search for new and alternative sources of energy. On the consumer side a strong incentive developed for energy to be used more efficiently. Interest in the production of synthetic fuels flared up and large sums of money were made available for research and study projects particularly here in the USA with a view to develop new or more efficient processes. It took some time for all these activities to show results. Dramatic progress was made in the area of efficient utilisation of energy especially after the second oil price shock in 1979. Oil refineries became more efficient, buildings were made more energy efficient, the automotive industry achieved a drastic saving through the production of lighter cars in combination with more fuel efficient engines. Similarly drastic fuel savings were realised in the aircraft industry. All in all a very large reduction in the consumption was achieved world wide and this at a time that new oil and gas sources were found and developed in many parts of the world. Non-Opec oil production increased steadily. As time goes on crude oil will again become more expensive because the recovery will become more expensive. However sufficient oil will be available for several decades to keep the price at such a level that synfuels as such will not be able to compete.

If we could improve the economics of producing synthetic fuels the situation will obviously change. What is the likelihood of a drastic improvement in technology? In this connection let us have a look at what has happened since, say 1975:

- Research and development in the USA concentrated on the direct liquefaction of coal. The main advantage of this process route is that it has a considerably higher thermal efficiency than the indirect routes, provided suitable coal is available. Development work in the USA as well as pilot plant work undertaken by

Sasol over a period of more than 10 years have demonstrated that suitable low ash coal can be liquefied at pressures of between 250 and 300 bar. This in contrast to the much higher pressures used by the Germans in their plants prior to and during the second world war. The reduction in pressure has become possible through the use of so-called hydrogen donorsolvents. Operating conditions of the direct liquefaction route remain severe however, and unproven on a commercial scale.

- There are the indirect routes to synfuels.

a) The new methanol-conversion process based on Zeolite catalysts has been developed for converting synthesis gas to gasoline via methanol and one commercial unit has been built in New Zealand based on natural gas. A catalyst has also been developed for gasoline and diesel production but it has not been proven on a commercial scale.

b) The well tried Fischer-Tropsch process, 2 variations of which are in commercial operation in the Sasol plants namely, fixed bed low temperature Fischer-Tropsch and fluidised bed high temperature Fischer-Tropsch. In the reactor section of the Fischer-Tropsch process there is still some scope for further development. Sasol has no less than 19 fluidised bed and 6 fixed bed Fischer-Tropsch reactors in operation in its plants. Early next year Sasol will commission a fixed fluidised bed demonstration reactor. This reactor will cost only half as much as a conventional circulating bed reactor of the type used at Sasolburg and Secunda, operating costs will be lower and efficiencies higher. Unfortunately this part of a synfuels plant represents less than 20% of the total capital investment and even a significant reduction in capital cost in this area will have a relatively small effect on the overall cost of a synfuels complex. Sasol has also recently successfully commissioned a fixed bed low temperature Fischer-Tropsch reactor operating at 45 bar in stead of the 25 bar of the original 5 reactors.

c) For the indirect routes, coal gasification is important. Although new generation gasifiers like Texaco and H T Winkler have been developed and commercially proven on a limited scale, these slagging gasifiers are not suitable for high ash content and high ash melting point coals. We at Sasol therefore still have to depend on the well tried Lurgi dry bottom gasifier which is also still the most reliable (85-90% availability) and lowest cost commercial gasifier. We have 97 Lurgi gasifiers in operation in the Sasol plants. A Mark V version of the Lurgi gasifier (5 m dia) with a capacity 70% larger than the Mark IV has been in operation at Sasol One for the last 8 years and a future Sasol plant will be based on Mark V. In recent years the operation of Lurgi gasifiers has been almost completely automated at Sasol.

The above improvements made in the indirect route in recent years have been marginal and although there is still room for improvements such as catalyst life and performance, materials of construction, control and instrumentation, these will also be of a marginal nature.

Overall the results of the massive Research & Development effort around the world since 1975 have been disappointing. One can therefore say today that regardless of the route no breakthroughs have been achieved or are expected that have the potential of fundamentally changing the economics of the production of synthetic fuels on its own.

The Opportunity

We know that crude oil as a source of energy will not last indefinitely and alternatives will have to be developed.

Before you become despondent as a result of the bad news of the first two scenarios, let us consider a third scenario, namely a different approach towards the production of synthetic fuels which does present an opportunity for the future.

According to the critics the drawback of the indirect Fischer-Tropsch route is its lack of selectivity and indeed if we are interested only in liquid fuels then Fischer-Tropsch is not the most efficient route. We usually find that when the feasibility of a potential synfuels project is studied, the byproducts are considered a disadvantage and either no value, fuel value or sometimes even a negative value as effluent is assigned to byproducts. The result then invariably is that the economics look unattractive. Even at Great Plains valuable gasification byproducts are burnt as fuel to fire their boilers. What should however be taken into account is that the coproducts are not only marketable but can have considerably higher values than the fuels.

I note that it has been reported that your studies of the feasibility of producing jet fuel from the gasification byproducts of Great Plains have led to the conclusion that the economics would only be attractive if it were coproduced with cresylics. This just confirms the point I am trying to make.

* The transparancy (Attachment 1) gives typical selectivities of the 2 Fischer-Tropsch processes employed in the Sasol plants. These primary products offer a wide variety of opportunities. If "synthetic fuels" should be looked at in broader terms the economics of these projects would become more attractive.

* The next transparancy (Attachment 2) shows typical European and US gate prices of petrochemicals which can be produced from Fischer-Tropsch primary products. You will note that the petrochemicals sell at two to ten times the price of transport fuels per ton. In fact, coproduction of higher value chemical products can be the way to ensure that when the next oil crisis comes along, you will already have your synfuels technology in place instead of having to start developing the technology and miss the boat again as in 1973 and 1979.

In 1974 when the oil price had increased dramatically, Sasol was well prepared and seized the opportunity to build a new synfuels plant. Others, especially in the USA, embarked on almost endless feasibility studies to such an extent that a study industry developed. Unfortunately by the time that they had determined economics and had their permitting in place, the capital costs had escalated, the oil price started dropping, and the opportunity was lost. This performance is likely to be repeated in the "user-unfriendly" environment created by the authorities, especially the USA.

Let me now illustrate this scenario with the Sasol experience:

As far back as 1950 the original planners of Sasol realised that the economics of the route most suitable for SA coal namely Fischer-Tropsch, would at the then ruling market price be marginal if transport fuels alone were to be produced. The lack of selectivity of Fischer-Tropsch towards gasoline and diesel was recognised as an opportunity rather than a disadvantage and it was decided to spend additional capital to recover the more valuable byproducts and so improve the market value of its products. Sasol one consequently started up as a petrochemical complex rather than just as a liquid fuels plant. Shortly after startup in 1955 Sasol was already marketing coal gasification byproducts such as ammonium sulphate, tar acids, creosote and Fischer-Tropsch byproducts such as waxes, acetone, MEK, ethanol and higher alcohols. Sasol survived the low oil prices prevailing during the 1960's by diversifying even further into the petrochemical byproduct area and projects were launched for the production of Ammonia/Nitric Acid/Ammonium Nitrate, Butadiene, Styrene, Ethylene and towngas. By 1970 already forty different byproducts were being marketed. Sasol has recently extended its manufacture of petrochemical byproducts by further diversifying into cresylics from coal, fertilizers and explosives and this year projects have been launched for the expansion of our Ethylene production facilities as well as for the recovery of propylene and the production of polypropylene. The growing petrochemical market continuously presents opportunities to market additional coproducts. Today Chemicals are the star performers of the Sasol Group and the non-fuel products being marketed have grown to 80 as can be seen on the next transparancy (Attachment 3) on which the non-fuel products being marketed by Sasol are listed by category.

Further promising possibilities are being studied and Sasol will no doubt continue diversifying in the future.

The question has often been asked how it is possible for Sasol to compete with crude oil. In part the answer lies in the fact that 25% of Sasol's income is obtained from chemicals and its share is still growing as illustrated in the previous transparancies. Going from gasification to the products of Fischer-Tropsch there are almost unlimited possibilities in terms of petrochemicals production. In SA we still have the problem of a limited local market and appreciable transport cost to foreign markets. In the USA petrochemical coproducts of a Fischer-Tropsch based complex should easily be absorbed by your very substantial internal market.

On the subject of the economical viability of Sasol, I would like to point out that Sasol is a private company and its shares are listed on the Johannesburg Stock Exchange. The price received for transport fuels is determined by the landed cost of imported products. The low price of transport fuels in SA is claimed to be second only to that of North America in the industrial countries. In March 1988 for instance, 93 Octane gasoline was sold at the pump in the Sasol marketing area for 82c/litre ($1,44/US gall) of which Sasol received 41 SA cents/litre, the rest being levies and taxes. Sasol shares are Blue Chips on the Johannesburg Stock Exchange and in spite of the low oil prices the substantial dividend has been maintained this year.

Parting Thoughts

The most attractive process scheme for a future "synfuels" complex in the USA could be based on coal via the indirect Fischer-Tropsch route producing liquid fuels with pipeline gas and petrochemicals as coproducts.

The best place to start such a venture could very well be right here in North Dakota, to be more specific, Great Plains. You have abundant coal at a reasonable price and you have the Great Plains plant, which has been a great technical success and with very able and highly skilled staff.

In this way the economic viability of Great Plains can be improved and the valuable know-how already accummulated can be retained and further expanded. Know-how is soon lost when a plant is shut down.

TYPICAL SELECTIVITY (CARBON ATOM BASIS) OF SASOL'S FISCHER-TROPSCH PROCESSES

	Fixed Bed	Fluidised Bed (Synthol)
	%	%
CH_4	4	7
C_2 to C_4 Olefins	4	24
C_2 to C_4 paraffins	4	6
Gasoline	18	36
Middle distillates	19	12
Heavy oils and Waxes	48	9
Water soluble Oxygenates	3	6*
	100	100

* The 6% Water soluble oxygenates are made up of:

- 5/6 Non-Acid Chemicals with following approximate composition:

Aldehydes	5%
Ketone	30%
Alcohols	65%

- 1/6 Acids with following approximate composition:

Acetic Acid	70%
Propionic Acid	15%
C_4^+ Acids	15%

ATTACHMENT 2

TYPICAL GATE PRICES OF PETROCHEMICALS COMPARED WITH TRANSPORT FUELS

	$/Ton
Gasoline	200
Middle Distillates	170
Ethylene	500 - 600 *
Propylene	350 - 400 *
Benzene	300 - 350 *
Toluene	250 - 280 *
Styrene	1400 - 1900 *
Phenol	900 - 1000 *
Acetone	370
MEK	1800

* Reference: ECN Bulk Chemical Prices May 30, 1988.

ATTACHMENT 3

CATEGORIES OF NON-FUEL PRODUCTS BEING MARKETED BY SASOL

WAXES	(22)
SOLVENTS	(12)
NITROGENOUS CHEMICALS	(4)
COAL TAR PRODUCTS	(7)
MINING CHEMICALS	(2)
ETHYLENE	
PROPANE	
C_{10}N-PARAFFINS	(3)
SULPHUR	
FERTILIZERS	(15)
EXPLOSIVES	(12)
TOTAL	(80)

"PRODUCTION OF AVIATION FUEL FROM GREAT PLAINS GASIFICATION PLANT BY-PRODUCTS"

BY: WILLIAM E. HARRISON III
WRIGHT AERONAUTICAL LABORATORY
U.S. AIR FORCE
WRIGHT PATTERSON AFB, OHIO

NO PAPER SUBMITTED

"METHANOL FUEL: CONVERTING NORTH DAKOTA LIGNITE INTO LIQUID TRANSPORTATION FUEL FOR THE NATION"

BY: GALEN ANDERSEN AND RALPH D. BARTZ
THE NOKOTA CO.
BISMARCK, ND

METHANOL FUEL - CONVERTING NORTH DAKOTA LIGNITE INTO LIQUID TRANSPORTATION FUEL FOR THE NATION

ABSTRACT

Authors: G. E. Andersen and R. D. Bartz

Methanol is a major chemical feedstock and promises to be a widely used fuel in both Otto-cycle or gasoline engines and Diesel-cycle engines.

Public policy considerations are the major driving force for the creation of a market for methanol as a transportation fuel. As mandated by Congress, there is a national commitment to reduce emissions from cars and trucks, and the strategy being developed by the United States Environmental Protection Agency includes methanol as a major component. In southern California, for example, the South Coast Air Quality Management District expects that, by 2007, up to 40% of passenger vehicles and 70% of trucks operating around Los Angeles will use alternative fuels with the majority of the market going to methanol.

The use of methanol in cars and trucks is also one of the most realistic methods of diversifying our energy sources away from the Persian Gulf.

Methanol is made from natural gas or from coal. The economics of producing methanol from natural gas largely depend on the availability and price of natural gas. As for coal, the economics depend on federal and state incentives to alleviate high fixed costs and the ability of the project to produce quality by-products.

Due to low availability and relatively high costs, North Dakota is at a disadvantage when considering the production of methanol from natural gas. But when we consider producing methanol from coal, North Dakota has the distinct advantage of being the first state with a commercial-size coal gasification plant. The successful completion and operation of the Great Plains Project has proven that North Dakota lignite can be gasified into carbon monoxide and hydrogen, the building blocks for both synthetic natural gas and methanol.

It is important, however, that the sulphur recovery systems at Great Plains be proven effective. Great Plains and future synfuel projects cannot operate without the trust and support of the State of North Dakota, nor will they reach their economic potential unless quality by-products uncontaminated by sulphur compounds can be produced and sold.

As we reach the Congressionally mandated deadlines in the early to mid-1990's for reducing emissions from the nation's cars and trucks and as the need to diversify our energy sources away from the Persian Gulf becomes more acute, it is expected that the market for methanol as a transportation fuel will increase dramatically. North Dakota is in an unusually good position to benefit from this new market for North Dakota's lignite.

METHANOL FUEL - CONVERTING NORTH DAKOTA LIGNITE INTO LIQUID TRANSPORTATION FUEL FOR THE NATION

SUMMARY OF KEY ISSUES

Authors: G. E. Andersen and R. D. Bartz

As we reach the Congressionally mandated deadlines in the early to mid-1990's for reducing emissions from the nation's cars and trucks and as the need to diversify our energy sources away from the Persian Gulf becomes more acute, it is expected that the market for methanol as a transportation fuel will increase dramatically. North Dakota is in an unusually good position to benefit from this new market for North Dakota's lignite.

BIOGRAPHICAL SKETCH

Galen E. Andersen

Galen E. Andersen is President of The Nokota Company. He joined the company in 1971 as it began to broaden its activities from oil drilling and exploration into coal and synfuels development. He served to Captain in the U.S. Army and, prior to joining Nokota, worked in New York City for Texas Gulf Sulphur Corporation. Mr. Andersen is a graduate of Washington and Lee University with a B.S. degree in Commerce and serves on the Executive Committee of the North Dakota Lignite Council, the Board of Directors of the ASEAN-U.S. Business Council and as company representative to the Council on Alternate Fuels.

Ralph D. Bartz

Ralph D. Bartz is Manager, Technical Services, for The Nokota Company. He joined the company in 1981 as it began preliminary design activities for the proposed Dunn-Nokota Methanol Project. He worked as a mining engineer for Consolidation Coal Company in southern Illinois and, prior to joining Nokota, worked in a similar capacity for American Natural Resources Company in both their Detroit and Bismarck offices. Mr. Bartz is a graduate of the University of Minnesota with a B.S. and M.S. degree in Geological Engineering.

METHANOL FUEL - CONVERTING NORTH DAKOTA LIGNITE INTO LIQUID TRANSPORTATION FUEL FOR THE NATION

LIST OF SLIDES

1. Centers of alcohol fuel development, including California, Brazil, Sweden, Japan, France, West Germany and New Zealand, from 1983 California Energy Commission report on methanol.

2. Indianapolis 500 race cars which use methanol for reasons of performance and safety.

3. Ford Crown Victoria with flexible fuel system which can run on any combination of methanol and gasoline.

4. Vehicle schematic of Ford's flexible fuel system.

5. GM's variable fuel vehicle, a 1988 Chevrolet Corsica, is being tested by the California Energy Commission.

6. GM bus with Diesel engine by Detroit Deisel Allison built to run on methanol.

7. U.S. Senate Bill 1518, Methanol and Alternative Fuels Promotion Act of 1987.

8. U.S. House of Representatives Bill 3399, Alternative Motor Fuels Act of 1987.

9. White House Cabinet Council Working Group on Methanol.

10. Cover from September 1984 issue of EPA Journal where the Environmental Protection Agency first began to publicize their finding that "the use of methanol can produce significant environmental benefits compared to the conventional fuels used in most U.S. automobiles."

11. Ford Escort designed for dedicated methanol use.

12. GM bus designed for dedicated methanol use.

13. The California Energy Commission will begin testing trucks with Diesel engines built to use methanol. Five manufacturers including Detroit Diesel, Cummins, Ford, Navistar and Caterpillar will supply engines.

14. Chevron and Arco, in cooperation with the California Energy Commission, will provide methanol pumps in 50 stations by January 1, 1989.

15. Location of Great Plains Coal Gasification Project.

16. Map of Beulah-Zap coal bed.

17. Ford Escorts built to use methanol fuel.

18. Ford flexible fuel vehicle being fueled from methanol pump at Arco service station.

"SYNFUELS TECHNOLOGIES - WHAT IS APPROPRIATE TO CHINA"

BY: BAO HAN-CHEN, DIRECTOR
ENERGY RESEARCH COMMITTEE,
CHINESE ACADEMY OF SCIENCE
BEIJING, PEOPLE'S REPUBLIC OF CHINA

SYNFUEL TECHNOLOGIES - WHAT IS APPROPRIATE TO CHINA ?

BAO HAN-CHEN

Energy Research Committee, Chinese Academy of Sciences
Beijing, People's Republic of China

ABSTRACT

Coal will remain as principal source of energy in China for a long time to come. World oil price will have little effect on this situation. Development of synfuel technologies is urgently needed to solve problems of efficiency, transportation, environmental protection and shortage of liquid and gaseous fuels.

The Chinese Academy of Sciences is responsible for most of the State-sponsored synfuel R & D projects including gasification, indirect liquefaction, and is also supporting research on super-critical gas extraction of low rank coals. A pilot plant base is now under construction for scaling up these processes.

The present status of these projects is overviewed and technologies appropriate to China are discussed.

INTRODUCTION

Energy is the most important issue facing modern China. Shortage in energy supply is one of the limiting factors of economical growth at present, and will remain as a bottleneck unless significant progress could be made in the area of exploitation and conversion technologies.

China has abundant resource of coal, but that of oil and gas is insufficient in comparison with the large population. At present, over 70% of the energy consumption of the country is derived from coal, and it is projected that coal will remain as the principal source of energy for a long time to come.

Overdependence on coal will inevitably bring forth a series of problems such as efficiency, transportation, environmental pollution and shortage in the supply of liquid and gaseous fuels.

Direct combustion of coal in out-dated industrial furnaces, kilns and numerous domestic stoves is the chief cause of low efficiency and serious air pollution in many cities. At present, only 20% of the urbanal residents is supplied with town gas. Pressure for increased production of town gas and industrial fuel gas is rapidly growing.

Prices of motor fuels and petrochemicals in domestic market are rising sharply, although world oil price has dropped to a low level in recent years. The gap between supply and demand is predicted to be broadening.

In many coalfields of China, such as those in Shanxi Province, coal production is limited by transportation. Although new railroads are under construction, it is believed that production there can easily exceed transportation capacity, cheap coal will always available in these areas.

Growing demand for synfuel and availability of cheap coal provide good opportunity for the development of synfuel tehcnologies. It is considered as a comprehensive solution of the above problems, an urgent need and also of long-term significane.

SYNFUEL PROJECTS

The main constraints of the development of synfuel industry in China are the investment intensiveness and sophisticated technologies involved. Since China is a developing country, technologies appropriate to China should be:

- suitable for Chinese coals
- affordable for smaller enterprises
- easily operable

The chief aim of the Academy's synfuel projects is to identify and develop technologies appropriate to China.

According to coordination understandings between fossil energy research organizations in China, the Academy is chiefly responsible for the development of fluidized bed gasification and indirect liquefaction processes, while other institutions are responsible for the development of direct liquefaction, moving-bed and entrained bed gasification processes.

The followings of the Academy's synfuel projects are included in State-sponsored projects in the 7th 5-year plan (1986 - 1990) :

- Ash Agglomerating Gasification
- High Octane Gasoline from Syngas
- Mixed Alcohols from Syngas

The followings are included as the Academy's important projects:

- Supercritical Gas Extraction of Low Rank Coals
- Partial Methanation

A pilot plant base is now under construction to scale up some of the above processes. This base will be open to other research institutes at home and abroad.

GASIFICATION

Facing growing pressure for increase of supply, many cities and even small towns are planning to set up or expand coalbased gas plants.

Cheap coke oven gas is used as town gas in many cities, where coking coals are available. In some of the gas plants, the ovens consume nearly half of the amount of gas produced. Moving bed producers can be used to produce low heating-value gas as plant fuel, thus expanding the volume supplied to the residents. These producers require lump coals or cokes and higher investment due to lower throughput.

Ash Agglomerating Gasification

The first objective of the Academy's ash agglomerating gasification project is to develop a gasifier of larger capacity and capable of using cheaper coal fines as feedstock for the production of plant fuel for these gas plants and other industrial heating purposes.

A 1 ton/day PDU was set up in 1983 in the Institute of Coal Chemistry, Chinese Academy of Sciences (ICC). 67 test runs covering six kinds of samples including coke breeze, lean coal, high ash meager coal, coking coal middlings, gas coal and anthracite have been carried out in this unit. Analysis of the samples are shown in Table 1. Typical experimental results are given in Table 2.

It should be pointed out that owing to the small size, the heating value of product gas is rather low. It is expected to increase considerably in a larger gasifier operated at higher pressure.

It was found from these test runs that

- The operability of the gasifier is good, it is capable of withstanding upsets;
- It is applicable to wide range of Chinese coals, including those with high ash content and high ash fusion temperature occuring in abundance around Shanxi Province;
- No tarry matter is found in waste water and the phenol content in it is less than 0.04 mg/., acceptable in China;
- The carbon content in the ash agglomerate is less than 10% and can be further reduced through secondary combustion, that avoids the disadvantages of conventional fluidized bed gasifiers;
- No trouble encountered with the construction material, thus the gasifier can be manufactured in China.

Ash agglomerating gasification may be considered as appropriate to China.

The design of a24 ton/day pilot plant has been completed, it will start operation around 1990. The next objective of this project will be the development to a pressurised gasifier for the production of syngas and fuel gas for IGCC.

Partial Methanation

Water gas is blended into town gas in many gas plants. If it were used alone, the CO content would be too high. It is worth noticing that in China, nearly every county or small town has a small synthetic ammonia plant starting with water gas production. Water gas producers are being manufactured in China at low costs. Workers familiar with this technology can be found even in remote places. So partial methanation of water gas provides a convenient way of producing town gas for small towns.

Dalian Institute of Chemical Physics of the Academy (DICP) has succeeded in developing a new type of heat resistant methanation catalyst. Satisfactory results were obtained in industrial-size single tube reactor tests.

A demonstration plant is now under construction in a small town (Wa Fang Dian, north of Dalian). Although the cost of the product gas may be 2 - 3 times that of coke oven gas, it would be acceptable in some coastal areas. Rapid deployment may occur around 1990.

Another option of obtaining town gas from water gas is the cogeneration of liquid and gaseous fuels through Fischer-Tropsch synthesis.

Some larger cities have chosen moving bed pressurized gasifiers for the production of town gas. The one at Shenyang has completed construction, but stopped soon after test runs owing to technical and economical problems. The other two, one at Harbin and one at Lanzhou, are now under construction. Due to high cost of imported gasifiers, the cost of the product gas may be a little higher than the gas from methanation of water gas. DICP is developing a sulfur-tolerant methanation catalyst for upgrading the product gas from this type of gasifiers.

Some smaller cities have chosen two-stage atmospheric gasifiers for the production of town gas. A demonstration plant using gasifiers imported from Poland is under construction. The product gas also contains too much CO (around 30%), partial methanation may be necessary.

INDIRECT LIQUEFACTION

Synthesis of High-Octane Gasoline from Syngas

In comparison with direct liquefaction, indirect liquefaction has better chance of development in China, because

- It can use wider range of coals as feedstock,
- Numerous small and medium ammonia plants can be easily expanded to produce liquid fuels, a way of reducing investment,
- Similarity of the ammonia and F-T synthesis make it easier to gather up teams of trained technicians and workers.

The conventional F-T synthesis, however, has a broad spectrum of products. it may be too complicated for smaller enterprises. Furthermore, the octane number of the gasoline fraction from conventional F-T synthesis is very low. Since gasoline derived from Chinese petroleum is also of low quality, unleaded high octane gasoline would have a favorable market in China.

ICC has developed a two-stage F-T Zeolite process, in which gasoline with octane number above 80 amounts to 65-80% of the hydrocarbons formed.

Two industrial size single-tube reactors were elected to test the operability of the catalysts and reactor system under industrial conditions. Duration test results show that

- Stability of the spherical fused Fe-catalyst in the 1st stage is satisfactory, no disintegration observed in 1000-hr run;
- Stability of the zeolite catalyst in the 2nd stage is also satisfactory, no regeneration required in 1000-hr run;
- Heat removal system works smoothly.

Table 3 summarized experimental results in laboratory and industrial size single-tube units. It can be seen that hydrocarbon yield and liquid yield are higher when precipitated iron catalyst is used in place of fused iron catalyst, this has yet to be proven in industrial size tube reactor.

DICP has been successful in developing a new type of supported Ru catalyst with very high selectivity for gasoline and diesel. Typical results are shown in Table 4. It is interesting to note that pretty high yield of liquid hydrocarbon is obtained in a simple single-stage process. Commercialization of this process is, however, dependent on the stability of the catalyst, availability and recoverability of metal Ru.

Synthesis of C_1-C_5 Alcohols

Another option of obtaining motor fuel from coal is to use alcohol fuels. The Institute of Engineering Thermophysics of the Academy has carried out a series of engine tests using M-100 and M-15. ICC is responsible for the synthesis of C_1-C_5 alcohols. Two types of catalysts have been developed, both have passed duration tests in 1-liter reactors using industrial size catalysts and syngas from a methanol plant.

Experimental results are given in Table 5. Further scaling up of these processes is now under discussion.

SUPERCRITICAL GAS EXTRACTION OF LOW RANK COALS

In all existing gasification and liquefaction processes, organic matter in coal is broken down under more or less drastic conditions. Would it be possible to obtain from coal optimum yield of solid, liquid and gaseous products with good quality under milder conditions? Investigations in ICC seem to indicate that supercritical gas extraction of low rank coals may be one of the answers to this question.

The advantages of this process may be summarized as follows:

- Fairly high yield of liquid product -- 30-50% of the organic matter convertible to oil (Tables 6 and 7);
- Relatively high H/C ratio in the liquid product -- less hydrogen required for upgrading (Figure 1);
- Extraction without using hydrogen -- lower investment and operation cost;
- No problem in separation of liquid and solid residue -- liquid product free of solid contaminates;
- High reactivity char and high heating value gas co-produced -- all products of good quality;
- Water enhancing liquid formation -- excessive drying of the feed unnecessary.

All these have been proven in a continuous flow system. A larger continuous extraction column is under construction. This may be an attractive and practical way of coproduction of good quality liquid, solid and gas from coal.

CONCLUSION

1. Development of synfuel technologies is an urgent need in China.
2. The main constraints of synfuel development in China are investment intensiveness and sophisticated technologies involved. Simpler processes using equipments manufacturable in China would be preferable.

REFERENCES

1. Bao Han-chen, China-Japan Symposium of Coal and C_1 Chemistry, September, 1985, 4.
2. Zhu Ya-jie, et al. ibid, 80.
3. Lin Heng-sheng, et al. ibid, 184.
4. Cheng Mao-yu, Proc. The 2nd Japan-China Symposium on Coal and C_1 Chemistry, May, 1988, 7.
5. Wang Yang, et al. ibid, 83.
6. Zhou Jing-lai, et al. ibid, 201.

Table 1 Analysis of Tested Coals

		Coke	Lean Coal	Meager Coal	Coking Coal Middlings	Gas Coal	Anthracite
Moisture		0.40	0.47	1.28	0.79	2.43	3.66
Volatile Matter		5.47	14.94	14.17	19.38	29.82	6.20
Fixed Carbon		76.76	74.37	53.96	47.39	47.71	66.62
Ash		17.37	10.22	30.59	32.44	20.04	23.52
Ultimate Analysis (d.a.f.)	C	95.34	88.76	86.06	83.77	79.76	90.71
	H	0.85	4.59	4.67	4.96	5.33	3.01
	O		1.00	0.64	8.10	12.78	4.75
	N		2.66	1.50	1.45	1.46	1.13
	S	0.63	2.99	7.13	1.72	0.67	0.40
Ash composition (wt%)	SiO_2	49.11	45.67	50.19	52.63	45.82	49.05
	Al_2O_3	31.11	38.98	35.03	32.17	39.82	32.87
	Fe_2O_3	7.00	7.61	6.02	5.93	5.48	4.74
	CaO	4.98	1.87	2.90	3.93	2.43	4.49
	MgO	0.82	0.72	0.38	0.61	0.72	1.42
	TiO_2	1.22	1.48	1.34	1.13	1.58	1.17
Ash fusion temperature, °C							
	T_1	1430	>1500	>1500	1500	>1500	>1500

Table 2 Typical Experimental Results

	Coke	Lean Coal	Meagre Coal	Coking Coal Middlings	Gas Coal	Anthracite
Bed temp. °C	1190	1125	1110	1090	1085	1100
Feedrate						
Coal kg/hr	20.0	48.7	32.8	52.3	42.0	56.1
Steam kg/hr	16.5	20.0	20.0	19.4	13.4	23.0
Air NM^3/hr	111.2	125.4	109.6	102.3	107.5	160.9
Heating value of gas Kcal/NM^3	794.7	1005.6	782.3	894.4	874.2	771.8
Gas Composition	Vol%					
CO	18.20	14.20	12.13	13.13	12.79	13.95
CO_2	13.53	12.44	16.73	9.63	10.69	10.61
H_2	8.06	14.70	12.41	14.24	13.19	11.13
CH_4	---	1.45	0.40	0.68	0.87	0.05
N_2	60.21	57.39	58.33	62.32	62.46	64.26
Carbon content in ash wt%	6.84	2.36	3.32	7.96	9.01	5.36
Ash Composition	Wt%					
SiO_2	47.71	44.99	51.09	52.22	51.53	52.08
Al_2O_3	35.71	36.61	32.72	32.43	33.91	32.69
Fe_2O_3	8.14	13.69	7.17	7.92	6.65	3.95
CaO	3.57	2.01	4.02	3.31	2.90	5.22
MgO	0.74	0.10	0.31	0.48	0.42	0.73
TiO_2	1.40	1.12	1.22	1.02	1.19	1.01

Table 3 Results of Long-Duration Tests in Two-Stage FT-Zeolite Process

Catalyst	Pptd Fe-zeolite	Pptd Fe-zeolite	Fused Fe-zeolit
1st stage cat. volume (ml)	10	100	Industrial-size single tube reactor Ø25mm
Temp. (C) 1st stage	230-255	225-230	280
2nd stage	320	320	350
Pressure (MPa)	2.5	2.5	2.5
1st stage GHSV (hr^{-1})	500	500	500
Feed Ratio (H_2/CO)	2	2	2
Recycle Ratio	0	3.0-3.5	3
C_5^+ yield gm/m^3(CO+H_2)	70-75	100-120	93.9
HC Distribution (wt%)			
C_1	5-10	4.0-5.5	12.7
C_2	2-4	1.0	7.0
C_3-C_4	15-20	15-17	20.3
C_5^+	70-75	72-80	60.0
C_{15}^+	trace	trace	trace
Aromatics in C_5^+	22-28	20-35	47.8

Table 4 Typical Results of F-T Synthesis on Supported Ru-catalyst (single-stage)

Reaction Temperature °C					225
Pressure (kg/cm^2)					25
GHSV					270
H_2/CO in syngas					2.2
C_5^+ yield g/m^3 (CO+H_2)					121.3
Hydrocarbon Product Distribution (wt%)					
C_1	C_{2-4}	C_{5-8}	C_{9-11}	C_{12-25}	C_{25}^+
1.74	2.70	28.32	30.27	36.87	0

Table 5 Experimental Results of C_1-C_5 Alcohol Synthesis (1-liter Reactor)

Catalyst	Zn-Cr	Cu-Co
Reaction Temperature °C	405	276
Pressure MPa	15	8
H_2/CO in Syngas	2.34	2.42
GHSV	4000	6000
Composition of ROH (wt%)		
C_1	73	51.8
C_2	2	28.1
C_3	3.8	10.4
C_4	15	5.4
C_5	0.8	2.1
C_6	0.4	0.9
Unidentified	5	1.3

Table 6 Analysis of Coals, Peats and Oil Shales Tested

Sample	Proximate Analysis %			Ultimate Analysis % (m.a.f.)				
	Ash (dry base)	Volatile matter (m.a.f.)	Total S(dry base)	C	H	N	S	O
Brown Coals								
Dayan HLJ	5.56	29.37	0.36	72.69	4.62	1.52	0.38	20.79
Shiaolongtan YN	10.99	33.82	1.16	69.61	4.42	2.03	1.31	22.63
Shengli IM	10.66	35.21	1.35	68.91	4.27	1.24	1.65	23.93
Fengmingcun YN	18.77	57.38	3.22	65.36	4.42	2.01	3.98	24.23
Shundian YN	6.84	59.23	0.89	68.26	5.23	1.06	0.96	24.49
Fanchi SX	19.93	62.54	0.31	67.11	6.21	1.34	0.38	24.96
Peats								
Baoqing HLJ	29.29	71.80		56.27	5.91	2.67	0.40	34.75
Norgai ZC	21.94	70.04		57.89	5.44	2.75	0.36	33.56
Oil Shales & Candle Coal								
Huangxian SD	52.36	66.38	0.68	72.56	6.64	2.06	1.42	17.23
Maoming GD	76.44	84.28	1.08	56.07	9.52	1.63	4.57	28.21
Puxian SX	6.10	51.14	0.62	86.23	7.14	1.63	0.66	4.34

Table 7 Extraction Results (Toluene as Solvent)

Sample	Temp. °C	Pressure MPa	Yield of extracted oil % (m.a.f.)	Gas and water formed % (m.a.f.)	Volatile matter of the feed % (m.a.f.)	Volatile matter converted to oil %
Brown Coals						
Dayan HLJ	410	19.7	24.18	10.79	29.37	82.3
Shiaolongtan YN	410	19.7	27.28	11.70	33.82	80.7
Shengli SD	410	19.7	21.24	9.66	35.21	60.3
Fengmingcun YN	410	19.7	34.87(45.71)*	12.04(1.38)*	51.38	60.1(89.0)*
Shundian YN	410	19.7	35.56(51.60)*	20.72(7.49)*	59.23	60.0(87.1)*
Fanchi SX	410	19.7	33.34	21.73	62.54	53.3
Peats						
Baoqing	410	20	34.5	30.2	71.80	48.0
Norgai ZC	350	20	34.6	28.7	70.04	49.4
Oil Shales & Candle Coal						
Huangxian SD	380	19.7	54.8	12.0	66.38	82.6
Maoming GD	380	25.6	51.8	3.8	84.28	61.5
Puxian SX	360	25.6	50.7	6.8	51.14	99.1

* Xylene as solvent

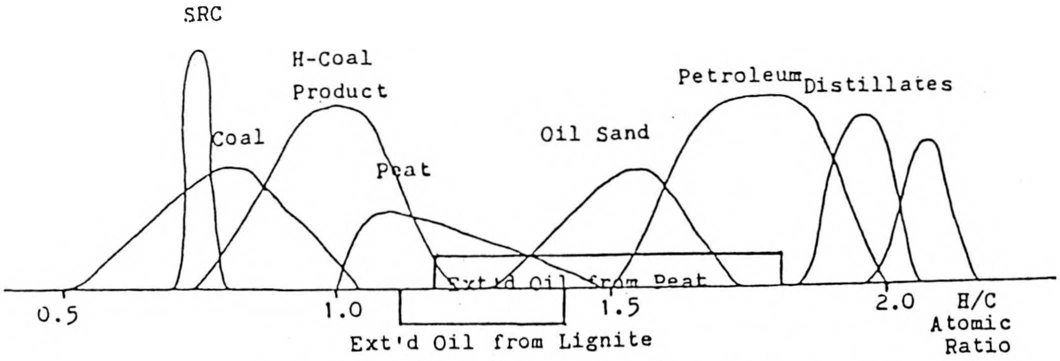


Figure 1 H/C of Coal, Petroleum, Oil Sand and Coal Liquids

SESSION 2: ENHANCED COAL UTILIZATION

SESSION CHAIRS:

MIKE MUJADIN
ANG COAL GASIFICATION CO.
BEULAH, ND

MICHAEL L. JONES
ENERGY & MINERAL RESEARCH CENTER, UND
GRAND FORKS, ND

1. "Overview of Underground Coal Gasification Issues & Opportunities"

   by: Gerald H. Groenewold
   Craig R. Schmit
   Frank W. Beaver
   Energy & Mineral Research Center, UND
   Grand Forks, ND

2. "Upgrading Experience & Studies on Australian Brown Coals"

   by: R.S. Higgins and D.J. Allardice
   Coal Corp. of Victoria, Australia

3. "Utilization of Coal-Water-Fuel Manufactured from Low-Rank Coal"

   by: W. (Bill) Irwin
   Canadian Pacific Consulting Services, Ltd.
   Calgary, Alberta

4. "LURGI's CFB Slagging Gasification the Way to Syngas, Fuelgas, & CO"

   by: P.K. Herbert and J.C. Loeffler
   Lurgi, Frankfurt, West Germany

5. "Advanced Concept for the Production of Co-Products"

   by: M.C. Jha, AMAX
   Golden, CO
   R.O. Ness, Energy & Mineral Research Center, UND
   Grand Forks, ND
   J.E. Coburn, Pellet Technology Corporation
   Houghton, MI

6. "Low Temperature Pyrolysis For Synfuel Production"

by: Radha Krishnan
Oak Ridge National Laboratory
Oak Ridge, Tennessee

7. "Assessment of Yugoslavian Lignite for Coal/Water Fuels"

by: Blazo Ljubicic and Zarko Bukarov
University of Novi Sad
T.A. Potas, Energy & Mineral Research Center, UND
Grand Forks, ND

"OVERVIEW OF UNDERGROUND COAL GASIFICATION - ISSUES & OPPORTUNITIES"

BY: FRANK W. BEAVER
CRAIG R. SCHMIT
GERALD H. GROENEWOLD
ENERGY & MINERAL RESEARCH CENTER, UND
GRAND FORKS, ND

UNDERGROUND COAL GASIFICATION - ISSUES AND OPPORTUNITIES

Frank W. Beaver, Craig R. Schmit, and Gerald H. Groenewold

INTRODUCTION

Underground coal gasification (UCG) is the process by which coal is consumed in situ in a controlled manner to produce combustible gases (Dockter, 1986). The key elements in this process, in addition to the coal, are water and oxygen. Some of the water is derived from the gasification setting, and the remainder, if needed, is injected from the surface as steam. Oxygen is introduced by injection, either in the pure form or as a component of air. Oxygen is necessary because most UCG operations occur in an inherently, chemically reducing environment below the water table. Oxygen injection provides the primary mechanism for regulating and, if necessary, ending the gasification process.

Injection of air/oxygen and steam, as well as the removal of product-gas, is accomplished using vertical or horizontal wells, or a combination of the two. Enhancement of coal-bed permeability between injection and product wells is generally required prior to the initiation of gasification to ensure maintenance of appropriate gasification rates and product-gas removal. Of the "linking" techniques that have been tested, reverse combustion and directional drilling have proven to be the most successful.

The UCG process results in product gas that can be upgraded by conventional techniques applied at the surface to yield low-grade substitute natural gas (SNG) if air injection is used and higher-grade SNG if oxygen is injected. The basic UCG product-gas constituents are hydrogen, methane, and carbon monoxide, which account for most of the heating value, as well as carbon dioxide, water vapor, and, if air is injected, nitrogen oxides. The primary sulfur species is hydrogen sulfide, the removal of which is readily accomplished using existing gas-processing techniques.

Unlike surface gasification, which is carried out in a reactor system designed, engineered, and constructed to contain and control the gasification process, in situ gasification takes place in a continually evolving hydrogeologic environment consisting of earth materials and the water moving through those materials. As a result, the UCG process and the setting are intimately interactive. This demands a comprehensive and multidisciplinary approach to in situ gasification that must begin with site characterization and be carried through all process design and evaluation phases.

It is apparent from the Rocky Mountain I (RM1) UCG test in Wyoming that UCG activities can be conducted with little or no adverse environmental impact if an integrated, comprehensive approach is taken which embraces site geological, hydrogeological, and geochemical characteristics. The next major step in advancing UCG technology to commercialization in the U.S. is the conduct of a long-term, multi-well test. Based on the results of the RM1 test, we feel that the most viable site for such a demonstration test is adjacent to the Dakota Gasification Company surface gasification facility near Beulah, ND.

DEVELOPMENT OF UNDERGROUND COAL GASIFICATION

Historical Perspective: 1896-1985

Consideration of in situ coal gasification began at least as early as 1896 (Barone and others, 1987), and speculative interest continued in the U.S., England, and the U.S.S.R. until 1928 when the first field test was conducted in the U.S.S.R. For the next two decades, UCG research and development efforts occurred largely in the Soviet Union with a major program that culminated in commercial demonstration projects in the 1950s and early 1960s. The end of World War II saw the initiation of UCG research activities in a number of other countries, most notably Great Britain and the United States, although the scope of the Soviet effort has yet to be approached anywhere. Unfortunately, Soviet research-and-development literature is largely unavailable.

The first field test in the U.S. was conducted at Gorgas, Alabama by the U.S. Bureau of Mines, but it was not until the early 1970s that the UCG research and development effort in the U.S. was focused and accelerated. Beginning in 1972, a variety of federal and private entities conducted a number of field tests generally designed to evaluate the UCG process as applied to low-rank coals in Texas, Wyoming, and finally Washington. In the wake of the last of these tests, which took place at Centralia, Washington in 1983, the status of UCG in the U.S. could be summarized as follows:

- The process, when applied to subbituminous coals, could be controlled in such a manner as to efficiently produce reasonable quantities of low- to medium-grade gas.

- Reverse "linking" to enhance permeability and, thus, gasification was the best available method, but drilled linkage offered substantial promise, particularly as a means of linking effectively over substantial distances.

- The use of horizontal process wells, either exclusively or in conjunction with vertical wells, offered the potential for both increased process efficiency and increased coal utilization.

- The use of injected oxygen rather than air produced superior process results, though optimum steam/oxygen ratios remained to be determined.

- The economics of UCG became increasingly favorable as progress continued in refining and applying the process.

- Responses to the potential environmental impacts of UCG in large part dictated the future development of the technology.

The last point was particularly critical since it required addressing commonly held perceptions that UCG was a high-impact technology and that the impacts might very well be insurmountable. This view had arisen because the tests conducted through 1983, which were process-oriented, were largely designed, sited, and conducted without the benefit of detailed site-characterization and environmental-monitoring programs. These tests had, on occasion, resulted in substantial environmental impacts. The potential effects of site geology including topography, structure (e.g. faults), stratigraphy, sedimentology, mineralogy, and hydrogeology (groundwater moving through earth material) were largely ignored. Consequently, potential prevention and mitigation measures were not apparent, leading to the perception that the impacts were inherently major and perhaps serious enough to threaten further development of the technology. Thus, the stage was set for the Rocky Mountain 1 UCG test, the first experiment to seriously address environmental impacts on the basis of detailed site characterization data.

Rocky Mountain 1 Field Test

The Rocky Mountain 1 (RM1) UCG test program in Carbon County, Wyoming was designed to respond, in large part, to both the process and environmental research needs noted above through:

- The use of horizontal holes as part of the two innovative UCG technologies being evaluated in an effort to increase both process efficiency and coal utilization.
- The evaluation of the effects of variation in the ratio of injected steam and oxygen on product-gas quality.
- The evaluation of the effects of oxygen injection rate variations on product gas quality.
- The collection of data that would be useful in evaluations of the economics of UCG.
- The conduct of an extensive environmental research and monitoring program that would involve: a) the detailed pre-test characterization of the site, b) the detailed evaluation of UCG-related environmental impacts, and c) the incorporation of environmental considerations in the test design to prevent or mitigate impacts, particularly those involving groundwater.

Furthermore, the RM1 program was designed to be managed and conducted by a multidisciplinary group of scientists and engineers representing a variety of entities including: the U.S. Department of Energy, the Gas Research Institute, Amoco, Union Pacific Resources, Lawrence Livermore National Laboratory, Stearns-Roger, Energy International, Project Construction Corporation, the Western Research Institute, and the University of North Dakota Energy and Mineral Research Center. The result, in effect, was a UCG test program that was more comprehensive and integrated than any previous UCG effort and one that was focused on both process and environmental issues. Significant progress in the development of UCG has resulted from the analysis and interpretation of the RM1 results to date.

The gasification phase of the RM1 program was completed on February 26, 1988, ending a 102-day period during which gasification was successfully undertaken for 45 days using the Extended Linked Well (ELW) technology, and for the entire 102 days using the Controlled Retracting Injection Point (CRIP) technology (Bloomstran and others, 1988). Although the analysis of process-related data will continue, it is clear that the technical objectives for this phase were largely attained.

Attempts to prevent or mitigate environmental impacts through the design of test and post-test activities at RM1 generally have proven, and are proving, to be successful. Both the collection and evaluation of environmental data are ongoing. Detailed pre-test site characterization supplemented by well-designed and carefully conducted environmental monitoring and research are, as anticipated, proving to be fundamentally important in understanding process-environment interactions. The results to date from the RM1 UCG test reveal that UCG can be environmentally safe and produce commercially valuable gas if the process is engineered and addressed by a multidisciplinary team with an emphasis on process-environmental interactions (Beaver and others, 1988a,b; Daly and others, 1987; Dindi and others, 1988; Gosnold and others, 1988; McCarthy and others, 1988). The process and environmental success of the RM1 test has provided major incentive for a UCG demonstration project in the western U.S.

ADVANTAGES OF UNDERGROUND COAL GASIFICATION

As a result of the RM1 UCG test, research and development of in situ gasification is more inviting than ever because:

- UCG product gas is comparable to the product gases from surface gasifier facilities, and therefore has the potential, upon upgrading, to be used in similar ways. This means that gas produced by in situ gasification has value in the short term as a supplement to conventional natural gas supplies, and in the long term as a source of replacement gas as conventional gas supplies dwindle.

- The RM1 program indicates that western subbituminous coal and probably lignite, are the best coals for UCG, thus placing an unforeseen premium on energy resources that otherwise are at a competitive disadvantage. Indeed, lignite, though it has by definition a lower heating value, may well be the better UCG feedstock due to its typically higher reactivity and water content.

- UCG technology can recover coal resources that are not otherwise exploitable because of the depth of the coal. For example, North Dakota has an estimated lignite resource of more than 500 billion tons. With an effective surface mining limit of 200 feet, this means that only six percent, or about 30 billion tons of North Dakota's coal resources are exploitable through mining. However, establishment of UCG as a viable gas-production technology to a depth of only 1500 feet would allow consideration of the remaining 90 percent, or 450 billion tons of coal, for exploitation. If only an additional ten percent of the coal proved exploitable by UCG, North Dakota's accessible energy-resource base would be increased dramatically, which would substantially benefit the state's and nation's long-term energy and economic outlook.

- The cyclic employment nature of current extractive mining technologies can be largely eliminated because of the continuity that long-term UCG operations would demand. There would also be an ongoing demand for skilled trades such as drilling and pipe fitting.

- UCG has the potential to be an economically competitive energy technology. According to a recent study done for the Gas Research Institute by Williams Brothers Engineering Company (Hill and others, 1984), UCG offers a projected scenario in which cost savings can largely be attributed to two areas: 1) low coal acquisition and handling costs reflecting the use of unmineable coal instead of the utilization of mined coal, and 2) lower capital costs associated with field systems that are basically composed of drilled wells and piping networks for injection and product gases, with limited support facilities.

- UCG emission and subsidence impacts are manageable. Process-related emissions and solid and liquid wastes at the surface are all minimal, as are surface and surface-water disruptions resulting from construction and support activities. Subsidence can likely be minimized by choosing coals for gasification only after a careful consideration of both the depth of the coal and the expected response of the overburden to extreme thermal conditions and high-stress conditions resulting from cavity development.

- The potential impacts on groundwater occurrence, flow, and quality can be minimized. The potential is significant for groundwater to be seriously impacted by in situ gasification because of the intimate relationship that exists between the UCG process and the hydrogeological setting within which it takes place. Not only does UCG affect the amount of groundwater in the area and the local groundwater flow conditions, it can also promote changes in the chemistry of the groundwater. However, the RMI test program, in particular, is providing conclusive evidence that it is possible to site, design, and conduct UCG operations so as to: 1) promote efficient use of the local groundwater during gasification, 2) control the migration of potential process-related contaminants and, therefore, the resulting changes in groundwater chemistry, 3) maintain process efficiency, and 4) allow the subsequent reestablishment of baseline conditions without the need for extensive remediation efforts.

- UCG would allow recovery of deeper coal in greater quantities, and could result in minimal or no disruption of potable groundwater resources by leaving shallow coal aquifers intact. Shallow coal seams are typically a valuable source of potable groundwater. Surface mining and reclamation typically result in groundwater that is two to three times more mineralized than groundwater originally found in coal aquifers. These shallow, presently mineable coal seams may ultimately be more valuable as groundwater sources than for the energy extracted.

- If UCG is conducted in an area that has also been surface mined to maximum depth, then maximum energy can be extracted with respect to the area disturbed and reclamation bond posted. Thus, UCG would provide for significantly increased energy-extraction efficiency.

- Our coal reserves are much more extensive than our petroleum reserves. UCG technology can allow us to take advantage of a secure energy resource that would be less sensitive to disruptions of any kind.

- UCG may be a viable component of scaled, integrated, combined-cycle, gas-turbine, power-generating facilities.

FUTURE OF UNDERGROUND COAL GASIFICATION

In spite of the significant progress that has resulted from the RM1 test program with respect to answering the technical and environmental questions surrounding UCG, the fact remains that it was a relatively short test involving only a few process holes. If progress toward commercialization of this very inviting technology is to continue, a long-term (12 to 24 months), large-scale (multi-well and multi-module) demonstration is an absolute necessity. Only with a thoughtfully designed, appropriately sited demonstration program of this scope can the variety of questions unique to commercial-scale UCG operations be adequately addressed. The RM1 UCG test has set the stage for the next step toward commercialization. The factors that remain to be addressed include:

- The sequential development of cavities in a manner that will ensure the maintenance of process efficiency, while minimizing the impacts to the environment.

- The UCG process-design technology that will be most effective over the long term.

- The process-well array that will promote the desired development of individual cavities and cavity sequences to ensure maximum gas production and resource utilization.

- The potential hydrogeological impacts in response to both the large amount of water that will be utilized and the substantial amounts of contaminants that may be generated.

- The environmental monitoring requirements necessary to adequately provide ongoing evaluation of impacts without imposing unnecessary regulatory burdens on the operator.

- The disposition of the large quantities of gas that would be generated by such a test.

SUMMARY - DEMONSTRATION PROJECT

UCG research and development to date indicates the necessity of a long-term, large-scale demonstration project to bring the technology to full commercialization. A very practical aspect of this process is the disposition of the large volume of gas that would be produced. The smaller-scale UCG tests produced quantities of gas that were small enough to be flared; this is not a viable option for a test of the type now required. Another option, transportation of the gas by pipeline, is simply not economical for more than a very short distances. The best solution is to use the gas close to the site of the test. The foremost such site is almost certainly the area in the vicinity of the Dakota Gasification Company (DGC) facility near Beulah, North Dakota. An association with the plant would allow the UCG product gas to be processed and used as a replacement for the liquid by-products of the surface gasification process, which are presently used as fuel but have more value as feedstock for the production of chemicals. An additional benefit associated with the area around the Great Plains plant is the available coal resource, which is typically highly reactive, has a high moisture content, and is located at depths of approximately 1100 feet in beds that are generally flat-lying, continuous (traceable for tens of miles), and, in several cases, 10 to 25 feet thick. Finally, the overburden in the area is well-suited for UCG, and the groundwater resources appear to be adequate to support a project of this scale. These combined conditions at the Great Plains plant site provide a unique opportunity for a UCG demonstration project.

A suggested outline for the required demonstration project follows:

1. Identification of UCG Project Support.

2. Identification of UCG Technical Advisory Team.

3. Identification of UCG Project Management Team.

4. Preliminary Economic Evaluation.

5. Site(s) Identification:

   A. Surface Ownership.
   B. Mineral Rights.

6. Characterization of Potential Sites to Establish Environmental Baseline

   A. Design/Selection/Installation of Monitoring Equipment:
      1. Drilling/Coring.
      2. Geophysical Logging.

        3. Seismic Surveys.
        4. Geothermal Probes.
        5. Hydrogeological Instruments:
            a. Piezometers.
            b. Water Table Wells.
            c. Lysimeters.
            d. Gas Sensors.
            e. Pressure Transducers.
        6. Integrated Control System.

    B. Collect Field Data:
        1. Geological:
            a. Topography.
            b. Stratigraphy.
            c. Structure.
            d. Mineralogy.
            e. Geochemistry.
            f. Coal Quantity.
            g. Coal Quality.
        2. Hydrogeological:
            a. Groundwater Occurrence.
            b. Groundwater Flow.
            c. Groundwater Quality.
            d. Groundwater Recharge Potential.

7. Site Selection Based on Candidate Site Evaluation.

8. Engineer UCG Process to Accommodate the Site and Economic Considerations.

9. Establish Environmental Monitoring Program.

10. Interface UCG Operations with DGC Facility.

11. Establish Process Monitoring.

12. Interface Environmental and Process Monitoring.

13. Initiate Test Burn.

14. Conduct Process Experiments.

15. Continue Environmental/Process Monitoring.

16. Ongoing Process/Economic Evaluation.

17. Termination of Test.

18. Evaluation of Experiment.

19. Commencement/Continuation of Commercial Operations.

We submit that the long-term, large-scale UCG demonstration project outlined above, and conducted in concert with the Dakota Gasification Company facility at Beulah, ND, is the most viable option available to enhance and stabilize North Dakota energy-resource utilization. Experienced professionals with the necessary expertise are available but may become dispersed in the near future if immediate consideration is not given to the continued advancement of the technology. We believe that this technology could become a secure cornerstone for energy independence and economic growth in North Dakota and other areas of the northern Great Plains.

REFERENCES

Barone, S.P. and Malavasic, K.F., 1987, Underground coal gasification: Overview of an energy alternative: Unpublished supplement to Proceedings of the Fourteenth Biennial Lignite Symposium on the Technology and Utilization of Low-Rank Coals, 14 p.

Beaver, F.W., Daly, D.J., Groenewold, G.H., and Schmit, C.R., 1988a, The role of detailed site characterization in undergound coal gasification operations: Examples from the Rocky Mountain 1 test, Carbon County, Wyoming (abstract), in Proceedings of the Fourteenth Annual Underground Coal Gasification Symposium: (in press).

Beaver, F.W., Groenewold, G.H., Schmit, C.R., Daly, D.J., Evans, J.M., and Boysen, J.R., 1988b, The role of hydrogeology in the Rocky Mountain 1 underground coal gasification test, Carbon County, Wyoming, in Proceedings of the Fourtheenth Annual Underground Coal Gasification Symposium: (in press).

Bloomstran, M.A., Galyon, G.D., and Davis, B.E., 1988, Rocky Mountain 1 UCG Operations: Submitted for publication in Proceedings of the Thirteenth Annual Underground Coal Gasification Symposium, 10 p.

Daly, D.J., Groenewold, G.H., and Schmit, C.R., 1987, The evolution of the design of environmental research associated with UCG: in Martin, J.W., and Barone, S.P., eds., Proceedings of the 13th Annual Underground Coal Gasification Symposium: DOE/METC-88/6095, pp. 309-316.

Daly, D.J., Stevenson, R.J., and Schmit, C.R., 1988, Natural coal combustion pyrometamorphism: Relevance to underground coal gasification, in Proceedings of the Fourteenth Annual Underground Coal Gasification Symposium: (in press).

Dindi, H., McCarthy, G.J., Stevenson, R.J., and Krantz, W.B., 1988, Laboratory characterization of overburden cores from Rocky Mountain 1 UCG test site, in Proceedings of the Fourteenth Annual Underground Coal Symposium: (in press).

Dockter, L., 1986, Underground coal gasification in the United States: A review, in Proceedings of the Twelfth Annual Underground Coal Gasification Symposium: United States Department of Energy Report DOE/FE/60922-H1, p. 2-13.

Gosnold, W.D., Beaver, F.W., and Schmit, C.R., 1988. Groundwater temperatures at the Rocky Mountain 1 underground coal gasification site, Carbon County, Wyoming, in Proceedings of the Fourteenth Annual Underground Coal Gasification Symposium: (in press).

Hill, V.L., Burnham, K.B., Barone, S.P., Rosenberg, J.I., and Ashby, A.B., 1984, Underground coal gasification: Its potential for long-term supply of SNG: Gas Research Insights (Gas Research Institute in-house technical series), 18 p.

McCarthy, G.J., Stevenson, R.J., Oliver, R.L., and Hassett, D.J., 1988, Mineralogical characterization of the residues from the Tono I UCG experiment: in Proceedings of the Fourteenth Annual Underground Coal Gasification Symposium: (in press).

"UPGRADING EXPERIENCE & STUDIES ON AUSTRALIAN BROWN COALS"

BY: R.S. HIGGINS
COAL CORP. OF VICTORIA
AUSTRALIA

UPGRADING EXPERIENCE AND STUDIES ON AUSTRALIAN BROWN COALS

by

R. S. Higgins, D. J. Allardice and G. J. Perry
Coal Corporation of Victoria
P. O. Box 428, Traralgon, 3844.
Victoria, Australia.

ABSTRACT

The extensive low rank coal deposits in Victoria, Australia, are estimated at over 200,000 million tonnes (Mt) of which about 33,000 Mt are readily recoverable reserves using present day open cut mining technology. At current rates of consumption these reserves would last over 800 years. Over the past 60 years the coal has been primarily used for power generation, although significant quantities have been used for the production of briquettes, town gas and char.

The Victorian State Government recognises that these coal resources are one of the State's key competitive strengths for economic development. The unique properties of the coal, together with the ease of open cut mining, make it suitable for a variety of new applications. Research and development activities are centred around applications which take advantage of the natural attributes and unique properties of the coal. The high reactivity and low ash content of the coal led to its selection for the Japanese brown coal liquefaction pilot plant currently operating in the Latrobe Valley, with support from Victoria.

Research and development of new brown coal based products together with many other areas of applied and fundamental research are being conducted in Victoria by Government research organizations, tertiary institutions and private industry, with the objective of establishing new industrial developments based on Victoria's vast brown coal resource.

Presented to "Opportunities in the Synfuels Industry" Symposium, Bismarck, North Dakota, August 1988.

1. BROWN COAL RESOURCES IN VICTORIA

In 1982 the Victorian Brown Coal Resource Development Study conducted by Kinhill Pty Ltd and associates (1) estimated the total geological resource of brown coal in Victoria to be 197,000 Mt (coal with less than 10% ash content, dry basis). More recent estimates have increased this figure to over 200,000 Mt (2, 3).

85% of the State's brown coal resource is located in the Gippsland Basin, the bulk of it in the Latrobe Region and within 300m of the surface. It has been estimated that a further 220,000 Mt of coal could occur in deep deposits within the Gippsland Basin (3), particularly offshore.

Smaller deposits occur in the Otway Basin (9,000 Mt) and the Murray Basin (20,000 Mt).

Kinhill (1) estimated that 54,000 Mt could be recovered with current open cut technology. However some of these reserves have specific constraints on their development and by exclusion of coal under townships and environmentally sensitive areas this 54,000 Mt of "usable coal" has been reduced to about 33,000 Mt of "readily recoverable coal". More than half of this recoverable coal is located in the central Latrobe Valley area.

An illustration of the significance of the Victorian brown coal reserves can be seen in Table 1 which compares the ratio of reserves to production for low rank coal (brown coal and lignite) producing countries of the world. This table shows that while Australia ranks second in brown coal reserves to USSR, it only ranks eighth in production. When the reserves to production ratio is considered, Australia with over 800 years is more than double that of most other countries, although USSR and USA both have over 500 years. In contrast the ratio for East Germany, the largest producer, is only 43 years.

By any standard, it can be seen that brown coal provides Australia and particularly Victoria with a resource which is largely under-utilized and offers substantial economic opportunities for future development.

2. BROWN COAL PRODUCTION

Coal production from the Latrobe Valley open cuts during 1986/87 was 40.50Mt and came from -

Yallourn North Extension Open Cut	0.21 Mt
Yallourn Open Cut	17.36 Mt
Morwell Open Cut	12.07 Mt
Loy Yang Open Cut	10.86 Mt

Brown coal was also mined outside the Latrobe Valley at Angelsea, 1.16 Mt, and Bacchus Marsh, 0.04 Mt.

The open cuts in the Latrobe Valley are unique because of the very thick coal seams and relatively thin overburden. Overburden varies from 10 to 30 m in thickness and the depth of coal varies from 60 m to a maximum in the Loy Yang open cut of 220 m so very high ratios of coal to overburden are achieved in practice. The overburden which contains no hard rock, consists mainly of a mixutre of sand and silicious clay, and bucket wheel excavators are used for both stripping overburden and recovering coal. The largest machines in operation in the Latrobe Valley are the 60,000 t/d bucket wheel excavators in the Loy Yang Open Cut.

Loy Yang open cut is the newest and potentially the largest open cut. It commenced production in 1984 and is designed to develop a capacity of 32 Mt/yr by the mid 1990's when it could be supporting 4000 MW of power generation.

The State Government through a "Coal For Industry Program", has announced that at least 5 Mt/yr of Loy Yang coal could be made available for processing by industry.

3. QUALITY OF VICTORIAN BROWN COAL

Victorian brown coal has been extensively surveyed and a comprehensive data base has been assembled on the properties, characteristics and utilisation parameters of the coal (4).

Latrobe Valley brown coals are soft and strongly banded, due to variations in depositional environments causing the formation of different coal types or lithotypes. Five lithotypes, based on colour, texture, degree of gelification, compaction of ground mass etc have been distinguished in Latrobe Valley coals (5). The presence of these coal types contributes to the variability in chemical and physical properties within coal seams (6).

Typical values for important coal properties for Latrobe Valley brown coals are shown in Table 2.

For a proper assessment of coal quality not only the properties of a coal must be considered, but also requirements of the the intended applications. The primary assessment of the quality of a low rank coal is usually for combustion and is based on bed moisture, ash content and net wet specific energy. The high moisture and oxygen contents of brown coals are usually considered major disincentives for its utilization, however, as will be shown later these properties are beneficial for some potential applications.

Average moisture contents of coal in the Latrobe Valley ranges between 52% and 67% bed moisture. The bed moisture is substantially higher than the moisture holding capacity of these coals (equilibrium moisture content at 97% relative humidity and 30°C), which varies from 31% to 42% (6).

Apart from thin bands of inferior coals (greater than 10% ash) normally found near the top and bottom of coal seams, the average ash contents of Latrobe Valley coals range between 1% and 5% on a dry basis. In areas of the Loy Yang deposit, substantial quantities of coal with less than 1% ash occur. The level of minerals and inorganics are generally lower than the ash (or ash yield) due to the high relative levels of exchangeable cations associated with the coal compared to discrete minerals. (7). Sodium, calcium, magnesium, iron and aluminium are frequently present in intimate combination with the coal substance as salts of carboxylic acids.

The occurrence of minerals is sporadic, is of less significance and is usually restricted to quartz, kaolinite, pyrite and marcasite.

Certain inorganic cations present can affect the combustion and fouling properties of the coal (8). High levels of calcium and magnesium lead to the formation of carbonates during hydrogention leading to reactor blockage problems (9). Calcium is also believed to contribute to the inferior weathering properties of briquettes manufactured from Morwell brown coal, compared with the better Yallourn coal on which briquette production is now based.

The Latrobe Valley coals show variations in ultimate analysis between seams and also within seams with changes in lithotype. While average values are listed (Table 2), observed variability can be (on dry basis); Carbon 64 to 71 per cent, Hydrogen 4.4 to 6.6 per cent, Oxygen 19 to 28 per cent, Sulphur 0.1 to 5 per cent, Chlorine 0.02 to 0.6 per cent and Nitrogen is fairly constant at approximately 0.6 per cent.

The high concentration of oxygen, present in the carboxylic, hydroxyl and carbonyl functional groups of the coal substance, is the most notable aspect of the ultimate analysis. The H/C ratio of brown coal approximates that of a high volatile bituminous coal, although much of this hydrogen is associated with oxygenated functional groups and is released as water during pyrolysis.

The high moisture contents of the brown coals are reflected in their relatively low net wet specific energies, which range from 6.5 to 11.5 MJ/kg (2800 to 4950 BTu/lb). All seams show a slight increase in specific energy with increasing depth beneath the surface, although significant variations with lithotype are also apparent.

4. UTILIZATION OF BROWN COAL IN VICTORIA

4.1 ELECTRICAL POWER GENERATION

Power generation has been and will continue to be the major user of brown coal for the foreseeable future.

Currently the total capacity of installed power generation plant in Victoria based on brown coal is 5460 MW, which generates about 85% of the electricity supplied to the State. The Loy Yang project, reflecting current projections in electricity demand, has been committed to 3000 MW with a decision on the timing for the final two 500 MW units deferred at this stage.

4.2 BRIQUETTE PRODUCTION

Briquettes produced from Yallourn coal have been available in Victoria since 1924 and production reached a peak of 1.9 Mt per year during 1966 but has declined since low cost natural gas became available from Bass Strait.

In 1986/87, 0.852 Mt of briquettes were produced (nominal design production capacity at the Morwell briquette factory is 1.3 Mt per year) from 2.3 Mt of process coal; the optimum production capacity at the Morwell briquette factory is now assessed to be 1.1 Mt per year, in view of the price of competing energy sources, the operating cost of the plant and the value of cogenerated electricity.

The briquettes are manufactured from Yallourn brown coal which is crushed to -8 mm, dried from its initial moisture content of 66% to 15%, and extrusion pressed without the addition of any binder in an Exter reciprocating ram press (Figure 1). The briquetting pressure is 9-12 MPa (6-8 tons/sq. in.) (10).

The uniformly shaped briquettes (nominally 58 x 37 x 43 mm) can be stored conveniently, transported economically, are readily ignitable and, given suitable equipment, can be burned slowly or at high rates. The net heating value of 21.3 MJ/kg, together with the low ash content (2.1% dry basis) and the low sulphur content (0.3% dry basis) make briquettes ideal for solid fuel heating applications and as a feedstock for value-added products.

The responsibility for briquette distribution and marketing was transferred to the Coal Corporation of Victoria on 1 January 1985 and new strategies are being vigorously pursued to increase export sales, as well as sales to Australian domestic and industrial customers. The past decline in briquette sales is being reversed based on the increased local use of briquettes as an industrial fuel and through exports. Exported briquettes are used as a fuel (domestic and commercial) and as a chemical feedstock for humic acid production for use in fertilizer mixes, and, potentially to produce activated carbon.

It should be recognised that the capital value of the briquette production facility has been fully written off and the briquette business is now being operated on a direct cost, marginal basis.

4.3 BRIQUETTE USE

Briquettes have been used for power generation, steam raising, industrial and domestic heating, town gas production and char production.

Consumption in 1986/87 was

- 240,000 t for use as auxiliary fuel in power stations
- 540,000 t to the industrial sector
- 50,000 t for export, and
- 20,000 t for domestic use.

The industrial sector covers use in boilers, ranging in capacity from less than 1 MW to 60 MW, and in a variety of furnaces and kilns.

The largest industrial boilers currently in service burning briquettes consume 30 t/hr using a spreader stoker fuel feeding system. Prior to 1983 power generating boilers using mill firing systems were in operation.

A wide variety of combustion systems are in use - mill firing for larger boilers, spreader stokers with moving grates, fixed grates or pneumatic feeders.

At the present time the largest industrial consumption is for the production of char, see Section 4.5, and other major industrial users are hospitals, the dairy industry and paper manufacturing. There are promising prospects for new ferrous and non-ferrous metallurgical reductant applications where the high reactivity, low ash and low sulphur provide unique advantages.

4.4 TOWN GAS MANUFACTURE

From 1956 to 1969 a Lurgi high pressure steam-oxygen gasification plant was operated using briquettes as a feedstock by the Gas and Fuel Corporation of Victoria. The plant ceased operation when Melbourne was converted to natural gas from the Bass Strait oil and gas fields.

The gasifiers were 2.5 m internal diameter Lurgi units with rotating step grates and solid ash discharge systems (Figure 2).

The initial Morwell plant was designed to produce approximately 425,000 m^3 per day of purified gas from six generators operating on a five plus one basis. In fact, it achieved a specific output per gasifier approximately double the design level. Although it was often down to two or three generators on line in the initial years due to operational problems, the plant was able to maintain an average output of 350 - 370,000 m^3 per day. After initial problems were overcome, plant output was consistently above the design level. In the early 1960's, output averaged 470 - 490,000 m^3 per day whilst in the final year of operation, the plant produced at the rate of approximately 650,000 m^3 of purified gas per day from six generators operating on a four plus two basis.

The plant produced town gas with an energy value of 16.4 MJ/m^3 at a rate of 1020 m^3/t of briquettes (thermal efficiency 76.8%). In its final year the plant consumed 229,000 t of briquettes compared with the original design capacity of 144,000 t.

Briquettes from Yallourn brown coal proved to be an excellent feed stock for the Lurgi gasifier. There were only two coal related problems experienced:

- high values of SiO2 in ash caused ash fusion under reducing conditions and consequent problems with the ash extraction system, and
- the low nitrogen content of the coal meant that ammonia production was low and resulted in crude gas condensate of low pH and aggressively corrosive characteristics.

Process and technology developments were made to overcome these problems (11).

4.5 CHAR PRODUCTION

Since 1970 Australian Char (Holdings) Pty Ltd has been manufacturing industrial carbon by carbonising Yallourn coal briquettes using direct-heating from circulating hot gases in vertical retorts. The process operates with a carefully controlled temperature profile through the retort to a final temperature of 800 °C. This minimises breakage and loss of lump strength in carbonising whole briquettes (12).

The product is a hard lump char (25 mm nominal diameter), and has a high purity (95% fixed carbon and low levels of contamination by iron, phosphorous, vanadium and titanium). It is marketed for use as a metallurgical recarburiser and reductant, and as a electrochemical reductant and chemical feedstock.

The annual production of this lump char is nominally 60,000 tonnes and in 1987/88 Australian Char processed 145,000 tonnes of briquettes. About 75% of the char is exported.

Australian Cement Ltd at Traralgon also produces char by carbonising briquettes in a partial combustion type retort from which the hot gases are used for drying the marl. Most of the char is used as an integral fuel in pelletised clinker which is fired in a vertical cement kiln. The plant produces about 18,000 t of char per annum.

A small proportion of the brown coal char produced in Victoria is the principal component in a high quality barbeque fuel.

4.6 AGRICULTURAL USES

Within Victoria there has been a small market for brown coal as a moisture holding, sterile, humus additive to potting mixes and similar special purpose agricultural products. Consumption is probably around 10,000 tonnes of coal/year for such purposes.

Some briquettes are exported to manufacturers of high value fertilisers for the production of humic acids. About 5,000 tonnes/year are supplied for this purpose.

4.7 ACTIVE CARBONS

Some exported briquettes and char have been used as feedstock for the production of activated carbons, but it is not known what quantities have been applied for this purpose. In addition, small scale commercial production of activated carbons from briquettes was trialled in Victoria in the 1970's (13).

4.8 PULVERISED DRIED BROWN COAL

During the years 1948 to 1953 and prior to the advent of diesel-electric locomotives, the Victorian Railways and State Electricity Commission of Victoria developed the technology for firing steam locomotives on pulverised dried brown coal (14).

Although this application was considered to be both practical and economic, the locomotive fleet was not converted as it became obvious that steam locomotives would be replaced by diesel-electrics.

5. AVAILABILITY OF BROWN COAL FOR NEW INDUSTRIES

The Victorian Government has identified the State's brown coal resources as one of its key competitive strengths for future economic development. The Government has therefore agreed to provide private enterprise with access to this low cost, high quality brown coal in the central Latrobe Valley. Previously this attractive coal had been reserved for future power generation.

To encourage this initiative the Coal Corporation of Victoria is offering at least 5 Mtpa of high purity Loy Yang coal as part of the "Coal For Industry Program". Low coal prices can be achieved by taking advantage of the economics in scale of operation at the Loy Yang Open Cut which will produce up to 32 Mtpa for electricity generation.

Run of mine Loy Yang coal is one of the lowest cost, high purity, organic carbon feedstocks available in commercial quantities in the world today. The weighted average and distribution of moisture, ash, specific energy and the main coal constituents over the whole open cut are given in Table 3. The data illustrate that Loy Yang coal is ideally suited to many premium applications due to its low levels of ash forming constituents and low content of specific elements of concern in potential applications.

In the late 70's and early 80's the dominant development interest was in converting Victorian brown coal to oil, with several significant project proposals submitted. Sophisticated liquefaction technologies are now financially unattractive with the present atmosphere of reduced oil prices.

Interest has shifted to value added products such as activated carbons and carbon reductants (chars) and to upgraded solid fuels (although the depressed export coal prices have reduced interest in this prospect).

Resulting from this program, one new carbonisation pilot plant is operating in the Latrobe Valley and detailed feasibility studies are under way on several value added product projects. The Coal Corporation of Victoria is confident that 1988/89 will see further progress towards new commercial applications based on Loy Yang Coal.

6. OPPORTUNITIES FOR INCREASED USE OF BROWN COAL

6.1 DEVELOPMENT OF BROWN COAL LIQUEFACTION TECHNOLOGY

From 1933-1938, a major research project on direct hydrogenation of Victorian brown coals was conducted at the Fuel Research Station U.K. by Baragwanath (15). The coal showed significant potential for liquefaction using the Bergius approach.

In the late 1970's coal research and development programs focussed heavily on conversion of coal to oil. In this regard, brown coals commanded special interest because of their high reactivity in liquefaction processes. The most active of the programs led to the Brown Coal Liquefaction (Victoria) pilot plant.

Other significant liquefaction studies on Victorian brown coal were conducted in West Germany by Rheinbraun as part of the Australian/FRG Joint Coal to Oil Feasibility Study (the Imhausen Study), by Mitsui SRC Co. in Japan, in the H-Coal process and in the Co-Steam process in North Dakota.

Although the urgency for such developments has diminished, there is still a case to continue these efforts to establish technology as a contingency against major disruptions or price increases in the world oil trade. While many of the world's major synfuels projects have been dropped, some brown coal projects are still active.

The Brown Coal Liquefaction (Victoria) Pty. Ltd. (BCLV) project, operated by a Japanese consortium at Morwell in the Latrobe Valley, is the largest low rank coal liquefaction project in the world. It uses a two stage hydrogenation process developed specifically for Victorian brown coal following preliminary studies going back to 1974 (16).

The construction cost of the pilot plant exceeded $A500 million, and the annual budget is $A70 million. The Japanese Government provides the bulk of this funding. Construction of Stage 1 began in November 1981 and it started-up in November 1985; construction of Stage 2 is also complete and integrated operation with Stage 1, to produce liquid transport fuel, is now in progress.

Stage 1 converts 50 t/d (dry coal basis) of brown coal to 30 t/d coal liquefied bottoms (CLB or solvent refined coal) and 5 t/d naphtha. The first stage uses a once through catalyst operating at 200-250 bar and 430-460 °C. In Stage 2, the CLB intermediate is further refined to produce a total yield of about 25 t/d of middle distillate and naphtha. The pilot plant represents a scale-up factor of 100:1 from the mini-pilot plant which has operated since 1979 at Kobe in Japan. Operation of the Morwell pilot plant is scheduled to continue until at least late 1989, and could be further extended.

While the current development at the BCLV coal to oil plant will continue on strategic grounds, this technology may not be economic until early next century. Nevertheless, the fact that the project is continuing reflects the Japanese Government's awareness of the strategic importance of having coal liquefaction technology available, despite the present depressed world oil prices.

6.2 PREPARATION OF ACTIVATED CARBONS

Among the unique characteristics of Victorian brown coals are their high surface area and porosity. These features are preserved and enhanced in carbonisation and make them ideal feedstocks for activated carbon production (13).

Activated carbon is an important adsorbent used in industrial and environmental applications and currently Australia imports all of its activated carbon requirements. In 1985/86 this amounted to 4263 tonnes with an average cost per tonne of over $A2000. The direct production of activated carbons from low cost, high purity brown coal derived feedstocks represents an attractive opportunity for development of a new brown coal based industry in Victoria for both local and export sales.

The Coal Corporation of Victoria, in a joint venture, has operated a 1 t/day pilot plant to produce activated carbons from a variety of brown coal derived feedstocks. Using this pilot plant good yields of medium to highly activated carbons have been obtained from brown coal char and briquette grus.

Laboratory scale investigations by the Corporation are continuing to prepare attrition-resistant carbons with high activity from brown coal. Attrition resistance is particularly important if carbons are used by the gold mining industry in the carbon-in-pulp (CIP) process. Both physical and chemical modification of brown coal feedstocks have been investigated to overcome the inherent softness of brown coal and produce activated carbons with acceptable levels of hardness.

In this work, digestion of brown coal with alkali promotes the collapse of the pore structure and the release of humic acid material. After drying this alkali treated coal forms a dense, relatively homogenous, gellified, brittle material, (17). Incorporation of potassium cations has been found to yield carbons of high surface area (1100 m^2/g) when this alkali treated coal is carbonized (18).

By the use of alkali digestion together with additional chemical modification followed by carbonization and/or steam activation, hard activated carbons with high surface areas can be produced from Victorian brown coal. Some of these carbons show an excellent capacity for adsorption of gold from cyanide solutions and therefore have potential to satisfy the stringent requirements of the CIP gold industry. This technology has signficant potential for commercialization.

Research is also being conducted on brown coal derived carbon adsorbents for compressed natural gas as a transport fuel (CNG).

6.3 ION-EXCHANGE MATERIALS FROM BROWN COAL

The high oxygen content of Victorian brown coal, half of which is attributable to the coal's carboxylic and phenolic functional groups, together with the coals large internal surface area make brown coal a potential medium for ion exchange. It has been found that pre-loading the coal with an alkali metal e.g. calcium, enhances the ion exchange capacity of the coal. (19). The use of calcium loaded brown coal has achieved 99% removal of metals from 1000 ppm solutions of copper, lead, mercury, uranium and cobalt. (19).

However Loy Yang brown coal without pre-treatment can also remove, by ion exchange, metal ions from aqueous solution to a significant extent (20). The degree of metal removal is dependent on the pH of the solution, the particular metal ion and its concentration.

Victorian brown coal due to its ion-exchange properties has the potential to remove metal species from industrial waste waters or hydrometallurgical liquors in a cost effective manner. Commercial prospects are being evaluated.

6.4 AGRICULTURAL/HORTICULTURAL APPLICATIONS

Victorian brown coal has many chemical and physical properties in common with soil organic matter which are essential to soil fertility. These properties include high water holding capacity, good nutrient holding capacity (due to ion-exchange) and open friable structure. It is believed that the high humic acid content of Victorian brown coal could play an important role in agricultural applications due to the plant growth promoting properties of humic acids. (21, 22).

Research work is also being conducted to use brown coal as a fertilizer support, by enriching the coal in nitrogen and phosphorus.

This is one of the few uses for brown coal where the high moisture content is not a disadvantage, as drying is not essential prior to horticultural or agricultural application.

6.5 DRIED BROWN COAL FUELS

With the prospect of the production capacity of the existing briquette factory being fully committed in the near future, efforts are continuing to identify lower cost methods for producing additional dried brown coal fuels.

A consultant study "Comparison of Technologies for Brown Coal Drying"(23) was conducted in 1984 to provide an independent and objective comparison, on both technical and economic grounds, of the diverse range of brown coal drying technologies that are either available now or under development. The costing of conventional drying technologies for brown coal is being kept under review, and development is continuing on a number of novel processes.

- **Solar Dried Brown Coal**

A Solar Dried Brown Coal Slurry pilot plant with a nominal capacity of 2200 t/yr has been constructed and operated in the Latrobe Valley by the State Electricity Commission of Victoria with Australian Government support. The process (Figure 3) requires wet milling of coal with water to a pumpable slurry which is dried in open-air ponds to provide a dense lump product (24). The test program is essentially complete and detailed evaluation of the data is under way.

Solar Dried Brown Coal has potential for low production costs at small-scale (350,000 t/yr) (23). However it does not benefit from economies of scale to the same extent as other drying technologies.

The process requires large land areas and the production is seasonally variable depending on climatic conditions.

- **Steam Fluidized Bed Drying**

Potter at Monash University (25) has developed a multiple effect steam fluidized bed drying process to produce fine granular dried brown coal. The multiple effect concept (steam from one stage providing heat for another) has the potential for low production costs and significant economies of scale (23).

A single stage varient of steam fluidised bed drying has been demonstrated in East Germany (26) and is also being investigated in West Germany. This technology has considerable potential for commercialisation.

- **Continuous Fleissner Process**

Brown coal can be dewatered by heating to above 200°c in autoclaves. Chemical change (essentially decarboxylation) at this temperature makes the coal hydrophobic and moisture contained in the coal is exuded in a liquid form.

Such non-evaporative processes have the added advantage of producing a lower fouling fuel, since dissolved inorganics, particularly sodium, are removed with the expelled liquid.

The conventional batch Fleissner process was developed for lump coal in Austria in the 1920's. An improved continuous process capable of handling a range of feed coal sizes with improved economics is now under development (27). Tests on Victorian brown coal have been encouraging and the feasibility of a demonstration plant is being assessed.

6.6 COAL WATER MIXTURES

Coal Water Mixtures (CWM) are attracting attention around the world as substitute fuels for oil, particularly in stationary combustion systems. With Victorian brown coals, the high initial moisture content of the coal leads to unacceptably low solids loadings, around 30%, in a pumpable coal-water mixture slurry, although the low ash content is a distinct advantage.

By heating the slurry under pressure, thermal dewatering occurs by the mechanism described for Fleissner above. This can lift the solids loading (after separation of water by centrifugation or other means) of a pumpable slurry to 60% for hard lignites, and to around 50% for Victorian brown coal. This process is being developed at the University of North Dakota for US lignites (28) in a pilot plant processing 2t/d at up to 330°C. It is a slurry version of the Evans-Siemon thermal dewatering process (29) which is essentially Fleissner drying in hot water rather than steam.

More recent work on Victorian brown coal at the University of Melbourne (on rheology) and Swinburne Institute of Technology (on coal surface properties) has demonstrated the potential, by a combination of drying and chemical densification of coal, to produce brown coal water slurries with more than 60% solids loading (30). This could produce a premium low ash, low sulphur, liquid fuel with an energy value considerably in excess of the original raw brown coal.

The successful development of brown coal-water mixtures with acceptable solids content would open many new avenues for brown coal utilisation with increased convenience and safety of the fuel. Potential applications include injection into pressurised fluid bed combustors or gasifiers (to overcome coal feeding problems) and slurry fuel injection into boiler furnaces, coal fired gas turbines and other industrial process heat applications. In the longer term there are opportunities for pipeline transport to coastal storage, for export or large scale power generation.

6.7 DRIED BROWN COAL COMBUSTION DEMONSTRATIONS

To facilitate the wider use of brown coal and dried brown coal fuels in industrial process heat applications, the Coal Corporation is supporting the demonstration of improved combustion technologies.

Studies in conjunction with CSIRO (31) have demonstrated the suitability of Victorian brown coals for combustion in fluidized bed systems, preferably in predried form, although Yallourn North Extension coal, with its lower moisture content (52%), was successfully burnt in ROM form (31).

A skid-mounted Tas-coal microniser and Stordy burner unit have recently been constructed for the Corporation, to demonstrate the potential for pulverised dried brown coal as an industrial fuel in Victoria (Figure 4 (32). The unit has a 3 MWt capacity, a 6 to 1 turn down ratio, and is designed to operate in an unattended mode.

The unit has successfully burnt briquettes and dried brown coal fuels (including solar dried brown coal). It is now intended to mount the unit in an operating boiler to further demonstrate its potential for unattended operation. Achieving unattended operation rating is essential if coal fired equipment is to compete commercially with comparable gas fired units which in Victoria have unattended rating up to 6 MWt.

7. CONCLUSION

Victoria has extensive reserves of high quality brown coal, coupled with sixty years of experience in large scale extraction and processing of this unique resource. This provides a key economic advantage to the State by ensuring the continued availability of low cost electricity and solid fuel and by providing the basis for new industries to produce value-added brown coal products for local and export markets.

Active research and development programs and facilitation initiatives are under way to assist in further realising the potential of this resource.

ACKNOWLEDGEMENTS

The authors wish to thank the Coal Corporation of Victoria for permission to publish this paper and their colleagues for assistance in its preparation.

REFERENCES

1. Kinhill Pty Ltd Victorian Brown Coal Resource Development Study, 9 Volumes. Victorian Brown Coal Council, Melbourne, 1982.

2. Gloe, C.S. and Holdate, G.R. Geology and Resources of Victorian Brown Coal in Monograph on the Science of Victorian Brown Coal Ed. R.A. Durie (to be published).

3. Stanley, D.R. Brown Coal Resources of Victoria. An Overview Geological Survey of Victoria. Unpublished Report 1986/25. 1986.

4. Higgins, R.S., Kiss, L.T., Allardice, D.J., George, A.M., and King, T.N.W. Properties of Brown Coals from the Latrobe Valley - A Basis for the Evaluation of Quality. State Electricity Commission of Victoria, Brown Coal Research Division. Report SC/80/17. 1980.

5. George, A.M. Brown Coal Lithotypes in the Latrobe Valley Deposits. State Electricity Commission of Victoria. Petrological Report No 17. 1975.

6. Perry, G.J., Allardice, D.J., and Kiss, L.T. The Chemical Characteristics of Victorian Brown Coal In the Chemistry of Low Rank Coals. Ed. H.H. Schobert, ACS Symposium Series 264 pp 1-14, 1984.

7. Kiss, L.T. and King, T.N.W. The Expression of Results of Coal Analysis. The Case for Brown Coals Fuel 56, 340-341, (1977).

8. Ottrey, A.L. and Johnson, T.R. Victorian Brown Coal Ash. Past, Present and Future Problems. State Electricity Commission of Victoria. Brown Coal Research Division Report GO/82/54 1982.

9. Perry, G.J., Gray, A. and Mackay, G.H. Carbonate Formation During Hydrogenation of Victorian Brown Coal. Fuel Processing Technology 10, 285-297, (1985).

10. Crockett, L.A. The Briquetting of Brown Coal in Victoria, Australia. Proc. Inst. Briquetting & Agglomeration Vol. 13 p. 237, 1973.

11. Bennett, B.B. Aspects of the Operation and Development of the Lurgi High Pressure Gasification Plant at Morwell, Australia. 8th Int. Gas Conf. Stockholm, 1961.

12. Kennedy, G.L. Production of Hard Char from Brown Coal Briquettes by Australian Char Pty Ltd. Proc. Inst. Briquetting and Agglomeration Vol. 12 p. 205, Vancouver, 1971.

13. Packer, L.J. and Garner, L.J. High Grade Granular Activated Carbons from Victorian Brown Coal. 5th Int. Conf on Coal Research, Dusseldorf p.255, September 1980.

14. Herman, H. Brown Coal p.508, Publ. by State Electricity Commission of Victoria, 1952.

15. Sinnatt, F.S. and Baragwanath, G.E. The Hydrogenation of Victorian Brown Coals. Fuel Research Station U.K., 1938.

16. Nakako, Y., Matsumura, T. and Takematsu, T. Coal Power '87, AusIMM Annual Conf. Newcastle Australia p.49, 1987.

17. Heng, S., Verheyen, T.V., Perry, G.J., McAllan, C.G. and Harris J.A. Effect of Chemical Pretreatment on Carbonization of Victorian Brown Coal. Proc. 1985 International Conf. on Coal Science Sydney, p.875 1985.

18. Durie, R.A. and Schafer, H.N.S. The Production of Active Carbon from Brown Coal in High Yields. Fuel 58, 472-76, (1979).

19. Cullen, G.V. and Siviour N.G. Removing Metals from Waste Solutions with Low Rank Coals and Related Materials. Water Res. 16, 1357-1366, (1982).

20. Lambert, J.D., Perry, G.J., Royston, D. and Lafferty, C. The Use of Victorian Brown Coal as a Ion Exchange Medium. Proc. Australian Coal Science Conference 1986 Vol 1, p. 142. Newcastle, NSW. December 1986.

21. Beames, G.H. Use of Humic Substances As Agricultural Plant Biostimulants. Proc. ACS Symposium on Structural and Chemical Analysis of Humic Substances. Denver, Colarado, 1986.

22. Heng, S. and Patti, A. Potential of Brown Coal as a Soil Conditioner and Fertilizer. Coal Corporation of Victoria Research Report 85/7, 1985.

23. Davy McKee Pacific. Comparison of Technologies for Brown Coal Drying. Coal Corporation of Victoria Report, 1984.

24. Anderson, B. Optimisation of Design Parameters for a Solar Dried Brown Coal Slurry Plant. Australian Inst. of Energy National Conference, Melbourne, 1985.

25. Potter, O.E., Beeby, C.J., Fernando, W.J.N. and Ho, P. Drying Brown Coal in Steam Heated Steam Fluidized Beds. Drying Technology 2, 219, (1984).

26. Weiser, R. Integrated Coal Drying in a Steam Generating Plant and Fluid Bed. Warme Technik 30, 104 (1985).

27. Fohl, J., Lugschneider, W., Tessmer, G. and Wallner, F. Removal of Moisture from Brown Coal 2. Thermal Dehydration. Braunkohle 39, 46 (1987).

28. Sears, R.C., Baker, G.G., Mass, D.J., Potas, T.A. and Patel, R. Production and Combustion of Hot Water Dried Low Rank Coal Slurries. 13th Biennial Lignite Symposium, Bismarck, North Dakota, 1985.

29. Evans, D.G. and Siemon, S.R. Pre-dewatering of Brown Coal before Combustion. J. Inst. Fuel 43, 413 (1970).

30. Boger, D.V., Leong, Y.K., Christie, G.B. and Mainwaring, D.E. Flow Behaviour of High Solids Brown Coal Water Suspensions as Liquid Fuels. Coal Power '87. Aus IMM National Conf. Newcastle, Australia 1987.

31. Thomas, J. A., Allardice, D. J., LaNauze, R. D. and Grave, N. C. Fluidized Bed Combustion of a Range of Brown Coal Fuels from Latrobe Valley. Proc. Aust. Coal Sci. Conference 1986, Newcastle, NSW, December, 1986.

32. Morley, W.J., Dixon, M. and McLean, D. Micronised Dry Brown Coal - A Viable Alternative to Oil and Gas. High Temperature Energy Technology Seminar, Australian Inst. of Energy, Melbourne, July 1988.

TABLE 1 - WORLD BROWN COAL RESERVES AND ANNUAL PRODUCTION

COUNTRY	ANNUAL PRODUCTION[1] Mt.	RESERVES Mt.	RESERVES/ PRODUCTION RATIO (YEARS)	COUNTRY	ANNUAL PRODUCTION[1] Mt.	RESERVES[2] Mt.	RESERVES/ PRODUCTION RATIO (YEARS)
East Germany	300.0	13,000[3]	43	Bulgaria	31.5	3,700	117
USSR	159.0	89,100	560	Romania	29.8	-	-
West Germany	120.7	35,150	291	Canada	26.5	2,117	80
Czechoslovakia	100.4	2,860	28	Spain	23.5	411	17
Yugoslavia	66.0	15,000	227	Turkey	22.9	1,728	75
USA	63.0	31,980	516	Hungary	21.4	4,000	187
Poland	57.7	12,000	208	Austria	3.1	60	19
Australia	37.0	43,300[4]	1,170	Italy	2.0	-	-
China	32.0	-	-	France	1.9	-	-
TOTAL					1,157.4		

NOTES:

1. The Annual Production figures are based on 1985 production estimates (ref. Braunkohle Vol 38, March 1986, page 60).
2. Reserve figures based on Survey of Energy Resources in 1983 by World Energy Conference unless noted otherwise).
3. Reserve figures based on the following reference:
   Concise Guide to World Coalfields IEA Coal Research, 1983 ISBN 92-9029-088-9
4. The Australian reserves figure is based on the Victorian Reserves quoted in "Victoria's Energy - Strategy and Planning Options" November 1985. No South Australian brown coal reserves have been included as these are small and have not been clearly defined.

TABLE 2 - TYPICAL ANALYSES FOR VICTORIAN BROWN COALS

	GIPPSLAND BASIN					OTWAY BASIN			MURRAY BASIN
	Yallourn	Morwell	Yallourn Nth Extn	Loy Yang	Gelliondale	Altona	Bacchus Marsh	Angelsea	
Seam	Yallourn	Morwell 1	Latrobe	Morwell 1 & 2	Gelliondale				
Moisture (%)	66.4	61.3	52.3	62.8	64.8	58.7	60.5	46.4	56.0
Ash (%db)	1.7	3.0	4.9	1.4	5.7	12.6	7.4	3.8	10.8
Volatiles (%db)	50.3	48.3	47.4	49.8	49.4	47.2	49.8	47.0	
Fixed Carbon (%db)	48.0	48.7	47.7	48.8	44.9	40.2	42.8	42.9	
Minerals & Inorganics (%db)	1.3	2.0	3.8	1.4	3.3		3.5	2.2	
Carbon (%dmif)	67.5	69.2	69.5	68.5	67.0	68.6*	67.6	70.1	
Hydrogen (%dmif)	4.8	4.9	4.9	4.8	4.8	4.9*	4.9	5.0	
Nitrogen (%dmif)	0.57	0.60	0.63	0.59	0.48		0.59	0.71	
Organic Sulphur (%dmif)	0.24	0.30	0.23	0.35	0.70		1.60	2.75	
Oxygen (%dmif)	26.9	25.0	24.7	25.8	27.0		25.2	21.5	
Total Sulphur (%db)	0.28	0.33	0.36	0.38	0.72	2.6	1.74	2.85	
GDSE (MJ/kg)	26.1	26.4	26.0	26.2	25.0	22.5	25.6	27.4	
NWSE (MH/kg)	7.8	9.1	8.8	7.9	7.0	7.4	8.3	13.1	8.9
Surface Area m^2/g	257.	270.	255.	259.	278.		208.	234.	

NOTES:
db - dry basis
* - Values are db not dmif
dmif - dry mineral and inorganic free basis
GDSE,NWSE - gross dry and net wet specific energies

TABLE 3

Loy Yang coal properties:
Analysis of bore hole samples, Loy Yang open cut

ITEM	WEIGHTED AVERAGE (all coal seams)	CUMULATIVE FREQUENCY DISTRIBUTION		
		5%	50%	95%
Moisture (% wb)	62.7	59.2	62.7	65.9
Ash (% db)	1.4	0.8	1.2	3.9
Volatile Matter (% db)	51.4	49.1	51.6	54.3
Carbon (% db)	68.4	65.6	68.8	70.7
Hydrogen (% db)	4.9	4.6	4.9	5.2
Nitrogen (% db)	0.5	0.4	0.5	0.6
Sulphur (% db)	0.4	0.2	0.3	0.7
Oxygen (% db) (by difference)	24.3	Not available		
Specific Energy MJ/kg				
- Gross Dry	26.6	25.1	26.7	27.8
- Net Wet	8.0	6.9	8.0	9.1

Loy Yang coal inorganic constituents:
Analysis of bore hole samples, Loy Yang open cut

CONSTITUENT (% coal db)	WEIGHTED AVERAGE (all coal seams)	CUMULATIVE FREQUENCY DISTRIBUTION		
		5%	50%	95%
Silica (SiO_2)	0.34	0.02	0.10	1.41
Alumina (Al_2O_3)	0.38	0.02	0.16	1.32
Potassium Oxide (K_2O)	trace			
Titanium Dioxide (TiO_2)	trace			
Pyrite/Marcasite (FeS_2)	trace			
Iron (Total) (Fe)	0.13	0.05	0.12	0.25
Calcium (Ca)	0.04	0.01	0.03	0.12
Magnesium (Mg)	0.08	0.03	0.06	0.17
Sodium (Na)	0.11	0.04	0.08	0.33
Chlorine (Cl)	0.14	0.05	0.10	0.37

wb - wet basis   db - dry basis

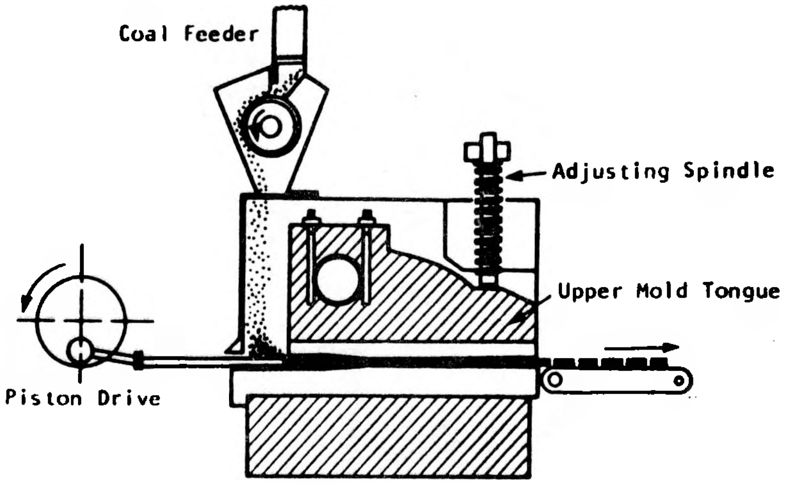


Figure 1 Principles of the Exter Briquetting Press

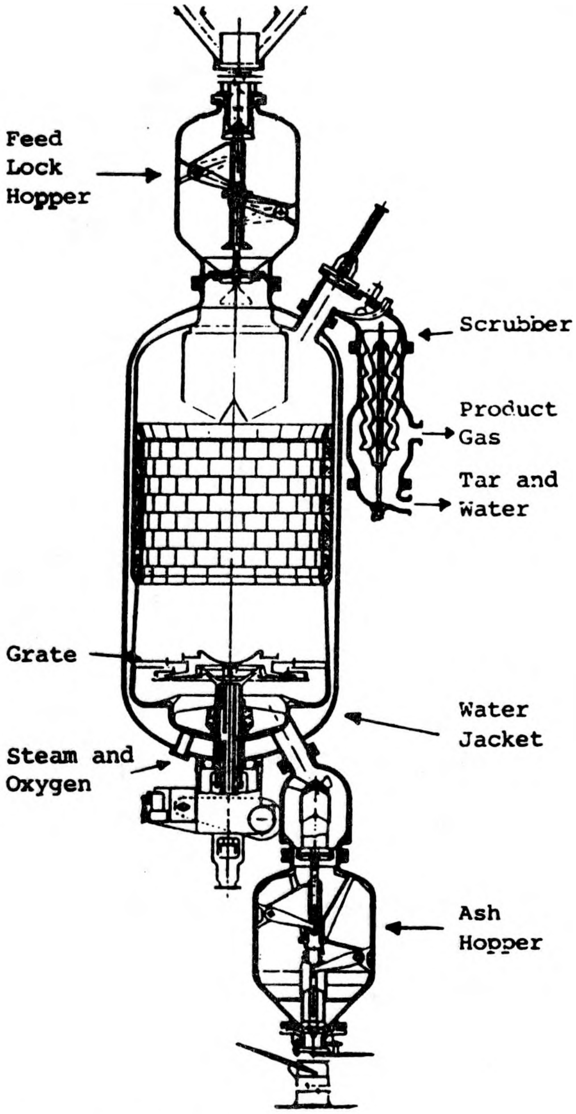


Figure 2 Morwell Lurgi Gas Generator

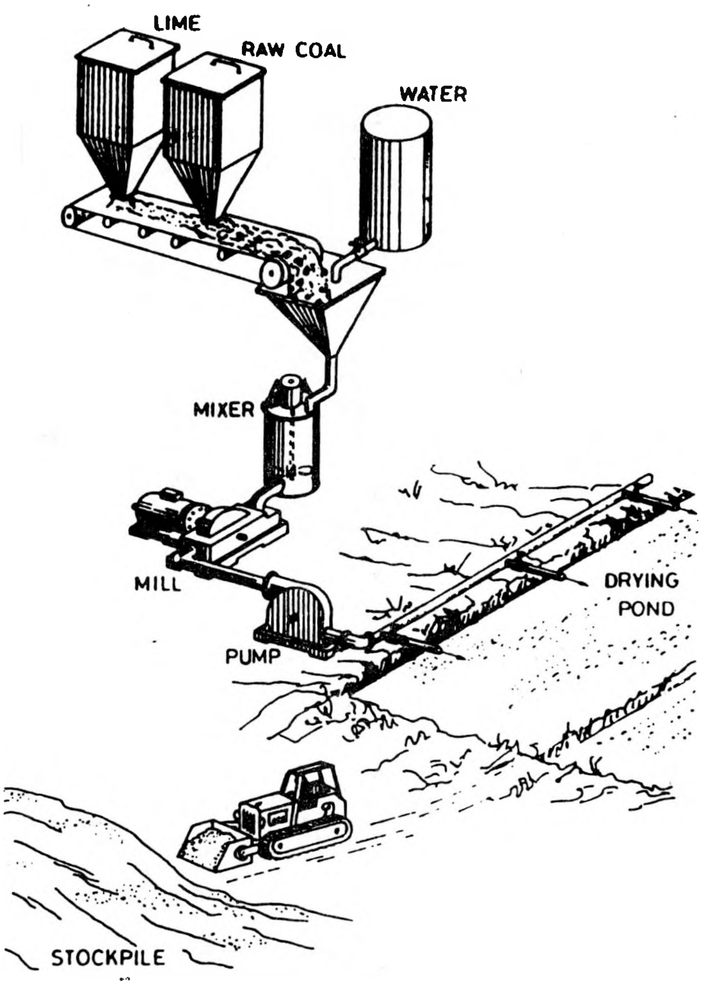
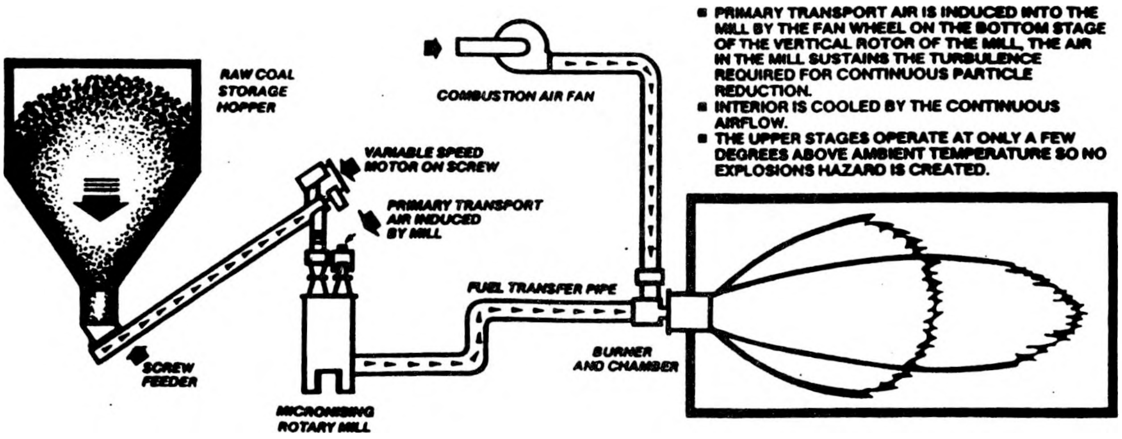


Figure 3 Solar Dried Brown Coal Slurry Process Concept



- PRIMARY TRANSPORT AIR IS INDUCED INTO THE MILL BY THE FAN WHEEL ON THE BOTTOM STAGE OF THE VERTICAL ROTOR OF THE MILL, THE AIR IN THE MILL SUSTAINS THE TURBULENCE REQUIRED FOR CONTINUOUS PARTICLE REDUCTION.
- INTERIOR IS COOLED BY THE CONTINUOUS AIRFLOW.
- THE UPPER STAGES OPERATE AT ONLY A FEW DEGREES ABOVE AMBIENT TEMPERATURE SO NO EXPLOSIONS HAZARD IS CREATED.

Figure 4 Diagram of Stordy-Tas-Microfire Demonstration Combustion System

"UTILIZATION OF COAL-WATER-FUEL MANUFACTURED FROM LOW-RANK COAL"

BY: W. (BILL) IRWIN
CANADIAN PACIFIC CONSULTING SERVICES, LTD.
CALGARY, ALBERTA

UTILIZATION OF COAL-WATER-FUEL MANUFACTURED FROM LOW-RANK COAL

W. (Bill) Irwin
Director, Coal Technology
Canadian Pacific Consulting Services Ltd.
Calgary, Alberta, Canada

ABSTRACT

The paper discusses the application of coal-water-fuel technology for low-rank coals, the high moisture content of which has until now been a constraint to their use as feedstock. Early development of the technology concentrated on using a good quality bituminous coal possessing low ash, high Btu values and favourable physical properties. It is argued that these higher quality bituminous coals will always find a market in their traditional dry bulk form, but some means must be found to utilize the plentiful reserves of cheaper sub-bituminous coals and lignite. The paper suggests this is now made possible as a result of a major technical breakthrough which can be characterized as being a means of simulating coalification. Since almost half of the world's abundant coal reserves are comprised of low-rank coals, this breakthrough offers the opportunity to exploit them for purposes other than mine-mouth generation of electricity. The diversity of these reserves is of equal significance since they can be found in many non-coal producing countries who are often heavily dependant upon imported oil as their prime source of energy. The author suggests that use of their own indigenous low-rank coal reserves by under-developed countries would promote more rapid social and economic development.

Paper Presented to
"SynOps 88 Conference"
Bismark, North Dakota, U.S.A.
August 28-31, 1988

Introduction

Within today's changing world, science and technology are the keys to freeing coal from its perceived image of being the product of a tired, old, and out-dated smokestack industry. There is an urgent need for those outside the research community to be made aware that technologies to clean and transform coal into alternative fuel form, exist, and are in fact ready to compete in the energy market place, head-to-head with all other sources of energy, particularly oil, which has dominated the energy scene since the early 1950's. Indeed, as the world seeks to reduce its dependency upon oil, a new multi-energy era is beginning to emerge, in which the range of energy options have been extended by the development of alternative coal-based fuels. To exploit this situation, the major marketing challenge facing today's coal industry, is that of changing coal's poor image. Utilization of these new fuels and the immediate environmental benefits to be gained from their use, would greatly help to improve that image. Their adoption in the world's energy mix would signal recognition of the contribution coal can make in improving environmental standards.

The Case For Coal-Water-Fuel

Of all the alternative coal-based fuels proposed to meet future energy needs, coal-water-fuels are among the most promising. Possessing the handling and storage characteristics of oil, with the flame and burning characteristics of coal, they can be considered a liquid fuel. Their attraction lies in the potential they offer for use as a direct replacement for oil in utility and industrial boilers. While not projected to sweep oil aside as a boiler fuel, they are expected to play an important role in the world's future energy mix, as a substitute for oil.

Because CWF behaves as a liquid, the disadvantages associated with coal in its dry bulk form, are eliminated to yield all the advantages and convenience enjoyed by oil. Transportation options extend to the use of long-distance pipelines in which lengthy shut-downs can be tolerated without incurring start-up problems. Environmental benefits derived from liquid storage and handling replacing that employed for dry bulk coals, include elimination of dust nuisance and spontaneous combustion problems.

The economic merits of coal-water-fuel (CWF) are attractive because on a Btu basis, coal is cheaper than oil. In quasi-liquid form, that differential is maintained since the more expensive cost of dry bulk coal handling and storage is avoided. To coal producers the technology opens up new markets for coal. To fuel users it offers price stability and security of supply. These commercial considerations are made further attractive as a result of a recent breakthrough in coal processing, which has enabled the range of feedstock coal from which CWF can be manufactured, to be extended to include cheaper sub-bituminous coal and lignite. Due to transportation economics, the use of such low-rank coals have until now been confined to the generation of electricity at the mine-site.

Coal-Water-Fuel Development

Mixtures of coal and water are commonly regarded as slurries. This is misleading. Slurries are an unstable mixture of coal and water, used only for transportation purposes. At the reception terminal, the coal and water are separated and the coal is burned conventionally as a dry pulverized coal.

Coal-water-fuel (CWF) on the other hand can be directly fired in a manner similar to oil. While generically it comprises a mixture of finely ground coal, water, and a chemical stabilizing agent, development of CWF technology has primarily centred around particle behaviour and surfactant chemistry with the aim of increasing the coal-to-water ratio while limiting any rise in viscosity.

Early development of CWF technology concentrated on good quality bituminous coal, possessing low ash, high Btu values and favourable physical properties. However, while such coals can be easily slurried, many do not possess the necessary combustion characteristics to provide trouble-free burning at the boiler front. Although CWF is produced from coal and is handled and fired like oil, it is different to either in its behaviour at the burner and extensive burner development work has been required to overcome these differences.

From worldwide commercial demonstration programs, it has been established that a stable CWF can be manufactured, transported, stored, handled and burned in utility and industrial boilers as a direct replacement for oil. For instance, in the past two years, some 15 commercial scale industrial demonstrations of CWF firing have been undertaken in 7 different countries. These demonstration projects have led to supply contracts and stimulated widespread interest among industrialists at large in the use of CWF as a substitute for oil. The resultant experience and know-how gained from these programs confirms that all links in the production/supply chain, must be viewed as part of the total technology. That is to say, the manufacture, transportation, storage, handling and combustion of CWF involves a total system which begins with the feedstock coal and extends through to its eventual energy conversion in the end-users facility.

Coal Characteristics

Although it is often thought of as being one of our mineral resources, coal is a sedimentary soft rock, rather than a mineral. It is a very complex heterogeneous mixture of organic compounds and minerals and one coal deposit may differ greatly from that of another. These differences can be the result of varying types of vegetation from which the coal originated, the varying depths of burial and the temperatures and pressures at those depths, as well as the length of time the coal has been forming in the deposit. This makes interpretation of quality data and prediction of a coal's behaviour during its treatment and utilization, a difficult task, one that to date has relied largely upon judgement based on knowledge gained from practical experience over a wide range of coals. Considering the origin of coal and the millions of years it took coalification to occur, this is hardly surprising.

However, in recent years, coal has become the focal point of the work of many chemists, who despite the lack of formal training in the subject, have succeeded in elevating coal chemistry from a black art, to a science. Nevertheless, mistakes are still made when assessing the processing and utilization needs of a coal. These are usually caused by poor interpretation of data and resort to the use of parameters based on generalizations. If each coal is characterized and its potential determined on a coal specific basis, such mistakes could be avoided. This calls for matching the specific properties of each coal with utilization needs. Although that fundamental rule applies for all coals, irrespective of the market being served, it is regularly ignored. The various types of coal are illustrated in Figure 1 which can serve as a useful guide when assessing a coal's utilization potential.

In the case of coal-water-fuel, it is particularly important at the initial feedstock selection stage to give priority consideration to the combustion characteristics of each candidate coal. Laboratory studies to determine the fuel formulation system can only be justified if these are considered suitable.

Feedstock Selection

Reference has already been made to the early development of CWF which concentrated on the use of high quality bituminous coals, that are readily slurried. However, coal quality and slurryability properties alone, are not an adequate selection guide, although to a limited extent, both can be controlled by modern processing methods. Combustion characteristics on the other hand are inherent features which cannot be changed by process techniques. It should be recognized therefore that since burning coal-water-fuel is burning coal, utilization considerations must prevail over those of processing, thus the criteria employed to ensure this, needs to be identified.

While process considerations for the control of ash, sulphur and heating values etc., have also to be identified and accommodated, the following coal properties are a pre-requisite for good combustion and trouble-free burning at the boiler front.

PROPERTY	CWF REQUIREMENTS
Volatility	High volatile content
Reactivity	High degree of reactivity
Agglomeration	Non-caking
Ash Fusion	High temperature to avoid slagging
Fuel Ratio	Acceptable level for good combustion

Since coal utilization in a liquid fuel market, involves different quality control standards to those employed in traditional dry bulk coal markets, the importance of these parameters cannot be overstated. Although other factors have to be taken into consideration, it should be recognized that it is the properties of the parent feedstock coal which will ultimately determine the fuel's acceptability. A feedstock coal that does not possess all of the necessary properties, could give rise to problems at the boiler front. However, for completeness, it is worth re-stating that the use of a CWF is dependant upon both coal and boiler specifics, with fuel formulation being tailored to suit each end-users needs. This is achieved by matching a specific coal's characteristics with utilization demands. Tailoring of the fuel should be viewed as being a similar production step to that involved in refining different grades of oil to suit utilization considerations.

Matching the specifics of an individual coal and a boiler as production criteria, contrasts sharply with the practices employed in traditional dry bulk coal markets. In the latter market, specifications are based on the average quality of each bulk consignment, and several different coals can be blended as a compensatory measure to control various properties in the final product. This is not yet a practical proposition in the manufacture of CWF, although it is technically possible under strictly controlled laboratory conditions. Product consistency, is an aspect that needs careful consideration at the feedstock selection stage, particulary in the case where multi-seam mining is being practiced at the coal source.

Until recently, the high moisture content of low-rank coals had been a major constraint to their use as feedstock for manufacture into CWF. That constraint has now been removed by hydrothermal drying, a new, non-evaporative drying technique which allows the range of feedstock coals to be extended to include sub-bituminous coal and lignite. Discussion of this major breakthrough, together with its technical and economic impact, follows.

Hydrothermal Drying

Coal-water-mixtures are promising alternative fuels proposed to meet future energy needs; however, until now, low-rank coals have not been seriously considered for this purpose due to their high inherent moisture contents.

This situation has been changed by a technical breakthrough at the Energy and Mineral Research Center at the University of North Dakota, whereby research has shown that the energy density of slurries made from high moisture coals such as lignite and sub-bituminous coal, can be significantly increased by hydrothermal treatment (hot-water-drying) of the feedstock. In many cases, the treated coals can be essentially slurried in the displaced inherent moisture to produce a liquid fuel having approximately the same, or greater energy density as the parent coal.

Hydrothermal treatment is relatively simple and can be envisioned as rapid coalification. A dilute water slurry of the feedstock is heated to temperatures above 240°C at saturated steam pressures for 5 minutes or less. After treatment, the dilute slurry is cooled, depressured and mechanically dewatered to produce a concentrated coal-water mixture fuel.

In simple terms, the coal is cooked and aged so that the surface properties of the dried product becomes similar to bituminous coal. This is due to a change in the coal itself whereby the pores shrink, and tars that form, tend to seal the pore entries. Figure 2 illustrates this and shows how the coal's structure is fundamentally altered. While not all that happens to the coal's micro-structure during hydrothermal drying is known and understood, accurate calorimetry measurement has confirmed that a significant decrease in surface area occurs.

Technical feasibility has been demonstrated in a 2.5 ton/day continuous Process Development Unit on more than 10 different feedstocks. Pumpable coal-water-mixtures with concentrations of 58-63 wt. % "bone dry" solids and with energy densities between 6,000 and 8,000 Btu/lb. have been produced from a variety of lignitic and sub-bituminous coals.

An example of the improvement gained from beneficiation via Hydrothermal Dewatering without additives, is seen from the following:

As-Mined Lignite	Lignite Coal-Water-Fuel
Solids = 56-68%	Solids = 58-63%
H_2O = 32-44%	H_2O = 37-42%

The main features that illustrate the superiority of hydrothermal dewatering, are:

- Simple concept
- Energy efficient
- Increased heating value
- Reduction of Alkaline ash
- Minimal water requirements
- Permanent reduction of inherent moisture
- Continuous high pressure process
- Low cost
- Premium Quasi-Liquid Fuel from high moisture feedstock.

The Case for Use of Low-Rank Coal as CWF Feedstock

Most of the coal currently being burned in the developed countries of the world, is high rank bituminous coal which generally has a high heating value and is low in moisture and non-combustible ash. Where these coals are readily available they are an alternative to valuable natural gas or oil, as a primary source of energy in their traditional dry bulk form. Development of CWF as a direct substitute for oil in industrial and utility boilers, has to-date also concentrated on the use of such coals.

In the light of this situation, why consider the use of sub-bituminous coal and lignite as feedstock for manufacture into CWF?

To answer that question it must be acknowledged that while the high moisture levels and low heating values of these low-rank coals are negative factors, they do have positive features in terms of their utilization potential. For instance, they ignite easier, burn faster and are often lower in sulphur than many bituminous coals. Also they are non-agglomerating, so that expensively micronized coal particles do not reform into bigger char puffs as slurry droplets evaporate prior to ignition. Finally because of their low mining cost, they are cheap coals.

Perhaps more importantly, almost half of the world's vast reserves of coal are comprised of these low-rank coals and their utilization cannot continue to be confined solely to on-site generation of electricity at the mine. Although the problems of mining, handling, processing, combustion and environmental control for these coals, are different to those for bituminous coals, the development of new technologies such as CWF, now makes them commercially attractive. This is of particular relevance in the case of underdeveloped countries, many of whom have no reserves of oil or high rank bituminous coal, but do have reserves of low-rank coals that are not currently being exploited. Utilization of these reserves would minimize the effect of fluctuations in oil prices and decreasing oil reserves, both of which pose a threat to the economic development and social progress in underdeveloped countries. Since recurring oil crises illustrate the threat which energy can represent to the world's economy, these countries are particularly vulnerable, thus reduced dependency upon imported oil must be a priority objective for them. If the philosophy outlined here, is adopted by those countries, a potential market becomes available to them for export of an energy resource to the industrialized world, where coal-water-fuels are already at the threshold of commercialization.

Those objectives are equally valid in the case of North America where substantial reserves of lignite and sub-bituminous coal are to be found in the western parts of both the United States and Canada. The transportation economics which has so far restricted their utilization in distant dry bulk-coal markets changes dramatically when serving a liquid market with a beneficiated CWF. As end-user confidence is established an increased market demand can be expected to follow.

Increased utilization of coal in the form of CWF should not be viewed as being incompatible with today's more stringent environmental control regulations. On the contrary, the emergence of new advanced clean coal technologies and improved methods of combustion are ideally suited for integration into CWF technology, all of which are design to burn coal cleanly.

TYPES OF COAL

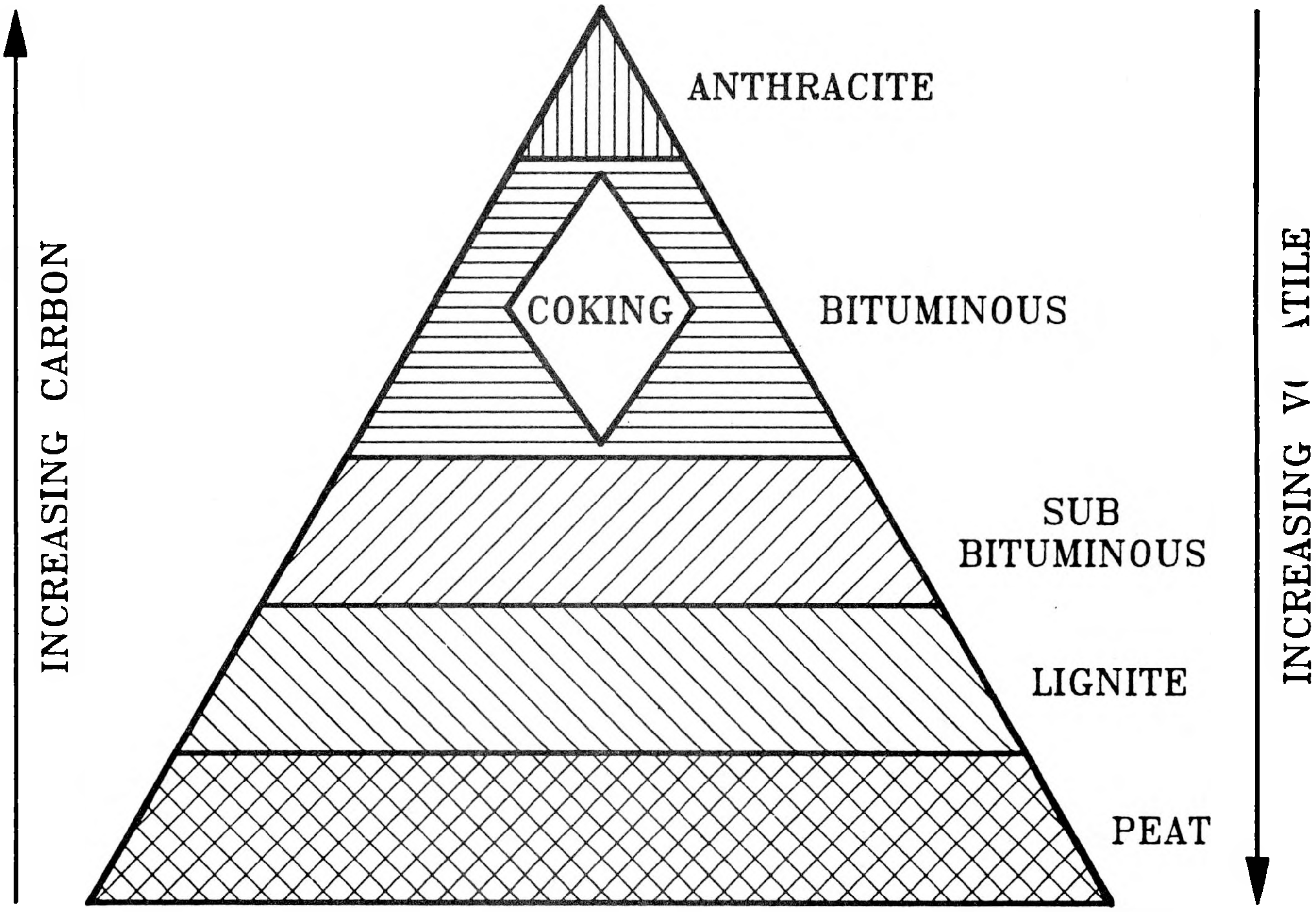


Figure 1

HYDROTHERMAL TREATMENT PROCESS

RAW COAL

Water exists in coal as:

1. **Free surface water.**
2. **Capillary water in pores.**
3. **Chemically bound water.**

HYDROTHERMALLY TREATED COAL

1. **Water expands out of pores.**
2. **Destruction of carboxyl groups releases carbon dioxide and associated cations, which reduces the number of hydrophilic sites.**
3. **Tars form and migrate to the surface where they plug micropore entrance.**

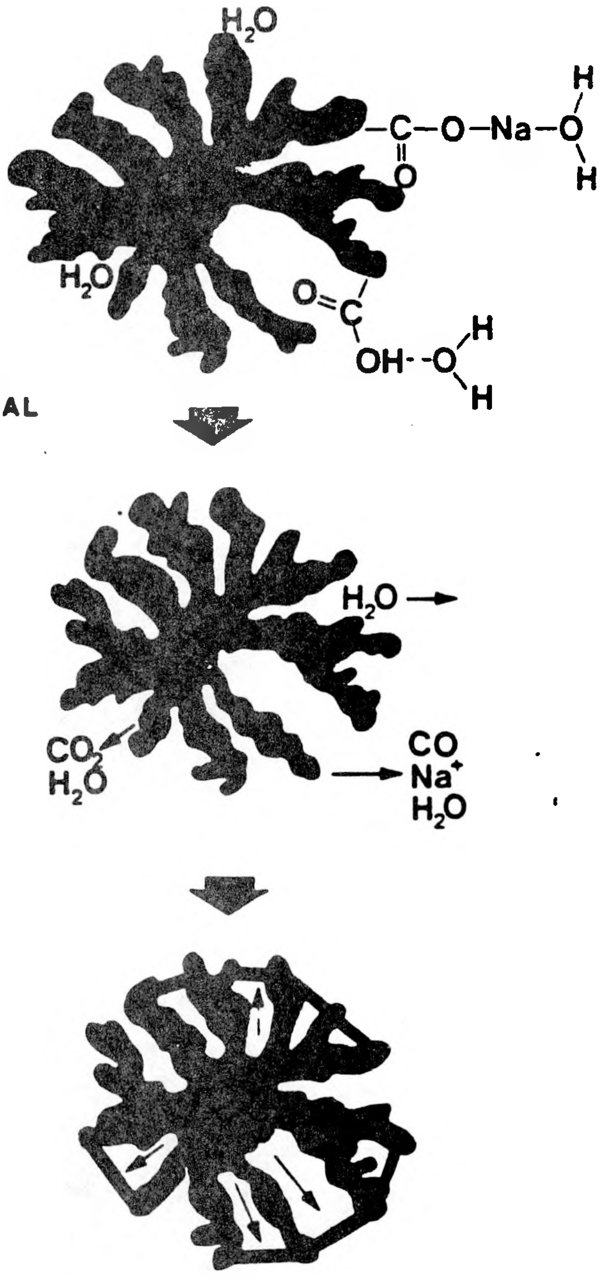


Fig. 2

"LURGI's CFB SLAGGING GASIFICATION THE WAY TO SYNGAS, FUELGAS, & CO"

BY: P.K. HERBERT AND J.C. LOEFFLER
LURGI, FRANKFURT, WEST GERMANY

"LURGI's CFB Slagging Gasification the Way to Syngas, Fuelgas, and CO"

by P. K. Herbert, Lurgi GmbH
J. C. Löffler, Lurgi GmbH

Abstract

CFB Gasification

Circulating fluidized bed (CFB) reactors have been developed by Lurgi over the past 25 years. Key applications included aluminium hydroxide calcination and combustion of a variety of fuels. Reactors have been built in commercial size units many times. For the last 7 years CFB technology has also been applied for gasification.

A variety of solid fuels like coal and lignite, wood and wood waste, other biomass and RDF have been gasified successfully in Lurgi's 3 MWth pilot plant. In extensive tests it could be proved, that the process is both technically feasible and environmentally acceptable. Even on gasifying RDF - the fuel with the highest potential for emissions in the product gas as well as in the ash - stringent environmental standard are being met. In particular dioxin was not detectable. Ash leaching tests have demonstrated that the ash is disposable in regular disposal areas.

Since late 1986 the first commercial CFB gasification unit is in operation in Pöls, Austria, producing low BTU gas for lime kiln firing from bark and wood wastes.

However, CFB gasification can do more than providing low BTU gas for calcination or similar processes. By using basically the same equipment, however with oxygen rather than air as gasification agent, the process will produce synthesis gas for a variety of applications. Pressurized CFB gasification is also considered in combined power cycles.

Production of CO in the slagging gasifier

High purity carbon monoxide is required for a variety of organic chemicals like phosgene, polyurethane, acrylic glass, and others. This can be produced in quantities as low as 1.500 Nm^3/h (4,100 lbs/hr) by gasifying coke with a mixture of oxygen and CO_2 as gasification agent in a countercurrent fixed bed gasifier with liquid ash withdrawal.

This technology had been applied on a large scale until after World War II. Meanwhile, the process has been improved to meet today's requirements, and it is now being offered on a commercial basis.

RÉSUMÉ

SURNAME:	Dr. Löffler
FIRST NAMES:	Johannes Christian
[redacted]	[redacted]
NATIONALITY:	German
FUNCTION:	Department Head
EXPERIENCE:	1971 - 1973 with Bergbau-Forschung GmbH, Process design of a formed coke plant for Ruhrkohle AG, Lurgi-Ruhrgas pilot plant operation. Hot briquetting plant operation. Since 1973 with Lurgi GmbH. Special duties, process design, basic and detailed engineering of coal gasification and adjacent units. Operation of the combined cycle Steag power station in Lünen / FRG. Assistance in various coal gasification tests in Sasolburg / South Africa. Start-up assistance for the Sasol gas expansion - prototype gasifiers. Lead commissioning engineer for Sasol II gasification. Lead commissioning engineer for ANG gasification, gas cooling, CO-shift conversion, gas liquor separation. Supervision of the CFB gasification in Pöls / Austria.
MAJOR PROJECTS:	WESCO, ANG, Sasol Gas Expansion (Special duties, process design); Sasol II process, basic, detailed engineering. Process coordination for the Hampshire coal gasification project. CFB gasification, process and design development.

EDUCATION:

1962 - 1968 mechanical and process engineering at the "Rheinische-Westfälische Technische Hochschule Aachen".

1968 Degree of "Diplom Ingenieur"

1968 - 1971 Dissertation on "Flow Behaviour of Degassing Bulk Materials"

1971 Degree of "Doktor-Ingenieur" (PhD) of the RWTH Aachen.

Lurgi's CFB and Slagging Gasification - the Way to Syngas, Fuel Gas and CO

by P.K. Herbert, Lurgi GmbH
J.C. Loeffler, Lurgi GmbH

Summary and Introduction

Lurgi's CFB gasification technology is now commercially available for gasification of biomasses, coals, and RDF at low pressures. High pressure gasification is being developed and will be available in a few years. A commercial 27 MW bark gasification unit is in operation since 1986 in a pulpmill in Austria. The process is well suited for the production of low BTU gas and synthesis gas. The low BTU gas can be used in lime kilns, cement kilns and CFB combustors as substitute of the total fuel or part of it. The synthesis gas can be used for various syntheses after purification and conditioning.

Many organic chemicals can be made from high purity carbon monoxide. In order to provide a source of CO at reasonable costs an attractive new process scheme has been developed based on well known technologies. Fuel for the fixed bed slagging gasification process is coke. Gas purification systems are available according to the requirements of the downstream syntheses.

Atmospheric CFB Gasification

Lurgi's Circulating Fluidized Bed or short - CFB - technology has been applied over the past 25 years for aluminum hydroxide calcination, other thermal reactions and for combustion. Since then a large number of commercial CFB plants - 35 for calcination and 25 for combustion - have been or are being built by Lurgi.

In 1980 the development of the CFB gasification process was started with gasification tests in our 3 MWth plant. Based on the successfull tests and the know-how collected in the commercial calcination and combustion CFB's the first large scale production unit was designed, constructed and started up successfully in 1985/86 in Poels/Austria.

Process Description

CFB reactors operate in the velocity regime between the classical fluidized bed - with defined surface - and pneumatic lift pipes. Particulates entrained in the gas leave the reactor and - after gas / solids separation in the recycle cyclone - are being recycled to the bottom of the reactor (Fig. 1).

This principle of operation is characterized by the maximum gas / solids velocity difference of all fluidized reactors ("slip velocity") and yields the following advantages:

- Intensive mixing of gas and solids
- High heat and mass transfer rates
- High gasification reaction rates (i.e. high specific throughput)
- Largely uniform temperature through the reactor
- Zero tar and oil production

A typical CFB gasification unit comprises the cylindrical refractory lined reactor, the recycle cyclone, the air preheater and the secondary cyclone.

The gasification reactions occur in the vertical reactor. The fuel fed to the bottom of the reactor by a screw feeder, the recycle material (mainly ash) and the gasification agent mix and react rapidly above the nozzle grate.

The solids are carried upwards by the product gas. The low temperature difference between reactor bottom and top (90°F) proves the good mass and heat transfer of this reactor type.

In the recycle cyclone the solids are separated from the product gas and returned to the reactor bottom through a standpipe and a seal. The gas then passes through the air preheater and cools down to approx. 1080°F.

After final dedusting in the sedondary, high efficiency cyclone the product gas is ready for immediate use or further treatment.

In the air preheater the gasification air is heated up to approx. 1020°F before it is injected into the reactor bottom through a nozzle grate. The ash is withdrawn through the central outlet of the nozzle grate.

Pilot Tests

In the Lurgi 3 MWth pilot plant biomasses like wood, bark, other agricultural wastes, RDF, lignite, bituminous and subbituminous coals, and petrol coke have been successfully gasified in test runs lasting over 3000 hours in total. Selected fuel data are given in Fig. 2.

Some of the test work was sponsored. EPRI (1) has supported tests with N.D. lignite and red wood which had very promising results. The German Ministry for Research and Technology - the BMFT - sponsored tests with German bituminous and with brown coal (2, 3) for basic CFB gasification process development and for a new combined power cycle based on CFB technology.

For the different fuels only minor hardware adjustments were required in the fuel handling system. Process parameters such as reaction temperature, steam/-air or steam oxygen ratio, fuel to gasification agent ratio, fuel moisture, etc. had to be adapted to each fuel. For the product gas analyses corresponding to the above fuels see Fig. 3.

The HHV's of the gas excluding the latent heat range from 125 to 155 BTU/SCF. In applications where gas cooling is not required approx. 20 BTU/SCF of latent heat of the product gas can be efficiently used.

When gasifying with air the steam required for the gasification reaction is usually introduced into the reactor by residual fuel moisture. In this case fuel moisture must be closely controlled. For biomasses hogged to minus 30 mm max. particle size a rotary dryer - see Fig. 4 - has proven to be the right choice for moisture reduction/control of the fuel.

Based on 25 years of experience with CFB technology, the CFB gasification pilot tests, operational experience with the 27 MWth bark gasification plant in Poels/Austria (see Fig. 5) and last but not least the fixed bed gasification know-how Lurgi can give full guarantees for commercial CFB gasification plants. For economic reasons 10 MWth is regarded as the minimum capacity of commercial CFB gasification units.

Application of CFB Gasification

Depending on feedstock and/or product requirements CFB gasification units can be air or oxygen operated at near atmospheric or elevated pressures. The latter is, however, still in the demonstration phase and will be available on commercial terms in a few years only.

For fuel gas production usually air and for synthesis gas a mixture of steam and oxygen is used as gasification agent.

Depending on the fuel composition the product gas contains pollutants. Some pollutant data are given in Fig. 6. In order to meet the environmental requirements these pollutants have to be removed.

- This can be done by the process using the product gas, if this process has the ability to absorb the pollutants. Such processes are the lime calcination, the cement production and the CFB combustion. These processes have a good potential for absorbing sulfur and/or chloride. They also tolerate a rather high dust concentration in the fuel gas and high temperatures and are thus well suited as processes downstream of CFB gasification units.

- If the process using the CFB product gas cannot accept or tolerate the pollutants the CFB gas is cleaned in a separate process step.

According to the fuel characteristics there are four major pollutants in the fuel gas. These are dust, consisting of approx. 65% carbon and 35% ash, ammonia, H_2S, and HCl. When gasifying biomass H_2S and HCl removal is not normally required and consequently only dust and NH_3 have to be removed in a process step as shown in Fig. 7. When using fuels with higher sulfur and chloride contents, chemicals - like sodiumhydroxide - can be added to the wash water for removal of these substances.

When producing synthesis gas the CFB gasification should be operated under elevated pressure with steam/oxygen. For gas purification and conditioning, gas cooling, CO conversion and Rectisol is required.

Another fuel well suited for the CFB gasification process is RDF. Thus RDF gasification is an alternative to conventional garbage combustion and has the following main advantages related to environmental protection:

- No dioxine formation: during a pilot test run with RDF, dioxine was not detectable in either gas or ash.
- Heavy metals, bound in the ash do not leach.
- Ash is disposable in regular disposal areas.

Low BTU fuel gas from RDF is suitable for the substitution of up to 60% of cement kiln fuel and can substitute approx. 40% of the fuel of CFB combustors. An RDF gasification scheme including RDF preparation is given in Fig. 8.

CFB gas produced from coal is being considered for ore reduction processes.

Another application under consideration is partial gasification of coal/lignite under pressure for combined power cycles - see Fig. 9.

CO Production with the Atmospheric Slagging Gasifier

The purpose of this process is to produce CO rich gas for various syntheses, such as diisocyanates, polyurethane, fatty acid derivates, acrylic glass etc. Hydrogen content of fuel and product gas should therefore be minimum. This leads to the following requirements:

- Minimum hydrogen in the gasification agent. For this reason a mixture of dry carbon dioxide and oxygen is used.

- Minimum hydrogen in the fuel; therefore high temperature cokes are best suited.

- High CO-contents; i.e. high gasification temperatures. This is achieved by a low CO_2/O_2 ratio of the gasification agent.

Process Description

CO gas can be produced by the process route as shown in Fig. 10. The process includes atmospheric slagging gasification, gas cooling and gas purification.

The atmospheric slagging gasifier is fueled with coke from the top. According to its countercurrent reaction the gasification agent (a mixture of CO_2 and O_2) is injected via tuyeres - as in blast furnace technology - into the bottom (hearth) of the reactor. The low CO_2/O_2 ratio of the gasification agent leads to temperatures above the melting point of the ash. The slag collects in the hearth, from where it is withdrawn intermittently.

The crude gas leaves the reactor at the top with CO-concentrations ranging from 90-92 % vol., depending on feedstock qualities. The remainder is mainly CO_2 and hydrogen. After removal of CO_2 CO-concentrations of 97 to 98.5 % vol. can be achieved. After desulfurization the gas is suitable for a wide range of syntheses.

Gasifier capacity ranges from 70,000 SCFH to much larger capacities.

Operating data and economics are given elsewhere (3).

Literature

1) P. Mehrling, H. Vierrath
"CFB Pilot Plant Gasification Tests"
EPRI Project No. RP 2656-3
Report in preparation

2) R. Rudisch, et al
"Development of a Coal Gasification Process in the Circulating Fluidized Bed under Elevated Pressure"
Final Report to BMFT, Rep. No. 03E-6094-A7

3) P. Mehrling
"CFB Pressurized Gasification in a Combined Power Plant"
Final Report to BMFT, Rep. No. 03E-6384-A

4) E. Lath, P. Herbert
"Make CO from coke, CO_2 and O_2"
Hydrocarbon Processing, Aug. 1986,
P. 55-56

Short C.V. of J. C. Loeffler

Johannes Christian Loeffler -
studied mechanical and process engineering at Technical University, Aachen, West Germany, between 1962 - 1971.
He holds an M.S. and a PhD degree in process engineering.
Since 1971 he is engaged in coal technology, in particular in LURGI fixed bed and circulating fluidized bed gasification. He holds the position of department head for fixed bed gasification at LURGI GMBH.

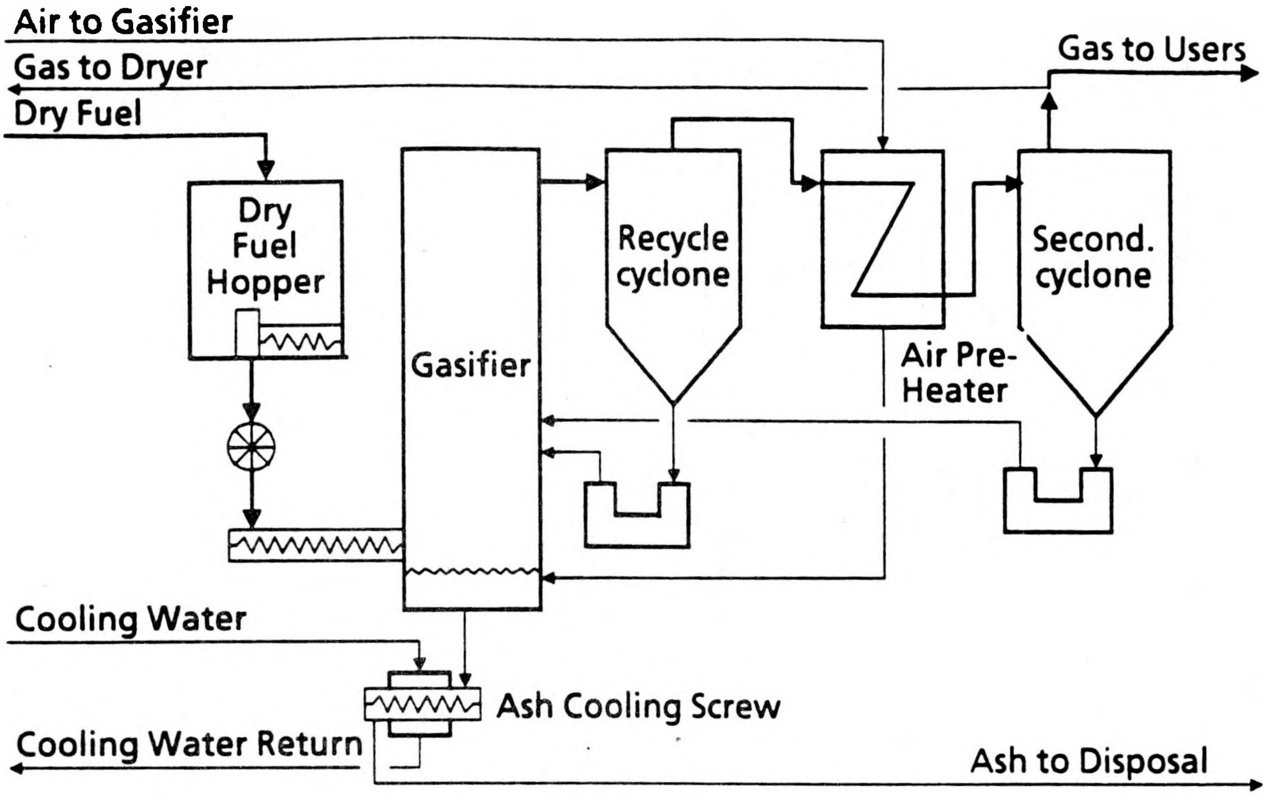


Fig. 1 Typical CFB Gasification Flow Scheme

Fuel		Bark	Wood	RDF	N. D. Lignite	Petr. Coke
C	wt%	52,00	51,30	53,30	71,70	90,90
H	wt%	6,10	5,90	7,80	4,70	3,40
O	wt%	41,40	42,60	36,70	21,30	0,22
N	wt%	0,50	0,10	1,50	1,20	1,75
S	wt%	–	0,08	0,30	1,09	3,73
Cl	wt%	–	0,02	0,40	0,01	–
Moist. *	wt%	15,00	30,00	15,00	38,00	8,60
Ash *	wt%	5,00	0,30	18,00	11,00	0,40

* related to as received fuel

Fig. 2 Pilot Plant Tests – Fuel Analysis – DAF - Fuels

Fuel		Bark [1]	Wood	RDF	N. D. Lignite	Petr. Coke [2]
React. Temp.	°C	800	820	920	840	1150
H_2	Vol%	20,2	14,2	19,3	13,5	33,7
CO	Vol%	19,6	18,8	15,2	17,2	40,9
$CH_4 + C_nH_m$	Vol%	3,8	4,8	5,6	1,3	0,6
CO_2	Vol%	13,5	14,8	13,3	12,2	17,0
N_2	Vol%	42,9	47,3	46,6	55,8	7,8

[1] Results from 27 MW unit in Poels

[2] O_2 - Gasification - N_2 content due to purge gas

Fig. 3 Pilot Plant Tests – Main Gas Components – Dry Gas

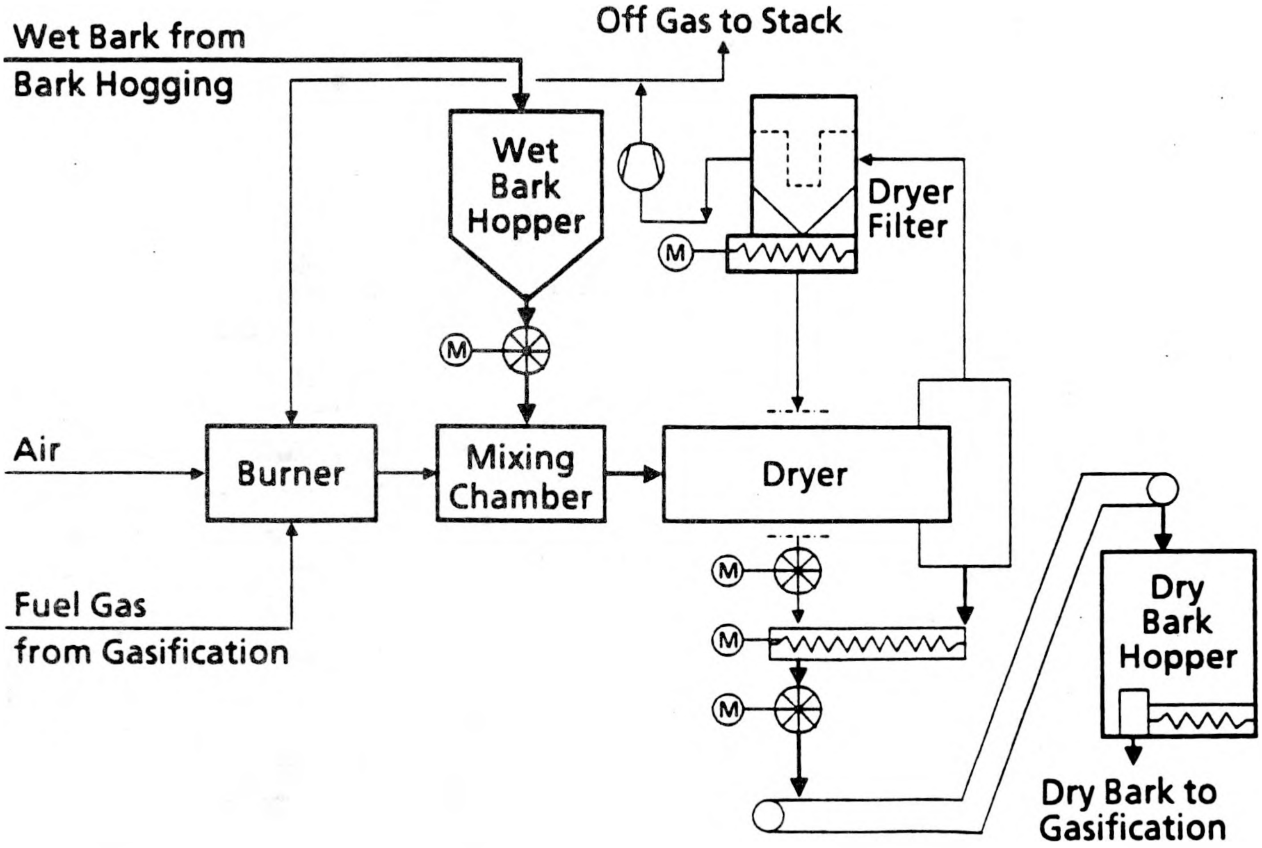


Fig. 4 Rotary Dryer System

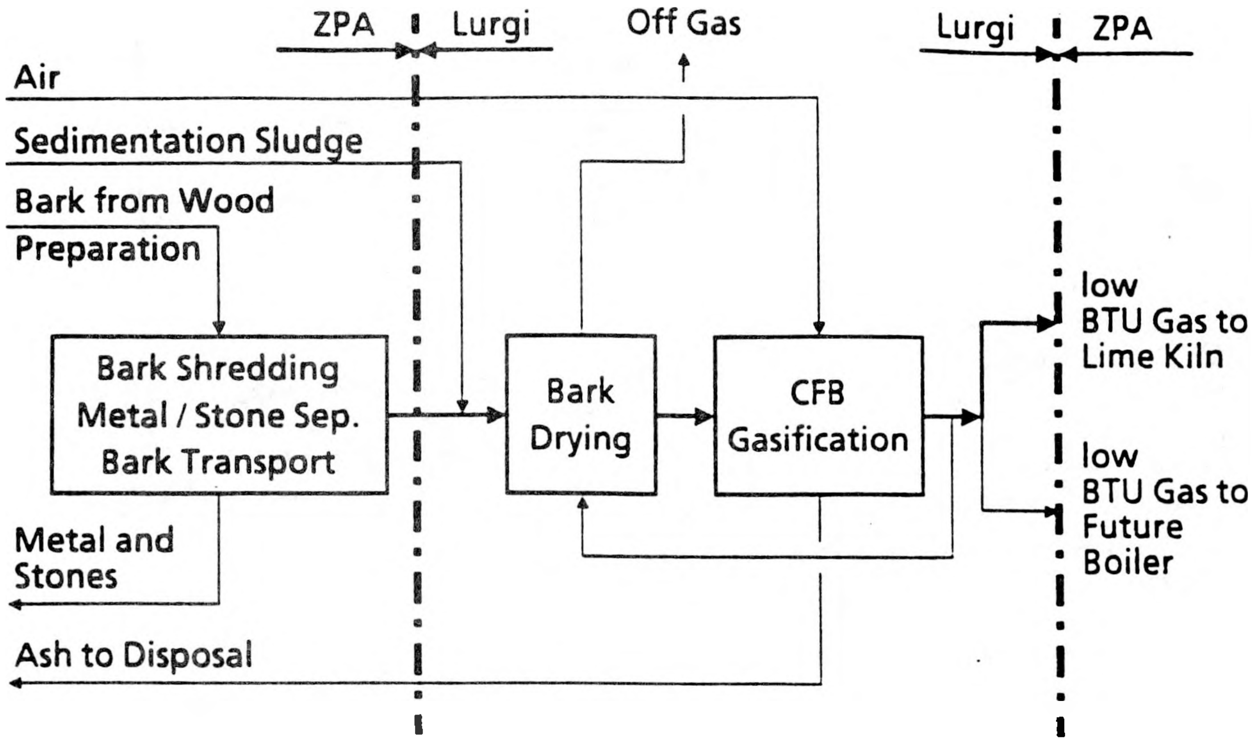


Fig. 5 Bark to low BTU Gas Process Poels

Fuel		Bark	Wood	RDF	N. D. Lignite	Petr. Coke
H_2S + COS	ppm V	–	47	490	140	4000
NH_3 + HCN	ppm V	8	27	840	19200	20000
HCl	ppm V	–	–	175	–	traces
Phenols	ppm V	–	15	–	0,3	–
Fatty Acid	ppm V	–	7	–	4	–
Dust	g/m^3_n	50	50	50	50	50

Fig. 6 Pilot Plant Tests – Gas Components – Pollutants

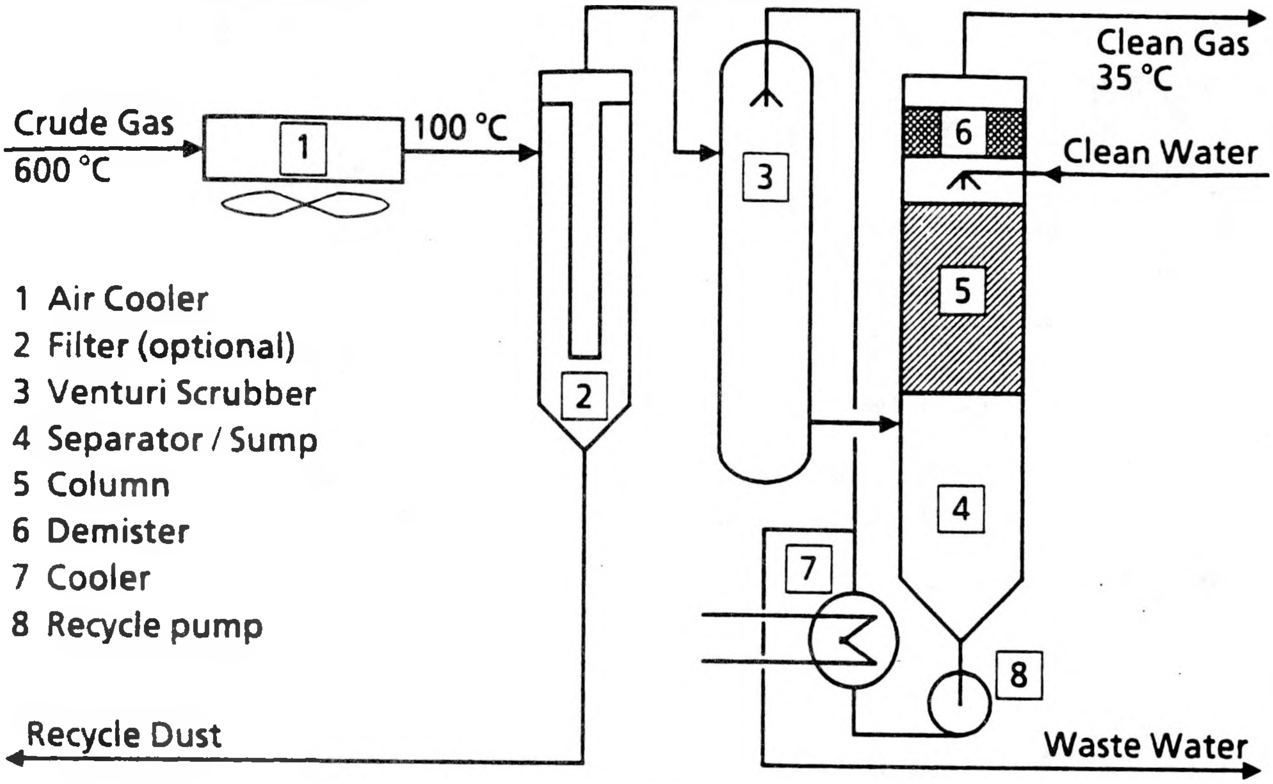


Fig. 7 Gas Cooling / Scrubbing Scheme

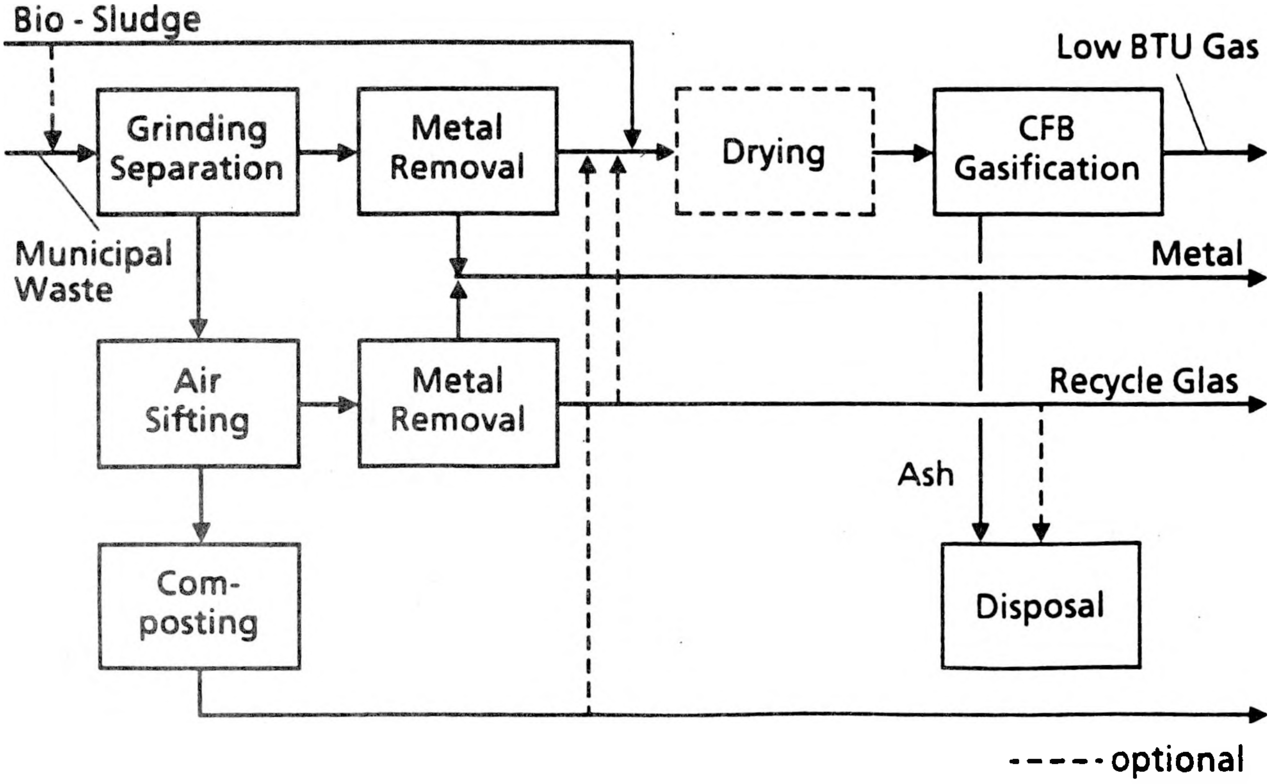


Fig. 8 Low BTU Gas from RDF – Gas Production Scheme

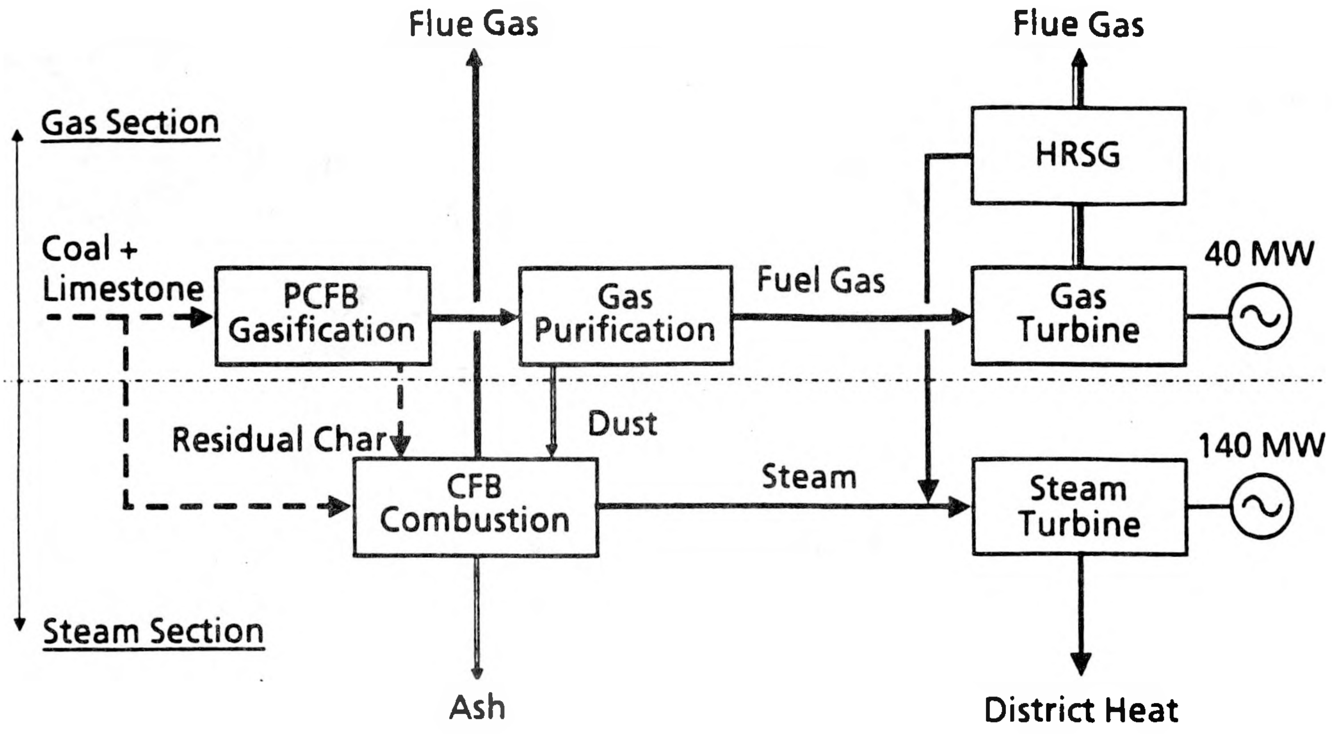


Fig. 9: PCFB - Combined Cycle - 180 MW

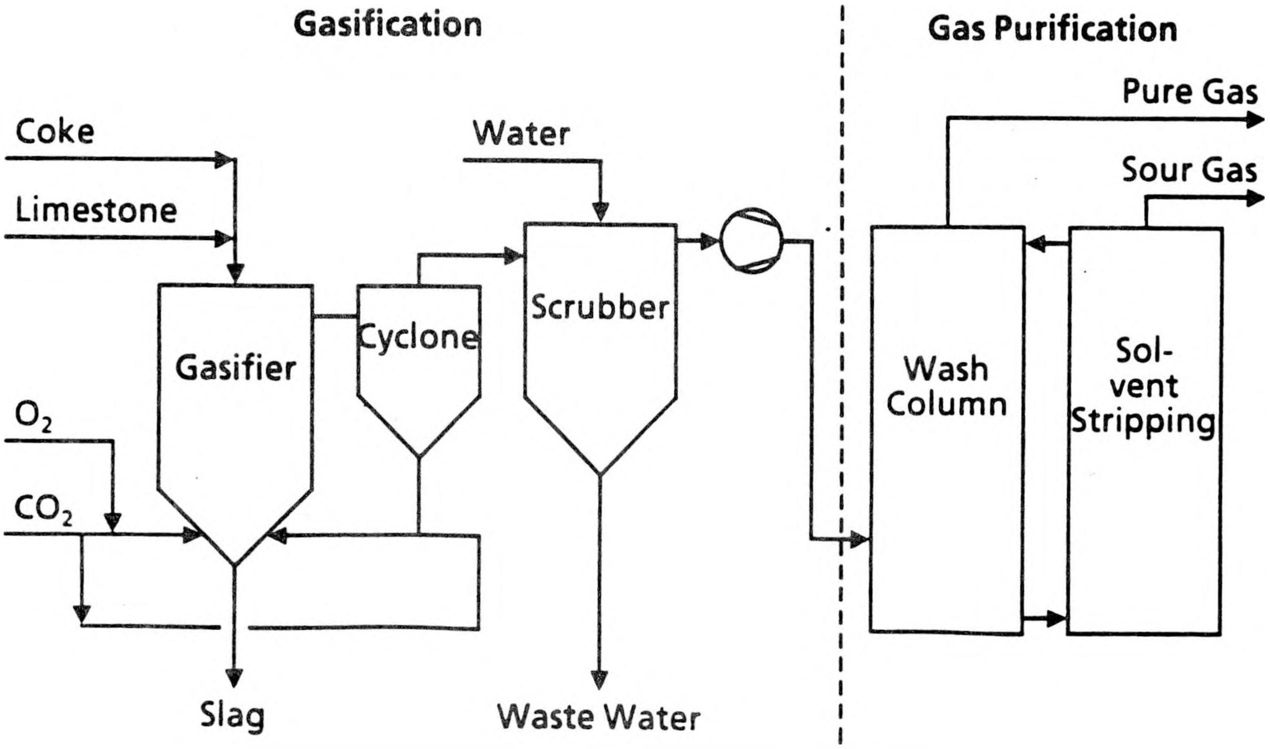


Fig. 10 Atm - Slagging Gasification – CO-Production Scheme

"ADVANCED CONCEPT FOR THE PRODUCTION OF CO-PRODUCTS"

BY: M.C. JHA, AMAX
GOLDEN, CO
R.O. NESS
ENERGY & MINERAL RESEARCH CENTER, UND
GRAND FORKS, ND
J.E. COBURN
PELLET TECHNOLOGY CORPORATION
HOUGHTON, MI

MILD GASIFICATION - PELLET TECHNOLOGY CORPORATION IRONMAKING PROCESS

by
M. C. Jha
AMAX Research & Development Center
5950 McIntyre Street
Golden, Colorado 80403

R. O. Ness
University of North Dakota
Energy & Mineral Research Center
15 N. 23rd Street
Grand Forks, North Dakota 58201

J. L. Coburn
Pellet Technology Corporation
601 Sharon Avenue
Houghton, Michigan 49931

ABSTRACT

AMAX, UNDEMRC, and PTC are working on a novel process that will benefit domestic coal, synthetic fuels, and steel industries. In this process, mild gasification (devolatilization) of coal is accomplished at low temperatures and near atmospheric pressures. The volatiles removed from the coal are converted to marketable synthetic fuel, such as Diesel No. 3 blending stock, and chemical feedstocks for phenol and benzene. The char is upgraded and utilized in the PTC-Cold Bond Agglomeration Process to produce carbon or carbon-bearing iron pellets for the steel industry. An atmospheric fluidized-bed combustion (AFBC) unit is used to incinerate process wastes and produce electric power. AMAX Coal is interested in developing this process for possible commercialization at one of its Midwestern mines.

The project is currently in the bench-scale testing phase following the technical and market evaluation studies. Process scale-up and evaluation studies are planned for the 1989-1991 period, and the design and construction of the commercial plant are scheduled for 1992-1994.

The work is presently funded by Morgantown Energy Technology Center (METC) of the Department of Energy (DOE) under Contract No. DE-AC21-87MC24267 to UNDEMRC with AMAX R&D and PTC as subcontractors.

INTRODUCTION

To expand the utilization of coal in a technically feasible, economically viable, and environmentally acceptable way, total gasification or liquefaction of coal has been investigated for several decades around the world. The commercialization of these technologies, particularly in the United States, has been limited by:

1. The high capital cost associated with severe process conditions necessary for total conversion of coal.

2. Market limitations imposed by plant location, product quality, and price competition from petroleum products.

As an alternative approach, Morgantown Energy Technology Center (METC) of the U. S. Department of Energy (DOE) has been investigating mild gasification of coal.[1] In this process, high-volatile coal is devolatilized at relatively low temperature (500 to 700°C) and near atmospheric pressure to produce three coproducts:

1. A low- or medium-Btu gas.
2. A valuable hydrocarbon condensate.
3. A reactive char.

To advance the concept further and bring it closer to commercial reality, METC awarded us a contract (No. DE-AC21-87MC24267) in the fall of 1987. The project is titled "Development of an Advanced, Continuous Mild Gasification Process for the Production of Coproducts".

Our team is headed by the University of North Dakota Energy and Mineral Research Center (UNDEMRC) and supported by AMAX and J. E. Sinor, Inc. UNDEMRC is primarily responsible for the process development work, particularly in the areas of mild gasification and upgrading of condensate. AMAX Coal, the third largest United States coal producer, is interested in commercialization of the technology, as it offers potential for business growth with new products and markets. AMAX R&D is coordinating the process development and evaluation studies and performing the char upgrading work.

J. E. Sinor, Inc. performed the market evaluation studies for various products. Based on this study, it was concluded that the best market for char would be the steel market, particularly if a novel process developed by Pellet Technology Corporation is used to produce carbon or carbon-bearing iron pellets to be charged into hot blast cupolas.

This paper discusses the selection of a product slate based on market and technology evaluation studies performed as the first task of the project. This is followed by a brief description of the mild gasification, char upgrading, and pellet production processes.

PROJECT OUTLINE AND SCHEDULE

Our goal is to design and build a 1,000-ton-per-day coal mild gasification plant at one of our Midwestern coal mines. The location of the mild gasification plant at the coal mine site not only cuts down the transportation costs but also provides the flexibility of utilizing some products on site.

To accomplish this goal, the project has been divided into three phases. The project schedule, as currently planned, is presented below:

Phase A. Concept Evaluation and Process Development (1987-1989)

- Task 1. Technology and Market Evaluations
- Task 2. Bench-scale Mild Gasification Studies
- Task 3. Bench-scale Char Upgrading Studies
- Task 4. Integrated System Studies

Phase B. Process Scale-up and Evaluation (1989-1991)

Phase C. Commercial Plant Design and Construction (1992-1994)

Task 1 of Phase A, Technology and Market Evaluation Studies, was completed in January 1988, and the results have been presented in two topical reports.[2,3] We are currently working on Tasks 2 and 3 of Phase A to test the process concepts on bench scale.

PRODUCT/MARKET SELECTION

Mild gasification produces three broad categories of products, as discussed earlier. For commercial success, it is essential that the product slate (relative quantity and quality) be selected to meet the existing and projected market requirements. The process technology can then be tailored to meet these goals.

The gas, condensate, and char products, as produced or after some upgrading, can be sold in following markets:

- Energy - Transportation and utility sectors.
- Other - Chemical, metal, and pollution control industries.

It should be obvious from Figure 2 that while the steam boiler presents a universal market for all the products, they cannot compete with the feed coal itself. The success of mild gasification would depend upon finding "other" applications for the products in markets where they will command premium price (in terms of $ per million Btu or $ per ton) in comparison to feed coal. With this criterion in mind, various upgrading and utilization methods were evaluated for all the three products in conjunction with the market assessment. The findings are presented below.

Gas

Of the three broad categories of products, gas represents the least tonnage. It is a mixture of CO, H_2, CH_4, CO_2, and H_2O with H_2S as a significant impurity. Thus, it would be difficult to sell this gas to an outside market. While it could be used on site to provide process heat, a better use would be to upgrade it and use its hydrogen content for liquid upgrading.

Liquid

Condensate produced during mild gasification is normally considered to be the most valuable product. This would, however, be true only if the liquid is stabilized and upgraded to premium fuels or converted to chemicals. If the liquid, as produced or after minimum upgrading, is utilized to raise steam, its value will be no better than that of residual oil from petroleum.

Several products were examined during the market evaluation studies. The findings are summarized below:

- Creosote and Cresylic Acid - Market too small.
- Diesel No. 1, No. 2, Aviation Jet Fuel, and Gasoline - Severe upgrading required, not competitive with petroleum.
- Diesel No. 6, Bunker C - No premium, market of last resort.
- Diesel No. 3 - Prime target (medium speed railroad engines), blend with DF No. 2, unlimited market, about $120 per ton.
- Chemical Feedstock - Phenol, Benzene, unlimited market, premium price, $200/ton or more.

Thus, the target products for our project are a diesel fuel blend stock and chemical feedstock for benzene and phenol. It should be noted here that the plant location in the Midwest helps significantly in reaching a large industrial market at low transportation costs for these products.

Char

In terms of tonnage, char is the main product of the mild-gasification process, representing as much as 50 to 70 percent of feed coal. In the past, many pyrolysis and carbonization processes were developed on bench or pilot scale but were not commercialized mainly because they considered char as a low-grade utility fuel.[4]

We explored a number of markets both in the energy and metals industries and concluded that char can be utilized as such or after upgrading as one or more of the following products:

1. Activated Carbon
2. Barbecue Briquettes
3. Boiler Fuel
4. Carbon Black
5. Coke
    a. Formcoke
    b. Metallurgical
    c. PTC Ironmaking
6. Graphite Electrodes
7. Gasifier Feed
8. Heat Engine Fuel

These products represent a range of market size from a few hundred thousand tons per year to a few hundred million tons per year and a product price from about $30 per ton to $500 per ton.

Based on the Midwestern location, resurgence in the United States steel industry, severe decline in domestic coke oven capacity, and relatively high price on the order of $80 to $120 per ton, the metallurgical coke market was identified as the most promising market. Our study also indicated that the Pellet Technology Corporation (PTC) ironmaking process, to be discussed in some detail later, provides an alternate and attractive method to produce carbon or carbon-bearing iron pellets for the iron and steel industry utilizing mild-gasification char. It is expected that some upgrading of char to reduce its ash, sulfur, and volatile contents, and thereby upgrading the carbon content, would enhance its value in this application.

PROCESS DESCRIPTION

Figure 1 shows a schematic flow diagram for the entire process. Major reaction vessels have been identified by numbers such as 1.1, 5.1, etc. These numbers have been used in the discussion that follows.

The plant will consist of the following five areas which are integrated to maximize the technical and economic feasibility of the process:

1. Mild Gasification
2. Liquid Upgrading
3. Char Upgrading
4. Pellet Production
5. Power Production

Each of these areas is described below in terms of its function and operational parameters.

Mild Gasification

Washed and sized coal will be fed to a mild gasification reactor (1.1 in Figure 1) where all of its moisture and most of the volatile matter will be removed. UNDEMRC has selected a fast fluidized-bed reactor for this application for the reasons summarized below.

1. Rapid heating rate.
    a. Maximizes condensibles yield.
    b. Minimizes gas production.
    c. Produces active char/carbon.
2. Long solid/short gas residence time.
    a. Decreases cracking.
    b. Minimizes gas formation.
    c. Improves condensible yield.
    d. Improves liquid product quality.

3. Efficient heat exchange.

4. Proven technology.

Steam and hot flue gas will be used to fluidize coal and provide heat. The temperature will be in the range of 500 to 700°C. Depending upon the caking characteristics of the coal and the desired char characteristics, two or more reactors may be used in a series. The last reactor will be used to cool and/or convert the char to activated carbon form. High temperature cyclones will be used to separate the particulates from the gas leaving the reactor system and return them to the bed.

Liquid Upgrading

The gas will be cooled in a spray condenser (1.2) using recycled water that will pass through an indirect heat exchanger. The gas will then be cleaned and upgraded (5.1) to produce hydrogen that will be used for upgrading the liquids (3.2). Waste gas and any sludge from this operation will be incinerated in an atmospheric fluidized-bed combustor (4.1).

The condensate from the spray condenser (1.2) will be separated into water and oil fractions based on the gravity difference (3.1). The oil will be hydrotreated (3.1) using hydrogen produced in the process. Two products will be collected. The lighter product will be a chemical feedstock suitable for production of benzene and phenol, both of which are high value commodity chemicals with huge markets. The heavier product will be a diesel fuel blend stock suitable for railroad engines. Unused gas, as well as the bottom fractions from this reactor, will be sent to the AFBC (4.1) for their fuel values.

Char Upgrading

The main objective of char upgrading is to increase its value in the designated application. The volatile matter content of the char will be lowered to the level desired in the PTC process by controlling the particulate residence time and temperature in the mild-gasification reactor. If necessary, an extra stage will be used for this purpose.

Because of the removal of moisture and volatile matter during the mild-gasification process, char will be higher in ash and sulfur contents than the parent coal. It is proposed to use inexpensive physical methods to upgrade the char (2.1). Dry gravity and/or magnetic separation methods are being considered for this purpose. This selection is based on the conjecture that most of the sulfur in the char will be present as pyrrhotite, which is magnetic. Also, the mineral matter (ash) rich particles will be heavier than the clean porous char particles. Exploratory bench-scale tests performed on the mild-gasification chars have shown good results.

The clean char from the upgrading operation will advance to the pellet production area. The dirty char, rich in ash, will be fed to the AFBC (4.1) as a fuel.

Pellet Production

We plan to utilize the upgraded char for the production of pellets that could be marketed to the metal industries, particularly the iron and steel industry. The process to be used is called the PTC-Cold Bond Agglomeration Process, which has been developed by Pellet Technology Corporation (PTC) of Houghton, Michigan.[5]

The clean char will be mixed with additives and pelletized on a disc pelletizer (2.2). The pellets will then be hardened in an autoclave (2.3). The hardening temperature used in the process (about 200°C) is much lower than temperatures used in the conventional pelletizing process (1,300°C). This not only results in lower process costs but also makes it possible to produce carbon or carbon-bearing iron oxide pellets using char as the carbon source.

Although it is not shown in Figure 1, one could have a direct reduction kiln or a cupola on site to process the carbon-bearing iron oxide pellets. Metallized iron pellets or iron from cupola will be sold in the open market, preferably to minimills which have a better growth potential in this country than the integrated steel mills. Carbon monoxide rich gas from the kiln or cupola will supplement the power production discussed below. Thorough intermixing of carbon and iron oxide in the PTC pellet dramatically reduces the reduction time required for iron production, as shown by Figure 3.

Power Production

The atmospheric fluidized-bed combustion (AFBC) unit (4.1) serves three purposes.

1. It is used as an incinerator for all the solid, liquid, and gaseous wastes from the plant. Lime will be used to control sulfur emissions.

2. It provides process heat, as hot flue gas or steam, to various reactors such as the mild-gasification reactor and pellet induration autoclaves.

3. It produces steam that will be converted to electric power. Part of this power will be used to satisfy the plant and mine requirements. The rest will be sold as another value-added product of the process. AMAX believes that cogeneration will be a major part of the future energy industry.

CONCLUDING REMARKS

In summary, UNDEMRC, AMAX, and PTC are working on a very promising process to produce synthetic fuel from coal. The process operates at mild temperature and pressure conditions, which will contribute to low costs. The sale of other value-added products such as carbon or iron pellets and electric power in local markets will further enhance the economics of the process. Simultaneously, the process provides a low cost method for production of iron, which should benefit our domestic steel industry.

REFERENCES

1. M. R. Ghate, K. E. Markel, Jr., L. A. Jarr, and S. J. Bossart (Editors), Proceedings of the Seventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Volumes I and II, Report DOE/METC-87/6079, Morgantown Energy Technology Center, Morgantown, West Virginia, June 1987.

2. W. G. Willson, et al., "Development of an Advanced Continuous Mild Gasification Process for the Production of Coproducts. Literature Survey Results", Topical Report for Work Performed Under Contract No DE-AC21-87MC24267, January 1988.

3. J. E. Sinor, "Development of an Advanced Continuous Mild Gasification Process for the Production of Coproducts. Industrial Market Assessment of the Products of Mild Gasification", Topical Report for Work Performed Under Contract No DE-AC21-87MC24267, January 1988.

4. Fuel and Mineral Resources, Inc., "Annotated Review and Classification of Char Producing Processes", Reston, Virginia, October 1987, Final Report for DOE Contract DE-AC01-85FE60601.

5. A. Goksel, T. A. Schott, F. Weiss, and J. Coburn, "PTC-Cold Bond Agglomeration Process and Its Various Applications in the Iron and Steel Industry", presented at the 20th Biennial Conference of the Institute for Briquetting and Agglomeration (IBA), September 27-30, 1987, at Orlando, Florida, and published in the same proceedings.

LEGEND

MILD GASIFICATION	1.1 AFBR 1.2 SPRAY CONDENSOR
CHAR CLEANING AND PELLETIZING	2.1 CHAR CLEANING 2.2 MIXER PELLETIZER 2.3 AUTOCLAVE
CONDENSABLE UPGRADING	3.1 GRAVITY SEPARATOR 3.2 HYDROTREATOR
PROCESS HEAT/STEAM GENERATION	4.1 AFBC
GAS CLEANING/SEPERATION/COMPRESSION	5.1 GAS CLEANING/SEPERATION

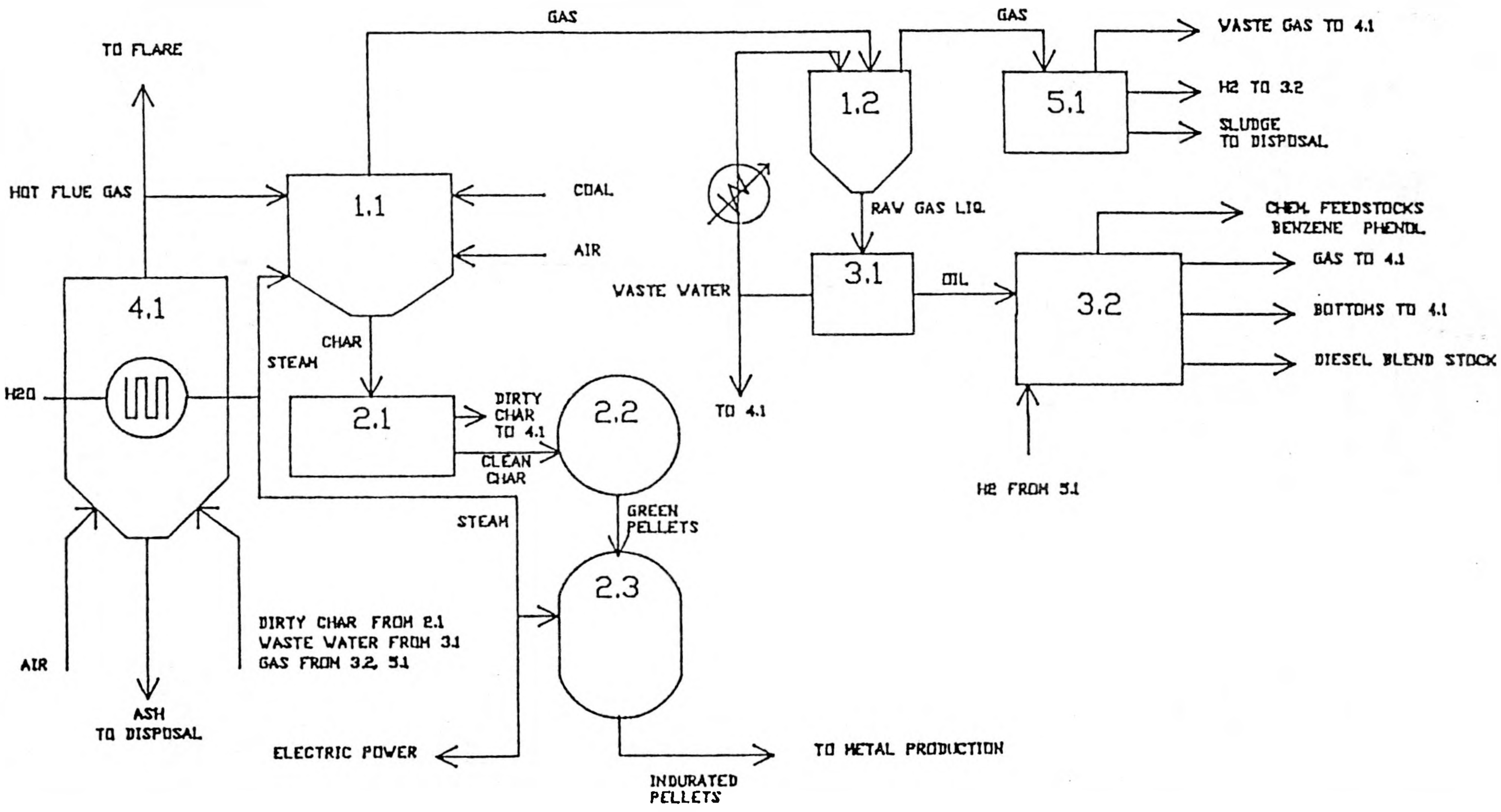


Figure 1. Schematic process flow diagram.

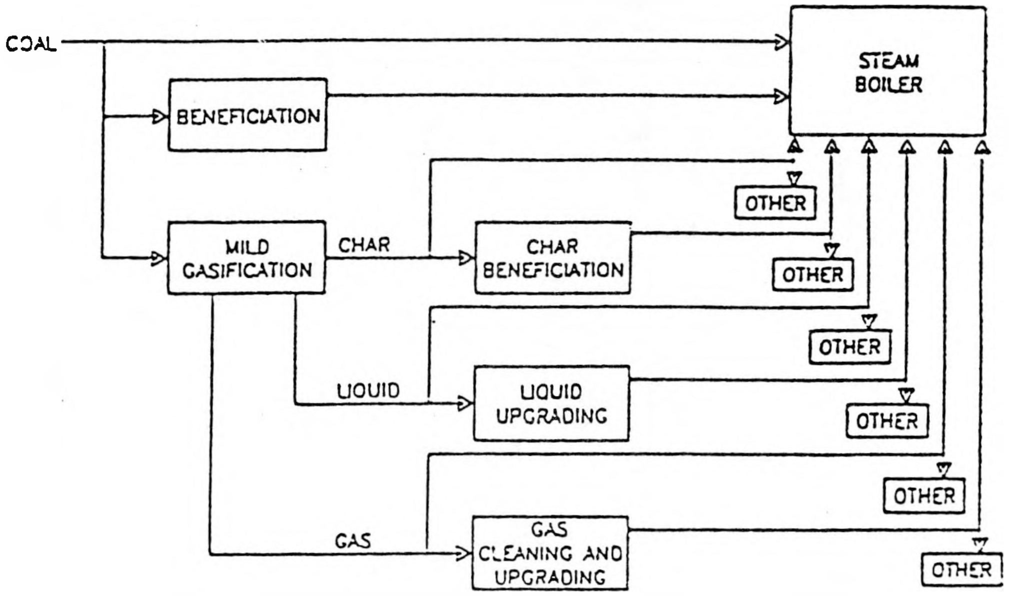


Figure 2. Alternate routes for coal utilization.

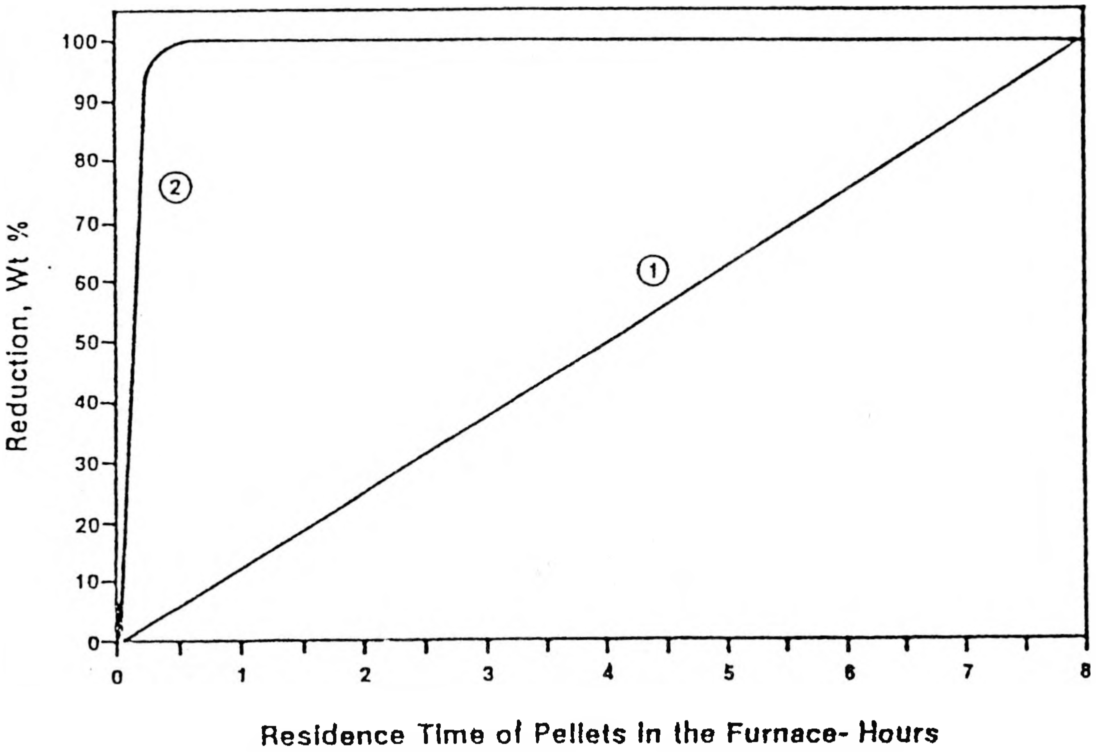


Figure 3. Comparison of reduction rates of oxides pellets in the blast furnace (1) and PTC carbon-bearing pellets in the cupola (2).

"LOW TEMPERATURE PYROLYSIS FOR SYNFUEL PRODUCTION"

BY: RADHA KRISHNAN
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

NO PAPER SUBMITTED

"ASSESSMENT OF YUGOSLAVIAN LIGNITE FOR COAL/WATER FUELS"

BY: BLAZO LJUBICIC, AND ZARKO BUKAROV
UNIVERSITY OF NOVI SAD
T.A. POTAS
ENERGY & MINERAL RESEARCH CENTER- UND
GRAND FORKS, ND

ASSESSMENT OF YUGOSLAVIAN LIGNITE FOR COAL/WATER FUELS

Blazo Ljubicic and Zarko Bukarov
University of Novi Sad, Yugoslavia
Todd A. Potas
University of North Dakota
Energy and Mineral Research Center

ABSTRACT

Yugoslavia has vast reserves of lignitic coal, although the majority of the lignite is of low quality and located in geographic areas that are difficult to mine. These lignites can contain over 40 wt% moisture, 25 wt% ash, and 4 wt% sulfur, all of which discourage their use in conventional pulverized coal mining and combustion. Some of the most promising reserves are located under and along the Danube River, making conventional strip mining totally unfeasible and pulverized coal combustion difficult. This lignite deposit (Kovin) is to be mined as a coarse coal/water slurry for the first time using dredging equipment mounted with bucket wheel excavators. Potentially, the most attractive way to utilize these reserves for power generation would be to combine the hydraulic mining technique with the following: aqueous ash removal, hydrothermal processing, solids concentration, and coal/water fuel (CWF) combustion. An agreement to investigate the technical and economic assessment of this approach has been signed by the University of Novi Sad in Yugoslavia and the University of North Dakota Energy & Mineral Research Center. A preliminary framework estimation of the CWF approach for the Kovin location is presented in this paper.

INTRODUCTION

The present economic conditions in Yugoslavia require rapid and expedient change in the structure of energy fuel consumption. Coal utilization was unjustifiably disregarded for many years in favor of imported oil and gas. This overbalance has led to a tremendous effort to identify and utilize all available domestic resources. The current fossil fuel consumption distributions are shown in Figure 1. Yugoslavia's dependence on imported energy is more than clear: over 60% of the oil and over 70% of the natural gas consumed annually is being imported. Considering this high dependence, alternate sources are required.

Prospects for increasing domestic oil and gas production are nonexistent. The same statement can be applied to many other energy sources. Nuclear energy has very strong opposition and is not likely to become an alternative. Hydro-electric potential is almost exhausted with no significant possibilities for new construction.

To meet energy demands in Yugoslavia two main directions are available: to increase coal production in accordance with estimated resources up to 200 million tons of coal per year; and strict control of energy conservation. The question is not will Yugoslavia rely on coal, but how, and at what rate, will this reliance grow. Coal consumption projections are under constant reevaluation and revision. A production increase of 130 million tons of coal per year would be as much or higher than all present energy imports. It is overly optimistic that all imported energy could be substituted with coal but the advantages for increased coal use are obvious.

The biggest coal potential exists as lignitic coal. There are three main lignite basins in Yugoslavia: Kosvo, Bosna and Kolubara. These areas are shown in Figure 2.

A problem in the utilization of the coal exists since the basins are not close to the major consumers. One area of major energy consumption is the county of Vojvodina (Figure 2), a main agricultural and industrial section of Yugoslavia. Currently, Vojvodina is trying to find the means to satisfy growing energy demands. The possibilities are:

- Mine mouth, power plant electric generation and transmission by long-distance power lines.
- Railroad transport of coal from one of the main lignite basins to consumers in Vojvodina.
- Pipeline transport of coal as CWF from one of the main basins to consumers in Vojvodina.
- Development of the largest coal deposition in Vojvodina, located mainly along and under the Danube River.

Mine mouth power plant electric generation, has certain advantages and is an established technology for lignite utilization. However, coal electric generation technology has been effectively frozen for the past 35 years. It takes, for example, the same amount of coal today to produce a kilowatt hour of electricity as it did in 1950. There is a need to be able to build smaller, more easily constructed power units, which can be quickly installed in any location to take full advantage of existing systems and possible co-generation. With these considerations, it was concluded that the best solution for Vojvodina would be to build seven coal-fired co-generating power plants. They will jointly produce electricity and heat for seven towns of 50 to 100 thousand people.

Given renewed emphasis on coal utilization, comparative transport costs play a key role. Coal slurry or coal/water fuel pipeline transport is an available alternative to unit train transportation. Although the principle is not new, it needs further investigations. The following is an introductory study on the possibilities of coal/water mixture transportation.

ASSESSMENT

Hydraulic Transport

Except for the availability of water, pipelines are geographically unlimited. Pipelines may be routed through and around mountains, cities, and other obstacles. However, routing and terrain have a large affect on construction cost, pipeline pressure and required pumping power.

Hazards associated with pipeline transport are breakage and plugging. While plugging does not occur on liquid and gas pipelines, line breaks and leaks do occur. System reaction is nearly the same for both cases. Stations upstream of the plug or break must dump slurry into holding ponds and introduce water for flushing. Plug removal or other repair may take more time than the relative stability of the CWF, which may settle in the pipeline. Pipelines that have throughput flow in the laminar regime may be subjected to freezing during periods of severe cold. Pipelines are best constructed underground, but some portions must be exposed. If the mixture freezes, pressure increase will be a function of viscosity increase, and a frozen section can act as plug.

The pressure drop during hydraulic transportation of coal/water mixtures has been extensively researched over a period of many years. Most theoretical models can be considered to be purely empirical, derived for the purpose of representing measured data. Thus, the representative models are limited by the quality and quantity of the data. It is imperative to recognize these limitations, both in model evaluation and application.

An impressive study of high concentration coal/water mixtures by Elliott and Gliddon indicated coal/water mixtures can be described by non-Newtonian fluid mechanics (1). CWF produced by control of particle size distribution often behave as Bingham plastic fluids in laminar flow up to a shear rate of about 100 s^{-1}. These conditions allow the designer to use established non-Newtonian theory as an estimation of energy loss.

Example:

Consider the transportation of stabilized CWF from Kovin to a cement factory containing 47% solids concentration at a rate of 45 m3/h, over a distance of 100 km at Beocin. Assuming laminar flow, i.e., 8V/D is less than 100 s^{-1}, then a typical pipeline diameter of 200 mm is realistic using a slurry velocity of 0.4 m/s. Using the equation given by Elliott and Gliddon, and rheological results, shown in Figure 4, an appropriate steady-state hydraulic gradient can be calculated as:

$$i_F = \frac{\Delta P_F}{\rho_M * g * L} = K' \left(\frac{8 * V}{D}\right)^{n'} * \left(\frac{4}{D * \rho_M * g}\right)$$

where:

i_F - hydraulic gradient attributable to mixture - wall friction losses [m of slurry/m of pipeline]
ΔP_F - pressure drop due to friction [Pa]
ρ_M - mixture density [kg/m^3]
g - acceleration due to gravity [m/s^2]
L - pipeline length [m]
V - cross sectional mean mixture velocity [m/s]
D - pipe diameter [m]

For Bingham plastic behavior constants n' and K' are given by:

$$n' = \frac{1 - \frac{4x}{3} + \frac{x^4}{3}}{1 - x^4}$$

$$K' = T_w \left[\frac{\eta}{T_w \, (1 - \frac{4x}{3} + \frac{x^4}{3})} \right]^{n'} \qquad [kg/m\ s]$$

$$x = \frac{T_o}{T_w}$$

where:

T_o - yield shear stress [Pa]
T_w - shear stress at pipe wall [Pa]
η - apparent viscosity [Pa S]

The mixture density is given by the expression:

$$\rho_M = \left[(\frac{\rho_S}{\rho_L} - 1) \ * C_w + 1 \right] * \rho_L$$

where:

ρ_S - density of solids [kg/m^3]
ρ_L - density of liquid [kg/m^3]
C_w - solids concentration [%]

For a given example the following result can be calculated:

$$\rho_M = [0.4 * 0.47 + 1] * 1000 = 1188 \ [kg/m^3]$$

$$n' = 0.1647$$

$$K' = 38.38 \ [kg/m\ s]$$

Given that D = 0.2 m and V = 0.4 m/s, we have:

$$i_F = 38.38 \left(\frac{8 * 0.4}{0.2}\right)^{0.165} * \left(\frac{4}{0.2 * 1188 * 9.81}\right) = 0.1 \ [m\ of\ sl./m\ of\ pipe]$$

$$\Delta P_F = i_F * \rho_M * g * L = 0.1 * 1188 * 9.81 * 1000 = 1165 \ [bar/km]$$

These results indicate an unacceptable pressure drop for economical hydraulic transport. High yield stress and high viscosity have to be reduced. Coal/water fuel rheology requires further investigation. An alternative approach could be hydraulic transport with lower solids concentration, and partial dewatering before combustion.

If the same example is calculated for a solids concentration, C_w of 45%, this results in:

$n' = 0.055$

$K' = 11.32$ [kg/m s]

and $$i_F = 11.32 \left(\frac{8 * 0.4}{0.2}\right)^{0.055} * \left(\frac{4}{0.2 * 1188 * 9.81}\right) = [0.022\text{m of sl/m of pipe}]$$

$$\Delta P_F = 0.022 * 1188 * 9.81 * 1000 = 2.56 \text{ [bar/km]}$$

Therefore, with 45 wt% dry solids, a reduction of only 2% solids, the pipeline pressure drop is lowered five times.

Project KOVIN

As a first step toward meeting the energy demands in Vojvodina, a potential solution was to activate the lignitic coal deposit along the Danube River. Project KOVIN is currently under way and is projected to operate with annual production of 4 million tons of coal and 600 MW of mine mouth power plant output. Coal characteristics of the deposit at Kovin are shown in Table 1.

Because of the Danube River, conventional strip mining is very difficult and uneconomical, making dredging technology the best alternative. The main coal seam is about 40 m deep with 20 m of overburden, and the second seam is between 60 and 80 m under the surface. Coal is to be mined as a coarse coal/water slurry using underwater bucket wheel excavators. Four dredgers will be operating on an artificially prepared pond. Two of them would be used for dredging the overburden layers above the coal with the remaining two for coal excavations.

A preliminary comparison study shows that hydraulic mining is more than twice as economical as open mine mouth techniques (2). At this point, Project KOVIN is conceived as a combination of underwater mining and conventional pulverized coal combustion. This may prove to be a poor combination, since both dry and wet coal handling equipment will be required with the solid coal drying being dangerous and difficult. This can be avoided if it is possible to prepare a coal/water fuel from the mined lignite through hydrothermal treatment. Hydrothermal treatment, currently being researched at the University of North Dakota Energy & Mineral Research Center (EMRC), improves the lignite characteristics to such a degree that it becomes possible to prepare concentrated CWF from the treated product (3). This would allow the coal to be handled as a liquid from the moment it is mined to utilization.

TABLE 1. PULVERIZED YUGOSLAVIAN LIGNITE ANALYSES

	As Received	Moisture-Free
Prox. Analysis (wt%):		
Moisture	26.4	NA
Vol. Matter	35.1	47.7
Fixed Carbon	22.2	30.1
Ash	16.3	22.2
Ult. Analysis (MF basis, wt%):		
Hydrogen	5.00	2.80
Carbon	37.75	51.28
Nitrogen	0.39	0.53
Sulfur	0.75	1.02
Oxygen	39.78	22.17
Heating Value (Btu/lb)	6390	8680
Ash Analysis (wt%)	% Elem.	% Ash
Silica	21.8	48.3
Alum. Oxide	11.2	21.9
Ferric Oxide	4.9	7.3
Titan. Oxide	0.6	1.1
Phos. Pentoxide	0.1	0.3
Calcium Oxide	6.0	8.6
Magnes. Oxide	1.9	3.2
Sodium Oxide	0.0	0.0
Potas. Oxide	1.3	1.6
Sulfur Trioxide	3.0	7.7

Existing coal grinding and physical cleaning techniques can be efficiently combined with slurry preparation for the lowest cost in a coal/water fuel scenario. An integrated system that ties together the coal mining, processing, transportation, and combustion into a more efficient operation is now possible. This is an improvement over a system where each component is considered separately, or when dry coal handling is considered. The mining, coal production, and utility industries should realize the opportunity of the synergism of integrated preparation and transportation systems. Once in place, such systems would reduce the price of using coal. Figure 3, a plant-site schematic of Project KOVIN, compares a typical dry coal handling and preparation to the proposed hydrothermal CWF processing scheme. The schematic features the planned 600-MW power station, the coal mining areas, and proximity of the development to the Danube River. Both the conventional and the CWF coal processing options will utilize 30 wt% as-received coal slurry from the hydroclone.

Experimental

Preliminary analyses and testing performed on a typical Yugoslavian lignite included proximate, ultimate, ash, heating value, and rheological analyses. The standard ASTM coal analyses procedures were used for the coal analyses. A Haake RV 100 concentric cylinder viscometer was used for the rheological determinations.

Feasibility testing for physical cleaning on the bench-scale was performed using Certigrav specific gravity solution at 1.3, 1.4, 1.5, and 1.6 sp. gr. levels, respectively, for both combustion grind and 1/4"-by-20-mesh coal (4). Hot-water drying was performed at 330°C and 2200 psi for a residence time of 5 minutes using the EMRC continuous hot-water-drying Process Development Unit (PDU) (3).

Results

Physical coal cleaning showed that it is possible to reduce the ash content of the Yugoslavian lignite from 22.2 wt% ash for the raw coal to 9.9 wt% for the 1.5 sp. gr. float product at a weight recovery of 73.4%. This cleaning was performed on 1/4"-by-20-mesh coal (6.3 to 0.85 mm). Similar results were obtained for a combustion grind (80% <75 μm) Yugoslavian lignite sample. These preliminary results show that removal of the heavier ash components from Yugoslavian lignite can be performed with excellent recoveries.

Preliminary hydrothermal treatment effects indicated significant alteration to the raw coal. Raw coal slurry solids contents were 37 wt% dry solids at a viscosity of 800 cP and a shear rate of 100 $\sec^{-1}$. This compares to a 47 wt% dry solids fuel produced with the hydrothermally treated coal at the same conditions. The flow behavior of the CWF is represented in Figure 4 as shear stress versus shear rate. The coal sample tested was oxidized before treatment (note the low moisture and hydrogen levels in Table 1). Moisture contents of 40 to 45 wt% are more common for these lignites. Oxidation of coal samples has been known to cause lower CWF performance after hydrothermal treatment. These preliminary findings indicate CWF of greater than 50 wt% dry solids are easily possible.

CONCLUSIONS

Feasibility studies will be performed to prove the economic and environmental benefits of the CWF technology. Therefore, it is too early for any final decision on Project KOVIN, although the possibilities for commercial implementation of CWF are at hand. The following conclusions are:

1. Preliminary experiments show that the Yugoslavian lignite responds to physical coal cleaning and hydrothermal treatment.

2. Handling and transport of coal and mining waste at Project KOVIN would be completely performed by efficient hydraulic equipment.

3. CWF technology avoids solids dewatering, thermal drying, and dry coal handling, which are difficult and hazardous coal processing options.

4. A CWF product would allow main consumers in Vojvodina to be supplied by pipeline or tanker transport using hydraulic equipment.
5. Co-generation at other power plant locations, including local electric generation and steam heating, becomes possible when these transport capabilities are in place.

Favorable investigation of hydraulic handling and transport combined with low-rank coal hydrothermal treatment may provide a solution to conventional lignite coal handling problems, allowing CWF technology implementation at Project KOVIN.

FUTURE PLANS

The implementation of Project KOVIN should be based on wide experimental work required to define the main design data and duty specification for the main equipment.

The main experimental activities necessary would be:

a) Complete characterization of coal and its superficial properties.

b) Optimization of the CWF characteristics (selection of particle size distributions compromising solids concentration, viscosity, and requirements for combustion and energy consumption).

c) Rheological and pumping characteristics require thorough investigation due to the importance of CWF transport via pipeline for Project KOVIN.

d) Combustion performance on promising bench- and pilot-scale coal utilization systems requires investigations.

These activities are being planned according to formal agreement and proposal submissions jointly made by the University of Novi Sad Institute of Hydraulics and Transportation and the University of North Dakota Energy and Mineral Research Center.

Project KOVIN is proposed to function as both a commercial and pilot plant defining the following technical features:

- to demonstrate commercial plant size and reliable operation.
- to serve as a pilot plant, used to investigate process parameters and types of equipment

The future of CWF technology in Yugoslavia is not tied directly to the price of oil as in industrially developed countries. Economic conditions, location of energy consumers, geographical considerations, and imported energy dependence all serve as driving forces for the commercial breakthrough of CWF technology.

REFERENCES

1. Elliott, D.E., and Gliddon, B.J., "Hydraulic Transport of Coal at High Concentrations", BHRA, Hydrotransport 1, G2-25, 1970.

2. "Preliminary Comparison Study for Open Mine and Hydraulic Mining at KOVIN Location", Mining Institute, Zemun, Yugoslavia, 1985.

3. Potas, T.A. et. al., "Pilot-scale Preparation of Low-Rank Coal/Water Fuels", Journal of Coal Quality, Center for Coal Science, Western Kentucky University, April 1987.

4. Malterer, T.J. et. al., "Screening of Low-Rank Coals for Low-Ash Fuel Preparation", 13th International Conference on Coal & Slurry Technology, Denver, CO, April 1988.

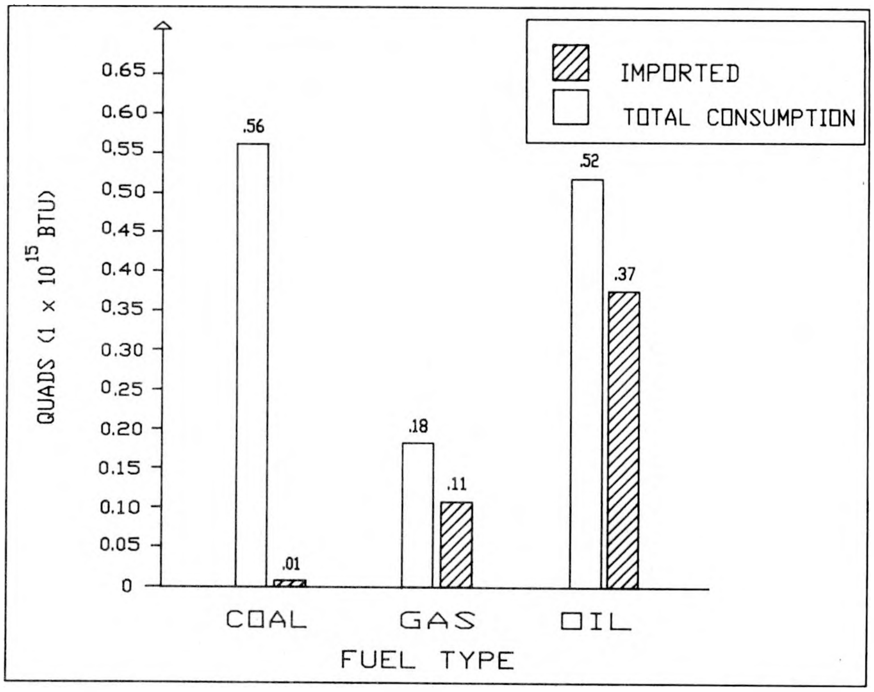


Figure 1 - Annual Energy Consumption for Yugoslavia

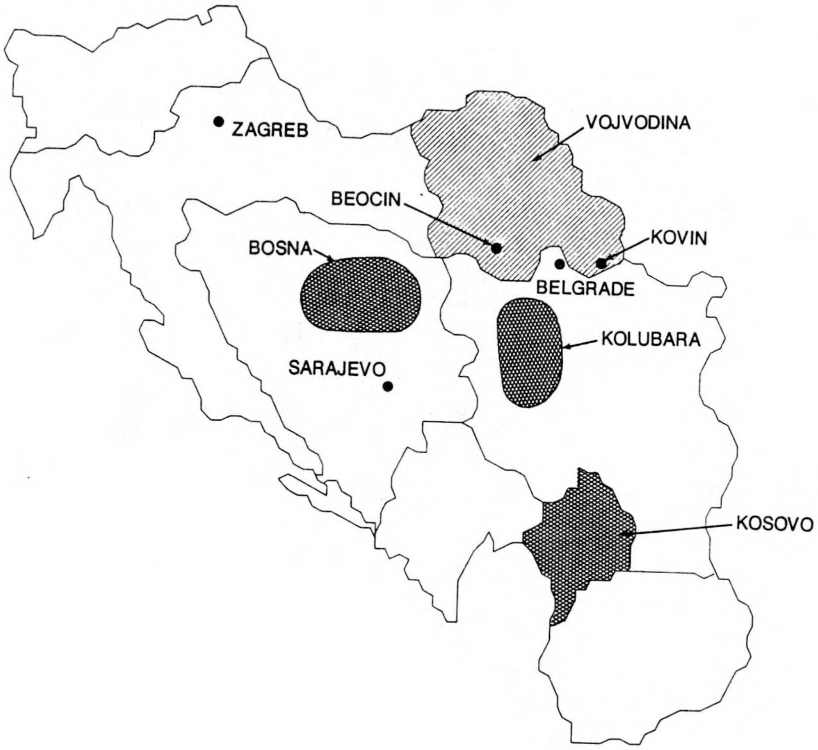


Figure 2 - Map of Yugoslavia, Including Major Lignite Deposits

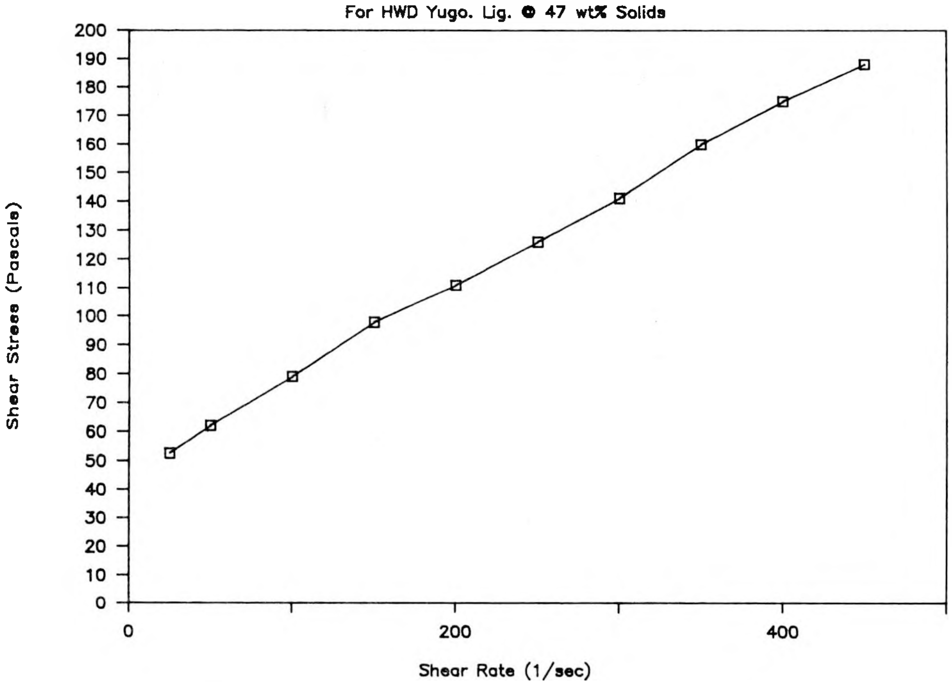


Figure 4 - Shear Stress vs. Shear Rate for CWF from Yugoslavian Lignite

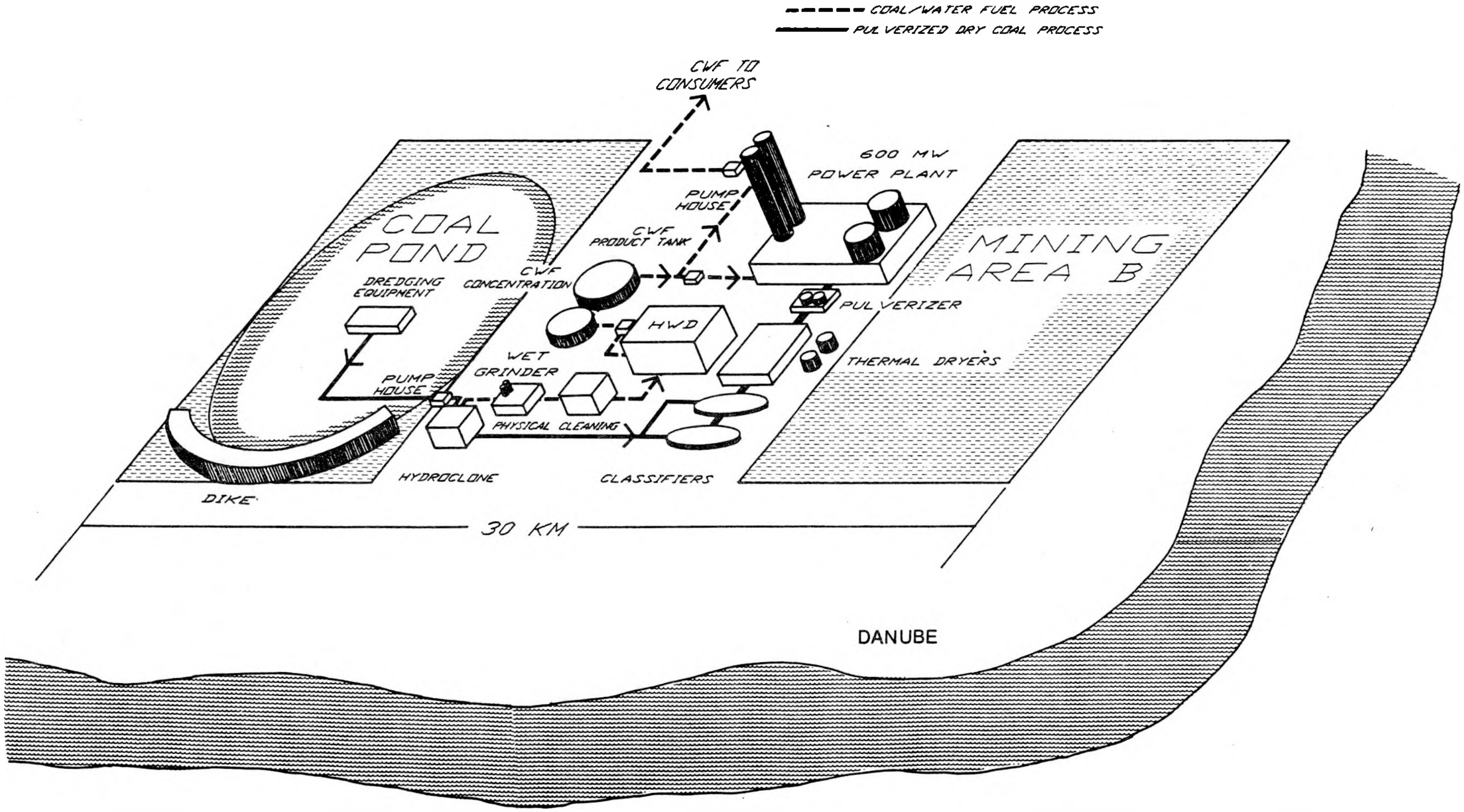


Figure 3 - Project KOVIN Plant-Site Schematic

SESSION 3: EMISSION CONTROL

SESSION CHAIRS:

JIM EVANS
GAS RESEARCH INSTITUTE
CHICAGO, IL

WILLIAM SCHOTT
BASIN ELECTRIC POWER CO.
BISMARCK, ND

1. "Sulfur Removed Through Liquid Redox Chemistry"

   by: D. Dalyrmple
   Radian Corporation
   Austin, TX

2. "Pilot Plant & Commercial-Size Testing to Resolve SO_2 Emission Problem at Great Plains"

   by: A.H. Kuhn and G.G. Baker
   ANG Coal Gasification Company
   Beulah, ND

3. "Advanced Flue Gas Cleanup Technologies Being Developed for Coal-Fired Utilities Boilers"

   by: C.E. Drummond
   Pittsburgh Energy Technology Center
   Pittsburgh, PA

"SULFUR REMOVED THROUGH LIQUID REDOX CHEMISTRY"

BY: D. DALYRMPLE AND TIMOTHY W. TROFE
RADIAN CORPORATION
AUSTIN, TX
J.E. EVANS
GAS RESEARCH INSTITUTE
CHICAGO, IL

ABSTRACT ONLY

ABSTRACT

Liquid redox chemistry has been employed for sulfur removal and recovery applications since the late 1950's. The first process to be used commercially was the Stretford process, which was used extensively in the United Kingdom in the 1960's as a replacement for the expensive iron sponge process in the treatment of sour town gas. Since that time, liquid redox chemistry has been found to offer advantages for a wide variety of sulfur control applications in the synfuels and other energy industries. Some of the inherent advantages are one-step conversion of H_2S to elemental sulfur, ambient temperature and pressure operation, regenerating catalysts, and applicability to very low and very high H_2S levels (several ppm to greater than 90 percent). These processes also remove sulfur while it is concentrated as reduced sulfur (H_2S) in the fuel rather than having to treat it as SO_2 in a much larger exhaust gas stream.

The need for liquid redox sulfur recovery processes in the synfuels and other energy industries is projected to increase as a wider variety of fuel forms are developed, many containing sulfur which must be removed. Current applications include treatment of natural gas, geothermal vent gas, enhanced oil recovery vent gas, coal-derived gas, coke oven gas, Claus plant tailgas, refinery and chemical plant fuel gases, and municipal anaerobic wastewater treatment plant off-gas.

In recent years, the Stretford process has been joined in the United States' marketplace by several other liquid redox processes including the the Unisulf, Sulfolin, LO-CAT, SulFerox, and Hiperion processes. This paper presents summary information on all six processes based on published literature, patent information, and contacts with users and designers. The liquid redox chemistry associated with each process is discussed along with known similarities and differences with respect to process design and equipment. Other areas covered include typical liquid redox sulfur recovery applications, the problem of conversion of inlet sulfur to non-regenerable by-product salts, environmental, health, and safety considerations, and capital and operating costs.

"PILOT PLANT & COMMERCIAL-SIZE TESTING TO RESOLVE SO_2 EMISSION PROBLEM AT GREAT PLAINS"

BY: A.H. KUHN AND G.G. BAKER
ANG COAL GASIFICATION COMPANY
BEULAH, ND

PILOT PLANT AND COMMERCIAL-SIZE TESTING
TO RESOLVE
SO_2 EMISSION PROBLEMS AT GREAT PLAINS

G. G. Baker, A. K. Kuhn and D. C. Pollock
ANG Coal Gasification Company

Abstract

The Great Plains Coal Gasification Project has demonstrated a remarkable success, both in start-up and by exceeding production goals for the first three years of production. The project has been plagued only by one shortcoming, removal of hydrogen sulfide to achieve the desired plant SO_2 emissions. In particular, two of the three feedstreams, the fuel gas and the Phosam off-gas, had to be bypassed since they made the Stretford Unit inoperable. In addition, H_2S removal efficiency for the main CO_2 waste gas stream was much lower than predicted and absorber packing had to be removed due to excessive fouling.

A pilot plant was built to simulate operation for any of the feedstreams. Investigations were made to explore benefits of pretreating the problem streams. Additives and alternative technologies were tested to determine how plugging of packing could be minimized. Synthesized feedgas and various concentrations of CO_2 were used to investigate the cause of packing plugging. Another series of tests determined, on a commercial-scale basis, the benefits of venturi modifications as well as different configurations of two-stage venturi operation. Alternative packings, such as hollow balls and Tripack, were studied in 6 inch and 30 inch pilot scale absorbers. Hollow balls have been installed in a full-size plant absorber showing encouraging results.

As a result of these various R&D activities, recommendations were made about pretreatment of the fuel gas and Phosam gas. The program already has led to a changeout in solution, switching from Stretford to Sulfolin chemistry. Venturi and packing test results through the end of January 1988 led DOE to prepare an application with the NDSDH on the basis of two-stage countercurrent venturies. More recent testing is showing that other alternatives may be more effective.

Introduction

The Great Plains Coal Gasification Project, which typically converts more than 16,000 tons/day of North Dakota lignite to 150 MMSCFD of substitute natural gas, was commissioned in 1984. Since start-up, the project has been an unparalleled success. The plant on-stream factor has been 80, 99, 103 percent for the last three years. Part of this success is due to the fact that the plant can be operated without difficulties at least 10 percent above the original design capacity of 137.5 MMSCFD of SNG production.

Although the initial start-up of the facility had its share of difficulties, all significant problems were resolved in a timely fashion and at reasonable cost except for the problems in the Sulfur Recovery Unit. This unit had been designed based on Stretford technology. Waste gas streams containing H_2S were to be first contacted with Stretford solution in venturis followed by a fixed bed absorber. Residual H_2S was to be less than 100 ppm by volume. The unit was to treat 3 major feedstreams: 1) The main CO_2 waste gas stream originating in the Rectisol Unit; 2) The non-condensibles from the Phosam Unit, an ammonia recovery process; and 3) the fuel gas originating from the Lurgi gasifier coal lock gas recovery system. Of the three, the Rectisol waste gas stream provides the bulk volume. Table 1 provides a composition for these 3 streams. Unfortunately, soon after admission of either of the Phosam or fuel gas feedstreams, the Stretford Unit experienced severe upsets. Excessive foaming of the solution occurred when processing Phosam-W off-gases and the lock gas caused severe problems in the sulfur melter operation. Upsets in sulfur flotation occurred with both feedstreams. As a result, these two process streams had to be bypassed and left untreated. Another disappointment was the H_2S removal efficiency obtained for treating the Rectisol waste gas. The venturi efficiency was less than expected and the absorber packing was plugged with sulfur in a matter of days. This problem could not be resolved and, in order to continue operation, the packing had to be removed.

The net effect of these difficulties, together with a higher than expected concentration of organic sulfur species in the plant's liquid fuels and waste gas, was that sulfur emissions substantially exceeded the original projected emission figures (Table 2).

At the time that these overall plant emission figures were established, the Great Plains project was in serious difficulties otherwise. After denial of any federal price support, the original partnership of pipeline companies defaulted on the loan and the government assumed ownership in accord with an earlier granted federal loan guarantee agreement. While the economics of continued operation under the new ownership were being evaluated, no commitments could be made on how to fix the sulfur emission situation. By the time appropriate state agencies started to press the issue, ANG and DOE had developed a test program to examine and improve the poor performance of the Sulfur Recovery Unit. This development program is now nearing completion and solutions for commercial plant implementation are being finalized. The remainder of this paper describes some of the highlights from the research and development activities.

Six-inch Pilot Plant

In 1986, a small Stretford pilot plant was built including a 6-inch absorber, reaction tank, four oxidizers, a sulfur slurry tank as well as a centrifuge and a balance tank (see Figure 1). All of these components are typical for a Stretford Unit. The absorber was made of glass thus permitting observation of irrigation patterns, fouling tendencies, packing behavior, etc. All three feedstreams identified earlier could be tested. The unit was designed to handle 12.5 SCFM of CO_2 waste gas requiring a 5 gpm liquid feed rate. Stretford solution could be supplied from either the commercial plant or made up as a virgin solution (Ref. 1).

Objectives of the pilot plant research program were as follows:

a. Investigate pretreatment needs for Phosam off-gas and fuel gas streams.

b. Investigate cause(s) for poor H_2S removal.

c. Explore benefits of alternative technologies.

During pilot plant operation, many process parameters were recorded together with observations about froth behavior, fouling of the packing, etc. This information was then used to evaluate the effects of different test parameters. Figure 2 shows some of the typical data that was collected for each run. Following are some of the lessons learned:

As in the commerical unit, processing the raw Phosam off-gas in the pilot plant caused uncontrollable foaming in the absorber and produced a very aerated structurally stable froth on the oxidizers. This froth proved to be difficult to blend into a sulfur slurry for further processing. Feeding raw fuel gas produced very finely dispersed sulfur particles in the wash liquor. This sulfur, if left in an unagitated state, would settle to the bottom of the vessels forming a slurry layer having the consistency of latex paint. In these tests, both gas streams tended to raise the carbon content of the melted product sulfur and increased the odor problems around the oxidizers and with the melted sulfur product. In addition, the problem of solids forming on the surface of the column packing was observed when processing these streams. After sufficient time, growth of solids in the lower stages of packing caused the absorber to flood.

Cooling and chilling these streams to 40°F produced a condensate, which contained significant quantities of organic substances. In the case of the Phosam off-gas, a major portion of the organic phase was isopropyl ether, a solvent used in another area of the plant (Phenosolvan Unit). Other compounds identified were acetone, pentanone, methyl-naphthalene, naphthalene, pyridine, and toluene. These organics are produced from gasification of the coal. Removal of these hydrocarbons reduced the severity of foaming in the absorber and also reduced the odor problems around the oxidizers.

Refrigeration of the fuel gas to 40°F produced less discernible effects. However, the apparent benefits were larger sulfur particles in the Stretford solution and froth production was better than when raw fuel gas was treated. Both sets of refrigerated gas tests were inconclusive regarding the impact on improved sulfur quality and sulfur melter operation. Plugging of absorber packing continued to occur while operating with these refrigerated feedstreams.

Plugging of absorber packing had also been a major issue while operating on Rectisol waste gas. For this reason, a number of pilot plant tests were carried out to determine if low levels of hydrocarbons or the high CO_2 content of the gas was responsible for the plugging phenomena. In addition to dilution of Rectisol waste gas with nitrogen, synthesized feed gas mixtures from pure nitrogen, carbon dioxide and hydrogen sulfide were also tested. Figure 3 shows the range of run lengths between absorber pluggings for gas mixtures containing various concentrations of CO_2. Runs made with pure N_2 and H_2S showed no sign of plugging for the duration of a 5-day test. Addition of CO_2, however, greatly accelerated the plugging and at 30 percent or higher concentrations of CO_2, it appeared that the absorber's service life was limited to about 15 hours. No significant difference in run length could be seen between the tests using synthesized feedstreams and those using dilutions of Rectisol waste gas. This latter finding suggested the plugging problem was due mainly to CO_2 and not to the hydrocarbons present in the gas.

A number of tests were performed to determine if changes in the Stretford chemistry, or additives such as citrate, thiocyanate and surfactants could reduce this plugging tendency. Out of a long list of runs, only citrate addition showed some benefit towards prolonging run times, although absorber plugging was still frequent. However, the solids that collected in the tower appeared to be less "sticky" than the usual deposits and could be removed mostly by water washing. One other test showed that absorber plugging could be eliminated if the Stretford process was operated without vanadium, using a high concentration ADA instead. However, the by-product formation rate was unacceptably high (7 g/l day versus .3 g/l day for a typical Stretford solution), and H_2S slip was considerable.

As the research program matured, the pilot plant was also used to explore alternative Redox technologies. Two processes were tested, Hiperion and Sulfolin. Most results from these tests are regarded as proprietary under licensor secrecy agreements. However, both tests revealed useful information. The Hiperion process allowed for much longer run length than when using Stretford solution and showed comparable H_2S removal efficiencies. The sulfur product, however, did not appear to be of equal quality as Stretford sulfur, and foaming problems were encountered when makeup chemicals were added.

The Sulfolin process provided good H_2S removal efficiencies and seemed to produce a sulfur that was less sticky than that made by Stretford. In addition, by-product formation rates were relatively low (0.1 g/l day). Plugging of the absorber still occurred although the Licensor offered suggestions for cleaning without requiring caustic washing. The sulfur that was produced by the Sulfolin process resembled that made by Stretford in both color and flotation characteristics.

Based partly on these pilot plant results and partly on the feedback received from SASOL's coal gasification plants in South Africa, Great Plains converted its Sulfur Recovery Unit from Stretford to Sulfolin chemistry in the fall of 1987. Making this change has improved the removal efficiency of the Sulfur Recovery Unit by about 2 to 3 percent and reduced SO_2 emissions by about 600 lb/hr. Implementation of chilling of the Phosam off-gas and the fuel gas will reduce the plant SO_2 emissions by about another 1200 lb/hr (at maximum sulfur coal).

Commercial-scale Venturi Testing To Achieve Higher H_2S Removal Efficiencies

Since encountering plugging problems with the packed towers, Great Plains was interested in exploring the benefits of multistage venturi arrangements. Early plant modifications were made to permit, on a test basis, attaining gas flow through two venturis in series. During these tests, some waste gas had to bypass the Sulfur Recovery Unit since venturis from two absorbers were operated in series rather than in parallel. Solution piping to the venturis was arranged for either parallel or countercurrent flow configuration. A temporary pump was installed to permit the countercurrent operating mode. Parallel flow was achieved with the existing solution pumps. The two-stage countercurrent arrangement requires less plant modifications than an arrangement with solution flow in parallel, but gas flow in series. The latter arrangement, on a full-scale implementation basis, would require additional oxidizer basins and other equipment, essentially a second complete facility. Costs for such an arrangement are excessive.

During the last several years, a number of single and two-stage venturi performance tests were carried out, initially with Stretford solution and more recently with Sulfolin solution. Early tests explored the impact of changes in venturi configurations. Nozzle dimensions and changes to the venturi tailpipe were compared. No significant improvements were found in these studies. The original design represented a fairly good arrangement. More recently developed data is of greater interest.

The following graph (Figure 4), shows various predicted removal rates near the expected ultimate plant capacity. For comparison purposes, long-term performance data obtained for single-stage venturi operation are shown. After an initial larger difference, Sulfolin solution still offers a couple percent higher removal rate than the earlier Stretford operation. Two-stage venturi operation, solution in countercurrent flow arrangement, raise the H_2S removal rates to the 90 percent level. Lean solution used in the countercurrent arrangement experiences pH depression and a reduction in active V^5. Both of these factors tend to decrease the removal rate in the rich liquor venturi stage. As a result, the overall removal rate is less than for the arrangement where both venturis receive the fully regenerated solution and would operate at similar removal efficiencies.

Although these tests were carried out with full-scale equipment, they include some uncertainty due to necessary plant adjustments to simulate appropriate oxidizer operating conditions. In case of the countercurrent arrangement, only one venturi of each absorber could be operated. Therefore, only 1/4 of the "B" Train gas flow and solution flow were required. Adjustments were made to the oxidizer operation to maintain a similar lean solution pH as measured for full capacity operation. It can only be assumed that the solution approximated the V^5 regeneration and CO_2 stripping (pH elevation) sufficiently close to produce comparable performance data. Continued operation has also shown that long-term solution performance must be monitored to determine the consistency of the data.

It must be pointed out that adding a second set of venturis such as contemplated for the countercurrent arrangement, requires pumping the total solution flow to elevated pressure for the second set of venturis. In addition to capital intensive plant modifications, the corresponding yearly operating expense is increased by over $1MM to cover the increased solution pumping requirement.

Alternative Absorber Designs

When absorber plugging problems were first experienced in the commercial unit, a number of packing modifications were briefly explored. Plastic versus stainless steel pall rings and Glitsch grid showed no long term improvement. Reduction in packed bed height and addition of sprays provided no satisfactory solution. After a series of unsuccessful commerical scale tests, the packing was removed from all absorbers.

These early commercial explorations, as well as the desire to achieve low SO_2 emissions, encouraged ANG and DOE to investigate alternative absorber designs (on a pilot scale). Mobile bed columns were studied with hollow balls and Tripack spheres used as the packing. Tests in a 6-inch glass column proved extremely encouraging with the service life of the units being extended from less than a day to several weeks. Since the column, at least at times, had to operate in a fluidized or moving bed mode, it was evident that scale-up from 6-inch pilot plant work to a commercial size absorber in excess of 12 feet diameter was not prudent. For this reason, a 30 inch diameter test absorber was installed to operate on plant solution and Rectisol waste gas. At the same time, a cold flow model made in plexiglass was built to allow studying the many aspects of bed configuration and liquid and gas distribution. Both units were installed in the Sulfur Recovery Process Area.

Numerous tests in the cold flow model identified the "do's" and "don'ts" for design of the internal members of the mobile bed column, while a smaller number of runs in the test absorber provided information on mass transfer, pressure drop and overall H_2S reduction. A long series of tests explored the impact of shallow versus deep beds, multiple beds with and without liquid redistributor as well as two different ball sizes. Benefits of compartmentalization were also investigated. A similar series of tests was also carried out with Tripack packing. The initial experimental results were very encouraging and after confidence was established, the steps toward scale-up to the commercial unit was taken. As a result, one of the four commercial absorbers was converted to provide full-scale performance data for mobile bed operation. Although modifications were kept to a minimum and bed depth was constrained by the existing tower dimensions, performance of the tower was found to be very promising. Pressure drop was less than expected using about one-half of that available and measured H_2S removal was better than anticipated. Overall absorption efficiency for the system was increased from around 75 percent to about 90 percent (Figure 4). As of June 27, after 28 days of operation, the tower has not plugged since being commissioned as a mobile bed unit and the pressure drop has remained unchanged. Initially, some degradation of the column packing was observed and this factor still remains one of the primary unknowns for complete acceptance of the technology. It is interesting to note that, at this time, the moving bed packed tower with 11 feet of packing promises a slightly better removal efficiency than a two-stage countercurrent venturi arrangement.

Conclusions

The above described R&D program has produced viable results and practical recommendations to reduce SO_2 emissions at Great Plains. The following options have been tested and demonstrated to reduce SO_2 emissions:

1. Convert to Sulfolin Technology.
2. Chill Phosam gas to permit processing in Sulfolin.
3. Chill fuel gas to permit processing in Sulfolin.
4. Improve H_2S removal efficiency either by:
   a. Two-stage venturi,
   b. Moving bed absorber.

In spring of 1988, DOE filed with the NDSDH for an operating permit. The filing was based on early Sulfolin performance data for a two-stage countercurrent venturi arrangement. As a goal, DOE would like to achieve the emission figures shown in Table 2, which is based on a 93 percent removal efficiency for the main and Phosam waste gases and processing fuel gas in the existing venturis. This 93% efficiency was based on commercial testing of venturis with fresh Sulfolin solution. Recent evaluations with aged Sulfolin solution as it exists today indicate the efficiencies may be 90% or less as shown in Figure 4. On the other hand, ANG had only pilot tested moving bed packing and could not assign high efficiencies to expected commercial performance without completing a commercial test. At the time of this writing, the commercial test is in progress and showing good results as indicated in the top curve of Figure 4.

Still a final comparison of options 4a and 4b cannot be made at this time. It appears that a sufficient volume of moving bed packing can be installed to equal or better the performance of a two-stage countercurrent venturi arrangement. This comparison must await a longer operating period for data collection and investigation of the cost of the necessary equipment modifications. It is hoped that by the time of this symposium, additional evaluations will have been completed.

Reference

Pilot Scale Stretford Research at Great Plains. Messrs. G. G. Baker, A. K. Kuhn and D. C. Pollock. Presented at the 1987 Stretford User Conference.

TABLE 1

Typical Analysis for Rectisol CO_2 Waste Gas, Phosam Off-gas and Gasifier Coal Lock Gas. Concentrations are in volume percent unless stated otherwise.

Gas Stream	Rectisol CO_2 Waste Gas	Phosam Off-Gas	Gasifier Coal Lock Gas
Component			
H_2	-	2.56	39.70
CO	0.18	1.36	14.40
CO_2	95.11	67.66	31.58
CH_4	1.00	1.09	13.00
C_2H_4	0.20		0.01
C_2H_6	1.39	0.026	0.47
C_3H_6	0.14		0.04
C_3H_8	0.25	0.009	0.31
C_4H_8	0.03		0.03
C_4H_{10}	0.03	2.55	0.03
C_5+	0.02	-	0.08
H_2S	0.79	1.13	0.23
COS	79 ppm	-	-
CH_3SH	0.02	0.009	0.013
C_2H_5SH	<10 ppm	0.004	0.003
CS_2	<10 ppm	-	-
$(CH_3)_2SH$	25 ppm	0.006	-
NH_3	<10 ppm	10.20	-
HCN	<10 ppm	-	-
N_2	0.79	0.702	0.02
O_2Ar	0.01	-	0.08
Benzene	0.01	0.26	0.048
Toluene	0.01	0.022	0.022
Ethyl Benzene	-	0.008	0.001
Xylene	-	-	0.003
Phenol	-	-	1 ppm
Acetone/MEK	0.01	3.31	-
Methanol	0.01	7.67	-
IPE	-	0.837	-
Propanol	-	0.031	-
2-Butanone	-	0.556	-

TABLE 2

SO_2 EMISSIONS AT GREAT PLAINS

		Original Design Basis	Current Plant @ Max S	After Proposed Changes (Max S
Coal Feed	T/D	14,000	16,700	16,700
SNG Production	MMSCFD	137.5	152.5	152.5
SO_2 Emissions				
from org. S	lb/hr	955	2,105	2,105
from H_2S	lb/hr	385	6,525	1,837
TOTAL	lb/hr	1,340	8,630	3,942

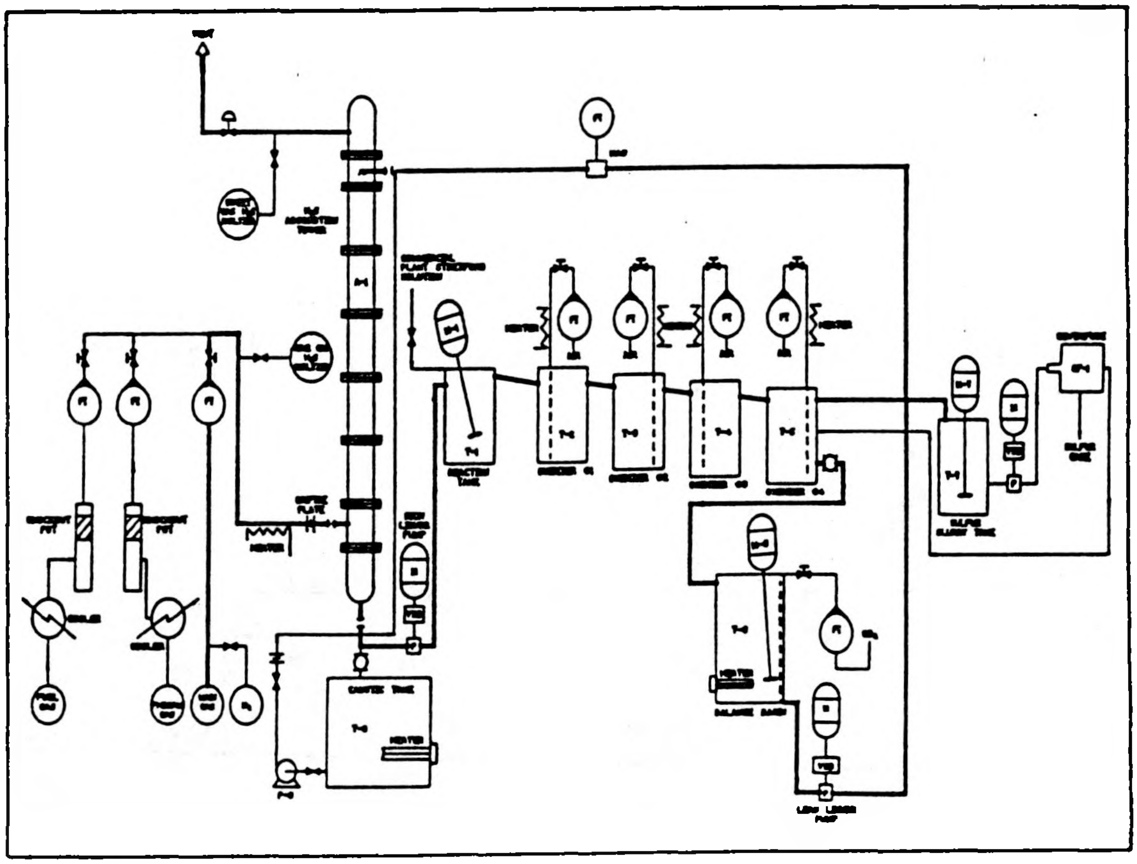


Figure 1. Simplified schematic of Great Plains Sulfur Recovery Pilot Plant

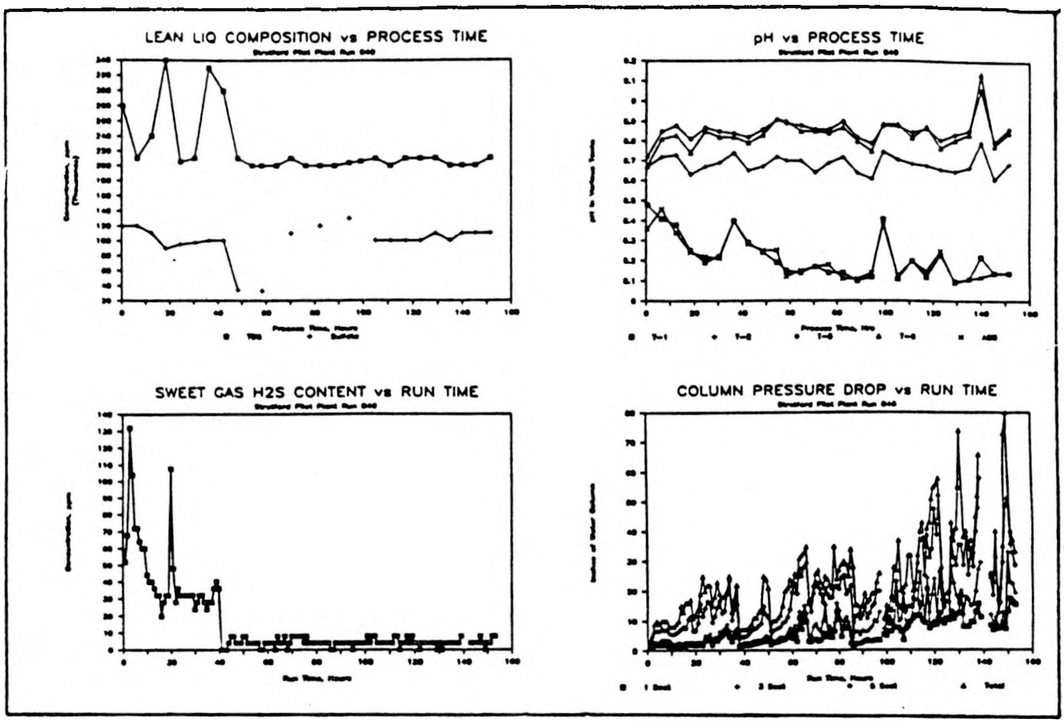
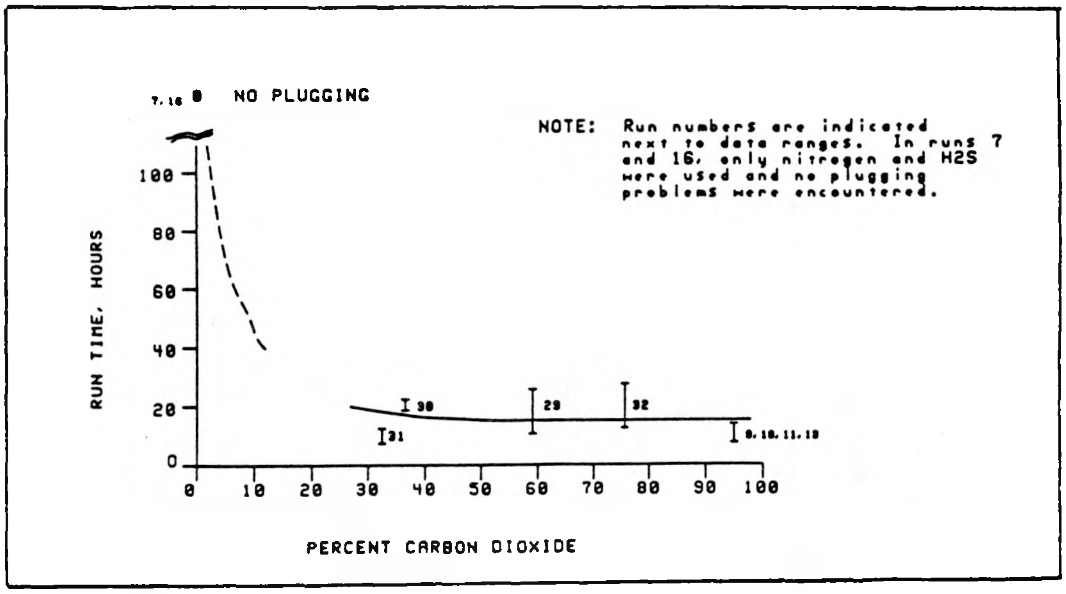
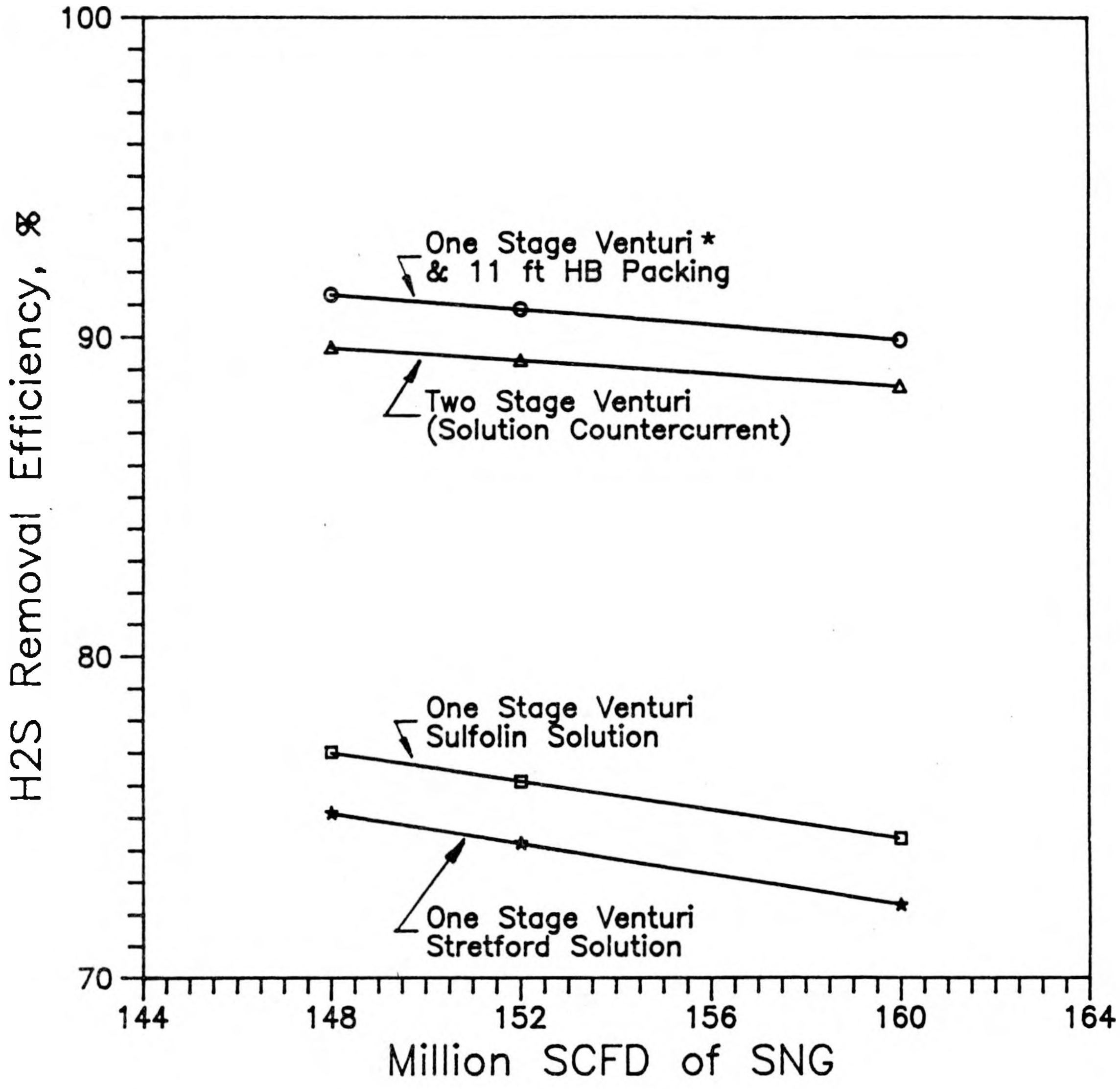


Figure 2. Examples of data output for pilot plant Run 49



NOTE: Run numbers are indicated next to data ranges. In runs 7 and 16, only nitrogen and H2S were used and no plugging problems were encountered.

Figure 3. Pilot Plant absorber plugging frequency as a function of the CO_2 Content of the feed gas



* Testing in progress.

Figure 4. H_2S Removal Efficiency vs. Plant Production Rate

"ADVANCED FLUE GAS CLEANUP TECHNOLOGIES"

BY: C.E. DRUMMOND
PITTSBURGH ENERGY TECHNOLOGY CENTER
PITTSBURGH, PA

NO PAPER SUBMITTED

SESSION 4:
SOLID WASTE CHARACTERIZATION/REUSE

SESSION CHAIRS:

WILLIAM GROSZ
BASIN ELECTRIC POWER COOP
BISMARCK, ND

FRANK BEAVER
ENERGY & MINERAL RESEARCH CENTER, UND
GRAND FORKS, ND

1. "Composition of Sulfur Waste Products and Possibilities of Their Utilization"

   by: Ivan Odler
   Technische Universitat Clausthal
   Clausthal-Zellerfeld, Federal Republic of Germany

2. "The Value of Mineralogical Characterization of Synfuel Solid Wastes as Illustrated by Lignite Fixed-Bed Gasification Ash"

   by: Gregory J. McCarthy
   North Dakota State University
   Fargo, ND

3. "Leaching Research - Characterization, Regulation and Metal Recovery"

   by: David J. Hassett
   Energy & Mineral Research Center, UND
   Grand Forks, ND

4. "Characterization and Utilization of Slag from the Texaco Gasification Process"

   by: E.F. de Paz, M.S. Najjar, and E.O. Wakefield
   Texaco, Inc.
   Beacon, NY

"COMPOSITION OF SULFUR WASTE PRODUCTS AND POSSIBILITIES OF THEIR UTILIZATION"

BY: IVAN ODLER
TECHNISCHE UNIVERSITAT CLAUSTHAL
CLAUSTHAL-ZELLERFELD
FEDERAL REPUBLIC OF GERMANY

COMPOSITION OF SULPHUR WASTE PRODUCTS AND POSSIBILITIES OF THEIR UTILIZATION

I. Odler
Technical University Clausthal
3392 Clausthal-Zellerfeld
Federal Republic of Germany

ABSTRACT

A wide variety of sulphur waste products may be formed in the desulphurization of flue gases. They include gypsum $CaSO_4.2H_2O$, anhydrite $CaSO_4$, calcium sulfite $CaSO_3.{}^1/2H_2O$, liquid SO_2, elementary sulphur and sulphuric acid H_2SO_4. If some advanced technologies are employed the obtained waste products may contain, beside a compound of sulphur (usually anhydrite), also variable amounts of ash components and free lime. The composition and properties of the various materials are reported and the possible ways of their utilization are discussed.

Different technologies have been developed to remove sulphur oxide from flue gas. In all instances this process is associated with the formation of a solid waste product in which the sulphur, originally present in the fuel, is chemically bound. The composition and quantity of the formed waste product varies widely depending on the desulphurization method employed and the quality and composition of the fuel used. Unless the possibility exists to use the desulphurization product further, the material has to be disposed of,which necessarily increases the costs of desulphurization. Thus, looking for possible ways to utilize such products makes good sense. In this paper the different sulphur waste products are described and the possibilities of their further use are discussed.

Presently, flue gas gypsum ($CaSO_4.2H_2O$) obtained by a wet absorption of sulphur dioxide (SO_2), present in flue gas, with lime ($Ca(OH)_2$ or $CaCO_3$) and subsequent oxidation of the primary formed calcium sulfite ($CaSO_3\ {}^1/2\ H_2O$) is the sulphur waste product produced in largest quantities. In principle, flue gas gypsum may be used for the same purposes as natural gypsum, however, there are some important differences between the two products that have to be taken into account:

Unlike natural gypsum which is usually available as a dry, crushed rock product, flue gas gypsum is obtained in the form of a wet thixotropic slurry with a water content typically between 7 and 10 per cent. Only by drying it, the material may be converted into a dry powder. This, however, requires an energy consumption of about 400.000 to 550.00 KJ/t. The particle size of the present gypsum crystals is usually rather uniform within a single product but may vary depending on the employed desulphurization technology between about 10 and 100 µm (Fig. 1). This different degree of aggregation means, that converting a plant (e.g. a cement plant) designed to use natural gypsum to the use of flue gas gypsum will necessarily require changes in the way how the material is stored, conveyed, handled and processed. This handicap, however, may be overcome, if the material is agglomerated prior to its use either by compacting or pelletizing.

As to the chemical composition, the calcium sulphate content of flue gas gypsum is usually rather high. Unlike natural gypsum it never contains calcite ($CaCO_3$) or clay constituents. On the other hand, it may contain some residual calcium sulfite, variable amounts of heavy metalls and also variable amounts of chlorides. The latter ones have to be removed by washing the material with water prior to the use of flue gas gypsum in the gypsum or cement industry. A typical composition of flue gas gypsum (after washing) as well that of natural gypsum is given in Tab. I.

In countries which produce large amounts of electricity in thermal power plants equiped with desulphurization units, the bare amount of flue gas gypsum produced may present a problem. So, e.g. in the Fed.Rep. of Germany the production of flue gas gypsum is expected to reach a volume of 3.9 million tonnes by 1990 which is to be compared with a present consumption of about 4.7 million tonnes/year of natural gypsum and anhydrite.

At the same time, the conversion from natural to flue gas gypsum would be complicated by the fact, that a large part of the latter product would need to be transported for long distances and would have to compete with natural gypsum or anhydrite available locally. Another factor that also has to be considered is the fact that the greatest part of flue gas gypsum is produced in winter months whereas the consumption of gypsum-based products peaks in the summer season. Thus, appropriate storage capacities would be needed to store the gypsum until it could be used. These conditions indicate that new applications and new products should be looked for to extent the present consumption of calcium sulphate.

In our laboratory we are presently studying the possibilities to convert flue gas gypsum into α-hemihydrate by an autoclave - free technology. Here the gypsum particles are treated in concentrated solutions of inorganic salts of high water solubility ($CaCl_2$, $MgCl_2$, $Mg(NO_3)_2$ etc.). Due to the presence of the salt, the boiling point of the solution may be raised to temperatures at which a spontaneous conversion of gypsum to α-hemihydrate takes place even at atmospheric pressure. To obtain good crystal morphology small amounts of suitable agents, such as organic carboxylic acids have to be added to the system. One great advantage of this process is the significantly lower investment cost as compared to the conventional autoclave process. On the other hand it is necessary to remove the residual amounts of salt by washing the final product with sufficiently large amounts of water and to dry it to obtain an α-hemihydrate powder. We believe that this technology is especially suitable for processing flue gas gypsum which is produced as a wet slurry with a high degree of dispersion and contains distinct amounts of soluble chlorides already in its original state. In this case the material has to be washed and dried-regardless of its future use - anyhow. Fig. 2 shows a α-hemihydrate product produced from flue gas gypsum by treating it in a $CaCl_2$ solution with added malic acid as a crystal shape modyfier.

Tab. I: Composition of natural and flue gas gypsum (Typical values) in wt %

	Natural gypsum	Flue gas gypsum
$CaSO_4.2H_2O$	75 - 95	98 - 99
Na^+ water soluble	< 0.1	< 0.1
K^+ water soluble	< 0.1	< 0.5
Fe^{+3} water soluble	< 0.1	< 0.1
Mg^{+2} water soluble	< 0.1	< 0.1
CO_3^{-2} water soluble	-	< 0.5
Cl^- water soluble	< 0.001	0.01-0.1
F^- water soluble	-	< 0.05
$CaSO_3.{}^1/2H_2O$	-	0.1 -1.0
$CaCO_3$+clay	5 - 20	-

Other products that may be formed in the removal of SO_2 from flue gas include elementary sulphur, liquid SO_2, sulphuric acid, ammonium sulphate calcium sulfite and anhydrite ($CaSO_4$). Large-scale desulphurization units producing these products are, however, rare or even non-existent and thus the amounts produced are rather low as compared to those of flue gas gypsum.

Out of products listed, elementary sulphur, liquid SO_2 and sulphuric acid have to be considered industrial chemicals rather than waste products, and may be utilized in the same way as identical products produced by the chemical industry. Ammonium sulphate may be used as a fertilizer.

Flue gas anhydrite may be interground with portland clinker - usually in combination with gypsum - to yield portland cement. Because of its high content of chlorides (up to 2% Cl^-) it may be used, however, just in limited additions. There exists also the possibility to use flue gas anhydrite in the production of anhydrous gypsum plaster by intergrinding it with an appropriate set accelerator. Here again a high content of water-soluble chlorides may limit or even prohibit its utilization.

Calcium sulfite obtained in the desulphurization process is presently not further utilized. In our laboratory we were able to prove, however, that it may be used as a set controling constituent in portland cement, just as natural or flue gas gypsum. There also exists the possibility of converting it into gypsum or anhydrite and using it in this form. In Tab.II the possible uses of different sulphur waste products are summarized.

As to their further utilization, wastes that contain ash components in addition to sulphur compounds represent a greater problem than the waste products mentioned so far. Such waste products are, or will be produced in the future in units that will employ some advanced SO_2 control technologies. These are either still under development or are just being introduced. It may be expected, however, that the importance of these technologies in flue gas desulphurization will rise in the coming years, and thus the volume of this kind of waste product.

Among these "advanced" technologies atmospheric fluidized bed combustion is most developed. Several full-scale units using this technology are already operating in West Germany and additional ones are under construction. The composition of this kind of "ash" may vary in a wide range, depending on the composition of the coal employed, the amount of added lime and the conditions of combustion. Tab. III shows the composition range of ashes from fluidized bed combustion analyzed in our laboratory. Fig. 3 shows REM photographs of a series of such ashes. Ashes from fluidized bed combustion may contain variable amounts of XRD-amorphous phases (produced by thermal decomposition of clay minerals present in the fuel) or glass. The main crystalline phases are usually quartz and anhydrite II. Other crystalline phases present include calcite, periclas, hematite, magnetite, feldspar, larnite and rankinite. The amount of free calcium oxide may vary in a wide range, just as the amount of residual carbon.

The utilization of ashes obtained in atmospheric fluidized bed combustion may be rather problematic. As long as the ash contains significant amounts of an amorphous or glass phase with puzzolanic activity and when simultaneously the free lime, the calcium sulphate and residual carbon contents of such ash are low enough, the possibility exists to grind the material with portland clinker to produce a blended cement. In doing so, the amount of SO_3 in the ash has to be taken into account and the amount of gypsum added has to be lowered accordingly. It seems obvious, however, that in the future only a small fraction of ashes produced by fluidized bed combustion may be utilized this way.

In our laboratory we are studying the possibilities to convert ashes from fluidized bed combustion into concrete aggregate. To do so, a blend of the ash with 10 to 20 per cent of ground portland clinker and with about 3 to 10 per cent water is compacted under high pressure into compacts about 1/2 to 1" large. After a few weeks of curing the product on air, hard water-stable particles are obtained which may be used as concrete aggregate (Fig. 4). This research work reached a state at which the construction of a pilot plant is being planed. It is obvious, however, that not each fluidized bed combustion ash may be utilized this way and a strict quality control of the material to be used, will be necessary to assure adequate quality of the produced artificial concrete aggregate. It is also obvious, that such approach may be justified only if the availability of natural rock aggregates is limited or if the costs of dumping the ash are prohibitively high.

In recent years the possibilities have been studied of binding sulphur present in the fuel by introducing lime (usually in form of $CaCO_3$) directly into the combustion chamber. By this furnace sorbent addition technology an ash is obtained that contains the present sulphur in form of anhydrite and

Tab. II: Possible utilization of products obtained in the removal of SO_2 from flue gases

	$CaSO_4 \cdot 2H_2O$	$CaSO_4$	$CaSO_3 \cdot {}^1/2\ H_2O$	$(NH_4)_2SO_4$	S, SO_2 H_2SO_4
Inorganic binders (Ca-sulphate based)	+	(+)	?	-	-
gypsum based building materials	+	(+)	-	-	-
Production of portland cement	+	(+)	?	-	-
Mining industry	+	+	?	-	-
Fertilizing	-	-	-	+	-
Chemical industry	-	-	-	-	+
Dumping	(+)	+	+	-	-

Utilization		
	possible	+
	conditionally possible	(+)
	questionable	?
	impossible	-

Tab. III: Composition and fineness of ashes from fluidized bed combustion

Al_2O_3	15	-	25	%
CaO total	6	-	26	%
CaO free	0.1	-	9	%
Fe_2O_3	5	-	15	%
FeO	0	-	11	%
K_2O	0.5	-	3	%
MgO	1	-	3	%
Na_2O	0.5	-	1	%
P_2O_5	0.1	-	1.2	%
SO_3	0.1	-	19	%
TiO_2	0.7	-	1.2	%
L.O.I.	(-)0.8	(+)	18	%
residual C	1	-	13	%
particle size	1	-	1000	µm
spec. surface (BET_{N_2})	0.15	-	10	m^2/g

variable amounts of residual lime in form of CaO, in addition to the inorganic constituents of the fuel. The composition of such product may vary depending on the fuel used and the amount of lime introduced. The amount of free lime in such ashes is usually rather high as excessive amounts of it have to be introduced into the combustion chamber to obtain an adequate desulphurizating effect. If mineral oil, rather than coal is used as fuel, the resulting desulphurization product almost exclusively contains anhydrite and free lime. On the other hand, the composition of such ashes may be rather unusual if this technology is used to burn toxic waste products. Fig. 5 shows a SEM-photograph of such waste product obtained in a pilot size experimental unit installed at our university. If the obtained product contains only negliable amounts of ash constituents and if its free lime content is also sufficiently low, it may be used as a set regulator in the manufacturing of portland cement, especially in combination with gypsum. But also products with moderate or high contents of ash components may be interground with clinker to yield in this case a "puzzolanic cement" however only if the ash component exhibits a sufficient puzzolanic activity. In this case the addition of redundant gypsum must be reduced or ommitted, taking the calcium sulfate content of the waste material into account.

Another sulphur waste product that also has to be discussed is one obtained by spray-drying a slurry formed in the scrubbing of flue gases containing SO_2 and ash particles with a suspension of lime. In this product, the sulphur is present in the form of a highly dispersed calcium sulfite. The ratio of calcium sulfite/ash may vary in a wide range depending on the degree to which the flyash had been removed from the flue gases prior to lime scrubbing. A third component of the material is the non-consumed residual calcium hydroxide whose amount also vary in a wide range. A SEM-photograph of this product is shown in Fig. 6. Its possible utilization will again very much depend on the existing calcium sulfite/ash ratio, the composition of the ash constituent itself and free lime content. In most cases it will be necessary to convert the present calcium sulfite into calcium sulphate e.g. by heating it on air to temperatures of around 400 °C. Then again the possible uses of such waste materials include their intergrinding with portland clinker, their conversion into an artificial concrete aggregate, or their use as a mortar mixture in which the present calcium sulphate acts as an anhydrous gypsum plaster. Here also a high content of chlorides may present serious problems and hamper the utilization of the waste material.

From the above one has to conclude that the composition and properties of sulphur waste products may vary in a wide range. This depends both on the composition of the used fuel and the SO_2 control technology employed. The present sulphur may be bound in form of different compounds and in variable amounts. The amount and quality of the present ash constituents may vary widely as well. In most instances sulphur waste products also contain variable but significant amounts of free lime and residual coal. Also, a variety of minor constituents may be present. All this makes a rational utilization of these materials rather difficult.

So far there are only few countries in which significant amounts of sulphur waste products are produced. In the future, however, the volume of produced sulphur waste products will go up steadily as the environmental conscieounseness of the public will increases new and stricter environmental laws will be passed and the existing power generating units will gradually be replaced be a new generation capable of cleaning the generated flue gas more effectively. One also may expect that the importance of advanced SO_2 control technologies will increase at the expense of processes yielding flue gas gypsum or other sulphur compounds free of ash constituents. Such development represents a challenge to those who will have to deal with the wastes produced. Presently it appears that ways may be found for the utilization of a significant fraction of the sulphur waste products, as long as sufficient funds will be made available for the needed research and development work. The amount and quality of sulphur waste products that will be produced in the future as well as the fraction of them that will be further utilized, rather than dumped, will ultimately not only depend on the technical feasibility of various solutions but also on their economics and on the readiness of the producers and users of these products to cooperate. Last but not least their successful utilization will also depend on the degree to which the governments will fund and push such effords, which may vary in different countries.

BIBLIOGRAPHIC SKETCH OF THE AUTHOR

[redacted] B.S. in chemical engineering and Ph. D. in ceramic engineering from the Slovak Technical University in Bratislava (Czechoslov.). Since 1968 worked at Clarkson College of Technology Potsdam NY, Westvaco Research Center Charleston SC und W.R. Grace, Cambridge MA. Now, professor of materials science and technology at the Technical University Clausthal, Fed. Rep. Germany (scince 1976).

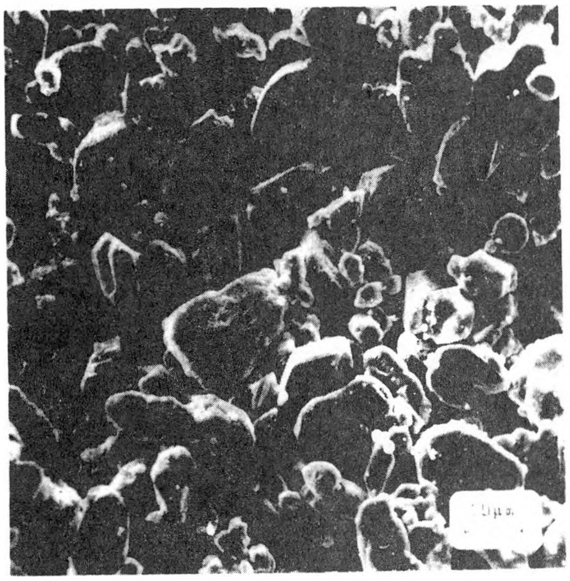


Fig. 1

SEM photographs of flue gas gypsum from three different power plants

Fig. 2

SEM photograph of a α-hemihydrate produced by an autoclave-free process from flue gas gypsum

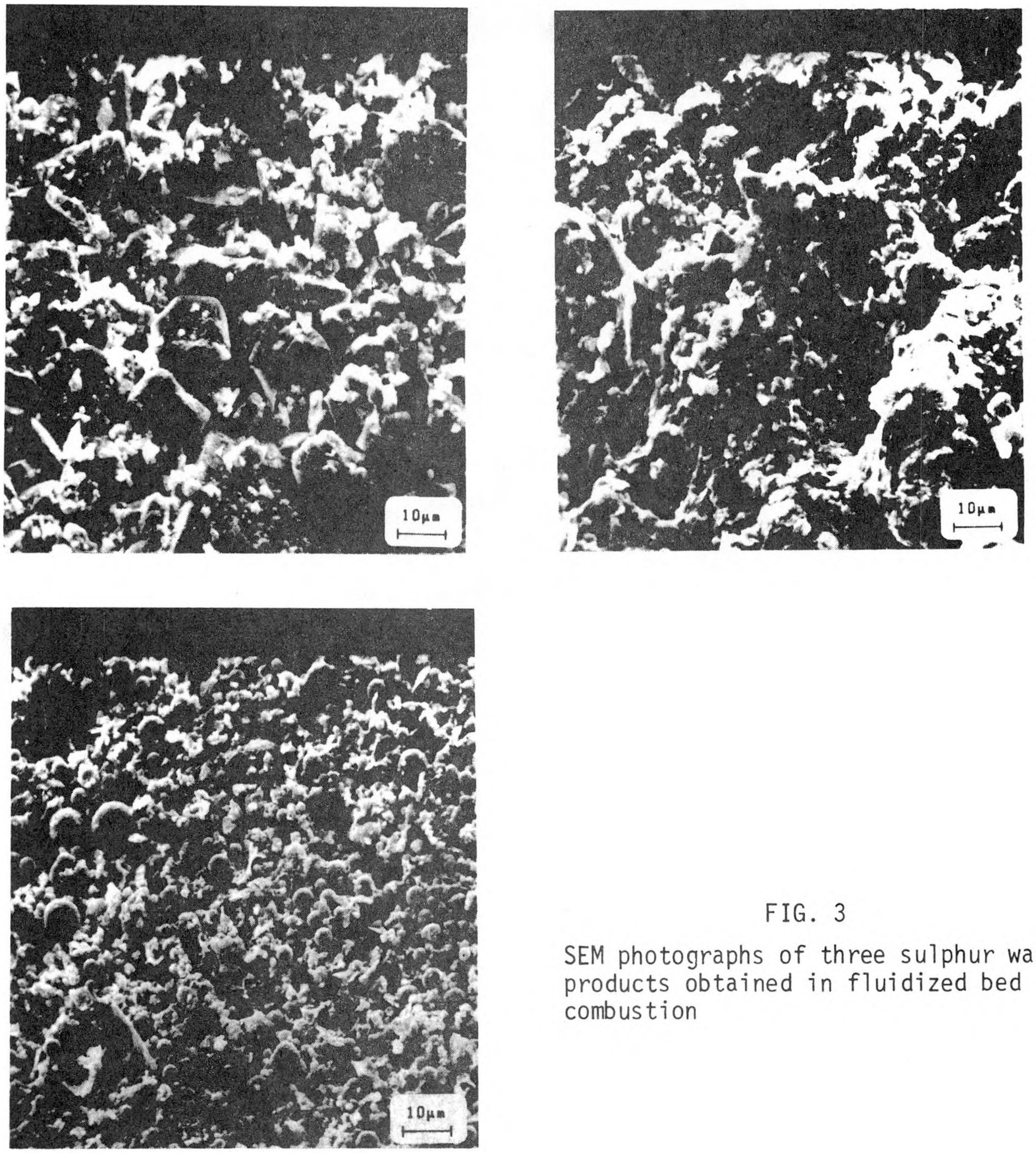


FIG. 3

SEM photographs of three sulphur waste products obtained in fluidized bed combustion

FIG. 4

Artificial concrete aggregate produced from fluidized bed combustion ash

FIG. 5

SEM photograph of a sulphur waste product obtained by furnace sorbent addition technology

FIG. 6

SEM photograph of a sulphur waste product obtained by scrubbing flue gase with lime

"THE VALUE OF MINERALOGICAL CHARACTERIZATION OF SYNFUEL SOLID WASTES AS ILLUSTRATED BY LIGNITE FIXED-BED GASIFICATION ASH"

BY: GREGORY J. MCCARTHY
NORTH DAKOTA STATE UNIVERSITY
FARGO, ND

THE VALUE OF MINERALOGICAL CHARACTERIZATION OF SYNFUEL SOLID WASTES AS ILLUSTRATED BY LIGNITE FIXED-BED GASIFICATION ASH

Gregory J. McCarthy
North Dakota State University
Department of Chemistry
Fargo, ND 58105

ABSTRACT

Mineralogical characterization the Great Plains Gasification Plant fixed-bed ash, and of its reactions with water, has led to an understanding of the self-hardening property of this ash. Laboratory modeling of the hydration reactions and the pHs generated by ash-water contact demonstrated that is a sodium aluminosilicate (carnegieite), and related phases, in the ash that generate the high pHs and form zeolites that result in self-hardening of the ash.

INTRODUCTION

Few would think of trying to find uses for, or dispose of, a solid waste from synfuels production without a chemical analysis. Equally or even more important is knowledge of the "mineralogy" of these wastes, the chemical compounds formed by its elements. It is these compounds that control both the reactivity of the ash in various utilization options, and the geochemical environment and secondary minerals that host the trace elements in disposed wastes.

The value of mineralogical characterization is illustrated with a summary of our research into the mechanisms of the unusual and sometimes troublesome self-hardening property exhibited by contact of the lignite ash from the Great Plains Coal Gasification Plant (GPGP) with water. During handling, this ash is wet sluiced. It was noted early in the the plant's operation that the ash would set-up into a concrete-like mass if sluicing stopped or if the ash collected in a quiet area of the sluice. In one instance, the resulting product had to be jack-hammered out of a sump. It was later discovered that additions of common salt, NaCl, to the sluice water would prevent this self-hardening. During the course of our investigations of the mineralogy and water reaction behavior of GPGP ash, the mechanisms for this self-hardening behavior and its prevention with NaCl additions was discovered.

Even before the Beulah, North Dakota, Great Plains Gasification Plant opened, the Gas Research Institute had initiated a studies of the characterization and utilization of the large quantities of ash to be produced by this plant. The research was performed by the North Dakota Mining and Mineral Resources Research Institute (NDMMRRI) utilizing faculty, staff and students at the University of North Dakota (UND) and North Dakota State University

(NDSU), and in close cooperation with GPGP personnel. Subsequent research dealt with codisposal of GPGP gasification ash and various ashes from the adjacent electrical generating station. These research programs are now complete and their results have been published in the series of articles listed at the end of this paper. Characterization of the mineralogy of the ash and of its water reaction products was an important component of the studies.

After we learned what solid phases constituted the gasification ash (McCarthy, et al. 1984, 1985; McCarthy, 1986; Stevenson, 1984; Stevenson and Larsen, 1985; Stevenson and McCarthy, 1986), and the leaching behavior of the ash (Hassett et al. 1985, 1986; McCarthy, et al. 1986), hydration of the ash was studied (Kumarathasan and McCarthy, 1987, 1988). The reactive phases in ash were then synthesized and studied individually, and then in pairs. Progress of the reactions and the formation of products were monitored by x-ray diffraction (XRD) on solids and pH measurements on solutions. In a final experiment, we compared the reactivity of an actual GPGP ash with and without addition of NaCl to the hydrating solution. Highlights of those studies are summarized here.

METHODS OF MINERALOGICAL CHARACTERIZATION

Mineralogical characterization of synfuels solid wastes is done principally by x-ray diffraction (XRD) analysis, and by electron microscopy (SEM) on an instrument equipped for elemental analysis. A summary of each method and its applicability to characterization of synfuels solid wastes follows.

When a crystalline solid is ground to a fine powder, spread out on a flat sample holder, and exposed to a monochromatic x-ray beam while being scanned over a range of angles, a series of peaks of varying intensity is produced at particular diffraction angles. Every crystalline compound (phase) has a characteristic set of angles and intensities of peaks. The situation is analogous to a fingerprint; with a file of XRD "fingerprints" and a system of retrieving them, any crystalline compound can be identified. The "fingerprint file" is called the Powder Diffraction File and there are various search/match methods in use that employ printed tables or computer files. XRD studies of synfuels solid wastes can be far from routine, as discussed by McCarthy (1986).

X-ray diffraction has certain limitations for solid waste characterization. Of these the most important is that it gives only an approximate chemical compositions of the phases identified. For this information, SEM characterization is required.

Scanning electron microscopy is a valuable tool in the delineation of the morphology (microstructure) and chemistry of particles and grains of material in a synfuels solid waste. For grains larger than about 2 μm, SEM characterization of mineralogy results in a knowledge of the composition, morphologic habit, and associations of all phases present in the waste material, including amorphous or glassy phases. The modern spectrometer-equipped SEM incorporates on-board computer routines for calculation of chemical analysis. When SEM is combined with XRD, one can complete the determination of mineralogy of crystalline phases, and can determine the chemical make-up of glassy phases.

EXPERIMENTAL PROCEDURES

Materials

Table 1 is a listing of the crystalline phases identified in GPGP gasification ash, and a similar ash produced from the same lignite in a Bureau of Mines fixed-bed gasifier in Minneapolis. A portion of the ash consisted of minerals from the lignite that had survived gasification. The bulk of the material was a series of high temperature reaction products. The surfaces of ash grains were found to be coated with various secondary phases resulting from ash hydration during sluicing. The ubiquitous ash phases, observed in all samples studied, are indicated by a mineral code. These shorthand codes will be used throughout this paper.

The individual gasification ash phases identified as being more water reactive were the sodium aluminosilicates carnegieite (Cg - $Na_{1+x}Al_{1+x}Si_{1-x}O_4$) and nepheline (Ne - $NaAlSiO_4$), the silicates bredigite (Bd - $Ca_{1.7}Mg_{0.3}SiO_4$), merwinite (Mw - $Ca_3Mg(SiO_4)_2$) and melilite, a solid solution phase of end members akermanite (Ak - $Ca_2MgSi_2O_7$) and gehlenite (Geh - $Ca_2Al_2SiO_7$). These phases were synthesized, as none were available commercially. At the start of the study it was thought, by analogy to the behavior of blast furnace slag in concrete, that the glass phases would play an important role in self-hardening. To simulate the glassy phases in gasification ash, mineral wool glass and two cyclone furnace slag glasses were provided by O.E. Manz Coal By-products Utilization Laboratory of UND. The mineral wool was prepared from a rapidly quenched melt of Beulah-Zap lignite ashes that is very similar in composition to the gasification ash. The cyclone furnace slags were also derived from North Dakota lignites, one with an exceptionally high calcium content. A gasification ash (GPGA-4) used in one of the experiments in this study was provided by the GPGP. This was a "dry" ash collected directly from a gasifier. Compositions of the glassy materials and GPGA-4, determined in the laboratories of D.J. Hassett of the NDMMRRI, are given in Table 2. Compositions of some of the important individual crystalline phases in the gasification ash, determined in the laboratories of R.J. Stevenson of the NDMMRRI, are given in Table 3. The actual compositions are much more complex than the nominal compositions of Table 1.

Modeling of Gasification Ash Hydration Reactions

Three sets of experiments were used to model gasification ash hydration reactions. Ten single phase solids were used in the first set. In the second set of experiments, carnegieite was mixed in a 1:1 weight percent (wt%) ratio of each of the other phases. In the third set of experiments actual gasification ash was used. For pH determinations, solids were mixed with water in a liquid to solid ratio of 10 to 1. To model hydration reactions, the ratio was one part of solids to two parts of water. The resulting pastes were placed in capped vials and stored in a dissector. Water placed at the bottom of the dissector maintained 100% relative humidity. The reactions were performed at room temperature (22-25°C). In the two-phase experiments, powdered samples of each phase were mixed in a 1:1 ratio before being mixed with the water. The same procedure was used with ground gasification ash. In the last experiment, NaCl instead of water was added to make the paste.

Sampling of all pastes was done at time intervals selected to be integer increments of the square root of time. The experiments ran for 81 days. Aliquots of samples removed were mixed with excess ethanol (to halt hydration reactions) and specimens were made for XRD analysis.

The reaction products were characterized by XRD. A pH meter equipped with a silver/silver chloride combination electrode was used to determine the pH of the solutions. Various buffers were used in calibrating the pH meter prior to the pH measurements. Corrections were made for electrode error due to the high sodium ion contents in many of the solutions. Solutions from the 81 day pH experiments were analyzed in the laboratory of D.J. Hassett.

RESULTS AND DISCUSSION

pH Experiments

The two sodium aluminosilicates, Cg and Ne, hydrated to give solutions that showed rapid rises in pH, leveling off at 13.0 after 25 days (Table 4), and both reactions resulted in extraction of significant portions of the available Na. However, 26% of the Na available in Cg was extracted compared to 13% of the Na in Ne. An even more significant difference in their hydration behavior is noted with the Al extracted. The Cg solutions showed 8% of the available Al extracted whereas the Ne solutions showed only 0.9% extracted. Both of these phases gave the highest values of pH. It appears that Na extracted from Cg into solution without any acid counter anion (such as SO_4) forms NaOH and is the principal reason for the high pH's observed when water contacts the lignite gasification ash. Raw pH measurements were as high as 13.8 before correction. Similar pHs were observed in the GPGP sluice water.

The three Ca-Mg-silicates, Bd, Mw and Ak showed similar pH behavior in these experiments. Bd and Mw reached a pH of 12.6 by the conclusion of the experiment. This pH is essentially the same as that of a saturated solution calcium hydroxide. The elemental analyses of the solutions from the slurries in contact with these phases show only Ca in solution; both observations are consistent with the pH behavior.

Results of pH experiments with the three glasses were interesting. The pH values were distinctly different and were apparently compositionally controlled. The mineral wool glass, which had the highest Na and Ca concentrations gave the highest pH values. The more acidic high-silica-alumina slag 1 gave much lower values. The high-CaO slag 2 gave an intermediate pH.

Hydration Experiments

After as little as nine hours of hydration, Cg had reacted partially to form zeolites, Na-X with minor Na-A (Table 5). By day 49 much of the Cg intensity had disappeared, and the originally formed Na-zeolite-X, which reached maximum XRD intensity at day 36, had largely transformed to Na-zeolite-A. Three forms of aluminum hydroxide were also observed in the Cg diffractograms. These observations suggest the following long-term reaction for Cg and water:

$$\underset{\text{carnegieite}}{24\ Na_{1.5}Al_{1.5}Si_{0.5}O_4} + 75\ H_2O = \underset{\text{Na-zeolite-A}}{(NaAlSiO_4)_{12}\cdot 27H_2O} + 24\ Al(OH)_3 + 24\ NaOH$$

It requires 0.37 mL of H_2O to hydrate 1.0 g of Cg fully according to this reaction, i.e. a L/S ratio of 0.37. With the 0.5 L/S of this experiment, there is an excess of water available to convert Cg into its hydration products. In the late stages of the reaction crystalline sodium carbonate was observed in the diffractograms (Table 5). Its likely origin is in carbonation reactions of the NaOH-rich solutions during exposure to the CO_2 in air during sampling.

The chemically similar nepheline paste gave less of a reduction in the original peak heights, and a smaller amount of zeolite formation. The zeolite is dominantly Na-A type. Carnegieite pastes showed self-hardening behavior while nepheline showed no self-hardening tendency.

Bredigite, a phase similar to the dicalcium silicate component of Portland cement, was the next most reactive phase. Its hydration products were similar to those of hydrated cement. Bredigite pastes exhibited self-hardening property by day 36.

The dominant solid phase observed in the glass paste was calcite. This suggests that Ca is the principal species leached from the glass and that it forms $Ca(OH)_2$ in the pore solutions which reacts readily with CO_2 on even the brief contact with any air during sampling of pastes. The products of the two slag hydration experiments were poorly crystallized calcium silicate hydrate phases. None of these three glasses exhibited self-hardening behavior.

These experiments suggested that Cg and Cg-like glass were responsible for the high-pH's observed when gasification ash contacts water, and that zeolite formation contributes to the self-hardening behavior of these ashes. Bredigite also appeared to contribute to self-hardening.

The logical next step in the modeling of hydration reactions in the full ash was to repeat the experiments with the key phase Cg combined with the other single phases. The results (Table 5) demonstrate that these phases interact upon hydration rather than hydrating individually. For example, the hydration of Cg + Bd produced gaylussite and straetlingite. Gaylussite requires Na from Cg and Ca from Bd; straetlingite requires Ca from Bd and Al from Cg.

Self-hardening correlated with the build-up of zeolite-A. The rate of zeolite formation was slower in these two phase pastes compared to the rate in the pure carnegieite paste, and closely tracked the rate of zeolite formation in hydrating gasification ash (Kumarathasan and McCarthy, 1987). A quantitative XRD method was used to determine the extent of hydration at the end of 81 day experiment:

Cg:	71%	
Bd:		54%
Cg+Bd:	Cg, 93%;	Bd, 80%

Apparently, the combination of phases enhances the hydration of each of the individual phases. These observations are important in suggesting the key role of dissolved Al in the overall model for gasification ash hydration.

Next, actual gasification ash (GPGA-4) was hydrated under identical conditions, both with deionized water (DW) and with 1M NaCl. GPGA-4 hardened by day 36, reached its final hardness by day 49. By day 64, there was no visible free water in the pastes. However, even after 81 days, GPGA-4 paste made with the NaCl solution had not hardened and excess solution was evident. XRD characterization (Table 5) showed that Cg in the GPGA-4 paste made with water had hydrated rapidly and the Na-zeolite-A phase had formed. The products were also characterized by calcium aluminate phases, suggesting that abundant Ca and Al had been mobilized into the pore solutions.

Hydration with the NaCl solution instead of water prevented the formation of zeolites and calcium aluminate hydrates. One possible explanation for the suppression of self-hardening is a Na common ion effect in which massive Na additions suppress hydration reactions of Na-containing phases. The immobility of Al, as evidenced by the lack of calcium aluminates, could be another important reason for the absence of the zeolite phases. The NaCl additions would change the ionic strength and complexation of pore solutions and this could also affect the mobility of key species.

CONCLUSIONS

Hydration modeling experiments with individual phases and mixtures of phases have led to the following conclusions concerning the self-hardening reactions of Beulah-Zap lignite fixed-bed gasification ash:

1. Carnegieite (and, it is assumed, Cg-like glass) is the most water-reactive phase in gasification ash. Its principal hydration reaction product is Na-zeolite-A. Extraction of Na accompanying the hydration of Cg leads to NaOH-rich, high-pH, solutions because there is no acidic counter anion also entering solution.

2. The rate and extent of self-hardening of gasification ash pastes correlate with zeolite formation. It is concluded that zeolite formation accounts for most of the early consolidation of gasification ash. This is in marked contrast to self-hardening fly ash, where some of the Portland cement hydration reactions and pozzolanic reactions with glass phases are the mechanisms. Bredigite and gasification ash glasses contribute to self-hardening from the formation of the poorly crystallized C-S-H and C-A-S-H gel-like phases responsible by the hydraulic activity of Portland cement. It appears that this is the mechanism for later stage self-hardening.

3. It takes both high-pHs and high concentrations of soluble alumina to form the Na-zeolites.

4. Additions of NaCl suppress both the formation of zeolites and the self-hardening of hydrating gasification ash.

One might ask how applicable these hydration-reaction and hardening mechanisms are to other types of gasification ash. The answer to this question is straightforward. This particular kind of zeolite-based self-hardening behavior will be confined to ashes that have the key precursor sodium aluminosilicate phases (carnegieite, possibly nepheline, and compositionally similar glasses that react like them). Dominantly crystalline ashes would be expected to form only with the low-temperature fixed-bed gasification technology; other technologies produce more homogeneous glassy slags with far lower reactivity to water. No other coals known to this author have the requisite high-sodium, low-alumina-silica contents of these North Dakota lignites. Therefore, the results, although interesting, are site-specific. The value of this study lies more in developing a generic approach to modeling water-reaction behavior than in producing generic results applicable any gasification ash.

ACKNOWLEDGMENTS

This research was supported by the Gas Research Institute, Chicago, IL, under Contracts 5082-253-0771, 5082-253-0926 and 5082-253-1283. Many of the experiments described here are part of the NDSU dissertation research of Miss Premkumari Kumarathasan. This paper would not have been possible without the enthusiastic collaboration of Robert J. Stevenson, David J. Hassett and Oscar E. Manz, and the leadership of Gerald H. Groenewold, all of the UND Energy and Mineral Research Center, and the cooperation of personnel from the ANG Coal Gasification Company.

REFERENCES

D.J. Hassett, G.J. McCarthy, K.R. Henke and E.D. Korynta (1985), "Characterization of a Lignite Ash from the METC Gasifier. III Correlations of Leaching Behavior and Mineralogy," in Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal I, edited by G.J. McCarthy and R.J. Lauf, Mat. Res. Soc. Symp. Proc. Vol. 43, (Materials Research Society, Pittsburgh, PA) pp. 187-194.

D.J. Hassett, G. J. McCarthy and K.R. Henke (1986), "Leaching Behavior of Fixed-Bed Gasification Ash Derived from North Dakota Lignite," in Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal II, edited by G.J. McCarthy, F.P. Glasser and D.M. Roy, Mat. Res. Soc. Symp. Proc. Vol. 65, (Materials Research Society, Pittsburgh, PA) pp. 285-300.

P. Kumarathasan and G.J. McCarthy (1987), "Laboratory Modeling of the Hydration Reactions of Lignite Gasification and Combustion Ash Codisposal Waste Forms," in Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal III, edited by G.J. McCarthy, F.P. Glasser, D.M. Roy and S. Diamond, Mat. Res. Soc. Proc. Vol. 86 (Materials Research Society, Pittsburgh, PA) 159-170 (1987).

P. Kumarathasan and G.J. McCarthy (1988), "Self-hardening Reactions in Lignite Gasification Ash" (to be published).

G.J. McCarthy, L.P. Keller, P.J. Schields, M.P. Elless and K.C. Galbreath (1984), "Mineralogical Characterization of Lignite Gasification Ash from a Low-Btu Fixed-Bed Gasifier. I. X-Ray Phase Analysis," Cem. Concr. Res. 14, 479-484.

G.J. McCarthy, L.P. Keller, R.J. Stevenson, K.C. Galbreath and A.L. Steinwand (1985), "Characterization of a Lignite Ash from the METC Gasifier. I. Mineralogy," in Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal I, edited by G.J. McCarthy and R.J. Lauf, Mat. Res. Soc. Symp. Proc. Vol. 43, (Materials Research Society, Pittsburgh, PA) pp. 165-176.

G.J. McCarthy (1986), "Qualitative X-Ray Phase Analysis of Lignite Gasification Ash. Illustration of a Strategy for Analysis of Very Complex Solids," Powder Diffraction, 1, 50-56.

G.J. McCarthy, D.J. Hassett, O.E. Manz, G.H. Groenewold, R.J. Stevenson, K.R. Henke and P. Kumarathasan (1986), "Technical Basis for the Co-Disposal of Gasification and Combustion Ash from the Plants at Beulah, North Dakota," in Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal II, edited by G.J. McCarthy, F.P. Glasser and D.M. Roy, Mat. Res. Soc. Symp. Proc. 65, (Materials Research Society, Pittsburgh, PA) pp. 301-310.

R.J. Stevenson (1984), "Mineralogical Characterization of Lignite Gasification Ash from a Low-Btu Fixed-Bed Gasifier. II. Scanning Electron Microscopy," Cem. Concr. Res. 14, 485-490.

R.J. Stevenson and R.A. Larsen (1985), "Characterization of a Lignite Ash from the METC Gasifier. II. Scanning Electron Microscopy," in Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal I, edited by G.J. McCarthy and R.J. Lauf, Mat. Res. Soc. Symp. Proc. Vol. 43, (Materials Research Society, Pittsburgh, PA) pp. 177-186.

R.J. Stevenson and G.J. McCarthy (1986), "Mineralogy of Fixed-Bed Gasification Ash Derived from North Dakota Lignite," in Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal II, edited by G.J. McCarthy, F.P. Glasser and D.M. Roy, Mat. Res. Soc. Symp. Proc. Vol. 65, (Materials Research Society, Pittsburgh, PA) pp. 77-90.

BIOGRAPHICAL SKETCH OF G.J. McCARTHY

Dr. Gregory J. McCarthy is Professor of Chemistry and Geology at North Dakota State University. He is internationally recognized for research into analytical x-ray diffraction, crystal chemistry and solid state geochemistry, and coal ash characterization and disposal. He has authored or co-authored more than 120 papers and book chapters. Among the eleven books that he has edited are a series of four entitled *Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal*, published by the Materials Research Society. After completing his doctoral studies at The Pennsylvania State University, Dr. McCarthy joined the faculty of the Materials Research Laboratory. In the 10 years at Penn State he rose to the rank of Research Associate Professor and was P.I or co-P.I. on numerous large research grants and contracts. His Penn State research included work on catalysts, phosphors, and nuclear waste disposal. He is the originator of the concept of converting high-level nuclear waste to insoluble rock-like ceramics. Dr. McCarthy is Past-Chairman of the Board of the JCPDS-International Centre for Diffraction Data and is an Editor of the x-ray analysis journal *Powder Diffraction*.

LEGAL NOTICE

This paper was prepared under the auspices the North Dakota Mining and Mineral Resources Research Institute as an account of work sponsored by the Gas Research Institute (GRI). Neither GRI, members of GRI, nor any person on behalf of either: (a) makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this paper, or that the use of any apparatus, method, or process disclosed in this report may not infringe privately owned rights; or (b) assumes any liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this paper.

TABLE 1

CRYSTALLINE PHASES IN GASIFICATION ASH IDENTIFIED BY XRD

Code	Name	Nominal Composition
	High Temperature	*Reaction Products*
Cg	Carnegieite	$NaAlSiO_4$
Ne	Nepheline	$NaAlSiO_4$
C_2S	Dicalcium Silicate	$(Ca,Mg)_2SiO_4$ (bredigite, Bd)
Ml	Melilite	$Ca_2(Mg,Al)(Si,Al)_2O_7$
Mw	Merwinite	$Ca_3Mg(SiO_4)_2$
So	Sodalite-structure	$(Na,Ca)_8(Al,Si)_{12}O_{24}(SO_4)_{1-2}$
Sp	Ferrite Spinel	$(Mg,Fe)(Fe,Al)_2O_4$
Hm	Hematite	Fe_2O_3
Pc	Periclase	MgO
Cc	Calcite	$CaCO_3$
	Ca-Na-Silicate	$(Ca,Na,Mg)_{2.2}SiO_4$
	Mullite	$Al_6Si_2O_{13}$
	Pyroxene	$(Ca,Na)(Mg,Fe)Si_2O_6$
	Kirschstinite	$Ca(Fe,Mg)SiO_4$
	Al-Spinel	$(Mg,Fe)Al_2O_4$
	Cristobalite	SiO_2
	Remnant Minerals	*from Lignite*
Qz	Quartz	SiO_2
Pg	Plagioclase	$(Na,Ca)(Al,Si)_4O_8$
	K-feldspar	$(K,Na)AlSi_3O_8$
	Pyrite	FeS_2
	Pyrrhotite	$Fe_{1-x}S$
	Ash Hydration	*Reaction Phases*
	Zeolite-A	$(NaAlSiO_4)_{12}\cdot 27H_2O$
	Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 25H_2O$
	Portlandite	$Ca(OH)_2$
	Gaylussite	$Na_2Ca(CO_3)_2\cdot 5H_2O$
	Thenardite	Na_2SO_4
	Brucite	$Mg(OH)_2$
	Gypsum	$CaSO_4\cdot 2H_2O$

TABLE 2

COMPOSITIONS (wt%) OF GPGA GLASS, CYCLONE SLAGS AND GPGA-4 GASIFICATION ASH

	Mineral Wool	Slag 1	Slag 2	GPGA-4
SiO_2	31.9	42.3	33.5	26.3
Al_2O_3	13.5	15.3	10.6	12.7
Fe_2O_3	9.5	13.7	11.7	9.5
CaO	22.9	19.3	33.1	20.5
MgO	8.4	5.2	8.5	7.9
Na_2O	7.5	a	1.3	8.8
K_2O	0.8		<0.1	0.6
SO_3	1.7	0.2	0.6	1.6

a. The Na_2O composition is not known, but is assumed to be approximately 1 wt%

TABLE 3

COMPOSITIONS OF SELECTED CRYSTALLINE PHASES IN LIGNITE GASIFICATION ASH

Carnegieite: $Na\quad Al\quad Si\quad O_4$
$(Na_{1.34}K_{0.02}Ca_{0.02})(Fe_{0.10}Al_{0.92})(Si_{0.69}Al_{0.29}S_{0.02})O_4$

Nepheline (Ne): $Na\quad Al\quad Si\quad O_4$
$(Na_{0.89}K_{0.16}Ca_{0.02})(Al_{1.00})(Fe_{0.04}Si_{0.94})O_4$

Bredigite (Bd): $Ca_4\quad Si_2\quad O_8$
$(Ca_{2.33}Na_{1.13}Mg_{0.69}Fe_{0.16}Ba_{0.01})(Si_{2.03}Al_{0.05}P_{0.02})O_8$

Melilite:
ackermanite (Ak): $Ca_2\quad Mg\quad Si_2\quad O_7$
gehlenite (Geh): $Ca_2\quad Al\quad AlSi\quad O_7$
$(Ca_{1.74}Na_{0.26})(Al_{0.44}Fe_{0.15}Mg_{0.35})(Al_{0.45}Si_{1.55})O_7$

Merwinite (Mw): $Ca_3\quad Mg\quad Si_2\quad O_8$
$(Ca_{2.83}Na_{0.20})(Mg_{0.91}Na_{0.03}Fe_{0.06})(Si_{1.93}Al_{0.03}Fe_{0.04})O_8$

TABLE 4

pH MEASUREMENTS IN EXPERIMENTS WITH SINGLE PHASES AND GLASSES (L/S = 10)

REACTION TIME (d)	Cg	Ne	Bd	Ak	Mw	Geh	Glass[a]	S1[b]	S2[b]
0.004	12.0	12.4	11.9	11.2	11.7	10.9	11.7	10.4	10.7
0.020	12.1	12.4	12.0	11.5	11.7	11.2	11.9	10.2	10.9
0.040	12.2	12.5	12.1	11.5	11.7	11.3	11.9	10.4	10.9
0.167	12.3	12.7	12.6	11.7	12.3	11.1	12.0	10.3	11.3
0.375	12.3	13.0	12.8	12.1	12.5	11.2	12.1	10.0	11.4
2	12.3	13.0	12.7	12.4	12.6	11.4	12.1	10.0	11.5
3	12.4	13.2	12.7	12.4	12.7	11.4	12.1	10.0	11.6
4	12.4	13.2	12.8	12.4	12.7	11.4	12.2	9.8	11.7
9	12.8	12.8	13.0	12.4	12.6	11.4	12.1	9.7	11.7
16	12.8	12.8	12.7	12.4	12.6	11.4	12.3	8.9	11.7
25	13.0	13.0	12.7	12.3	12.6	11.4	12.2	8.9	12.0
36	13.0	13.0	12.7	12.3	12.6	11.3	12.2	8.9	11.9
49	13.0	13.0	12.7	12.3	12.6	10.9	12.2	8.9	11.8
64	13.0	13.2	12.6	12.3	12.6	10.6	12.2	8.4	11.7
81	13.0	13.0	12.6	12.2	12.6	10.2	12.2	8.3	11.7

a. Gasification ash glass prepared as Mineral Wool by O.E. Manz of UND EMRC.

b. Slag 1 (intermediate CaO); Slag 2 (high CaO)

TABLE 5

SELECTED RESULTS FROM THE MODELING EXPERIMENTS ON HYDRATION REACTIONS OF GPGP ASH (L/S = 0.5)

PHASE	HYDRATION PRODUCT[a]	PDF[b]	COMMENTS/APPEARANCE OF HYDRATION PRODUCT
	CRYSTALLINE REACTION PRODUCTS IN SINGLE PHASE EXPERIMENTS		
Cg	Na-zeolite-X [$Na_{88}Al_{88}Si_{104}O_{384}(H_2O)_{220}$]	a	late in 1st day
	Na-zeolite-A [$(NaAlSiO_4)_{12} \cdot 27H_2O$]	11-590	16th day
	Gibbsite [$Al(OH)_3$]	29-41	16th day
	Nordstrandite [$Al(OH)_3$]	24-6	late stages
	Beyerite [$Al(OH)_3$]	20-11	early stages
	Natron [$Na_2CO_3 \cdot 10H_2O$]	15-800	late stages
Bd	Brucite (Ca-substituted) [$(Mg,Ca)(OH)_2$]	7-239	9th day
	Calcite [$CaCO_3$]	5-586	9th day
	C-S-H's:		
	Tobermorite-11A [$Ca_5(OH)_2Si_6O_{16} \cdot 4H_2O$]	19-1364	early stages
	[$Ca_2SiO_4 \cdot H_2O$]	29-373	mid and late stages
	[$Ca_2SiO_4 \cdot xH_2O$]	11-211	
	[$Ca_xMg_6Si_8O_{20}(OH)_4 \cdot xH_2O$]	7-357	
	[$2CaO \cdot SiO_2 \cdot H_2O$]	3-594	
		3-649	
	Portlandite [$Ca(OH)_2$]	4-733	early stages
Glass	Calcite		mid stages
	Tacharanite (poorly crystallized) [$Ca_{12}Al_2Si_{18}O_{51} \cdot 18H_2O$]		mid stages

a. Nominal formula given for first citation only.
b. PDF number given for first citation only.

TABLE 5 (cont.)

SELECTED RESULTS FROM THE MODELING EXPERIMENTS ON HYDRATION REACTIONS OF GPGP ASH (L/S = 0.5)

PHASE	HYDRATION PRODUCT[a]	PDF[b]	COMMENTS/APPEARANCE OF HYDRATION PRODUCT
	CRYSTALLINE REACTION PRODUCTS IN TWO PHASE EXPERIMENTS		
Cg+Bd	Zeolite-A		by 36 day
	Gibbsite		mid and late stages
	Beyerite		
	Gaylussite $[Na_2CO_3 \cdot CaCO_3 \cdot 5H_2O]$	21-343	49 day
	Straetlingite $[Ca_2Al_2SiO_7 \cdot H_2O]$	29-285	late stages
	Tobermorite		49 day
Cg+Glass	Zeolite-A		36 day
	Gibbsite		36 day
	Gaylussite		
	Straetlingite		late stages
	Calcite		late stages
	Tobermorite		
	CRYSTALLINE REACTION PRODUCTS IN EXPERIMENTS WITH GPGA ASH		
GPGA-4 with DW	Na-zeolite-X		mid stages
	Na-zeolite-A		36 day
	C-S-H (tobermorite)		
	Gaylussite		mid stages
	Portlandite		
	Thaumasite-like phase $[Ca_3Si(OH)_6(SO_4)(CO_3) \cdot 12H_2O]$	25-128	36 day
	Calcium aluminum oxide carbonate hydrate	36-129	36 day
GPGA-4 with 1M NaCl	Calcite		49 day
	C-S-H (tobermorite)		
	Gaylussite		
	Portlandite		
	Halite		64 day

---

a. Nominal formula given for first citation only.
b. PDF number given for first citation only.

"LEACHING RESEARCH-CHARACTERIZATION, REGULATION AND METAL RECOVERY"

BY: DAVID J. HASSETT
ENERGY & MINERAL RESEARCH CENTER, UND
GRAND FORKS, ND

LEACHING RESEARCH - CHARACTERIZATION, REGULATION, AND METAL RECOVERY

David J. Hassett

ABSTRACT

Leaching is often thought of as a technique used primarily to determine the hazardousness of waste materials. In this respect, the EPA extraction procedure (EP) and the soon to become official toxicity characteristic leaching procedure (TCLP) usually come to mind. To a scientist interested in obtaining information about the true nature of a material, leaching can play a much larger role than the simple determination of hazardousness. Leaching tests, properly applied, can be used to determine much information about the properties of trace and major constituents in materials with complex mineralogical compositions. Leaching is playing an increasingly important role in the complete characterization of materials. Leaching, combined with bulk chemical analysis, provides an important piece of information in a complete characterization scheme. From a regulatory point of view, leaching tests are becoming more fully understood and as would be expected, more reliable in the accuracy of the information they provide. The increased reliability has come about through an evolutionary process during which the regulatory leaching test protocols have been refined. Regulatory leaching today, relying on the EP tox and the TCLP tests, often provides false or misleading information. Newer generic leaching tests, such as the synthetic groundwater leaching procedure (SGLP) developed at the University of North Dakota, present the possibility of rectifying some of the problems with the current regulatory procedures. In metal recovery, leaching is important not only as a research tool, but also as a commercial means to resource recovery. There have been many advances recently that have made possible the recovery of metals, including aluminum, from coal ash by the use of simple leaching procedures. The important aspects of the use of leaching for these three important applications: characterization, regulation, and metal recovery, will be discussed in this paper. Examples of uses of leaching for characterization as well as the regulatory aspects of leaching will be discussed. Data demonstrating the different interpretations of materials that can be derived through various leaching tests will be presented. The use of leaching for metal recovery as well as a method developed to alter mineralogy of low-rank coal gasification ash for the application of leaching recovery of aluminum will be discussed.

INTRODUCTION

Leaching, for the characterization of materials, is a laboratory technique used in routine as well as research applications. The regulatory uses of leaching, although important, often overshadow the research aspects of this simple and versatile technique. Leaching can be applied in a number of ways; batch leaching, both long and short term, and column leaching are the commonly used techniques. This paper deals primarily with the topic of batch leaching as applied to research in the North Dakota Mining and Mineral Resources Research Institute laboratories. Column leaching, while a viable technique, is complex enough to be the topic in itself of another publication.

The question of the advantages of the study of chemical phenomena in a static (batch) system versus a dynamic (column) system raises some interesting philosophical problems. For example, when studying the trace element attenuation properties of sediments or soils in column systems, one must be concerned that reaction terms are, first of all, probably always second order and that there are multiple reaction sites of varying strength with multiple species competing for them. In addition, the amount of material sorbed or attenuated at any one point in the column can only be determined by sectioning the column and analyzing the material for attenuated species. In a column, diffusion into the stationary phase may also account for a portion of the measured attenuation. The advantages of batch leaching are that it allows the researcher to alter one variable at a time, in otherwise complex systems, and to observe resulting changes in chemical equilibrium. Batch leaching usually provides results in a relatively short period of time compared with most column techniques. In batch leaching, a high liquid-to-solid ratio minimizes the effect of diffusion of chemical species into the stationary phase while allowing for accurate measurement of amount sorbed per unit mass of solid. Multiple experiments for the stepwise integration of phenomena with the manipulation of a single variable per set of experiments can provide much valuable information not easily obtainable in column experiments. By conducting column experiments, a direct observation of the phenomena under dynamic conditions is obtained which is not possible in batch experiments. The changes in a carefully controlled batch system may also be observed over long periods of time. One leaching experiment performed at the University of North Dakota (UND) Mining and Mineral Resources Research Institute (MMRRI) has been underway for over 400 days with chemical analysis at regular intervals. Normally, leaching experiments are used to determine properties of materials in relatively short periods of time. Regulatory leaching tests, for example, are carried out using tests with leaching times of less than 24 hours. Even these short-term leaching tests allow for the accurate prediction of leachability, providing the tests are carried out in a manner that approximates the natural conditions which they are designed to simulate.

The key to designing leaching tests lies in using carefully thought-out protocols. This is very important since the outcome of the tests can have a profound effect. In the case of regulatory leaching, this may be the difference between a hazardous or a non-hazardous classification. For an ore body containing gold or other precious metals, the outcome of an inaccurate test could be disastrous to the investors.

This paper presents an overview of some of the various applications of leaching for research and regulatory applications. Three batch leaching test will be frequently referred to in this paper. These are:

1. EPA-EP (1) - The EPA-EP method was designed to define whether a material is a hazardous waste in a municipal landfill where the presence of organic matter would presumably give mildly acidic conditions due to the presence of acetic acid from the microbial degradation of cellulosic and other organic materials. The procedure uses a leaching test with dilute acetic acid as the leaching solution. A liquid-to-solid ratio of 20:1 is used in this test and an equilibration time of 24 hours with agitation on an orbital shaker. The test calls for the addition of 0.5N acetic acid solution up to a limit of 4 mL per gram of ash to maintain a pH of 5.0.

2. Toxicity Characteristic Leaching Procedure (TCLP) (2) - Philosophically this test is designed to provide the same information as the EPA-EP. This will soon become the official test, replacing the EPA-EP. The major changes are:

    A. End-over-end agitation

    B. Addition of all of the acid at once as a dilute acetic acid solution or as an acetate buffer, depending upon the alkaline nature of the waste material being tested.

    C. An 18-hour equilibration time instead of 24 hours

3. Synthetic Groundwater Leaching Procedure (SGLP) - The SGLP differs from the TCLP only in that the leaching solution is defined as whatever is appropriate to simulate the conditions the waste material is likely to encounter under natural disposal conditions. In North Dakota, this is usually a sodium sulfate, bicarbonate-buffered solution with the following composition (in mg/L): 436 Na; 338 SO_4; 726 HCO_3; pH=8.3-8.7.

4. ASTM D3987-81 (3) - This leaching test uses a liquid-to-solid ratio of 4:1 with reciprocal agitation. The leaching solution is distilled water and a 48-hour equilibrium time is used. A revision to this test changes the liquid-to-solid ratio to 20:1 with an 18 hour equilibration time and end over end agitation.

LEACHING RESEARCH

Characterization

Leaching is one of the more often used, and at the same time misused, laboratory tests for the evaluation and prediction of the effects of materials on the environment. The characterization of the leaching properties of materials for the purpose of predicting field effects must be carried out in a manner that simulates field conditions; therefore, flexibility is essential in the test protocol. In this respect, the current regulatory leaching test fails. Except when disposal will take place in sanitary landfills, the criterion of simulating field conditions eliminates the EPA extraction procedure (EP) and the toxicity characteristic leaching procedure (TCLP) as viable predictive techniques. This is important since there are large volumes of materials, such as coal conversion ash, that are disposed in monofills where leaching conditions are extremely different from the acetic acid leach used in the regulatory tests. The problems associated with the regulatory application of leaching tests is discussed more thoroughly in the section on regulation.

Leach testing is used frequently in the laboratory, either directly for the determination of properties of materials, or as a preliminary screening step for another type of testing or research protocol. Laboratory leaching is frequently applied for sample preparation, when analytical techniques, which require solutions, are applied to the analysis of solids.

Attenuation of Trace Elements

The attenuation of trace elements by near-surface sediments has been evaluated by the research application of batch leaching test protocols (4). The use of batch procedures allows the evaluation of individual variables one at a time as is impossible in column leaching. Column leaching can be used to predict field phenomena, but data from these tests are difficult, if not impossible, to interpret in the absence of the detailed information on the effect of individual variables provided by data from batch leaching tests. The use of batch leaching for the characterization of these individual components of the complex real world scenario has resulted in the elucidation of a number of trace element attenuation mechanisms.

Using batch leaching tests, the effects of pH, ionic strength, and concentration of the trace elements have been determined in the measurement of the trace element attenuation properties of near-surface overburden sediments. The sediments studied were obtained from coal mining areas of North Dakota, Montana, Wyoming, and Texas. Batch leaching allowed the evaluation of one variable at a time on the system under study, while incorporating all of the other variables in the test design. In a column test even the determination of the effect of one simple variable such as pH on the system is difficult since the observer can only accurately measure the pH of the solution entering and the pH of the solution leaving the column. The changes within the column remain a mystery and the effect of pH as a variable remains unknown except as an overall effect. Any changes brought about by, or phenomena occurring at, discrete pH values remain hidden within the column.

Leaching Characteristics of Gasification Ash

Four different leaching tests were applied to eight specimens of fixed-bed gasification ash produced from North Dakota lignite in three different types of gasifiers (5). The specimens were leached using the EPA-EP leaching test, the synthetic groundwater leaching procedure, the ASTM D3987-81 method, and a long-term leaching test. The short-term tests were applied as a part of an overall characterization protocol along with bulk chemical analysis, physical testing, and mineralogical characterization by X-ray diffraction. Although they provided valuable information on the overall leachability of select elements from ash samples, the short-term tests did not indicate how gasification ash would react with water over periods of weeks or months. To address the leaching properties of gasification ash under conditions relevant to disposal, a long-term leaching test was begun. The long-term leaching experiment was carried out at two liquid-to-solid ratios of 20:1 and 2:1. In the 20:1 experiment, 1000 grams of ash were mixed in with 20 L of carboy. In the 2:1 experiment, 9.8 kg of ash were mixed with 19.6 L of water in a 20 L carboy. Agitation was accomplished by rolling the carboys on their sides. The carboys were purged with nitrogen during of the experiment. Sampling of the solution was done at regular intervals ranging from hours at the start of the experiment to four weeks near the end of the experiment. The experiment was continued for 120 days.

Most of the analyses indicated trends that would be predicted. Concentrations of elements and other measured parameters increased rapidly at the beginning of the experiment and continued to increase, although, slowly, for the duration. Several elements exhibited very different behavior. At the start of the 2:1 test, aluminum and boron concentrations increased rapidly, but toward the end they actually decreased. This can be explained by the formation of secondary hydrated phases in this solution, which was more alkaline than the experiment performed at a liquid-to-solid ratio of 20:1. This has been confirmed by characterization of leaching residue by X-ray diffraction.

Leaching Characterization of the Effectiveness of Codisposal

Leaching tests have also been used to measure the effect of codisposal of various coal gasification residues and waste materials on the leachability of select trace elements (6). Leaching characterization, along with chemical analyses and mineralogical characterization by x-ray diffraction, provided the means to study and understand the phenomena observed. It was determined, during the course of this research, that the formation of secondary hydrated phases provided a major means for reducing the overall leachability of select, potentially problematic, trace elements such as arsenic and selenium. Codisposal mixtures cured for up to 28 days exhibited lower leachability of these select trace elements as measured by short-term (< 1 day) leaching tests. Long-term leaching tests, in excess of 300 days, along with mineralogical characterization of residues from the leaching test confirmed that the formation of ettringite-like secondary hydrated phases were responsible for the reduction of leachability, observed in the short-term leaching of cured samples.

In the long-term leaching, the solution concentration of boron, aluminum, arsenic, and selenium increased rapidly to a maximum level and then gradually decreased over the course of the test. Results from leaching experiments, designed to measure the fixation of trace elements in codisposal mixtures, indicated that the overall success with codisposal had been good. Fixation factors ranged as high as 337, indicating a reduction of leachability of a factor of 337, to as low as 3 for As, B, Mo, Se, and V. Even the lowest reduction of 3 is a significant reduction. Fixation factors were derived by dividing the calculated leachability of the individual components, as a weighted summation, by the measured concentration. The values for the individual components had been determined experimentally and assumed no fixation. Leaching values were determined using the TCLP and the SGLP. This is an excellent example of the use of innovative leaching techniques in research.

Regulation

The evaluation of hazardousness can be accomplished in a number of ways, but the most expeditious and cost-effective manner for certain categories of hazardousness is through batch leaching procedures. The most commonly used batch procedure is the EPA-EP which will soon be replaced by the soon-to-be-official TCLP. The EPA-EP is currently the regulatory test for the determination of hazardousness on the basis of leachable toxic or regulated materials. The EP was "designed to simulate the leaching a waste would undergo if disposed of in a sanitary landfill." This leaching procedure is designed to simulate leaching at pH 5 using dilute acetic acid. It is assumed that this leaching condition would simulate not only the pH, but also the type and source of the acidity. The general assumption was that cellulosic and other municipal wastes would generate acetic acid through microbial degradation. The assumptions are good and the test is based on a sound protocol.

Several sources of waste, however, would almost never be disposed of in a municipal landfill. One general category is coal conversion ash. The SGLP, the generic test of leachability described earlier, was developed to provide leaching data for just this type of waste material.

The generic leaching test was developed at the North Dakota Mining and Mineral Resources Research Institute, based on several objectives. These were:

1. To simulate natural groundwater conditions with respect to groundwater chemistry.

2. To be flexible enough to be site specific.

3. To be directly comparable to the TCLP.

The SGLP, as developed, used a leaching solution which simulated groundwater from central and western North Dakota. The solution was made by dissolving 0.50 grams of sodium sulfate and 1.00 grams of sodium bicarbonate in 1 liter of distilled deionized water. The analysis of this (synthetic groundwater) leaching solution is as follows:

Na	436 mg/L
SO_4	338 mg/L
HCO_3	726 mg/L
pH	8.3 - 8.7

This sodium sulfate-bicarbonate buffered water is typical for central and western North Dakota where the water is slightly alkaline (bicarbonate buffering) and the primary mineralization is from sodium sulfate. This was the composition of the solution used for leaching in all of the experiments performed with the SGLP method; however, since the test is generic, any composition could have been used to simulate the groundwater chemistry from any location.

Results and Discussion

A comparison was made between the TCLP, the SGLP, the original EPA-EP extraction procedure, and the ASTM leaching test.

We felt it would be useful to see how these four tests compared in an extraction of an alkaline coal conversion waste. Gasification ash from the integrated facility at Beulah, North Dakota, was chosen for our comparative leaching tests. The results of these tests are shown in Tables 1 and 2. Table 1 shows the results of analysis for major components and Table 2 shows results for select trace and minor components.

Several trends are immediately apparent in these two tables. In Table 1, pH indicates that the waste is highly alkaline in nature. In the case of a highly alkaline waste such as this, the effect of the relatively small amount of acid used is negligible, although the absence of any acid or bicarbonate buffering is indicated in the extremely high pH seen in ASTM leaching. Unfortunately, the liquid-to-solid ratio used in this test is different than that of the others, making direct comparisons difficult, if not impossible. This is the primary drawback to the use of the ASTM leaching procedure. Accordingly, the discussion of results from this leaching procedure will be limited. The results are interesting, however, and have been presented for comparison with the understanding that the different liquid-to-solid ratio used makes interpretation difficult.

Results for the ASTM leaching procedure reflect the higher solid-to-liquid ratio and the highly alkaline nature of the leachate. In general, the concentrations reported are higher with the ASTM leaching procedure except for elements whose solubility would be limited in an alkaline system. Notable in this respect are the elevated values for aluminum, potassium, sodium and vanadium, and the lower values for barium, calcium, magnesium, and strontium in comparison to values generated in the other leaching tests. In some cases, these values, which are different from EP leaching values, are similar to results from the the SGLP test. The reasons for this are related to the alkaline nature of both of these leaching procedures, but interpretation or correlation is complicated by the difference in liquid-to-solid ratio.

Notable trends among elements can be seen in a comparison between the EP and TCLP leaching procedure. These differences reflect the larger amount of acid which can be used in the EP procedure. Calcium, barium, magnesium, and strontium are most notable and have higher concentrations in the EP leachates than the TCLP. An elevated sodium value is noted for the TCLP, probably caused by the presence of highly alkaline particles. This elevated sodium value is most likely due to the nonhomogeniety of the ash rather than the differences in the leaching procedures.

Comparison of results of the SGLP, EP, and TCLP tests also indicated notable trends. The more alkaline nature of the SGLP test is apparent in the lower values for barium, calcium, and molybdenum as well as in the elevated values for arsenic and, to a lesser extent, selenium. There are other differences in the concentrations of elements, but discretion must be used in the interpretation of small differences in trace element concentrations in leachates generated from nonhomogeneous materials such as coal conversion ash.

Metal Recovery

Metal recovery, from aluminum in coal ash to gold and platinum in ore deposits, is generally evaluated in a batch leaching test of one kind or another. Many of the laboratory assays, relying on atomic spectroscopy, utilize batch leaching procedures as the front-end sample preparation step. Of great interest to the energy industry is the recovery of materials from coal conversion ash. Leaching procedures for the recovery of aluminum and a number of other important metals from ash have been developed. Many of these, unfortunately, depend on the modification of ash mineralogy prior to leaching and are uneconomical at this time.

Recovery of Aluminum From Ashes of an Integrated Coal Gasification Facility

Gasification ash presents a major problem in disposal because of the large volume of waste produced and because of the potential for classification as a hazardous material. Gasification ash could be reclassified as a hazardous waste either from a reevaluation of RCRA limits or from the inclusion of new elements in the RCRA list. The recovery of materials of value from what would normally be considered a waste material could have a major impact on the cost of disposal.

Various methods of batch leaching were investigated. Both acid and alkaline leaching solutions were considered (7). The experimental techniques for the recovery of aluminum or other leachable materials from gasifier ash were divided into categories as follows:

1. Unmodified Ash

    a. Acid Leaching
    b. Alkaline Leaching

2. Modified Ash

    a. Acid Leaching
    b. Alkaline Leaching

Initially, the acid leaching methods were given low priority and emphasis due to the alkaline nature of the ash. Ash from most low-rank coals is highly alkaline and would consume large amounts of acid. In any leaching scheme, the alkaline procedures would be favored because initial contact between the ash and water produces an alkaline solution. To utilize an acid leach, all of this natural alkalinity would have to be neutralized. For this wasteful use of acid to be economical, the process would have to yield some valuable products. Aluminum was recovered at between 76 and 96 percent in various acid-leaching experiments using strong mineral acids. Unfortunately, silicon was also efficiently recovered and the resultant acidic solution containing silicon formed a gel, presenting difficult material handling problems. In addition to the material-handling problems, the solution of silicon and aluminum also presented a relatively difficult separation problem as most inexpensive techniques for removing one of these elements also removed the other. Even the gel contained silicon and aluminum.

The solution to this problem was to modify the ash mineralogy to make a material that would lend itself to leaching without the liberation of large amounts of silicon. A process called the lime-soda sinter process (8) developed by Murtha and Burnet at Iowa State University, Ames Laboratory, proved to be the most versatile ash modification process for our application. This process, which requires the addition of sodium carbonate and calcium carbonate to the ash followed by sintering, forms insoluble dicalcium silicate and calcium aluminate as well as sodium aluminate. Both of these aluminum-containing compounds release their aluminum when subjected to leaching by dilute alkali. An economic analysis of this process indicated that it was not profitable. This is due to the relatively high cost of ash modification, primarily in energy costs, and to the low amounts of aluminum in ash from low-rank coals. The aluminum content expressed as aluminum oxide, in the samples studied, ranged from 11 to 15 percent. An excellent annotated bibliography discussing methods for the recovery of metals from ash presents more complete discussions of this and many other methods (9).

Recovery of Other Materials of Value by Leaching

There is a potential for the recovery of other valuable materials from ash. Depending on the source, there may be concentrations of materials such as gallium and germanium that could be recovered, either for profit or to offset costs of disposal. In addition, ash from burning oil contains other valuable metals, such as vanadium and nickel from metallo-porphyrins that could also be considered for recovery.

The uses of leaching for the recovery of materials of value from ash and other sources appear almost limitless. Leaching, for instance, is an established technique for the recovery of materials of value from ore bodies. Recent research at the EMRC MMRRI has focused on the leaching recovery of platinum-group metals and gold using innovative leaching technology. Currently much of the recovery of these materials depends on cyanide and thiourea leaching. These process, especially the commonly used cyanide leach, are extremely hazardous and, in the current conservative regulatory climate, are very expensive to permit. A relatively new process using halo-hydantoins has proven to be a viable alternative to these two processes, particularly to the cyanide leach. Cyanide leaching, one of the more efficient processes for the recovery of precious metals, has with it the hideous potential for disaster due to the high toxicity of cyanide. The use of halo-hydantoins, which are relatively safe to handle, would provide a desirable alternative.

SUMMARY

It can be seen, from the examples given, that there is considerable potential for innovative uses of leaching as a means of acquiring knowledge through fundamental research. In the regulatory sense, leaching is one of the criteria for the determination of hazardousness. This use of leaching for regulatory purposes, although only in the formative or developmental stages, has with it established procedures (the EPA-EP and TCLP) which, with the modifications that come from research and increased knowledge, can provide a means to predict environmental impacts of a variety of materials and waste products. The example given for regulatory uses of leaching provided examples of potential problem areas in the determination of hazardousness. Examples of the use of four leaching procedures indicated that there could be very different interpretation of leaching characteristics depending on the test used. The data indicated the need for a regulatory leaching procedure that reflects local conditions. This could be provided through a test such as the SGLP. The acceptance of a generic regulatory leaching procedure as a complementary test to the EP, or soon-to-become-official TCLP, would allow for more valid assessment of hazardousness as it applies to the field disposal of solid wastes. The generation of leaching data directly relatable to local conditions of leachability is crucial to the generation of scientifically valid data from which to make sound decisions. In the area of resource recovery, leaching is well established. Current research efforts are underway to improve some of the established leaching practices to remove the problems associated with the use of toxic materials such as cyanide. In short, laboratory leaching, often forgotten in this age of computerized high-tech instrumentation, is a powerful and versatile tool which a trained scientist can use to open many doors.

REFERENCES

1. U.S. Environmental Protection Agency, Federal Register 45(98) 33121-33133 (May 19, 1980), ISSN 0097-6326.

2. U.S. Environmental Protection Agency, Federal Register, 51(9) 1750-1758 (January 14, 1986), ISSN 0097-6326.

3. American Society for Testing and Materials, 1983 Annual Book of ASTM Standards - Water and Environmental Technology, Part 31, p. 1258 (1979).

4. Hassett, D.J. and G.H. Groenewold, "Attenuation Capacity of Western North Dakota Overburden Sediments: Final Report for Department of Energy Contract DE-AB 18-80FC10120," MMRRI Bulletin 86-04-MMRRI-01, 105 p. (1986).

5. Hassett, D.J., K.R. Henke, and G.J. McCarthy, in Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal II, edited by G.J. McCarthy, F.P. Glasser and D.M. Roy, Mat. Res. Soc. Symp. Proc. Vol. 65, (Materials Research Society, Pittsburgh, PA, 1986) pp. 285-300.

6. Hassett, D.J. and D.F. Hassett, "Fixation of Leachable Elements in Composite Waste Forms from North Dakota Lignite Coal Conversion Ash" in Fly Ash and Coal Conversion By-Products: Characterization, Utilization, and Disposal IV, edited by G.J. McCarthy, F.P. Glasser, D.M. Roy, and R.J. Hennings, Mat. Res. Soc. Symp. Proc. Vol. 113 (Materials Research Society, Pittsburgh, PA, 1987) pp. 333-340.

7. Manz, O.E., D.J. Hassett, D.F. Hassett, D.L. Laudal, and R.C. Ellman, Characterization Extraction and Reuse of Coal Combustion Solid Wastes, Volume III: Technical and Economic Feasibility of Bulk Utilization and Metal Recovery for Ashes from an Integrated Coal Gasification Facility, Final Report to the Gas Research Institute, October 1986.

8. Burnet, G., and M.J. Murtha, "New Developments in the Lime-Soda Sinter Process for Recovery of Alumina from Fly Ash," Proceedings, Fifth International Ash Utilization Symposium, Atlanta, Georgia, February 25-27, 1979, U.S. DOE, MERC/SP-79/10, pp. 68-84.

9. Burnet, G., M.J. Murtha, and J.W. Dunker, Recovery of Metals from Coal Ash, An Annotated Bibliography, 4 p., January 1984.

TABLE 1
COMPARATIVE LEACHING RESULTS FOR MAJOR CONSTITUENTS OF GASIFICATION ASH

Element	EP	TCLP	SGLP	ASTM
pH	10.9	11.6	11.0	12.1
Si	2.4	19	6.5	13
Al	6.2	9.4	210	1200
Fe	<0.1	<0.1	0.45	1.6
Ca	960	73	13	17
Mg	0.68	<0.01	0.98	0.89
Na	1500	2600	1181	3130
K	37	32	22	95
SO_4	471	550	623	1310

TABLE 2
COMPARATIVE LEACHING RESULTS FOR TRACE CONSTITUENTS OF GASIFICATION ASH

Element	EP	TCLP	SGLP	ASTM
As (ppb)	4	12	373	860
B (ppm)	17	10	4	8
Ba (ppb)	2800	770	180	190
Cd (ppb)	<1	<1	<1	<1
Cr (ppb)	<30	<30	<30	90
Cu (ppb)	<30	<30	<30	<30
Hg (ppb)	<0.3	<0.3	<0.3	<0.3
Mn (ppb)	<50	<50	<50	<50
Mo (ppb)	581	464	148	592
Ni (ppb)	<20	<20	<50	<50
Pb (ppb)	<2	<2	<2	<2
Se (ppb)	1	2	10	12
Sr (ppm)	51	7	0.5	0.7
Ti (ppb)	<20	<20	<20	<20
V (ppb)	240	400	260	620
Zn (ppb)	<20	<20	<20	<20

"CHARACTERIZATION AND UTILIZATION OF SLAG FROM THE TEXACO GASIFICATION PROCESS"

BY: E.F. DE PAZ, M.S. NAJJAR, AND E.O. WAKEFIELD
TEXACO, INC.
BEACON, NY

CHARACTERIZATION AND UTILIZATION OF SLAG FROM THE TEXACO GASIFICATION PROCESS

Enrique F. de Paz *** Mitri S. Najjar
Texaco Research Center - Beacon
P. O. Box 509
Beacon, New York 12508

Edward O. Wakefield
Texaco Research Laboratory - Montebello
Texaco Inc.
P. O. Box 400
Montebello, California 90640

PRESENTED:
OPPORTUNITIES IN THE SYNFUELS INDUSTRY SYMPOSIUM
BISMARK, NORTH DAKOTA
AUGUST 28-31, 1988

ABSTRACT

The operability of processes utilizing coal as a feedstock, depends on, among other things, their ability to process the mineral matter present in the coal. For this reason, it is very important to analyze and characterize the mineral products from these processes in such a way as to be able to predict their behavior during processing.

This paper discusses and provides examples of how techniques such as x-ray diffraction and optical and scanning electron microscopy are utilized to characterize slags from the Texaco Coal Gasification Process. These results are combined with other measured slag properties, such as viscosity, to assist in the selection of the operating conditions for the gasification process. In addition, the paper provides a brief review of Texaco's effort to identify and evaluate potential applications for the solidified slag product.

Introduction:

There are many processes which use coal as a feedstock. No matter what the final product may be--chemicals, fuels, electricity, etc.--the success of the operation depends on, among other things, their ability to effectively process the mineral matter in the coal. Ineffective processing of the mineral matter may lead to reduced efficiency or operating difficulties. In extreme cases, the characteristics of the mineral matter and its corresponding products may constrain the economic optimum operating conditions. For these reasons, it is very important to be able to determine and understand how the operating conditions of a particular process will affect coal ash transformations and the properties of the resulting flyash or slag. Therefore, to be of value, slag or flyash characterization techniques must provide insight into what is or may be occurring in the process.

Texaco Coal Gasification Process

The Texaco Coal Gasification Process (Figure 1) has been used commercially for over 10 years to convert coal into clean syngas (CO/H_2 mixture). The syngas is subsequently used as a feedstock for a variety of products. For example, the Tennessee Eastman Company, Ube Industries (Japan), and Synthesis Analge Ruhr (Germany) produce acetic anhydride, ammonia and oxo-alcohols, respectively. On the other hand, the Cool Water Program uses the syngas to generate electricity.

In the Texaco process, a finely ground coal/water slurry and oxygen are injected through a burner into a high pressure refractory lined reactor. The organic material in the coal reacts with the oxygen to generate the heat required to maintain the reactor temperature and to produce the syngas. The mineral matter melts into a slag, most of which impinges on the walls of the reactor. The syngas passes from the gasifier and is cooled in a water quench or by generating steam in a syngas cooler. The gas is then treated to remove contaminants (particulates, H_2S, etc.), after which it is used to manufacture chemicals or as a clean burning fuel. The slag flows down the gasifier walls to the slag outlet at the bottom of the gasifier. The slag is cooled and collected as a granular material in a water pool in the quench vessel or at the bottom of the radiant syngas cooler. The solidified slag is periodically removed from the process through a water-sealed lockhopper system.

Characterization Techniques and Results

The techniques presently being used to characterize slags from the Texaco Coal Gasification Process are listed in Table 1. To illustrate how the results of the various characterization techniques are interpreted, combined and related to the processing of the mineral matter in the gasification process, two coal slags will be used--slag A, from a western coal, and slag B from an eastern coal. The results of the elemental analysis, the x-ray diffraction and ash fusion tests for these two slags are shown in Table 2.

The elemental analysis of a slag, by itself, does not provide very much information about the process. However, by comparing it with the corresponding low temperature ash analysis, we can gain information about possible refractory wear and volatile vaporization during gasification. A substantial increase of any of the components from the refractory in the slag may be indication of incompatability of the refractory with the slag. This information is particularly useful if the refractory component detected in the slag is not present in the coal ash. A lower concentration of volatile species, such as sodium, in the slag than in the low temperature coal ash indicates possible vaporization of these components during gasification. The vaporized components will then condense and dissolve in the quench water or condense on cool downstream surfaces where they might contribute to deposit formation. As is usually the case, the comparative analyses in Table 2 show that there is little or no compositional difference between the ash and the corresponding slag for both of these coals, implying that in both of these cases, there was no vaporization of volatile components and no significant refractory wear.

The x-ray diffraction analysis indicates whether a slag is glassy (amorphous) or crystalline. In addition, if a slag does contain crystalline phases, x-ray diffraction will generally identify those phases. The presence of crystallinity in a slag, as will be shown later, may be an indication of undesirable slag flow properties.

Although the ASTM ash fusion test is still performed routinely, Texaco has found that this test is inadequate for predicting slag flow behavior in the gasifier. In some cases, the slag flows out of the gasifier at lower temperatures than the measured ash fusion temperature, while in other cases, the required temperature is considerably higher than the ash fusion temperature. We find that the best method for evaluating slag flow characteristics is using a high temperature viscometer--especially one designed to generate flow curves (shear rate vs. shear stress).

While most coal slags are newtonian fluids throughout the typical operating temperature range of the Texaco Gasification Process (2200-2700F), some demonstrate flow characteristics that may lead to slag flow problems in the gasifier. For example, Figures 2 and 3 show the measured flow curves for slags A and B at various temperatures. Slag A is newtonian at all the measured temperatures as indicated by the approximately straight shear rate/shear stress correlations passing through the origin. Slag B, however, is newtonian only at temperatures of 2600F and higher. Below this temperature the slag exhibits a yield stress which increases rapidly with decreasing temperature. In the gasifier, the shear stress or force for slag flow down the gasifier wall is the pull of gravity on the slag layer, i.e. the weight of the slag. This stress, in turn, generates a corresponding shear rate or velocity gradient within the slag. With a newtonian slag, flow is initiated immediately after the slag hits the gasifier wall. However, if a yield stress is present the slag will not flow immediately after hitting the wall. Instead, the slag layer on the wall will build up until it is heavy enough to overcome the yield stress at that particular temperature. Based on the flow curves for slag B, the slag layer thickness required to overcome its yield stress at 2400F will be approximately one and a half times that required at 2500F and 8 times that at 2550F. When the yield stress is exceeded, the layer of slag will flow downward to the slag outlet. If the slag layer is thick enough, it may cause the slag to bridge across the outlet, and lead to slag removal problems.

A yield stress generally indicates the presence of a somewhat rigid structure within a material. The yield stress is the force required to break down this structure before flow can be initiated. Yield stresses are typical of concentrated solid-liquid mixtures, such as coal slurries. In slags, yield stresses are caused by the formation of crystalline phases in the slag melt. However, the detection of crystalline phases alone does not necessarily indicate non-newtonian flow behavior. While crystallization generally increases the viscosity of all slags, it is the abundance and/or shape of the crystals which are the main factors contributing to the non-newtonian behavior of slags.

Determination of the abundance and shape of the crystals in a slag requires the use of optical and/or electron microscopy. These techniques, along with the energy dispersive x-ray (EDX) analysis capability of the scanning electron microscope, can be combined to obtain a semi-quantitative determination of the various phases present in a slag. Figure 4, shows an optical photomicrograph of a thin section of slag B, along with the corresponding EDX analyses of the various phases. The photomicrograph shows the large quantity of needle-shaped crystals which are dispersed throughout the glassy matrix. These needles, some of which are up to 300 microns long, form the woven network structure which is the source of the yield stresses previously shown in Figure 3. The EDX analyses show that, while the glassy matrix is similar to the bulk elemental analysis, i.e. Si>Al>Fe>Ca, the needles are mostly Al and Si, with the aluminum present in larger proportions. Based on this analysis, we can conclude that the needles are the mullite crystals detected by the x-ray diffraction analysis. The other crystalline phase, fayalite, apparently contributes very little to the non-newtonian flow behavior of the slag. Generally, we have found that a slag having a composition in the mullite region of a phase diagram, will precipitate these needle-shaped mullite crystals readily and will exhibit significant yield stresses.

As stated previously, non-newtonian flow characteristics are undesirable since they may cause slag removal problems. To minimize this possibility, the gasifier can be operated at high temperatures, where the slag is totally newtonian - in the case of slag B, 2600F or higher. However, very high process temperatures are undesirable since they decrease process efficiency. A more effective alternative is to modify the slag flow characteristics by injecting additives with the coal slurry. For example, Figure 5 shows how the addition of 15 weight percent dolomite (based on the coal ash content) will prevent formation of mullite crystals and eliminate yield stress down to a temperature of 2300F. This example demonstrates another important application of slag viscometry. It may be used to identify and evaluate fluxing additives before they are used in a plant.

Along with the techniques described in this paper, there are other analytical techniques that will enhance our understanding of the mineral transitions and reactions occurring during gasification. These techniques include infrared spectroscopy to identify clay-type minerals in the low temperature coal ash, differential thermal and gravimetric analysis (DTA/TGA) and hot stage x-ray diffraction to study the conversion of a coal to a slag and any subsequent crystallization which may occur during the slag cooling process.

Utilization of Slag

The solidified slag from the Texaco Coal Gasification process is a granular material ranging in size from 16 mesh to less than 325 mesh. The slag is stable and non-hazardous, so that landfilling is an acceptable means of disposal. However, There are cases where the slag has or is being used as a raw material for other industries. In Japan, a Texaco licensee, using a proprietary process, has modified the slag to produce a hollow light weight aggregate (U-Light) to be used for the manufacture of a light-weight gypsum-like wallboard and other building materials. In another instance, the slag has been used as a supplementary feed to a cement kiln, so as to benefit from the fuel value of the small amount of unconverted carbon present in the slag.

The apparent success of these slag applications suggest that the slag may be a suitable or a preferable raw material for other industries. Therefore, Texaco is working together with representatives from various industries to evaluate the potential of the slag as a raw material for those industries. Some of the applications for which the slag is being considered are as follows: cement, concrete products, roofing materials, landfill cover, soil amendments, road base materials, asphalt, filter media, blasting grit, tire manufacturing, rubber, paint and plastic extenders and artificial aggregates. While these applications are being evaluated, Texaco is continuing its effort to identify other industries for which the slag may be a suitable feedstock.

TABLE 1

SLAG CHARACTERIZATION METHODS

FUNDAMENTAL ANALYSIS

ELEMENTAL ANALYSIS
X-RAY DIFFRACTION
OPTICAL MICROSCOPY
SEM/EDX

PHYSICAL PROPERTY DETERMINATION

ASTM ASH FUSION
HIGH TEMPERATURE VISCOSITY

OTHER TECHNIQUES

INFRARED SPECTROSCOPY
TGA/DTA
HOT STAGE X-RAY DIFFRACTION

TABLE 2

CHARACTERIZATION RESULTS

ELEMENTAL ANALYSIS

Component	Ash A	Slag A	Ash B	Slag B
SiO_2	53.21	54.14	41.72	40.17
Al_2O_3	15.50	14.48	26.33	28.05
Fe_2O_3	6.31	6.33	23.11	21.05
MgO	2.77	2.78	1.16	1.23
CaO	17.18	17.24	3.01	4.33
Na_2O	3.11	3.10	0.41	0.56
K_2O	0.79	0.79	2.33	2.14
TiO_2	0.91	0.93	1.46	1.68
P_2O_5	0.22	0.20	0.46	0.79

X-RAY DIFFRACTION ANALYSIS

Ash A:	Quartz (SiO_2)	**Slag A:**	Amorphous (Glass)
Ash B:	Quartz (SiO_2) Hematite (Fe_2O_3)	**Slag B:**	Mullite ($3Al_2O_3$ $2SiO_2$) Fayalite ($2FeO$ SiO_2)

ASTM ASH FUSION RESULTS (REDUCING GAS)

	A	B
Initial Deformation Temperature (F)	2116	2112
Softening Temperature (F)	2147	2114
Hemispherical Temperature (F)	2202	2244
Fusion Temperature (F)	2336	2431

FIGURE 1

TEXACO COAL GASIFICATION PROCESS

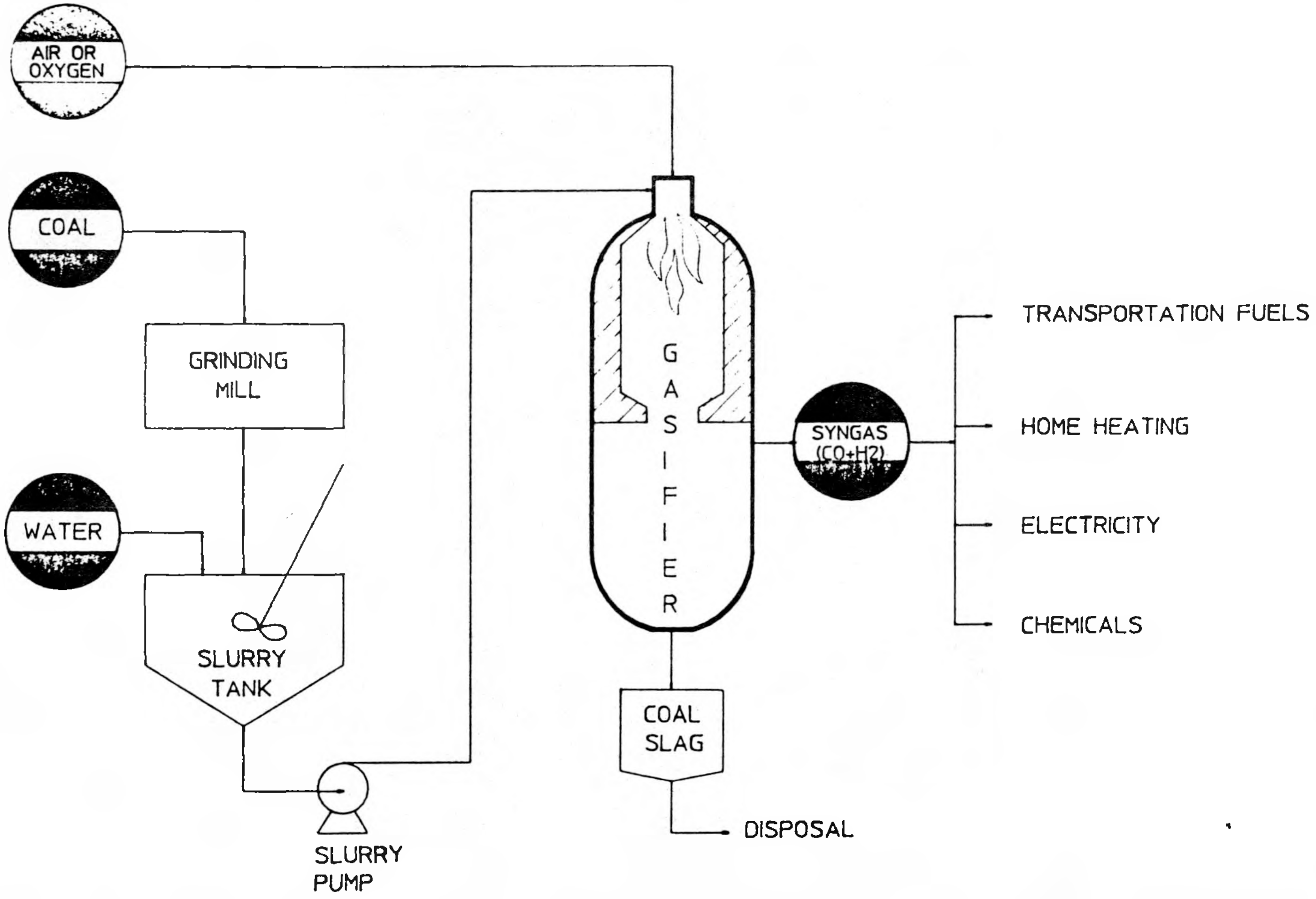


FIGURE 2

FLOW CURVES OF SLAG A SHOWING NEWTONIAN BEHAVIOR

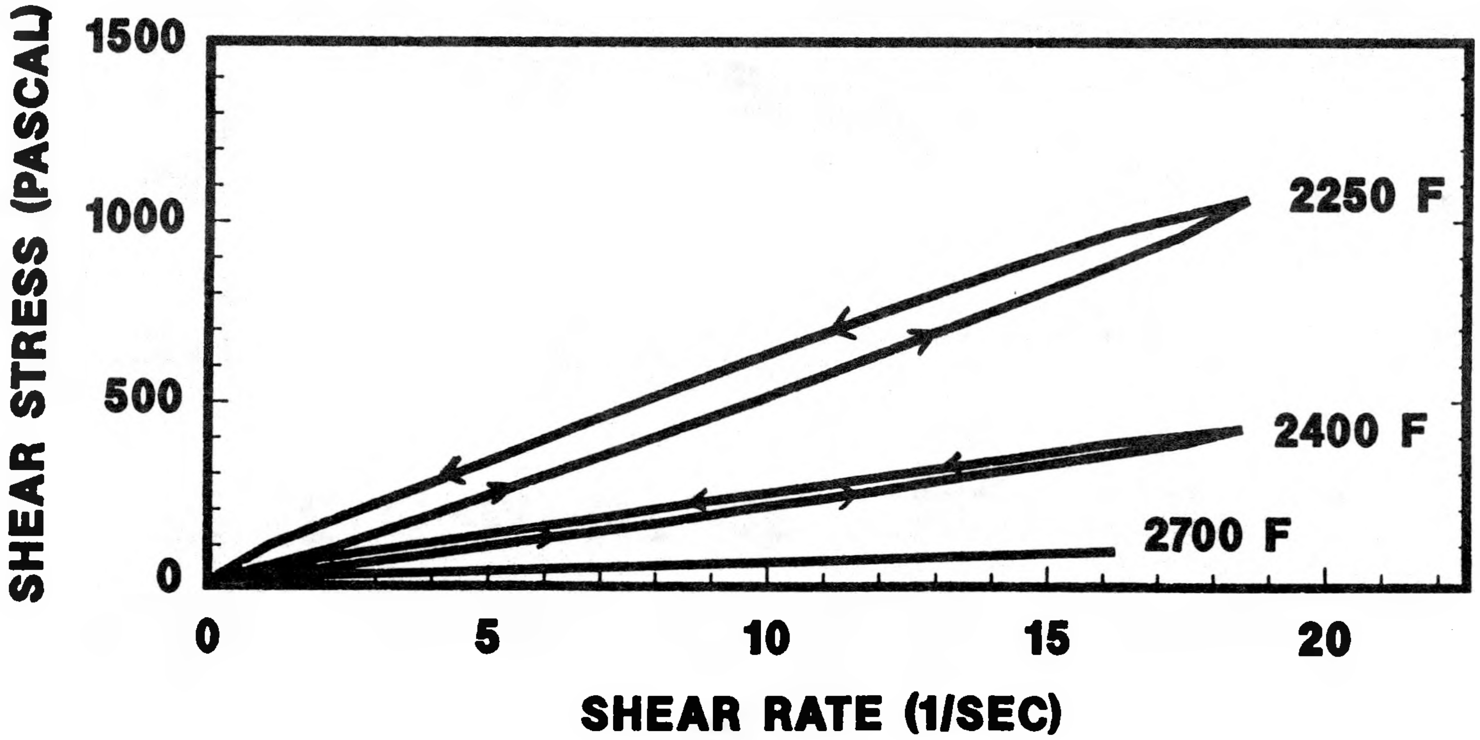
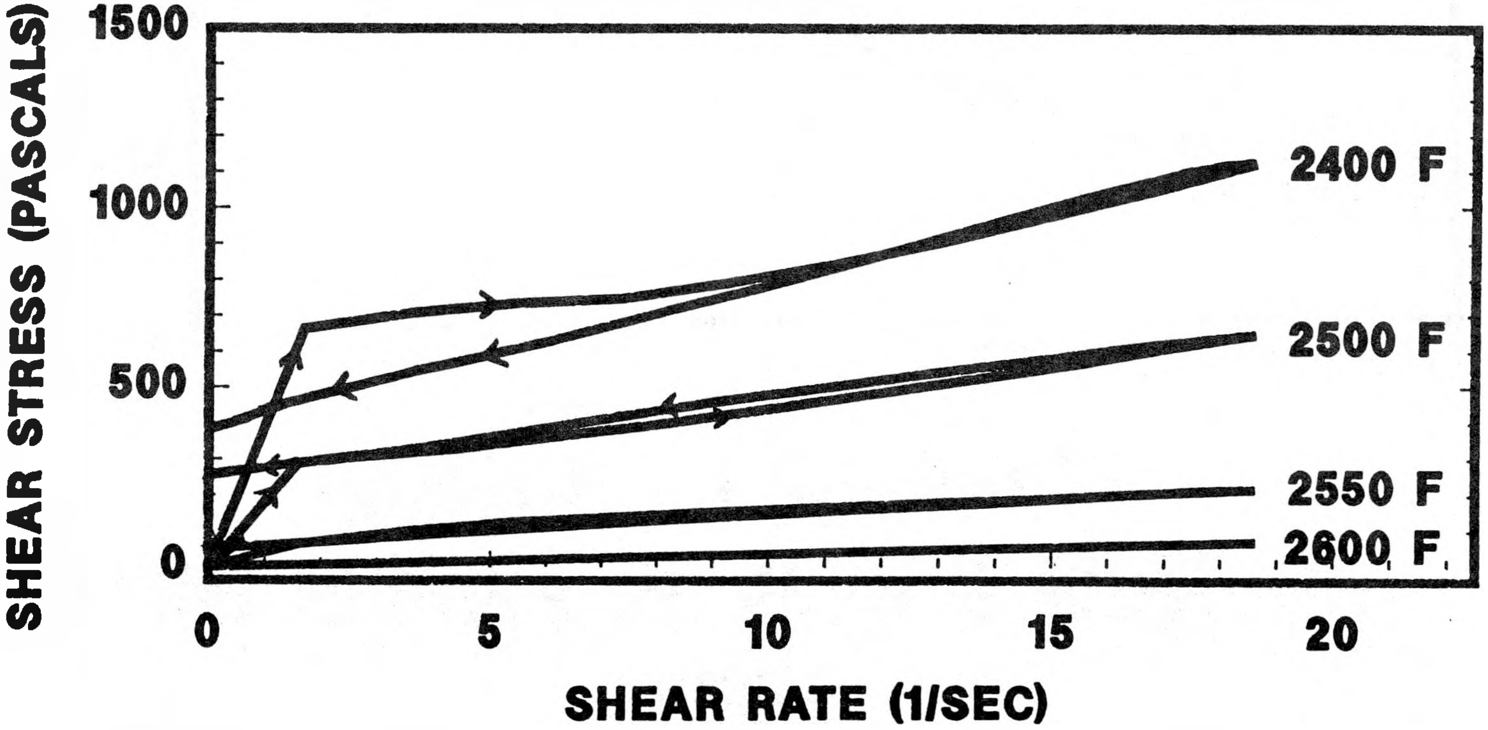
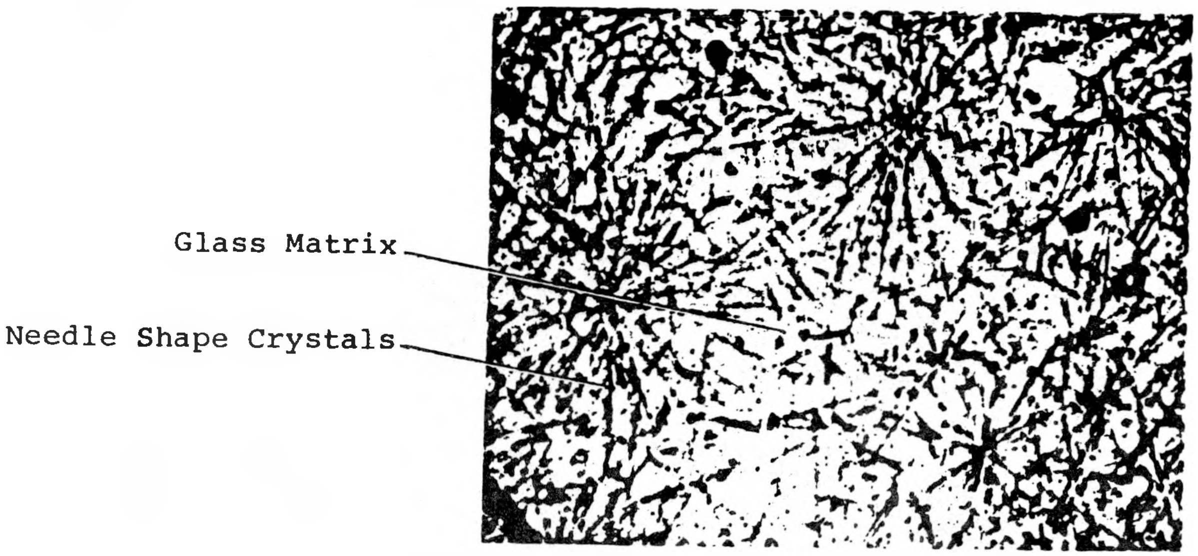


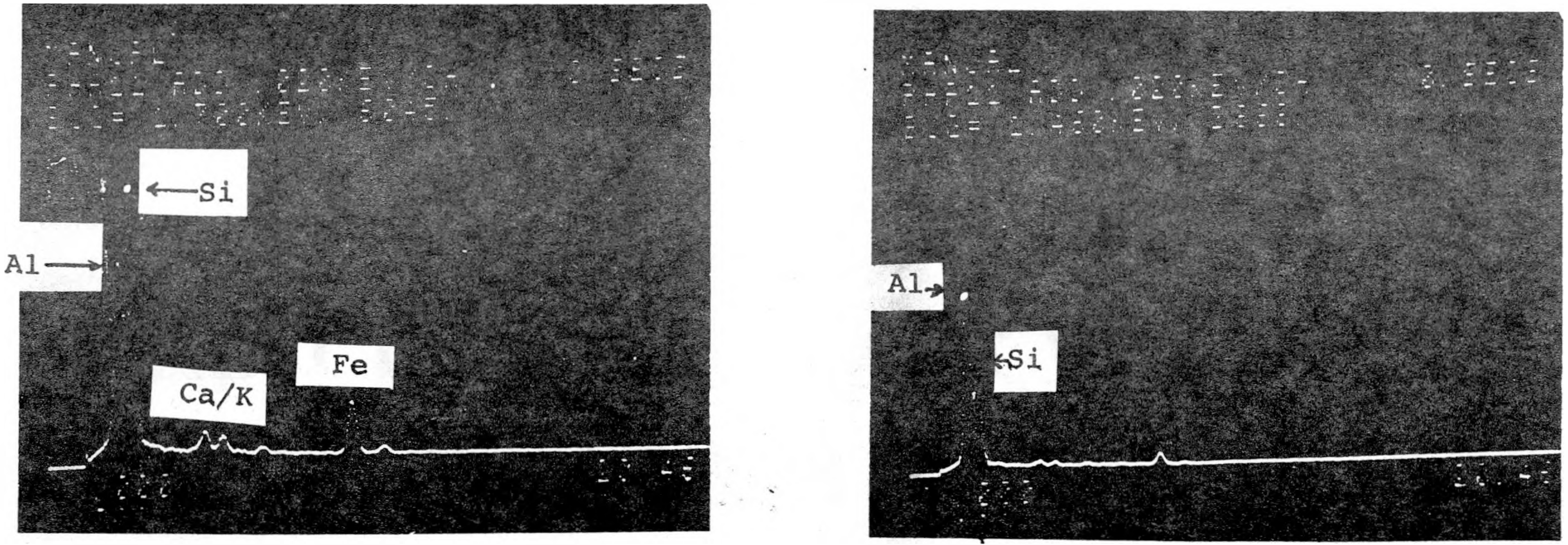
FIGURE 3

FLOW CURVES FOR SLAG B SHOWING DEVELOPMENT OF YIELD STRESS





Transmitted Light Photomicrograph of Slag B (F.O.V. = 0.6 mm)



EDX Analysis of Glass Matrix

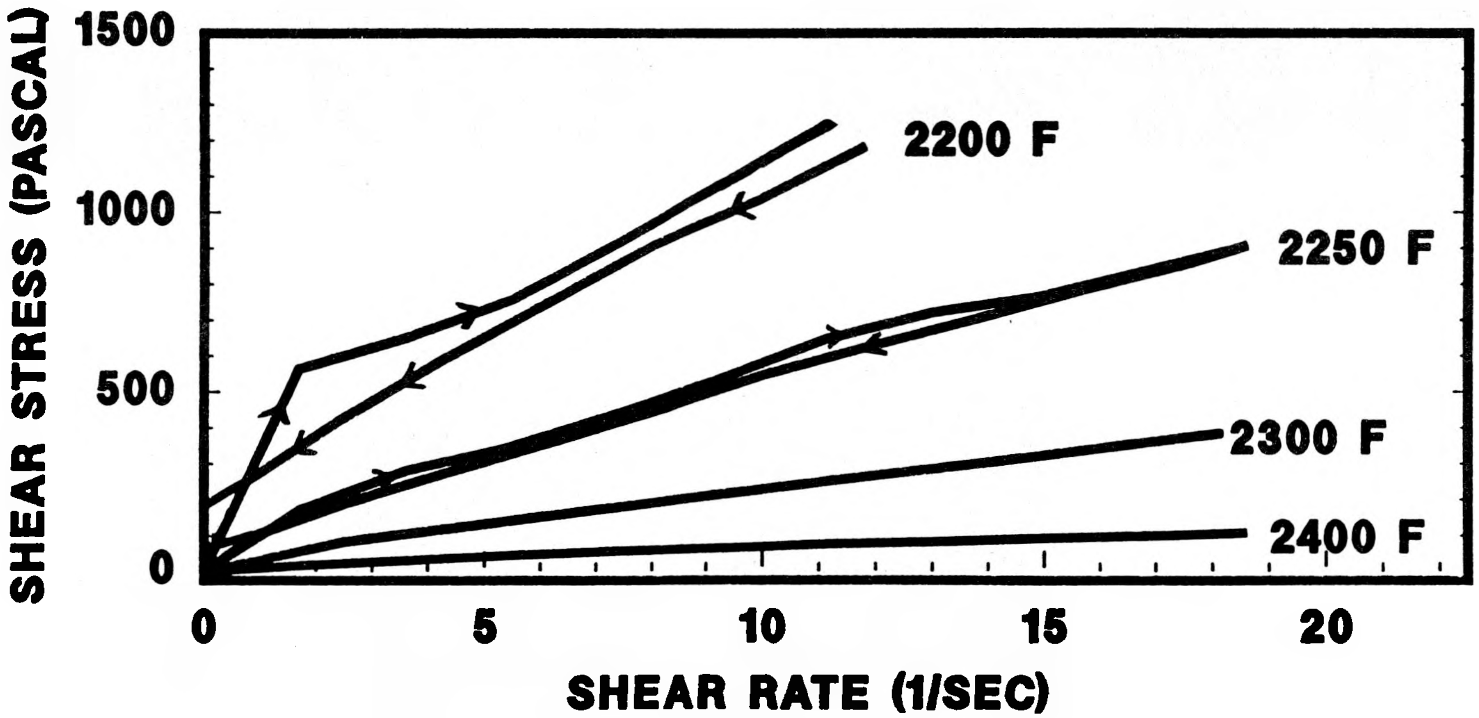
EDX Analysis of Needle Shape Crystals

FIGURE 4

Optical and Scanning Electron Microscopic Analysis of Slag B

FIGURE 5

EFFECT OF 15% DOLOMITE ADDITIVE ON FLOW CURVES OF SLAG B



SESSION 5: BIOREMEDIATION

SESSION CHAIRS:

MARY BROMEL
ANG COAL GASIFICATION CO.
BEULAH, ND

CHARLES TURNER
UNIVERSITY OF NORTH DAKOTA
GRAND FORKS, ND

1. "The SASOL Experience with Purification and Reuse of Synfuel Wastewaters"

   by: Andries Brink
   SASOL Ltd.
   Johannesburg, R.S.A.

2. "Bioremediation at Great Plains Gasification Plant"

   by: Mary Bromel
   ANG Coal Gasification Co.
   Beulah, ND

3. "Characteristics & Treatability of Synfuels Wastewater"

   by: Charles Turner
   University of North Dakota
   Grand Forks, ND

4. "Wastewater Treatment for Integrated Gasification Combined Cycle Power Plants"

   by: David L. Peterson
   CH2M Hill
   Gale Mayer
   Energy & Mineral Research Center, UND
   Grand Forks, ND

5. "Anarobic Biological Testability of Synthetic Fuels Wastewater"

   by: Steve Hrudey
   University of Alberta
   Edmonton, Alberta, Canada

"THE SASOL EXPERIENCE WITH PURIFICATION AND REUSE OF SYNFUEL WASTEWATERS"

BY: ANDRIES BRINK
SASOL LTD.
JOHANNESBURG, R.S.A.

THE SASOL EXPERIENCE WITH PURIFICATION AND REUSE OF SYNFUEL WASTEWATERS

by A Brink
General Manager, Research and Development
Sasol Technology (Pty) Ltd

ABSTRACT

At the Sasol One plant at Sasolburg the wastewater is treated biologically in trickling filters. The bio-effluent is used for ash handling, where further purification takes place, before being sent to the Vaal river. The Sasol Two and Three plants at Secunda have been designed as zero effluent plants. The treatment scheme comprises bio-treatment in activated sludge units, followed by adsorption on activated carbon and anion exchange. Plant performance is reviewed. New approaches being studied include anaerobic digestion of the water-soluble fatty acids and conversion of these acids to bioprotein.

INTRODUCTION

The oil from coal process as practised by Sasol produces two major wastewater streams : stripped gas liquor and an aqueous organic acid stream. Raw gas liquor from the Lurgi gasifiers is solvent extracted to remove most of the phenols and then steam-stripped to remove dissolved CO_2, H_2S and ammonia. The stripped gas liquor at Secunda typically has the following composition:

TOC	500 - 600 mg/l
Kjeldahl-N	300 - 450 mg/l
Fluoride	100 - 140 mg/l
Chloride	50 - 80 mg/l
Sulphur as sulphate	300 - 400 mg/l

The organic component consists of residual phenols, mainly dihydric, organic acids and hydantoins.

The second main wastewater stream is a 1-1,5% aqueous solution of the lower fatty acids: mainly acetic acid with decreasing amounts of propionic, butyric and valeric acids. In the fluidised version of the Fischer-Tropsch process (Synthol) substantial amounts of the lower oxygenates are produced as co-products; the alcohols and ketones are recovered as saleable products but an aqueous acid bottoms stream remains for disposal.

The wastewater treatment schemes are quite different for Sasolburg and Secunda and they will be discussed separately.

SASOLBURG SYSTEM

The process flow diagram is given schematically in Figure 1. The essential steps are biological purification in trickling filters and contact with ash. The coal processed at Sasolburg has a high ash content (30% and more). Ash from the gasifiers is fairly coarse but the ash from the boilers is fine and presents a large surface for chemical reaction. The dirtiest stream, gas liquor, is first brought into contact with the alkaline ash and excess $Ca(OH)_2$ is then precipitated with CO_2. Considerable purification is achieved as shown by the following typical figures :

	Before	After
COD, mg/l	1 380	660
NH_3/N, mg/l	220	120
Fluoride, mg/l	50	15
Sodium, mg/l	11	83
Conductivity, µS/cm	1 240	1 220
Boron, mg/l	6,5	8,6

Unfortunately the gas liquor also picks up soluble components from the ash, notably sodium and some boron. The ash-treated gas liquor is then combined with other wastewater streams from the Sasol plant, including blowdown from a cooling tower operating on gas liquor as cooling water, from other industries in the Sasolburg area and also with domestic sewage from the town of Sasolburg and the combined streams are biologically purified in trickling filters. The effluent is used for more ash handling and then stored in a series of stabilisation/equalisation ponds before being sent to the Vaal river.

Because the treated effluent from the Sasolburg plant is diluted with river water, the requirements (permit standard) for this effluent have been less strict than the general standard in South Africa. Some typical figures are given below, for those parameters where the effluent does not always comply with the requirements.

		Typical effluent	Permit standard	General standard
COD,	mg/l	70 - 147	100	75
NH_3/N,	mg/l	9 - 27	15	10
F,	mg/l	3,4 - 4,8	4,0	1,0
Na	mg/l	174	170	90 above intake
B	mg/l	3,5 - 4,3	3,5	1,0
Conductivity,	µS/cm	1 270	1 600	750

Steps have been implemented to address the sodium problem. These include incineration of the organic-contaminated streams and evaporation of the clean sodium-containing streams. The philosophy behind permits and standards is being studied at the moment and the principle of waste load allocation is being considered. This could affect the limits imposed on fluoride and boron, for instance.

SECUNDA SYSTEM

The Sasol Two and Three plants at Secunda are situated close to the watershed which separates the catchment areas of rivers flowing eastwards to the Indian Ocean and rivers flowing westwards to the Atlantic Ocean. In the absence, therefore, of any substantial watercourse which could act as a receiving stream for a partly treated plant effluent, as at Sasolburg, consideration had to be given to purifying the plant effluent to such an extent that the treated water could be recycled for use in the plant, in the first instance as cooling water.

The process which was installed consists of the basic steps outlined schematically in Figure 2. The gas liquor is cooled down from 90°C to about 30°C in a conventional cooling tower. An optional fluoride precipitation unit was included because at the design stage it was not certain what the fluoride level in the gas liquor would be. The activated sludge unit is basically of the plug-flow type with sludge recycle. The second zone from the inlet was designed as an anoxic zone, which is supplied with a small amount of Synthol acid water to serve as a carbon source for the denitrification of any nitrites/nitrates formed. A further, patented (1) feature of the activated sludge unit is that cations, mainly sodium, can be supplied as recycle in the form of blow-down from the cooling water system. The anions in the wastewater feed (fluorides, chlorides and sulphate precursors) are present mainly as the ammonium salts. If the ammonium ions are removed biologically through nitrification, other cations have to be supplied, hence the recycle.

Flocculation of the bio-effluent was intended to be by means of polyelectrolytes as the more conventional coagulants such as ferric chloride or alum would introduce anions which have to be removed further downstream. After dual-media filtration and activated carbon treatment the water is passed through weak-base anion exchangers in the bicarbonate form. The reactions concerned are:

$$\mathrm{R - N + H_2O + CO_2 \longrightarrow R - NH{\cdot}HCO_3}\ \text{(carbonation)}$$
$$\mathrm{R - NH{\cdot}HCO_3 + NaCl \longrightarrow R - NH{\cdot}HCl + NaHCO_3}\ \text{(alkalization)}$$
$$\mathrm{R - NH{\cdot}HCl + NH_4OH \longrightarrow R - N + NH_4Cl + H_2O}\ \text{(regeneration)}$$

Operational Experience

The Sasol Two plant, followed some years later by an identical Sasol Three plant, was designed as a zero effluent plant. Has this objective been achieved? The answer is: Yes, but a qualified yes.

At Secunda the wastewater treatment system is not at the tail end of the process chain but it is an integral part of that chain. It is a vital part of the chain in the sense that if the wastewater plant is out of action, production must stop since the effluent cannot be disposed off. This has never been the case, neither was it ever necessary to curtail production because of problems at the wastewater treatment plant. In this sense the zero effluent plant has been a success. But several problems have been encountered, the most important of which are:

(a) Difficulties were experienced with the activated carbon regeneration unit. As a result the adsorption units were run well beyond the breakthrough stage, which in turn led to excessive fouling of the anion exchange resin. This led to bypassing of these units and to-day they are used only sporadically. In addition cyanide corrosion problems were experienced on the ammonia recovery plant, which were solved by injecting polysulphide. Thiocyanate is formed as a product, which is converted to sulphate in the bio-plant. As a result the sulphate concentration in the feed to the anion exchangers is well beyond design. These factors combined with the built-in recycle of cooling tower blow-down have resulted in a gradual build-up of non-biodegradable organic matter and inorganic ions in the circulating cooling water. The organic content of the cooling water make-up, for instance, has increased over the past six years from 200 to over 700 mg/l COD. Apart from the fact that flocculation of the bio-effluent has become virtually impossible, this build-up of organic matter does not appear to have deleterious consequences. Bio-fouling is being controlled through the use of bio-dispersants and the occasional dosing of biocides. The increase in concentration of inorganic ions is more serious and fouling of heat exchanger surfaces by a scale consisting mainly of calcium fluoride has become a problem.

(b) The design called for evaporation from the process cooling tower to be slightly greater than the intake of wastewater to be treated. To achieve this negative balance, the extent of air-cooling was deliberately somewhat curtailed. In practice a positive water balance has been experienced most of the time with the result that storage dams had to be built to contain the excess water. The situation has deteriorated to the extent that something has to be done in the near future to solve the positive water balance problem.

(c) It has proved difficult to achieve satisfactory nitrification/denitrification at all times. At present the activated sludge unit is run in such a way that nitrification is not achieved to any great extent. The cooling water make-up is high in ammonia, but this does not affect its quality as cooling water, except that chlorine can not be used as biocide.

Remedial Action Being Considered

Fluoride precipitation

The design called for optional fluoride precipitation on the incoming gas liquor. It became evident, though, that fluoride precipitation would be much more efficient on the cooling-tower blow-down, where the fluoride content is much higher. Testing work is in progress to optimize this operation which includes cold precipitation of fluoride with lime, removal of excess lime in the bio-system and, if necessary, exchange of sodium for calcium ions.

Anaerobic digestion of organic acid stream

The organic acid stream is warm and concentrated, which implies that anaerobic digestion should be considered as a candidate process option. Laboratory tests were followed by a 5 m^3 pilot plant. Results of the pilot plant, which has now been on line for more than a year, are so encouraging that the design and construction of a commercial plant can be considered. The anaerobic unit is followed by an aerobic polishing unit, organic removal is excellent: *ca* 90% in the anaerobic unit and 97-98% in the aerobic unit.

Conversion of the organic acids to bio-protein

Very promising results were obtained by researchers at the University of Pretoria (2) who grew a culture of the fungus, *Geotrichum candidum*, on the acid stream. The dried fungus should make an *excellent protein* component in animal feeds or even in processed food for human consumption. Plans are underway to test this concept on pilot plant scale.

DIRECT USE OF STRIPPED GAS LIQUOR (SGL) AS COOLING WATER

The direct use of SGL as cooling water has been intensively studied at Sasolburg since 1972. A demonstration cooling tower was erected in 1976 and this tower has been in continuous use without any serious problems being encountered. The decision to adopt this approach for the Great Plains project was based on development work on experimental cooling towers at Sasolburg.

Main features of the use of SGL as cooling water are:

- Heat transfer is excellent as a result of minimal fouling.
- Rate of corrosion is very low: 0,125 mm/yr on carbon steel.
- Air pollution is much less than might be expected and well below accepted environmental norms.
- Extensive breakdown of the organic components takes place : *ca* 65% reduction in CSB.

- Foaming can be a problem, but can be controlled with anti-foam addition.

In general it can be said that SGL can be successfully used as cooling water in a tower designed for low drift losses and with the right type of packing.

REFERENCES

1 Brink, A, Hitzel, H and Rolke, D. U.S.P. 4 483 772.

2 Kuhn, A L and Pretorius, W A. "Fungal purification of an industrial effluent containing volatile fatty acids by means of a crossflow-microscreen technique", Paper to be presented at IAWPRC Conference, Brighton, U.K., 18-22 July, 1988.

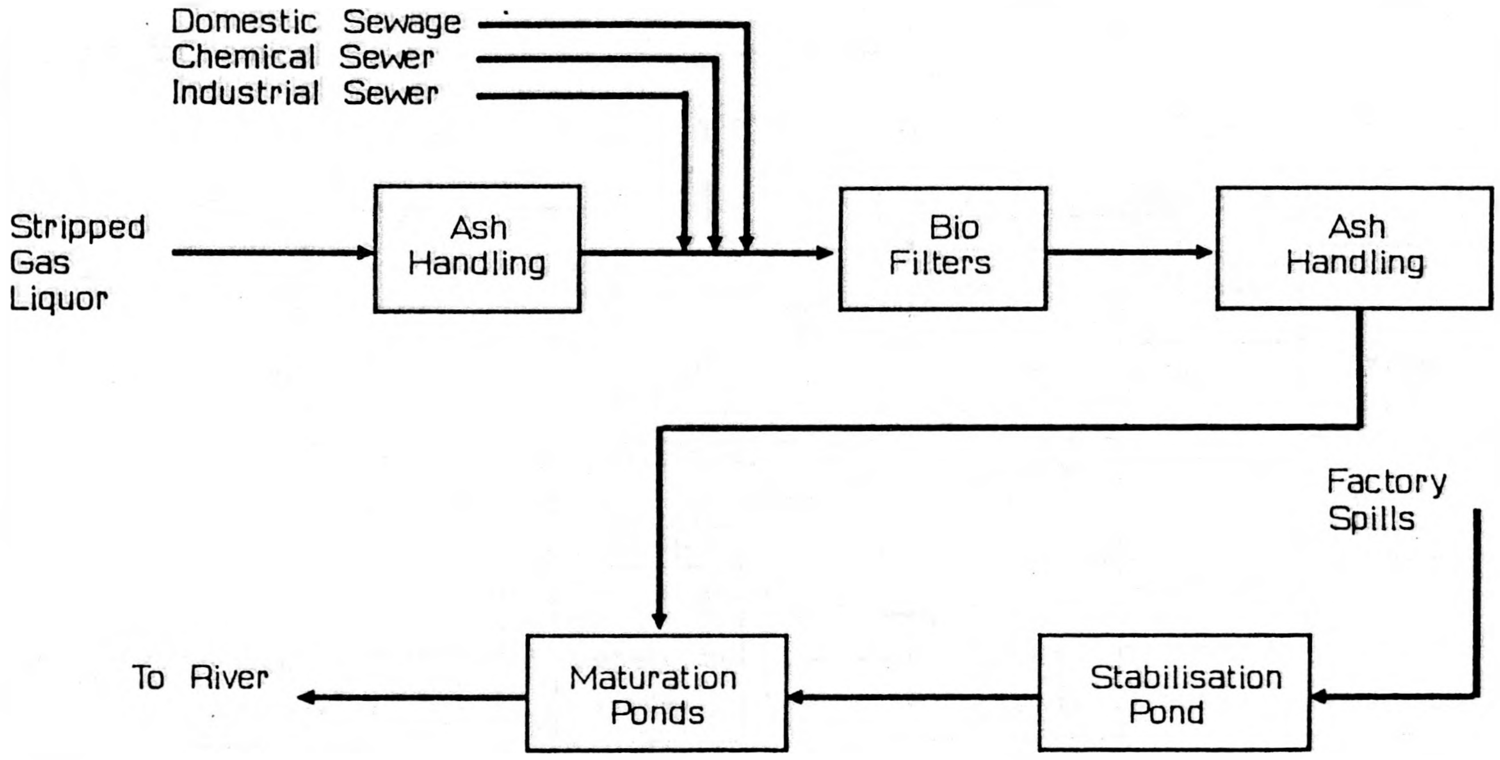


FIGURE 1 WASTE WATER TREATMENT AT SASOLBURG

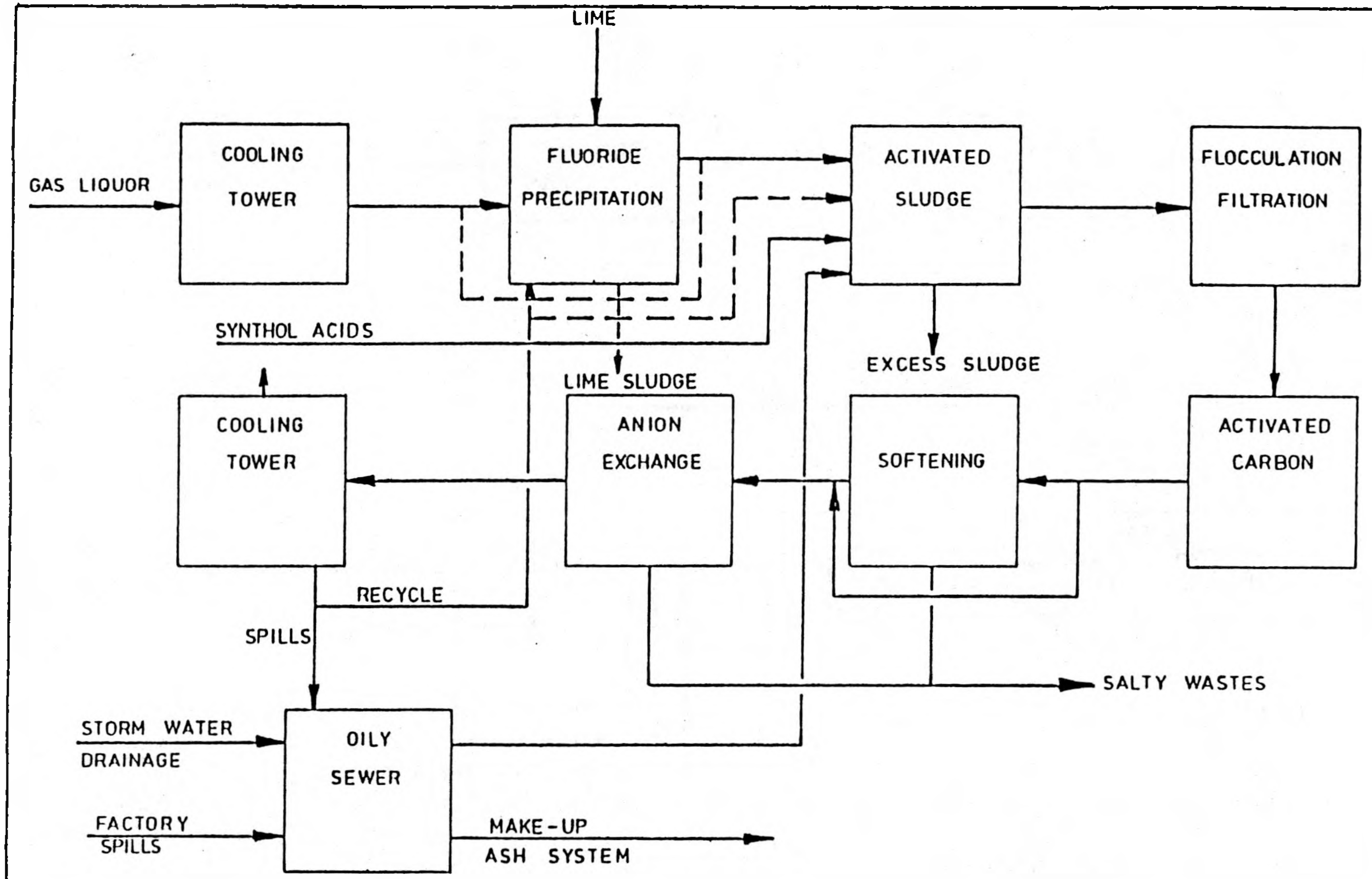


FIGURE 2 WASTEWATER TREATMENT AT SECUNDA

"BIOREMEDIATION AT GREAT PLAINS GASIFICATION PLANT"

BY: MARY BROMEL
ANG COAL GASIFICATION CO.
BEULAH, ND

ABSTRACT

Bioremediation at Great Plains Gasification Plant

Authors: Bromel*, M., J. Helander, J. Luer, M. Griffin, B. Striefel
ANG Coal Gasification Company
Beulah, ND 58523

The organic nature of coal gasification wastes, none of which may be discharged into the environment, has provided many areas for research and development in bioremediation. The cooling water system is a multifaceted process wherein evaporation, biological oxidation, and heat transfer function of six different wastewater process streams are accomplished. An aerobic, heterotrophic, nonfermentative bacterial population, averaging 4×10^8 CFU/ml of cooling water over four years of operation, achieves 99.9%, 99.6%, and 95% reduction respectively of the fatty acid, phenolic and total organic carbon concentrations present in the organic waste streams comprising the cooling water makeup. Four year population studies of the microbial consortium in the cooling water have shown the predominant genera to be Pseudomonas, Alcaligenes, Moraxella, and Acinetobacter in descending order of dominance. Gram positive genera such as Micrococcus, Corynebacterium, and Bacillus occur with lower frequency and are more sensitive to process upsets than the nonfermentative gram negative bacilli.

Mixed cultures of these hydrocarbon-degrading microorganisms, adapted to the organic wastes in the tower, have been used to degrade the aliphatic and aromatic hydrocarbons present in sludges in waste ponds if the ponds are aerated and microbial inorganic nutrients are added.

When mixed cultures of cooling water bacteria were added to topsoil into which tarry sludge had been injected, significant reduction (60-90%) of the anthracenes and naphthalenes as well as the short chain aliphatics were achieved in one week with 98% reduction of the aromatics in three weeks.

*Presenter

INTRODUCTION

The high concentrations of phenolic and other aromatic as well as aliphatic hydrocarbon wastes from coal gasification processes in a zero discharge plant has necessitated utilization of the degradative capabilities of microorganisms in the disposal of these wastes. Microorganisms that degrade these chemicals can be isolated from the soil of hazardous waste sites (2, 17) or, as in the case of the ANG cooling water, from processes where native water organisms have been adapted to organic wastes.

Early experiments between 1950 and 1970 in Britain (3,4,11,14 16) and Germany (8) showed that, under suitable conditions, microorganisms obtained from sewage and soil were able to grow in spent gas liquors. The phenols, organic acids, thiocyanate and other compounds in these liquors were oxidized by the microbiological consortia sufficiently well to permit discharge of the effluents into local sewers. Most of this work, however, was carried out in small scale activated sludge units or in pilot-scale packed towers.

A few studies have been reported where bioactivity in cooling towers has been encouraged (8) rather than suppressed with biocides as is the common practice in the cooling tower industry. The most successful operation of this kind was in Toledo, Ohio, where the Sun Oil Co. used refinery wastewater as feed for their biotowers and achieved phenol, COD, and TOC removals of 99.4%, 62%, and 67% respectively (11). McGuire and Dishinger (13) found that the use of biocides resulted in higher phenol concentrations in cooling towers at an oil refinery and stated that biooxidation was a significant removal mechanism.

Presently there is substantial incentive for synfuel developers to choose zero liquid discharge schemes in their plant design. Conservation of water resources and regulatory restrictions on discharge of treated effluents are but two of such incentives. Design engineers of the Great Plains Coal Gasification Project at Beulah, North Dakota, the first large commercial synfuel plant in the USA, incorporated this zero discharge concept when they designed the reuse of process condensates as cooling tower makeup water. They viewed the cooling tower as a process unit where evaporation, biological oxidation and heat transfer would take place concurrently (7).

There are two methods used to achieve bioremediation of organic wastes from coal conversion facilities:

1. Use genetically engineered organisms that have been modified in the laboratory to degrade particular substrates more efficiently than can the "wild-type" organisms.
2. By the technique of selective enrichment on the substrate(s) to be degraded, "adapt" wild-type organisms to become more efficient.

The present study reports the use of these adapted microorganisms for not only the oxidative degradation of tars, oil, volatile fatty acids, polyhydric phenols, and aliphatic or aromatic hydrocarbons in cooling water but also in soils and sludges.

MATERIALS AND METHODS

Chemical Sample Collection

Grab samples for chemical analysis were obtained daily from the cooling water (CW) return pump, the cooling tower surge pond (CTSP), the dissolved air floatation (DAF) sand filter effluent, stripped gas liquor (SGL), and the liquid waste incinerator (LWI) pond.

Analytical Chemical Methods

Biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) were determined according to Standard Methods (1); total or dissolved organic carbon (TOC or DOC) by a Dohrman carbon analyzer (Santa Clara, CA); volatile fatty acids, thiosulfate, thiocyanate and sulfate by an ion chromatograph (Model 220, Dionex Corp., Sunnyvale, CA); monovalent phenols by gas chromatography (Hewlett-Packard 5790, Avondale, PA); divalent phenols by HPLC (Beckman Instruments, Berkely, CA); heavy metals, phosphate, selenium and arsenic by ICP (Perkin-Elmer 6500, Norwalk, CA); oils and tars by a modification of ASTM #D3921; and polycyclic aromatic hydrocarbons by GC-MS (Model 5987 Hewlett-Packard, Palo Alto, CA).

Microbiological Sample Collection

Wastewater samples were collected daily for planktonic population assay in presterilized Whirl-Pak bags (Nasco, Inc., Ft. Atkinson, WI) from the DAF, CTSP, and CW areas listed above. On numerous occasions samples scraped from deposits in heat exchangers were collected for analysis of sessile populations.

Microbiological Analytical Methods

Aliquots (0.1 ml) of 10-fold serial dilutions of samples in phosphate buffered sterile water were spread in triplicate on plates of the following growth media: Tryptic Soy Agar (TSA) for the total aerobic heterotrophic count (TAC); Hektoen Enteric Agar (HEK) for the gram negative and coliform counts; Rose Bengal Agar (RBA) amended with 40 ug/ml gentamicin for the yeast and other fungal count. Sulfate reducing bacteria (SRB) were enumeraged in pour plates of API agar. All plating media were purchased from Difco Laboratories, Detroit, MI.

Plates were incubated for 72h at 30°C and then left at room temperature for an additional 24h for maximum recovery of slow-growing strains. Anaerobic cultures (SRB) were incubated in Marion Biobags (Marion Scientific, Kansas City, MO) for 10 days.

At the end of the incubation periods, colony counts were tabulated and representative colonies of various morphological types were subcultured to TSA slants for subsequent identification after gram staining to determine purity. All gram negative isolates were identified with the API 20E and/or the Rapid NFT nonfermenters identification system (Analytab Products, Plainview, NJ). Gram positive bacilli were identified by morphological types and fermentation patterns. Gram positive cocci were identified by DMS Staph-trac and Raid Strep (Analytab Products). Yeasts were identified with API 20C (Analytab Products).

For predominating population studies plates of the 10^{-7} to 10^{-8} dilutions containing at least 30 colonies but less than 50 were used. Each colony was subcultured to slants of nutrient agar or TSA and incubated for 24h. Identification of each isolate was then made with API 20E or Rapid NFT and by gram stain and cellular morphology.

Wet mounts of each undiluted wastewater sample or heat exchanger deposit sample or soil and pond sludge sample were performed with light, phase and epifluorescence microscopy with 0.05% aqueous (wt./vol.) acridine orange dye solution (Sigma Chemical Co., St. Louis, MO) as the fluorescent stain.

Antibodies raised against ATCC cultures #13541 (Desulfovibrio desulfuricans), #19365 (Desulfotomaculum orientis), #19377 (Thiobacillus thiooxidans), and #19859 (Thiobacillus ferrooxidans) in goats and conjugated with fluorescein isothiocyanate, were procured from Triple J Farms in Redmond, WA.

RESULTS AND DISCUSSION

Cooling Water System

The original source for the bacteria in the cooling water system was the water from Lake Sakakawea introduced into the cooling tower in 1984 before start up of the plant. Growth substrates for these bacteria are the various organic chemicals (Table 1) coming into the tower from the primary make-up stream, stripped gas liquor (SGL) (Figure 1), which is the aqueous condensate from gasification after tars, phenolics and ammonia have been removed. Enough residual dissolved organic material remains, however, in the cooling water (CW), along with fixed ammonia and phosphate as microbial nutrients, to allow a very stable, unshockable population of aerobic, non-fermentative, heterotrophic gram negative bacilli (TAC) to flourish at an average population density of 3 to 4×10^{8} organisms per milliliter of cooling water (Figure 2).

After a change in enumerating procedures in April of 1987 an average 10^{4}/ml sulfate reducing anaerobic bacterial population has been maintained in the CW (Figure 2). Microbially induced corrosion, however, has been almost non-existant with corrosion rates in the carbon steel piping and heat exchangers less than 2 mm/year whereas the typical corrosion rate in a plant of similar size to Great Plains is 5-15 mm/year from soft deposits in heat exchangers (7). Under deposit samples from heat exchangers when examined by fluorescent antibody to sulfate reducers or iron oxidizers have only rarely shown the presence of these corrosion bacteria.

Monthly identification of the most frequently occurring members of the CW bacterial population were performed and over the four years that the tower has been in service four bacterial genera have consistently predominated (Table 2), i.e. Alcaligenes, Pseudomonas, Acinetobacter, and Moraxella. All of these have been reported to be efficient hydrocarbon degraders in both marine and fresh water and soil (2). The only other significantly frequent genera present were Flavobacterium and Micrococcus. Most conspicuous by their very low frequency of occurrence at higher dilutions were the gram positive group (except for the micrococci). The CW with its largely hydrocarbon, fatty acid and phenolic composition had obviously selected for the gram negative, non-fermentative, strictly aerobic microorganisms. Gram positive rods and cocci were seen at 10 to 10^3/ml concentrations but never in significant numbers and anaerobes (other than the SRB) were not able to withstand the high oxygen tension of the tower.

When a concerted study was made of the most frequently isolated genus, Pseudomonas, the results on Table 3 were obtained. What was most surprising to find in this large heterogeneous taxonomic genus (20) was the predominating presence of P. vesicularis which, with P. testosteroni, constitutes a very distantly related ribosomal RNA homology group to all other pseudomonads (15). Ballard (5) found that these two species have unique properties (e.g. require several growth factors) not found in any other Pseudomonas species, so occurrence in the cooling water is worthy of further investigation. Gunsalus et al (10) reported that the initial attack on many aliphatic and aromatic hydrocarbons by the pseudomonads is due to the participation of their oxygenase enzymes which make the pseudomonads of great importance in the degradation of oil components and in the treatment of oil spills.

Acinetobacter, according to Sar and Rosenberg (19), elaborates an exopolysaccharide with emulsifying properties called "emulsan" which could account for the degraded look of the tar balls under the microscope. We also have some evidence (unpublished data) that, in a mineral salts medium with Mexican crude oil as the carbon source, Acinetobacter will emulsify the oil in one week. We are presently investigating the use of Acinetobacter cells in very high concentrations to emulsify waste hydrocarbon sludges of very high viscosity so that they may be pumped to the incinerator.

Alcaligenes species, isolated almost as frequently as Pseudomonas, and more frequently in cold weather (see Table 2) has been described by Westlake et al (21) to constitute more than 50% of the microbial population in a shale oil enrichment procedure. Alcaligenes and Flavobacterium are ubiquitously distributed in both marine and fresh waters and both have been implicated in phenol degradation (21) which was corroborated by our experiment with the primary substrates in the cooling water (see Table 4).

In order to determine which of our four predominant genera was responsible for the degradation of phenol, catechol and fatty acids, these substrates were used in an in vitro study at various concentrations as the sole carbon and energy source and with ammonium sulfate as the nitrogen source (Table 4). Acinetobacter after one week had degraded 92% of the 200 ppm catechol, all of the acetic and propionic acid but was not a competant phenol oxidizer. In the cooling tower, however, Acinetobacter degrades only a small portion of catechol; the rest is polymerized in this highly oxidized, alkaline environmental to humic acid. Alcaligenes degraded (oxidized) all of the 500 ppm phenol in seven days but could not degrade the catechol and took two weeks to degrade the volatile fatty acids. Pseudomonas vesicularis and P. stutzeri were both capable of phenol degradation with 26% and 40% of 1000 ppm phenol respectively degraded in seven days. Both degraded all of the fatty acids except formic in two weeks and P. vesicularis was capable of reducing 40% of the 200 ppm catechol concentration in one week and has since been adapted through selective enrichment to grow on 1000 ppm phenol in mineral salts as the sole carbon and energy source.

The resistance of this microbial consortium of dominants to chemical and physical changes was remarkable. The consortium not only maintained an average concentration of $4x10^8$ cells/ml over summer and winter but also seemed impervious to chemical shock (on several occasions when Phosam was malfunctioning the microorganisms withstood over 4500 ppm ammonia). Most significant to waste management are the reductions in organic chemical concentrations, achieved by the consortium (Table 1). Thus, 94% of the total organic carbon was reduced with 100% reduction of methanol, monovalent phenols, and volatile fatty acids.

As a result of this radical departure from conventional cooling systems operation (12) and after some fine tuning, today the ANG cooling tower: 1) provides an outlet for low level heat generated in plant processes; 2) evaporates enormous volumes of water generated in the coal gasification process avoiding additional quantities of lake water; 3) degrades biologically the tons of organic wastes present in the process waters fed to the cooling tower. The stable, almost non-shockable microbiological populations have saved many millions of dollars as they function in what may be best termed a "king-sized" trickling filter.

Soil Disposal of Hydrocarbon Wastes

Since the tower bacteria so successfully degraded the hydrocarbons in the CW, we decided to see if a mixed culture of CW bacterial dominants could degrade API sludge (a very viscous oil and tar mixture) mixed with soil and how long it would take to accomplish the degradation. Four plastic tubs, each containing 40 pounds of top soil from the mined area, and each fitted with a leachate catchment vessel, were placed outside the laboratory so that ambient weather conditions would prevail. On August 7, one liter of mixed culture (10^{13} organisms/ml) of bacteria from the tower (grown on nutrient agar) was raked into the top three inches of soil of Tubs 2 and 3, and an initial concentration of $3x10^8$ bacteria per gram of soil was determined. A urea phosphate fertilizer was added (1.2 pounds/tub) to the soil in Tubs 3 and 4. Tub 1 served as the control with only the indigenous soil bacteria present.

In August of 1987 one liter of API sludge was applied to each tub and raked into the top three inches of soil (there were eight inches soil in the tubs). A baseline GC-MS scan was made of the sludge-soil mixture (Figure 3) and the aromatic nature of coal gasification API sludge was apparent since the four largest peaks on the chromatogram were aromatics. One week after the third weekly application of API sludge to the tubs the aliphatic and aromatic sludge constituents practically disappeared (Figure 4). Two weeks after the third sludge application there was 100% biodegradation of all compounds in Tub 2. Indigenous soil bacteria in Tub 1 achieved 96% reduction of the sludge constituents and only the fertilizer carrier waxes were still present in Tubs 3 and 4.

Leachate (collected only once after a heavy rain in September 1987) contained less than 1 ppm total organic carbon in Tubs 1 and 2. This indicated that either the polycyclic organics from the sludge were mineralized *in situ* or were complexed with the natural humic materials in the soil. *Bollag* (6) has described cross coupling of humus constituents and xenobiotic substances and Guerin and Jones (9) reported that polycyclic aromatic hydrocarbons (PAH) may be rendered innocuous in soil and sedimentary aqueous environments without being completely mineralized by condensation with soil humics.

Thus we have shown that an adapted microbial consortium from the tower can be used to degrade (or mineralize) organic constituents in sludges from coal conversion plants.

Bioremediation of the Liquid Waste Incinerator Pond (LWI)

The LWI waste pond at ANG receives the most diverse hydrocarbon wastes of any pond in the plant. Caustic and acidic washings from equipment cleanup are also discarded in this 2.5 million gal.-capacity lined pond. After 4 years of use, the sludge depth at the bottom of the pond has increased to many feet of an extremely viscous and, in places, very hardened nature so that it cannot be pumped to the incinerator for burning.

An experiment to determine if *Acinetobacter calcoaceticus*, (known to degrade hydrocarbons (2) and to produce an extracellular oil-emulsifying agent into its environment) could both degrade the PAH's and other organics as well as emulsify the tarry waste, was set up as follows:

Flask #1 (100g LWI sludge + 120 ml deionized water)

Flask #2 (100g LWI sludge + 10g cell slurry of Acinetobacter cells + 110 ml deionized water)

Flask #3 (100g LWI sludge + 10g Acinetobacter cells +10 ml bacterial nutrient (1 part N:9 parts P:1 part K) in 100 ml water)

Flask #4 (100g LWI sludge + 120 ml Acinetobacter culture filtrate)

The flasks were shaken for one week on a rotary shaker to achieve both mixing and aeration.

After one week the sludge in all four flasks was homogenized and appeared pumpable but after standing the water separated from the sludge in Flasks 1, 2, and 4. While the remaining sludge was more liquid than its original state in Flasks 1, 2, and 4, it was only in Flask 3 with the bacteria plus nutrient that the water did not separate (i.e. an emulsion was formed) and the sludge emulsion appeared homogeneous.

All four samples were submitted for a GC-MS scan to determine differences in biodegradation of the organics (particularly the PAH's) in each case (Figure 5). While there was very significant reduction of the phenanthralene and anthracene peaks and complete reduction of the trimethylnaphthalene by the bacteria alone, the 100% reduction of aromatic and aliphatic peaks in Flask 3 with the bacteria + bacterial nutrient illustrates the necessity for bacterial nutrient in any in situ bioremediation situation.

This study also demonstrated the necessity for mixing and aeration of watery hydrocarbon sludges if bioremediation is to be accomplished since the hydrocarbonoclastic bacteria are all obligate aerobes and must attach to a hydrocarbon-water interface in order to function in biodegradation.

LITERATURE CITED

(1) American Public Health Assoc. 1985. Standard methods for the examination of water and wastewater. 16th ed., New York.

(2) Atlas, Ronald M. 1981. Microbial Degradation of Petroleum Hydrocarbons: An Environmental Perspective. Microbiol. Rev., p.180-209.

(3) Badger, E.H.M. 1955. The bacterial oxidation of gas liquor. Trans. Inst. Gas. Engrs. 105:653.

(4) Badger, E.H.M. and Jackman, M.I. 1960. Loadings and efficiencies in the biological oxidation of spent gas liquor. Part 2. Coke and Gas 22:426.

(5) Ballard, R.W., Doudoroff, M., Stanier, R.Y. and Mandel, M. 1968. Taxonomy of the Aerobic Pseudomonads: *Pseudomonas diminuta* and *Pseudomonas vesiculare*. J. Gen. Microbial. 53:349-361.

(6) Bollag, J.M. 1983. Cross-coupling of humus constituents and xerobiotic substances, p. 127-141. In R.F. Christman and E.T. Gjessing (ed.), Aquatic and terrestrial humic materials. Ann Arbor Science, Ann Arbor, MI.

(7) Crocker, B.R., Bromel, M.C., and Pontbriand, M.W. 1987. A case history of a coal gasification wastewater cooling tower at the Great Plains Coal Gasification Project. Tech. Paper No. TP87-2:2, Cooling Tower Inst. Annu. Meet., New Orleans, LA.

(8) Graham, P.W. 1969. Kinetic aspects of the treatment of phenolic wastes. In Advances in Water Pollution Research. Proc. 4th Int. Conf., Prague. Ed. Jenkins, W.H., Pergamon Press.

(9) Guerin, William F., and G.E. Jones, 1988. Two-stage mineralization of phenanthrene by estuarine enrichment cultures. Appl. Environ. Microbiol. 54:p. 929-936.

(10) Gunsalus, I.C., Tyson, C.A., Tsai, R.L., and Lipscomb, J.D. 1971. Chemico-Biological Interact. 4:75-78.

(11) James, E.W., W.F. Maguire and W.L. Harpel. 1976. Using Wastewater as Cooling System Makeup Water. Chem. Eng. Aug. 30:95-100.

(12) McCoy, J.W. 1980. In Microbiology of Cooling Water. Chem. Publ. Co. New York. pp 73-75.

(13) McGuire, L. and T. Dishinger. 1984. Chlorine dioxide solves biofouling problems in a refinery cooling tower used for phenol destruction. Cooling Tower Inst. Annu. Meet., TP-84-6.

(14) Noble, T.G., Jackman, M.I., and Badger, E.H.M. 1964. The biological treatment of gas liquor in aeration tanks and packed towers. J. Inst. Sewage Purif., 5:440.

(15) Palleroni, N.J. 1984. In Bergey's Manual of Systematic Bacteriology, Vol. 1 (Kreig, N.R. Ed.), pp 141-199, Williams and Wilkins, Baltimore.

(16) Pankhurst, E.S. 1959. The biological oxidation of spent gas liquor. J. Appl. Bact. 22:202.

(17) Perry, J.J. 1979. Microbial Cooxidations Involving Hydrocarbons. Microbiol. Rev. 43, 59-72.

(18) Phillips, D.H. 1983. Fifty years of benzo(a)pyrene. Nature (London) 303:468-472.

(19) Sar, N., and E. Rosenberg. 1983. Emulsifier production by Acinetobacter calcoaceticus strains. Curr. Microbial. 9:309-314.

(20) Stanier, R.Y., Palleroni, N.J., and Doudoroff, M. 1966. The Aerobic Pseudomonads: A Taxonomic Study. J. Gen. Microbial. 43:159-271.

(21) Westlake, D.W.S., Belicek, W., and Cook, F.D. 1976. Microbial utilization of raw and hydrogenated shale oils. Can. J. Microbial. 22:221-227.

	DAF	IMPURE H_2O	CTSP	MEE DIST.	SGL	CW	% REDUCTION
pH	4.37	11.5	8.55	9.51	9.83	8.27	
DOC	654	---	906	227(TOC)	1232	1778	94
TSS	30	0.00	599	---	13.2	2645	
TAR	25.9	---	440	---	16.15	1429	
OIL	95.5	---	---	---	90.9	262	75
COND.	5655	4797	6752	1939	2731	10,556	
METHANOL	---*	0.01	---	---	---	0	100
TDS	---	1000	---	---	---	---	
BOD_5	---	---	---	---	---	2820	
NH_3 TOTAL	176.7	---	592.79	592.23	1656	810	60 (fixed NH_3)
SV PHENOLS	96.0	---	27.29	1.22	5.7	1	100
HYDROQUINONE	9.25	---	9.18	9.25	8.6	8.6	
RESORCINOL	9.25	---	8.50	9.25	---	8.8	
CATECHOL	9.25	---	10.18	9.25	244.7	8.7	99.8
FORMIC	4.64	---	16.67	5.0	118.6	4.6	
ACETIC	17.8	---	116.25	7.5	383.6	15.6	
PROPIONIC	5.4	---	10.86	5.0	101.7	6.4	99.9
BUTYRIC	5.0	---	5.0	5.0	28.2	4.6	
ISOBUTYRIC	5.0	---	6.38	5.0	6.0	4.6	
As	---	---	---	---	---	1.0	
Ca	26	---	25.7	---	3.98	47.3	
Cl	228	---	137.6	17	15.9	194.6	
Fe-TOT	2.09	---	3.27	---	1.0	3.5	
Mg	15.23	---	8.01	---	1.3	15.3	
Na	860.0	---	941	---	105.3	1600.1	
PO_4	86.26	---	135.39	19.76	88.4	408.6	
SCN	---	---	---	---	---	124.4	
Se	---	---	---	---	---	1.0	
SO_4	2288.08	---	1703.44	160	---	2990	
NaCN	---	100	---	---	---	0	100

*--- Analysis Not Performed

Table 1 - Chemical Contributions to Cooling Tower Make-up Streams
100 Day Average - 1988
(in ppm, except pH)

1985 (3 MO)	1986 (6 MO)	1987 (12 MO)	1988 (4 MO)	1988 (MAY)
1. ALCALIGENES	1. PSEUDOMONAS	1. ALCALIGENES	1. MORAXELLA	1. ACINETOBACTER
2. PSEUDOMONAS	2. ALCALIGENES	2. MORAXELLA	2. PSEUDOMONAS	2. MORAXELLA
3. ACINETOBACTER	3. ACINETOBACTER	3. ACINETOBACTER	3. ALCALIGENES	3. PSEUDOMONAS
4. MORAXELLA-FLAVOBACTERIUM	4. MORAXELLA	4. PSEUDOMONAS	4. BORDETELLA	4. ALCALIGENES
5. MICROCOCCUS	5. PROVIDENCIA	5. MICROCOCCUS	5. FLAVOBACTERIUM	5. MICROCOCCUS

<u>Table 2</u> - Bacterial Genera Most Frequently Isolated From Cooling Water (Ranked by Most Frequent (1) to Least Frequent (5))

	2/22 85 CW	3/15 85 CW	10/14 85 CW	1/17 86 CW	4/18 86 CW	4/18 86 Plume	11/10 86 CW	Number Isolated	% Total
P. (other)	2	--	12	4	--	1	--	21	15
P. aeruginosa	1	--	1	1	--	--	1	4	3
P. diminuta	--	--	--	--	--	--	3	3	2
P. stutzeri	1	7	--	3	--	1	3	15	12
P. paucimobilis	--	--	--	2	7	2	4	15	12
P. putida	--	--	--	1	6	--	2	9	7
P. pseudoalcaligenes	--	--	--	--	--	7	19	20	14
P. testosteronii	--	--	--	--	3	2	5	10	7
P. vesicularis	--	--	--	--	40	--	--	41	30

Total Isolated = 130

*Identified with API-20E or RAPID NFT (ANALYTAB PRODUCTS)

Table 3 - Speciation of Pseudomonas Isolates*

	Conc ppm	ACINETOBACTER			ALCALIGENES			PSEUDOMONAS STUTZERI			PSEUDOMONAS VESICULARIS		
CATECHOL *	200	92			6			4			40		
	400	11			6			5			6		
	800	4			3			4			5		
VOLATILE ACIDS **		1 wk	2 wk		1 wk	2 wk		1 wk	2 wk		1 wk	2 wk	
Formic	200	53	100		0	77		0	76		0	47	
Acetic	300	100	100		49	100		48	100		52	100	
Propionic	100	100	100		15	100		12	100		20	100	
N-Butyric	100	5	100		12	100		6	100		14	100	
Iso-Butyric	100	19	100		60	100		59	100		56	100	
						100							
PHENOL		24h	7dy	9dy	24h	7dy	9dy	24h	7dy	9dy	24h	7dY	9dy
	100	27			13			79			38		
	500		2			100			100			100	
	1000			3			29			26			40

* Shaken for 1 week

** 1 and 2 week shaking period

Table 4 - Percent Biodegradation of SGL Substrates (Catechol, Volatile Acids, Phenol) By Cooling Tower Bacterial Isolates

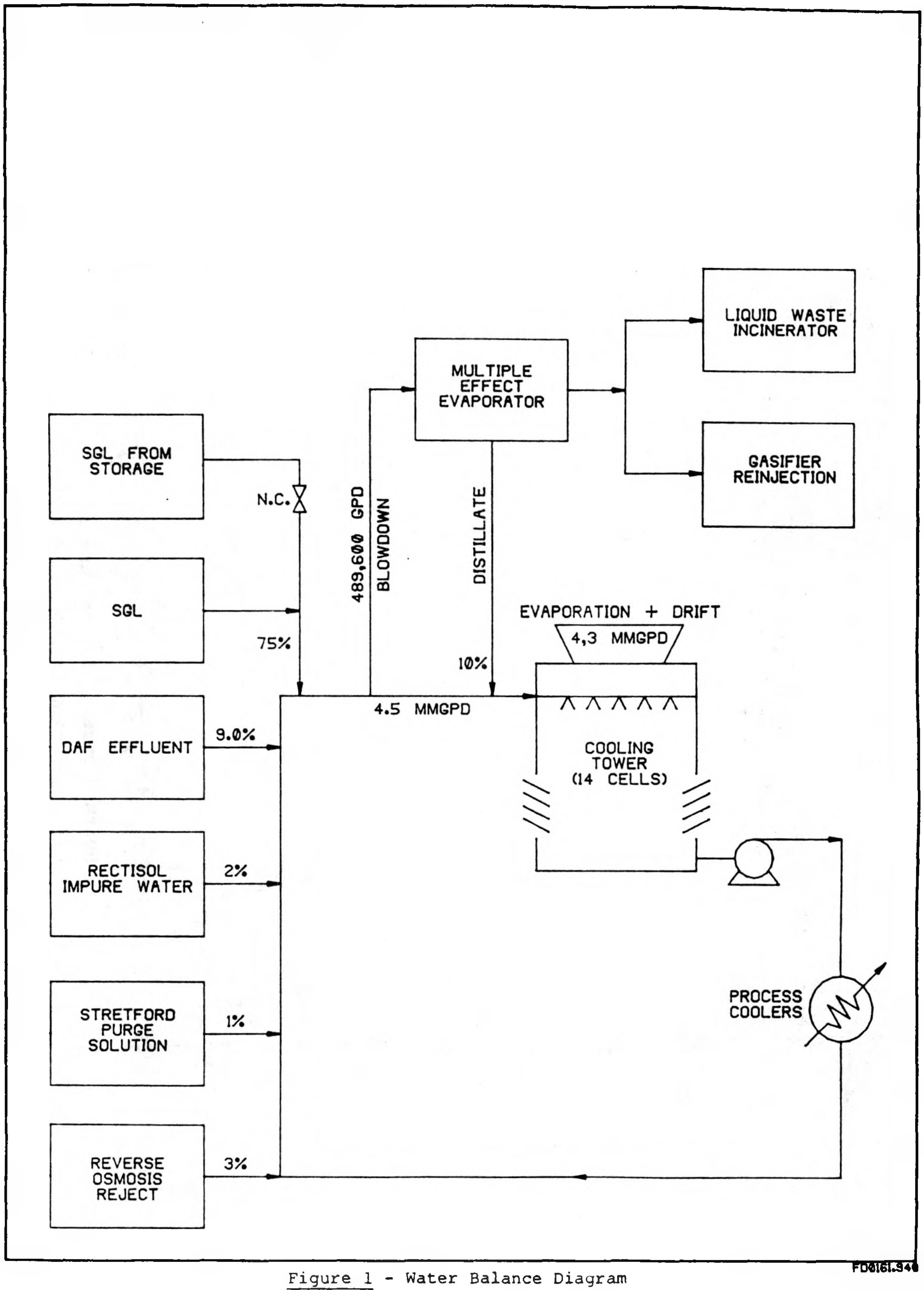


Figure 1 - Water Balance Diagram

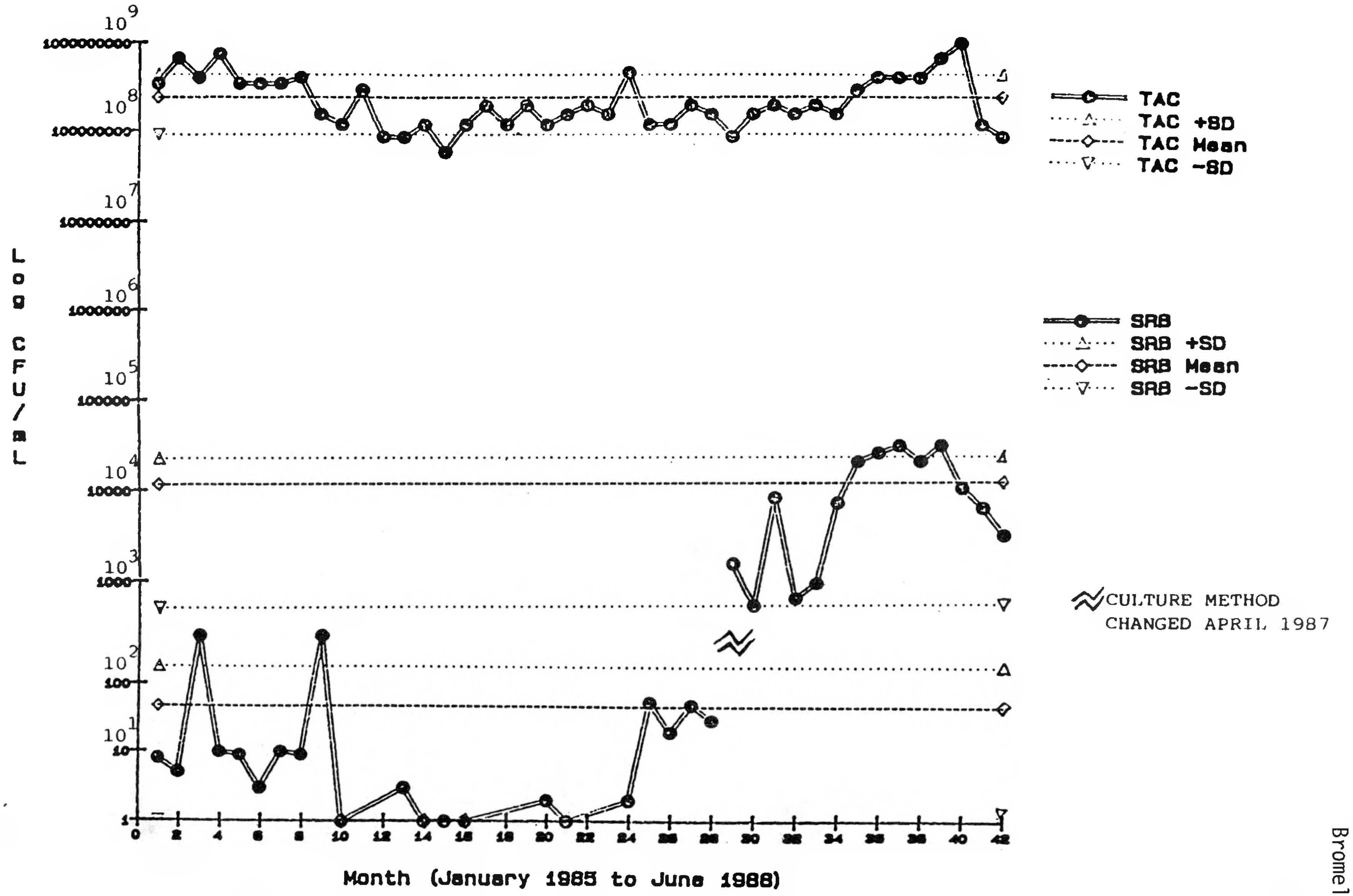


Figure 2 - Monthly Average: Total Aerobic Counts
Sulfate Reducer Counts

FIGURE 3

ORIGINAL SOIL PLUS SLUDGE

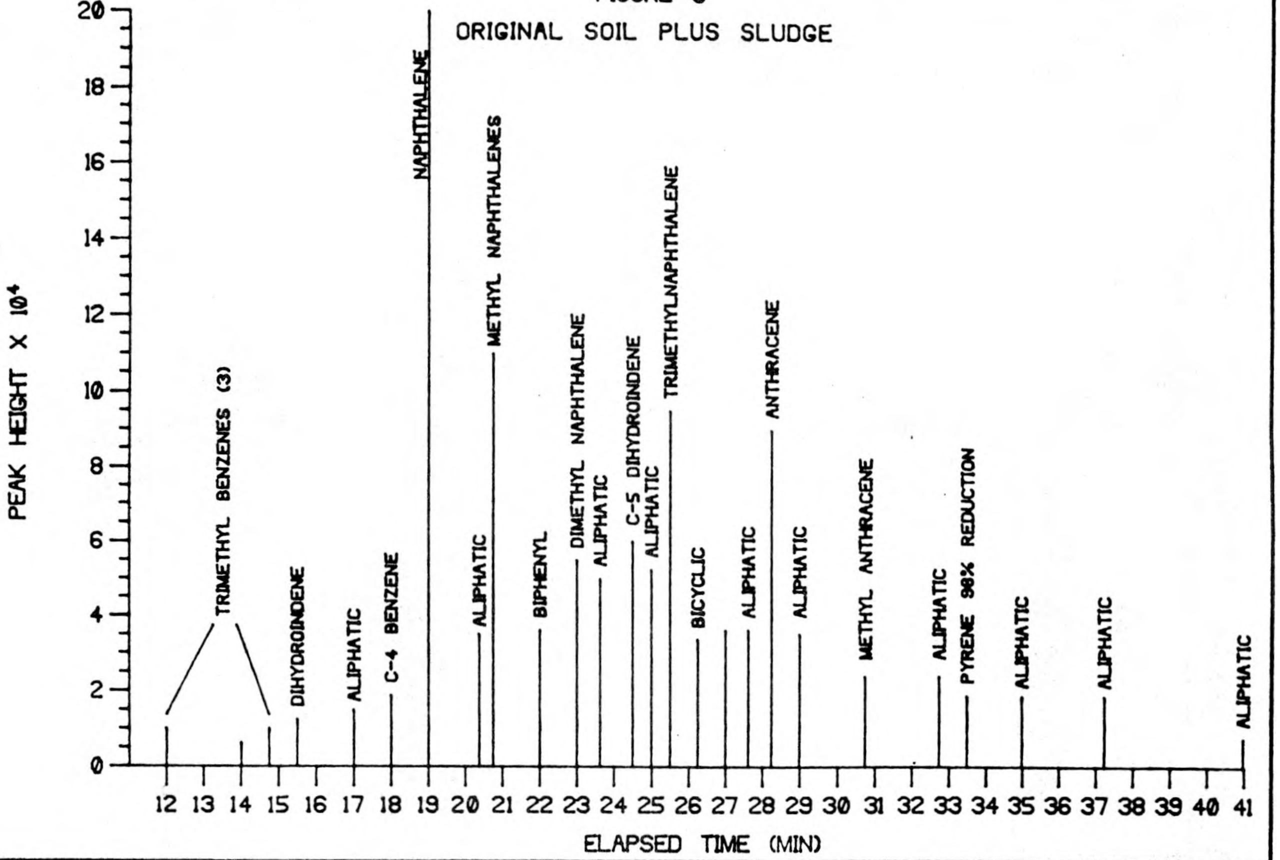
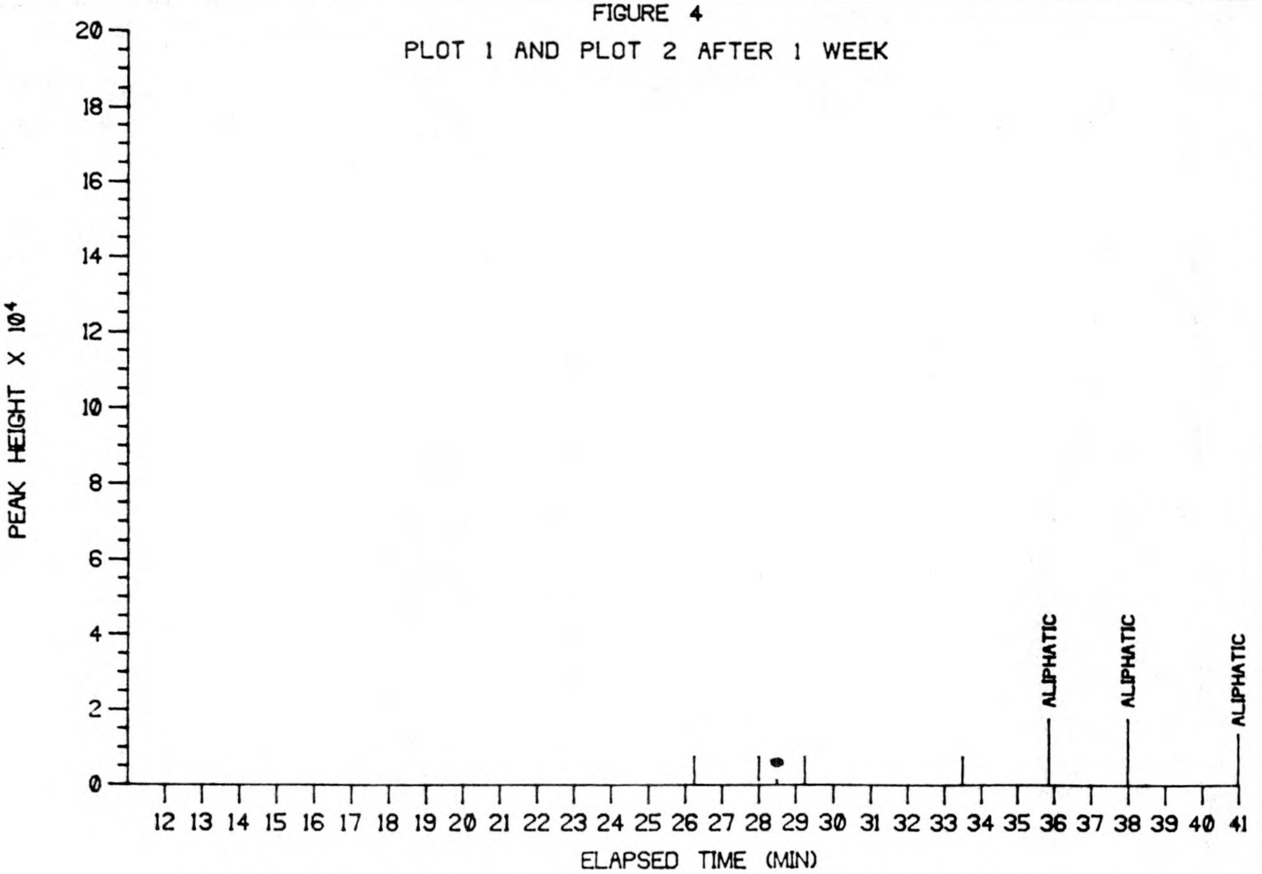


FIGURE 4

PLOT 1 AND PLOT 2 AFTER 1 WEEK



FIGURES 3 AND 4 - API SLUDGE AND SOIL

G00294.940

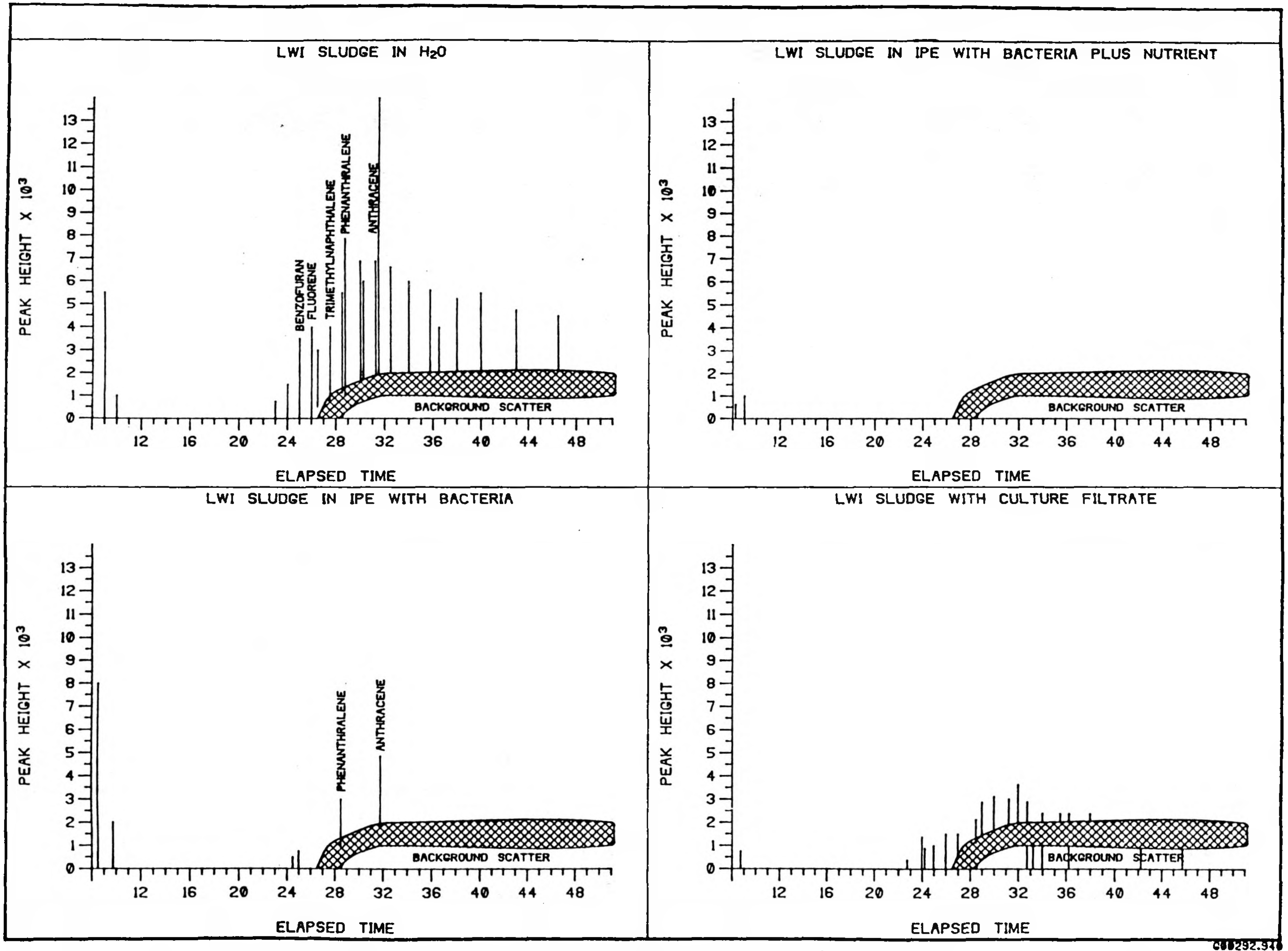


Figure 5 - PAH Oxidation by Acinetobacter in One Week

"CHARACTERISTICS & TREATABILITY OF SYNFUELS WASTEWATER"

BY: CHARLES TURNER
UNIVERSITY OF NORTH DAKOTA
GRAND FORKS, ND

CHARACTERISTICS & TREATABILITY OF SYNFUEL WASTEWATERS

Charles D. Turner

Associate Professor of Civil Engineering

Energy and Mineral Research Center
University of North Dakota
Grand Forks, North Dakota 58202

For presentation at the Opportunities in the
Synfuels Industry Conference
Bismarck, North Dakota
August 28-31, 1988

INTRODUCTION

Synfuels processes, such as the Lurgi dry-ash gasification process, produce wastewater with high concentrations of both organic and inorganic contaminants. Some of these contaminants, such as phenol, sulfur, and ammonia, are recovered as byproducts to the extent that recovery is economically efficient. The remaining contaminants are difficult to remove prior to discharge and create operational problems if recycled back into the process. Cost-efficient production of synfuels can only take place if the technologies for waste management are developed prior to prototype plant construction.

This paper reviews the characteristics and treatability of wastewaters from KILnGAS, Great Plains Gasification Plant, Texaco Coolwater, and UND EMRC gasifiers. Each of these wastewaters was collected on-site and subsequently transported, characterized, and treated at EMRC.

Characterization of these wastewaters has shown general similarities between all except for Texaco which has unique attributes due to the high temperatures encountered at the gasifier outlet. Despite general chemical similarities, each wastewater has characteristics which make the design of treatment systems similar yet distinctive for each wastewater.

Treatment involved physical, chemical and biological processes which were operated at EMRC using bench and process development unit (PDU) systems. This paper discusses the methodology of biological wastewater treatment modeling, the status of genetically engineered bacteria in synfuel wastewaters treatment, and the used of coupled biological fluid bed reactors for predenitrification treatment of synfuel wastewaters. The future of biological treatment in the synfuels industry is reviewed in view of these research results.

WASTEWATER CHARACTERIZATION

Wastewaters from GPGP, KILnGAS, UND-EMRC, and Texaco were characterized at EMRC. The numerical values shown in Table 1 are the means for each parameter. These wastewaters were pretreated by solvent extraction and ammonia stripping except for the Texaco wastewater which required only ammonia stripping. The analyses were conducted on the wastewaters during the bench-scale and process development unit (PDU) model operational periods.

Key parameters for biological treatment are BOD, COD, and ammonia. The GPGP, KILnGAS, and UND-EMRC wastewaters are similar with BOD values ranging between 630 and 1300 mg/L and COD values between 2400 and 2970 mg/L. Ammonia concentrations were 140 mg/L for KILnGAS, 850 mg/L for GPGP, 760 mg/L for UND-EMRC, and 590 mg/L for Texaco. Texaco wastewater contained low concentrations of BOD and COD at 340 and 670 mg/L, respectively. The BOD was exerted primarily by the 2200 mg/L of formate present in the wastewater. The high temperature and other operating conditions of the Texaco gasifier produced a wastewater with the low molecular weight compound, formate ($HCOO^-$), as the principle organic constituent. Other compounds of interest are the phenols, thiocyanate and thiosulfate. GPGP wastewater is practically free of these compounds while KILnGAS and UND-EMRC wastewaters have relatively high concentrations. Neither boron or selenium are shown in the table but both are generally present and are not removed by biological systems.

Table 1

Characteristics of the Synfuels Wastewater Used in Process Modeling at UND-EMRC

Parameter	GPGP[1] (mg/L)	KILnGAS[2] (mg/L)	UND-EMRC[3] (mg/L)	Texaco[4] (mg/L)
TSS	<50	26	<50	<20
TDS	2500	5550	3400	1120
BOD_5	1100	630	1300	340
COD	2400	2970	2780	670
TOC	660	720	850	400
Alkalinity	1100	570	1500	840
Ammonia	850	140	760	590
Cyanide	<5	13	5	3
Thiocyanate	ND	135	150	19
Thiosulfate	7	760	NA	11
Acetate	NA	67	ND	7
Formate	NA	14	ND	2200
Phenols	<5	97	100	<5
Methanol	130	3	200	ND
pH	8.5	9.2	9.2	8.8

All values except pH are in mg/L.
ND = none detected
NA = not available
1,2,3,4 are data references listed in bibliography.

BIOLOGICAL SYSTEM SELECTION

Biological wastewater treatment systems originated in the 1890s. A rapid strength reduction was observed when wastewater was applied over the surface of gravel media having a biological slime. The first municipal trickling filter systems were constructed in the 1910s and activated sludge systems followed in the 1920s[5]. Most industrial wastewater receiving treatment prior to the 1960s was discharged to municipal facilities where the wastewater was mixed with municipal sewage. Biological systems treating only industrial wastewater were not common. Therefore, most biological industrial wastewater treatment systems in use today are derivatives of systems designed to treat municipal strength wastewater.

Table 2 is a comparison of pretreated synfuels wastewater characteristics with those of domestic wastewater. This table also lists new source performance standards (NSPS) for wastewater discharge based on related industries such as coke plants and petroleum refineries.

Table 2

Synfuels Characteristics Compared with Domestic Wastewater Characteristics and NSPS Standards

Constituent	Synfuels SGL (mg/L)	Domestic[6] (mg/L)	NSPS Criterion (mg/L)
BOD	340 - 1300	200	30
COD	670 - 2970	400	150 - 400
TSS	<50	240	25
Ammonia	140 - 850	15	25
Phenol(4AAP)	<5 - 100	<0.1	0.1

Total suspended solids (TSS) shown in Table 2 are 240 mg/L for municipal wastewater and less than 50 mg/L for all synfuels wastewaters. Because of the low suspended solids concentrations, removal prior to biological treatment is not necessary. The BOD concentrations for GPGP, KILnGAS, UND-EMRC, and Texaco wastewaters are 5.5, 3.1, 6.1 and 1.7 times higher, respectively, than those found in domestic wastewater. Ammonia concentrations were 850, 140, 760 and 590 mg/L, respectively, as compared with 15 mg/L in raw domestic wastewater.

The characteristics of synfuels wastewater differ greatly from those of domestic wastewater. Until the late 1960s, biological wastewater treatment systems were designed using empirical criteria derived from municipal wastewater treatment plants to size treatment units. For example, an activated sludge reactor would be sized based on the pounds of BOD per 1000 ft^3

per day that similar reactors had treated in the past. During the last twenty years, design engineers have started using design equations based on the kinetics of the biological reactions that take place in the reactor. These kinetic design equations are particularly useful when designing treatment systems for industrial wastewaters.

MODELING AND TREATABILITY

As shown in Table 1, each synfuels wastewater is different even though they contain similar organic constituents. All have high ammonia concentrations. Because of these differences, the kinetic constants will be different for each wastewater. The design engineer must determine these kinetic constants. The methodology for determining these constants is through actual treatment of the wastewater in small, pre-prototype, models.

These models are classified as (1) bench-scale, (2) process development unit (PDU), and (3) pilot scale. Bench-scale models for an activated sludge system will be 5 to 20 liters and are small enough that they can be operated on a laboratory bench, hence the name. Figure 1 is a schematic of an activated sludge bench-scale model. A PDU for the same process, as shown in Figure 2, may be 100 liters or more in size. Pilot scale systems can be 1000 liters or larger and are generally constructed on or near the wastewater generation site. As the size of the model increases, so does the reliability of the kinetic and treatability data obtained from the model. The only constraint is cost. Bench scale models are less costly to construct and operate than the larger models.

Treatability testing of a wastewater includes not only the kinetic data but process stability, reliability, and removal of problem constituents such as ammonia and priority pollutants. Important design variables are the hydraulic residence time (HRT) and mean cell residence time (MCRT). The size of the reactor is dependent on the HRT while process stability and the ammonia removal are dependent on MCRT.

System performance is very important when evaluating the removal of priority pollutants and ammonia from synfuel wastewaters. Table 2 shows the NSPS criteria that might be anticipated for a synfuels plant. These criteria include standards for phenol (0.1 mg/L) and ammonia (25 mg/L).

For example, a 99% removal rate for wastewater with 100 mg/L of phenol means that the standard would be exceeded by a factor of 10. Biological removal of 99% of the phenol would be considered excellent but a polishing step such as activated carbon filtration would be necessary to meet the discharge standard of 0.1 mg/L for phenol.

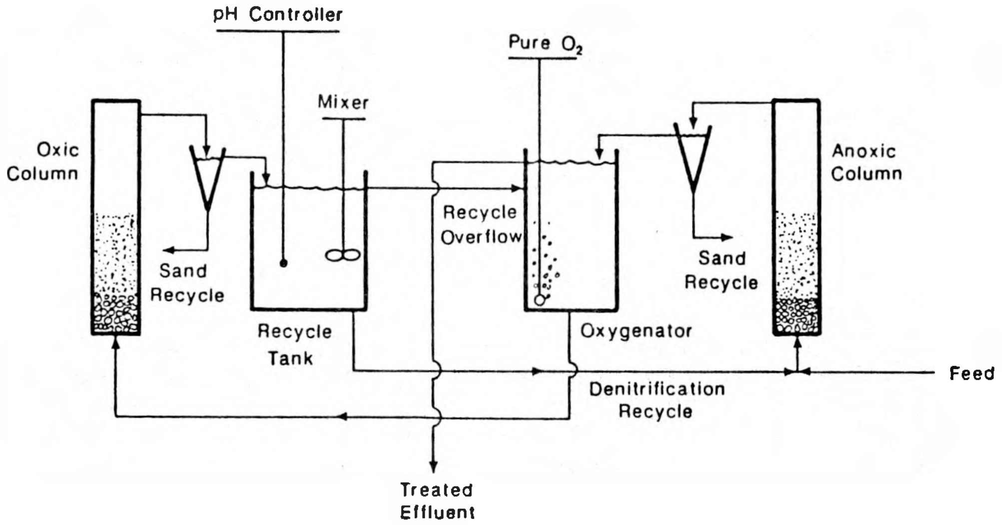


Figure 1. Schematic of a bench-scale, coupled biological upflow fluid bed reactor.

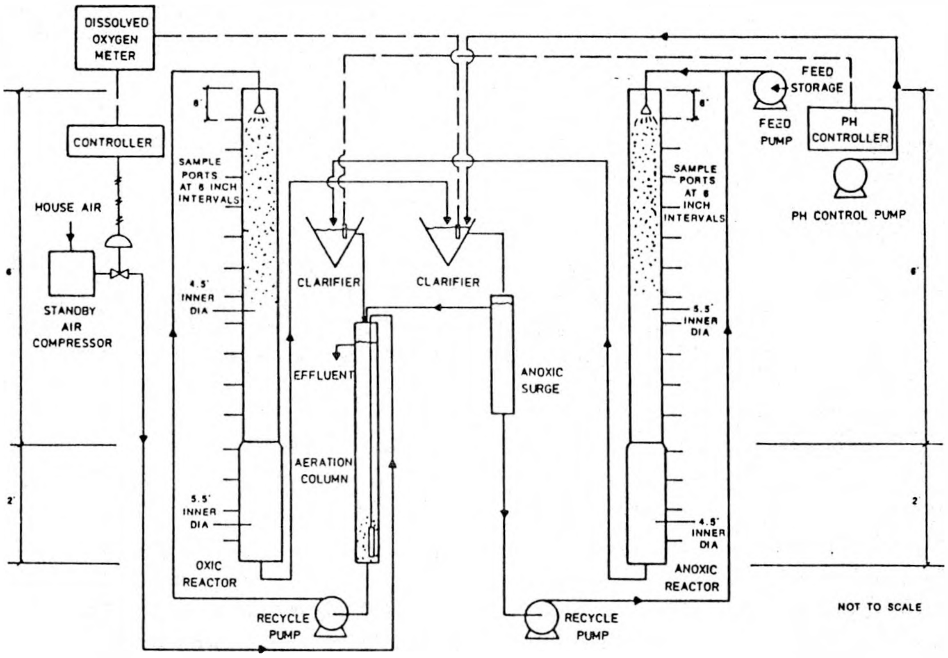


Figure 2. Schematic of process development unit (PDU) coupled biological downflow fluid bed reactor.

Treatability testing on synfuel wastewaters at EMRC has shown that the removal of specific compounds occurs in a predictable sequence. This sequence, from first to last, is as follows: alcohols, low molecular weight fatty acids, phenol, thiocyanate, and ammonia. This sequence is also related to process stability with the most stable systems able to remove ammonia. Since ammonia concentrations are high in synfuel wastewaters and NSPS standards would limit ammonia to a maximum of 25 mg/L, its removal is important for discharge systems. Once again, if ammonia concentrations can be reduced by 90%, most synfuel wastewaters would not meet the 25 mg/L standard and polishing operations would be required.

Nitrification of synfuels wastewater is not always readily achieved. GPGP wastewater has nitrified eaisly while UND-EMRC wastewater required activated carbon addition. Texaco wastewater nitrified at a MCRT of 40 days which was higher than expected given its low organic content. Kilngas wastewater resisted all attempts to develope nitrification.

ACCLIMATION AND ENGINEERED BACTERIA

Wastewater treatment system acclimation is a two part process involving short and long term phases. Biological treatment systems rely on bacteria to convert the contaminants into cell mass and energy for respiration and motility. Each bacterial species has a special niche in which it can utilize a limited range of substrates or contaminants under certain environmental conditions. There is no one general purpose bacteria. Short term acclimation, then, involves natural selection of bacterial species that can utilize the available substrate in the process environment.

Short term acclimation is a necessary component of synfuel wastewaters modeling studies. The desirable procedure is to have access to a bacterial culture that has been acclimated to a similar wastewater and use this culture in the start up of the new system. At EMRC, Pseudomonas and Arthrobacter have been the two dominant genera that populate bench scale and PDU models treating synfuels wastewater[7]. Systems treating municipal wastewater contain these two genera as well as Achromobacter, Cytophaga, Flavobacterium, Alcaligenes, Vibro, Aeromonas, Bacillus, and Zoogloea[8]. Nirtrosomonas and Nitrobacter are common to all systems where nitrification occurs.

Long term acclimation, as used in this paper, is defined as the adaptation of bacteria to utilize previously non-biodegradable or poorly biodegradable compounds as substrate. Most synfuel wastewaters are composed of a complex matrix of organic and inorganic compounds. Complete removal of the biodegradable compounds in a synfuel wastewater generally leaves

20 to 40 percent of the original COD in the effluent. If a previously non-biodegradable compound is subsequently removed, the bacteria have adapted in some way to utilize this compound.

One possible mechanism for this phenomena is genetic transfer of DNA that can produce the enzyme necessary to utilize a particular compound. This DNA can be contained in extrachromosomal genetic structures termed plasmids that exist within bacterial cells. An important characteristic of plasmids is that they can reproduce autonomously. A second mechanism for production of a suitable enzyme is through natural genetic mutation. Natural mutation is generally a function of selective pressures present in the ractor which come about due to substrate availability and growth conditions.

One form of genetic engineering involves the use of plasmids, restriction enzymes and DNA polymerases to construct DNA hybrid plasmids with genes from diverse sources. The cells containing hybrid plasmids can be tailored to utilize certain substrates very efficiently. Plasmids can also be transferred from cell to cell in nature by a process called conjugation.

Conjugation, along with transformation and transduction, are three methods of genetic transfer[9]. Conjugation occurs through cell to cell contact during which DNA genetic elements are transferred between cells by the plasmids. Figure 3 is schematic representation of this process. Through conjugation, one bacterial cell containing the plasmid DNA necessary for the utilization of a particular compound can initiate the transfer of that DNA to the other cells. Through this process, previously non-biodegradable compounds can be used as substrate.

Substrate utilization, brought about by DNA transfer from plasmids, is difficult to document during modeling studies because the time of occurrence and the compound acted upon are not predictable. Conjugation may have occurred at EMRC during bench scale modeling of the activated sludge process using UND-EMRC SGL. This wastewater contained 880 mg/L of 5-5-dimethyl hydantoin which was thought to be non-biodegradable. Hydantoin was monitored during the previous year and had never been biodegraded in the system. Suddenly, over a one month time period, hydantoin was reduced to less than 100 mg/L as shown in Figure 4[10]. Environmental conditions such as temperature and pH had remained constant throughout this period. Although other mechanisms could have caused sudden utilization of hydantoins as substrate, DNA replication by plasmids through conjugation remains a strong possibility.

The question arises as to why genetic engineering of bacteria containing the desired plasmids has not revolutionized the field of biological treatment in environmental engineering. One part of the answer is the regulatory restrictions surrounding

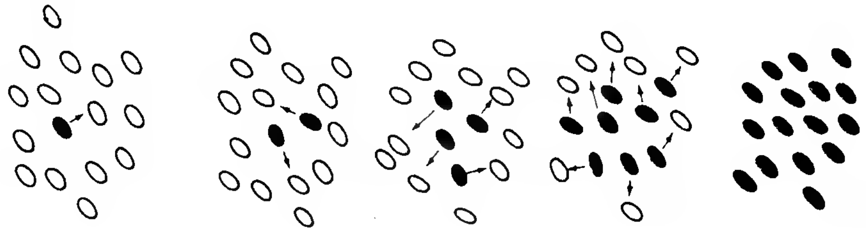


Figure 3. Representation of plasmid transmission between bacterial cells by conjugation.

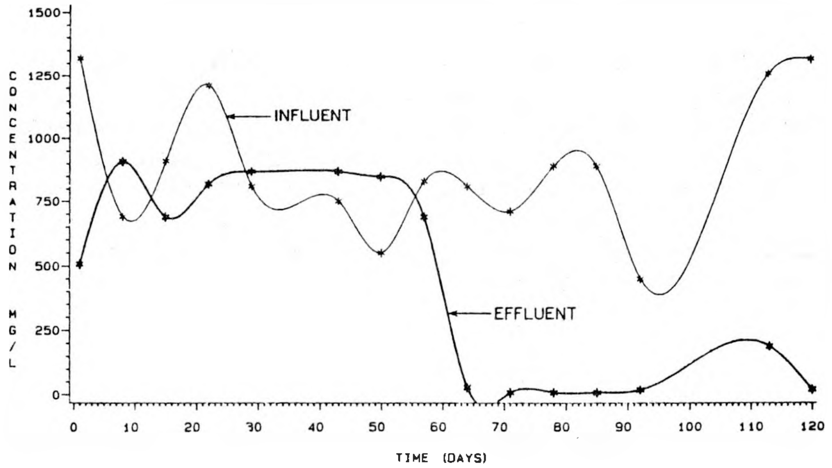


Figure 4. Removal of 5-5-dimethyl hydantoin from UND-EMRC wastewater in the second stage of a PAC activated sludge reactor.

the introduction of genetically engineered bacteria into the environment. Maintenance of strict controls was argued for by Sharples in Science[11]: "The dominant premise of evolutionary theory is that natural selection, the dominant force responsible for adaptations of organisms to their environments, operates on genetic alterations or novelties - mutations, rearrangements, and acquired accessory elements, such as plasmids - to produce evolutionary change. It follows that at least some genetic alterations (emphasis added) improve the abilities of organisms to survive, reproduce, compete for resources, or invade new habitats."

Based on Sharples's statement, it would seem that most engineered bacteria are destined to be non-reproductive when placed in the open, highly competitive environments that biological wastewater treatment systems provide. Davis[12] makes this argument in a parallel article with Sharples: "The reason is that a recombinant cannot be dangerous unless it can survive, and such survival, like earlier successes in evolution, depends upon a harmonious balance (coadaptation) of the total genome. Hence to be effective any new genes from a distant source will not fit well in the recipient genome, so they can be expected to produce noncompetitive (or even nonviable) monstrosities, rather than dangerous monsters."

Genetically engineered bacteria are not currently being used to treat synfuels wastewater. Their future use appears to be many years away, though genetic adaptation can and likely does occur naturally during long term acclimation.

Currently there are several companies marketing both liquid and dry bacterial cultures. Vendors claiming to market "genetically engineered" bacteria for use in wastewater treatment systems are in reality selling bacteria that have been acclimated to a specific wastewater. Some of these cultures may be excellent for initial startup of a system. However, once established, bacteria must reproduce on their own for a system to be economically viable.

SYSTEMS FOR THE FUTURE

EMRC has been actively involved in the testing and development of biological wastewater treatment systems for synfuel wastewaters. Table 3 is a summary of biological systems that have been modeled using synfuel wastewaters at EMRC.

As mentioned earlier, most of the systems tested in Table 3 were developed for the treatment of municipal wastewater which has characteristics very different from synfuel wastewaters. Although high BOD wastewaters can be treated by modifying the design and operation parameters such as HRT and MCRT, wastewaters with high ammonia concentrations are not well suited to treatment by any of the systems listed except the coupled fluid bed. Predenitrification modification of the activated sludge process can make it suitable for the removal of nitrogen from wastewater as with the coupled fluidized bed.

Table 3

Summary of Biological Systems Modeled
Using Synfuel Wastewaters at EMRC

Parameter	GPGP	KILnGAS	UND-EMRC	Texaco
AS	yes	yes	yes	yes
AS 2-Stage	yes	yes	yes	no
AS w/ PAC	yes	yes	yes	no
AS w/DENIT	yes	no	no	no
RBC	yes	yes	yes	yes
COOL TOWER	no	yes	yes	yes
TF	no	no	yes	no
FLUID BED	yes	no	no	no

AS = activated sludge
AS 2-Stage = activated sludge with second stage nitrification
AS w/PAC = activated sludge with powdered activated carbon addition
AS w/DENIT = activated sludge with nitrification and denitrification
RBC = rotating biological contactor
COOL TOWER = cooling tower with synfuel wastewater as makeup
TF = trickling filter
FLUID BED = coupled fluidized bed with predenitrification

In the coupled biological fluid bed reactor nitrification occurs in the aerobic column and denitrification takes place in an anoxic column. The influent wastewater is added as the carbon and energy source for denitrification in the anoxic column. The nitrified wastewater is cycled back through the anoxic reactor for denitrification. This arrangement is termed predenitrification. Figures 5 illustrates biological process coupling and Figure 6 shows the physical bench scale layout for the process in figure 6.

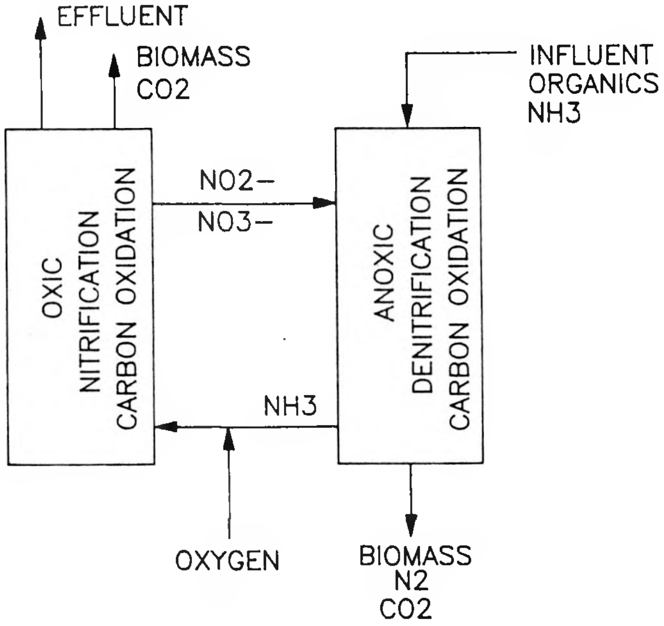


Figure 5. Biological process schematic for a predenitrification coupled fluid bed reactor.

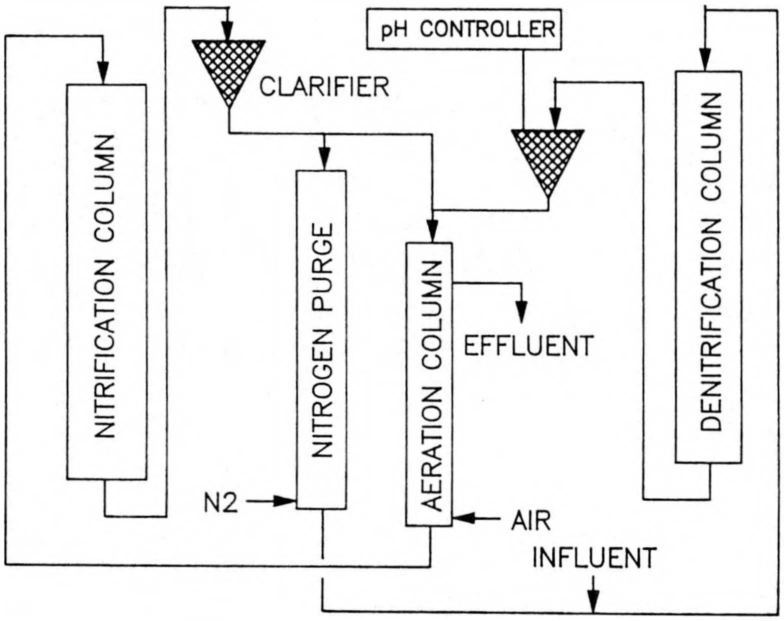


Figure 6. Schematic of a bench-scale predenitrification coupled biological fluid bed reactor.

The biochemical reactions in the denitrification process are the anaerobic conversion of the nitrate ion to the nitrite ion followed by conversion to nitrogen gas. The process is known as anoxic denitrification because the biochemical pathways are not anaerobic, but rather a modification of aerobic metabolism performed when oxygen is limiting. Most denitrifying bacteria are normally aerobic heterotrophs that require organic carbon as an energy and carbon source, but can grow anaerobically by using oxygen from nitrate and nitrite.

Municipal wastewater contains approximately 15 mg/L of ammonia and 200 mg/L of BOD. The BOD/NH_3 ratio is 13:1. The quantity of oxygen required to covert the ammonia to nitrate is relatively small compared to the BOD. If denitrification is desired, methanol is added as a carbon source in separate anoxic reactor.

Synfuel wastewaters contains concentrations of ammonia often in excess of 400 mg/L. A typical BOD/NH_3 ratio would be in the range of 2.5:1. The ideal BOD/NH_3 ratio is 2.8:1. This ideal ratio provides the quantity of chemically bound nitrate oxygen, generated form the conversion of ammonia to nitrate, that is just sufficient to oxidize all of the BOD in the anoxic column. Additional oxygen is not required to oxidize the BOD.

UND-EMRC has used coupled biological fluidized bed to treat GPGP wastewater. The process has proven successful with this wastewater as shown in Figure 7. Influent BODs varied between 1200 mg/L and 1600 mg/L with a mean value of 1250 mg/L. The mean effluent BOD_5 concentration was 240 mg/L which was an 81 percent reduction. The BOD_5 load on the anoxic reactor was a consistent 4 to 5 $kg/m^3 \cdot d$ during the last 80 days of operation. This value assumes that all BOD is removed in the anoxic reactor. The BOD removals, just as the COD removals, remained relatively constant throughout the test period.

Ammonia removal performance is shown in Figure 8. The influent and effluent ammonia concentrations indicate that very little ammonia removal occurred until after day 140. Influent ammonia concentrations averaged 1090 mg/L while the effluent ammonia concentrations eventually stabilized at 200 mg/L to 400 mg/L in the effluent. During this period, ammonia reduction varied from 60 percent to 90 percent and was very stable.

The coupled predenitrification process can be an ideal choice to treat synfuel wastewaters where ammonia and/or nitrogen removal is a goal. The process can eliminate: 1) oxygen for BOD removal, 2) an external carbon source for denitrification, and 3) the extra reactor vessel required when denitrification and BOD removal are separate operations.

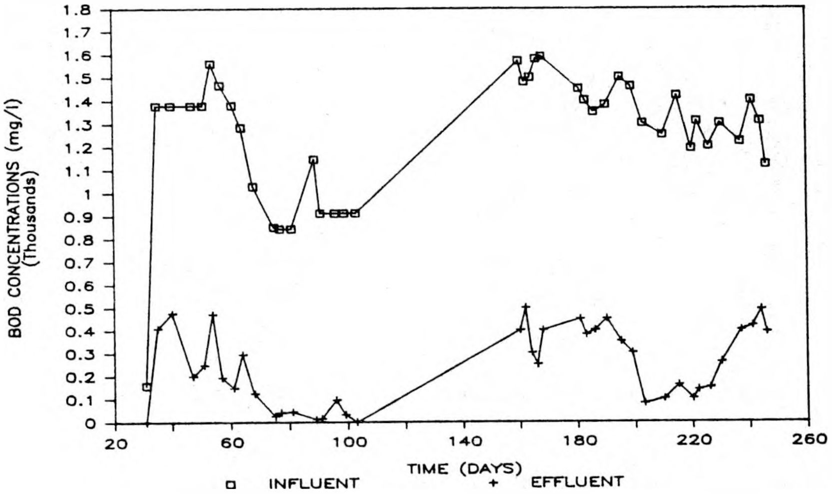


Figure 7. BOD removal from GPGP wastewater in a bench-scale coupled biological fluid bed reactor.

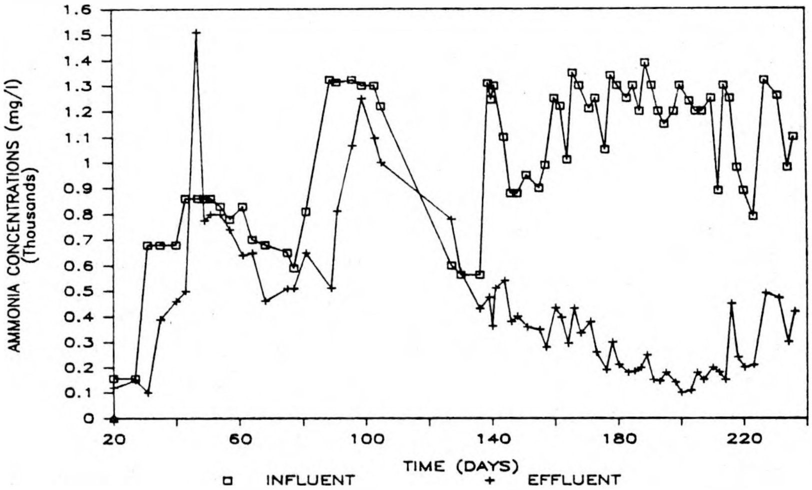


Figure 8. Ammonia removal from GPGP wastewater in a bench-scale coupled biological fluid bed reactor.

CONCLUSIONS

* GPGP, Kilngas, UND-EMRC wastewaters have similar chemical characteristics with a complex organic matrix represented by high CODs while Texaco wastewater has a COD that, without solvent extraction, is much lower than the others. All of these wastewaters have high ammonia concentrations.

* Treatability testing of synfuel wastewaters is needed for waste treatment process design because of variability in synfuel wastewaters and the presence of ammonia and priority pollutants that require removal to very low concentrations if the wastewater is to be discharged.

* Bench-scale models provide preliminary data suitable for determining treatability and the suitability of selected processes. PDU and/or pilot scale models are needed to obtain reliable design data.

*Genetically engineered bacteria are not available for use in synfuel wastewater treatment systems. The inability of genetically engineered bacteria to reproduce in an open system as well as regulatory restrictions make it unlikely that "super bugs" will have an impact on synfuel wastewaters treatment in the near future.

*Predenitrification processes such as the coupled biological fluidized bed system are ideally suited for synfuels wastewater treatment when either ammonia reduction or complete nitrogen removal is necessary.

ACKNOWLEDGEMENTS

Funding for this research was provided for in part by the United States Department of Energy and the Electric Power Research Institute (EPRI). CH_2M Hill was the senior partner in the EPRI research.

BIBLIOGRAPHY

1. Turner, Charles D., Chong Seng Ong, and John R. Gallagher, "Coupled Biological Downflow Fluid Bed Reactor Treatment of Synfuels Wastewater," Proceedings of the 43rd Annual Purdue Industrial Waste Conference, May, 1988.

2. Moe, Thomas A., Gale G. Mayer, Charles D. Turner, and Charles A. Wentz, "Integrated Coal Gasification Wastewater Treatment," presented at ASCE National Spring Convention & Energy Specialty Conference, Atlantic City, New Jersey, April, 1987.

3. Turner, Charles D., and Kevin Wernberg, "Using Rotating Biological Contactors for the Treatment of Coal Gasification Wastewaters," Proceedings of the 41st Industrial Waste Conference, Butterworth Pub., May, 1986.

4. Stepan, Daniel J., "Biological Treatment of Texaco Coal Conversion Wastewater by the Activated Sludge Process," Master of Engineering Design Paper, Department of Civil Engineering, University of North Dakota, Grand Forks, North Dakota, May, 1988.

5. Viessman, Warren, and Mark J. Hammer, Water Supply and Pollution Control, Harper and Row, 1985.

6. Tchobanoglous, George and Edward D. Schroeder, Water Quality, Addison-Wesley Publishing Co., 1985.

7. Turner, Charles D., Thomas Moe, and C.A. Wentz, "Stripping of Phenols in Model Cooling Towers" paper presented at AIChE Spring National Meeting in Houston, Texas, March 29 - April 2, 1987.

8. Reynolds, Tom D., Unit Operations and Processes in Environmental Engineering, Brooks/Cole of Wadsworth, Inc., 1982.

9. Brock, Thomas D., Biology of Microorganisms, Prentice-Hall Inc., 1979.

10. Turner, Charles D., Paula Diepolder, and John Strain, "Biological Nitrification and Hydantoin Removal in Coal Gasification Wastewater," Proceedings of the 40th Annual Purdue Industrial Waste Conference, May, 1985.

11. Sharples, Frances E., "Regulation of Products from Biotechnology," Science, Vol. 235, 1329, March 13, 1987.

12. Davis, Bernard D., "Bacterial Domestication: Underlying Assumptions," Science, Vol. 235, 1329, March 13, 1987.

"WASTEWATER TREATMENT FOR INTEGRATED GASIFICATION COMBINED CYCLE POWER PLANTS"

BY: DAVID L. PETERSON
CH2M HILL
GALE MAYER
ENERGY & MINERAL RESEARCH CENTER
GRAND FORKS, ND

WASTEWATER TREATMENT FOR IGCC POWER PLANTS

D. Peterson, B. Eis
CH2M HILL

G. Mayer
University of North Dakota
Energy and Minerals Research Center

ABSTRACT

The use of coal gasification to produce electrical power in combined-cycle generating plants is an important development in the synfuels industry. Integrated gasification—combined-cycle (IGCC) power plants will be used in the future as an alternative to conventional coal-fired plants to produce electrical power. The characterization of environmental emissions from such plants is a leading topic of investigation.

As part of its support of the development of IGCC power plants, the Electric Power Research Institute (EPRI) is sponsoring studies on environmental impacts and wastewater treatability. Bench-scale treatability tests have recently been completed on wastewater collected from demonstration runs of the KILnGAS and Texaco gasifiers. These tests have shown that biological treatment can effectively reduce the concentration of organics in these wastewaters when pretreatment is provided by steam stripping and, in the case of KILnGAS wastewater, solvent extraction.

INTRODUCTION

One of the promising opportunities in the synfuels industry is the use of coal gasification to produce electric power in combined-cycle generating plants. IGCC power plants will be an important alternative to conventional coal-fired power plants as additional generating capacity is required in the future. Interest in integrated gasification—combined-cycle (IGCC) power plants has been fueled by recent, successful operation of such plants at Cool Water, in Dagget, California, at Westfield, Scotland, and other locations (Ref. 1). Gasifiers that are being considered for combined-cycle generation include KILnGAS, British Gas/Lurgi, Texaco, Shell, Kellogg-Rust-Westinghouse, and Dow.

In conjunction with commercial-scale demonstration projects, studies are being completed to assess the environmental impacts of these new systems. Treatment of the wastewater condensate from the gasification process is an important environmental consideration with IGCC plants. Little commercial experience with treatment technologies exists for this condensate. Treatment and disposal of wastewater from an IGCC plant is best addressed early in the project planning phases.

The Electric Power Research Institute (EPRI) has joined other organizations in sponsoring a number of IGCC demonstration plants. EPRI'S sponsorship includes investigation of environmental emissions. Results of treatability testing of wastewater collected from demonstration runs of the KILnGAS and Texaco gasifiers were recently published (Ref. 2).

This paper describes the wastewater sources from IGCC power plants and summarizes the results of KILnGAS and Texaco treatability testing.

IGCC POWER PLANTS

A general schematic of an IGCC power plant is shown in Figure 1. Although the process details vary among the different commercial systems being developed, the integrated concept is similar for all systems. Synthesis gas is produced in the coal gasification process, and the gas is scrubbed and cooled to remove particulates and condensables. Sulfur is then removed from the cooled gas stream in the sulfur removal and recovery processes. The clean synthesis gas is burned in a gas turbine. Steam that is recovered in a heat recovery steam generator (HRSG) is used to recover the heat generated in the gas turbine and power the steam turbine.

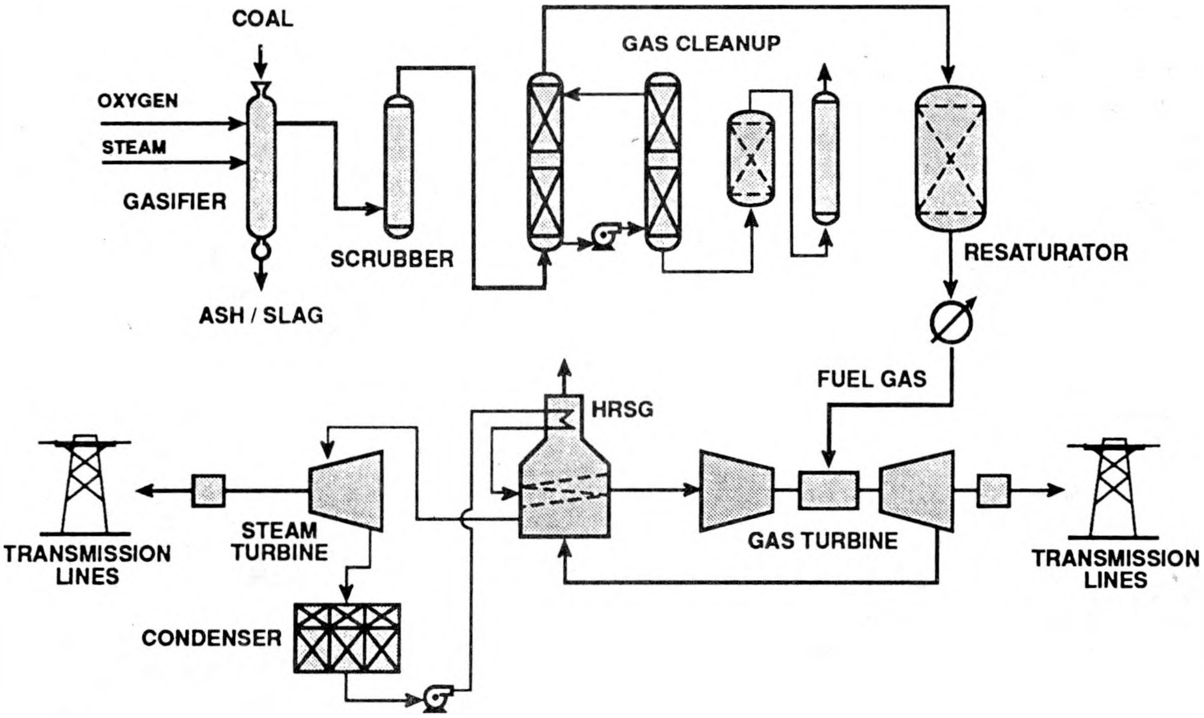
IGCC power plants are considered to have a number of advantages over conventional coal-fired power plants including:

- Reduced Air Emissions—SO_2, NO_x, and particulates can be removed more efficiently from the synthesis gas stream than from flue gas
- Phased Construction—Modular plant expansion increments, perhaps beginning with a gas fired turbine, reduce capital exposure and allow on-line capacity to match demand more closely.
- Fuel Economy—Coal-to-bus-bar efficiencies meet or exceed those of conventional plants.
- Load Matching—Units can be operated for base load power generation or to provide peaking service.

WASTEWATER SOURCES

The principal sources of wastewater from an IGCC power plant are shown in Figure 2. Many of these waste streams are similar to those from conventional coal-fired plants; the cleanup technologies for these streams in IGCC plants will be similar also. The principal additional sources

Figure 1. **IGCC Plant Schematic**



for IGCC power plants are the gasification condensate or gas liquor and the blowdowns from sulfur removal and recovery.

GAS LIQUOR

The principal source of contaminated wastewater from IGCC power plants is the condensate formed during the quenching and cooling of the synthesis gas. Commonly referred to as "gas liquor," this wastewater contains varying amounts of organics, ammonia, acid gases, dissolved salts, and metals, depending on the gasifier and coal type. The treatment and ultimate disposal of this process wastewater is one of the principal concerns in developing an overall water management strategy for an IGCC plant.

The representative gas liquor characteristics, shown in Table 1, illustrate the variability among gas liquors depending on the gasifier and type of coal used. The type and concentration of organics are largely dependent on the type of gasifier, particularly the temperature regime and the path of reactants in the gasifier. The gasifiers currently being considered for commercial IGCC plant range from the fixed-bed British Gas/Lurgi gasifier, which produces a low-flow stream with high concentrations of organics, to the entrained-bed gasifiers (Texaco, Shell), which produce gas liquor containing only simple organic acids. Fluidized-bed gasifiers typically have higher organics concentrations than do the entrained-bed gasifiers, with little or no tar formation.

The quantity of metals and inorganics in the gas liquor is principally a function of the type of coal processed. For example, the high chloride concentration shown for the KILnGAS gasifier is attributable to the chloride content of the coal.

Figure 2. **IGCC Power Plant Wastewater Sources**

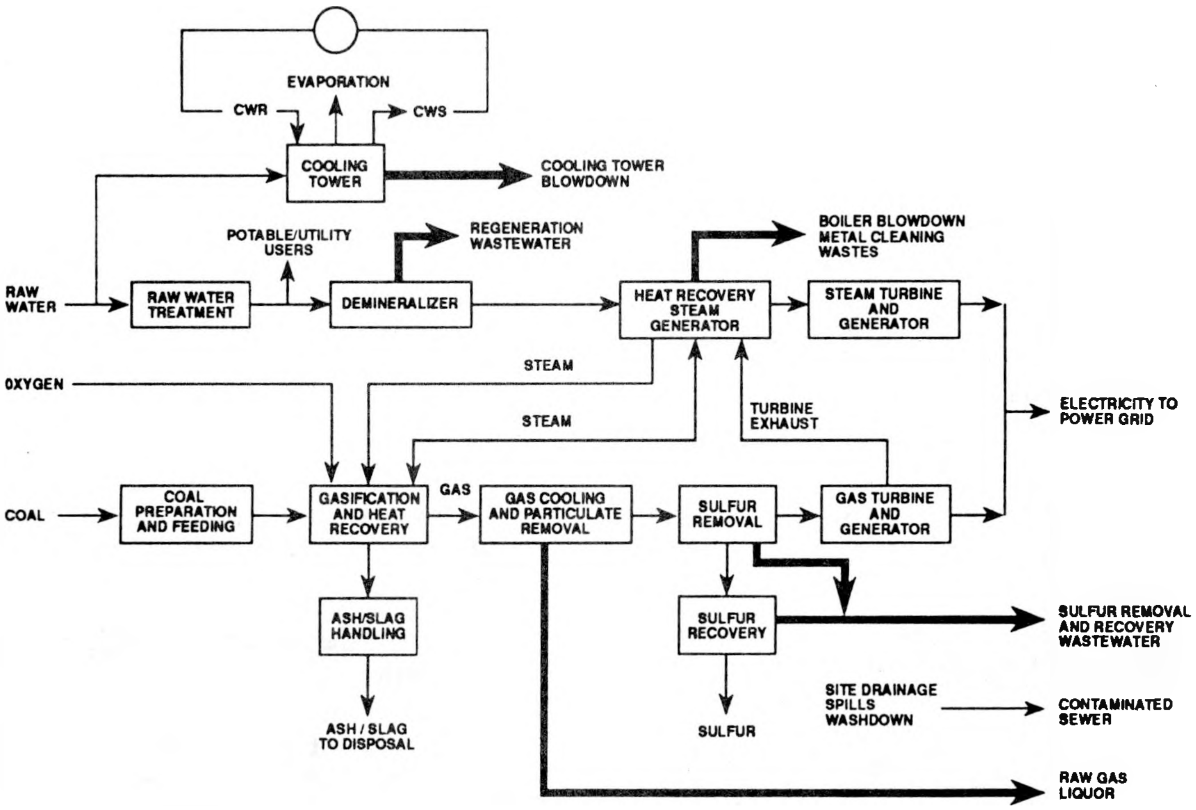


Table 1. **Raw Gas Liquor Characteristics**

	Gasifier and Coal Type			
Constituent Concentration (mg/l)	**BGC/Lurgi[a] Pitts. No. 8**	**KILnGAS[b] Ill. No. 6**	**Texaco[c] Utah**	**Texaco[b] Ill. No. 6**
Chemical Oxygen Demand (COD)	20,000	5,520	460	1,100
Biochemical Oxygen Demand (BOD)	—[d]	1,730	30	130
Phenolics				
Total	3,000	750	<5	<5
Mono	1,500	340		
Ammonia (NH_3)	15,000	1,500	4,300	2,100
Thiocyanate (SCN)	,000	160	2	27
Thiosulfate (S_2O_3)	—[c]	1,380	70	17
Cyanide (CN)	50	4	14	20
Sulfide (S—)	100	ND	50	80
Chloride	2,000	1,300	80	3,500
Fluoride	10	80	7	40
Boron	—	50	40	40
Metals				
Arsenic	2.9	<0.005	0.02	<0.01
Selenium	3.7	0.3	0.1	0.01
Sodium		50	125	40

---

[a] Estimated from data presented in Phase 1: Reference 3.

[b] Reference 2.

[c] Reference 1.

[d] No data available.

Volatile metals such as arsenic, selenium, and mercury will also carry over into the gasification condensate.

SULFUR REMOVAL AND RECOVERY (SRR) WASTEWATER

The quality and quantity of wastewater generated by the sulfur removal and recovery processes will vary with the type of process selected. They are often low or intermittent flow, but can have high concentrations of contaminants. Examples of wastewater characteristics for these wastewaters are shown on Table 2.

EPRI TREATABILITY TESTING PROGRAM

Treatability testing was recently completed on wastewater collected from demonstration runs of the KILnGAS and Texaco gasifiers. The processes that were tested as part of the treatability program are shown in Table 3.

Table 2. **Sulfur Removal, Sulfur Recovery, and Tail Gas Cleanup Wastewaters**

	SCOT[a]	Rectisol[b]	Selexol[a]
Flowrate (gpm)	100	50	5
Constituent Concentration (mg/l)			
COD	450	140	17,000
BOD	1,000	100	3,000
NH_3	3,300	74	6,800
H_2S	640		3,250
CN	25	74	300
SCN	48		55
TOC	100		2,800

[a] Reference 2.
[b] From EPA Pollution Control Technical Manuals.

KILnGAS TREATABILITY TESTING

The KILnGAS gasifier is a rotating, air-blown, ported kiln that operates at about 60 psig. Wastewater was collected in 1984, when the gasifier was operating on Illinois No. 6 coal, and transported to the University of North Dakota Energy and Minerals Research Center (UNDEMRC) for characterization and treatment.

SOLVENT EXTRACTION

The KILnGAS wastewater was first treated by solvent extraction with di-isopropyl ether (DIPE) to remove phenolic compounds. Solvent extraction pretreatment was found to be an essential step for effective performance of the biological treatment process. Without this pretreatment, dispersed biological growth, low concentrations of biomass, and poor organic removal rates occurred.

The solvent extraction process removed greater than 70 percent of the phenolic compounds and the BOD_5 from the gas liquor. Di- and tri-methyl phenols were reduced to nondetectable levels. The results are summarized in Table 4.

STEAM STRIPPING

In order to meet low effluent ammonia discharge targets and improve biotreatment performance, the KILnGAS gas liquor must also be treated by steam stripping to remove ammonia prior to biological treatment. Test results for steam stripping are included in Table 4. Ammonia was reduced to 150 mg/l by steam stripping with caustic addition.

The gas liquor collected for the EPRI testing had comparatively low alkalinity and a high fixed-ammonia concentration. Caustic addition was necessary to reduce ammonia concentrations significantly. Figure 3 shows the relationship of adjusted pH level to ammonia concentration after steam stripping. To reduce ammonia below 200 mg/l, a feed pH of 10.5 to 11.0 was necessary. Approximately 3 grams per liter of caustic were required to reach this pH and achieve the ammonia concentrations shown in Table 4.

BIOLOGICAL TREATMENT

Pretreated KILnGAS gas liquor was processed in activated sludge biological reactors for removal of organics. Gas liquor that was pretreated by steam stripping only created difficulties in the bioreactors—dispersed growth, poor settling, and low removal efficiencies.

The performance was measurably improved with wastewater pretreated by solvent extraction and steam stripping. The biological system was operated over five different operating conditions to evaluate process performance and to develop process design parameters. The solids concentration in the bioreactors (mixed liquor volatile suspended solids or MLVSS) was increased to desired concentrations for these test conditions. The MLVSS concentration over the testing period is shown in Figure 4. Target organic removal efficiencies for BOD_5 were produced during days 190 to 220, when MLVSS concentrations were approximately 1,000 mg/l. The activated sludge operating parameters during this period are summarized in Table 5. Table 6 shows the average effluent concentrations and removal efficiencies at these operating conditions.

The biochemical oxygen demand (BOD_5) of the KILnGAS gas liquor was reduced to less than 20 mg/l by the biological process; however,

Table 3. EPRI Treatability Testing Program

Unit Process	Desired Constituent Removal KILnGAS	Texaco
Solvent Extraction	Phenol, BOD_5, COD	--
Steam Stripping	NH_3	NH_3, HCN, H_2S
Biological Treatment	Organics, NH_3	Organics, NH_3
Chemical Precipitation	F, B,	B
Granular Activated Carbon Adsorption (GAC)	COD, color, phenol	---
Ion Exchange (clinoptilolite)	NH_3	NH_3, B
Ozonation	COD, color	BOD_5, COD
Cooling Tower	BOD_5, COD, phenol	BOD_5, COD
Wet Air Oxidation	Organics	---

Table 4. Solvent Extraction and Steam Stripping Results

		Solvent Extraction		Steam Stripping	
Parameter	**Raw Gas *Liquor* (mg/l)**	**Effluent *Concentration* (mg/l)**	**Removal *Efficiency* (percent)**	**Effluent Concentration (mg/l)**	**Removal Efficiency (percent)**
pH	8.5	8.5	—	9.5	—
Ammonia	1,360	1,320	0	150	87
COD	4,870	3,200	35		
BOD	1,610	320	80		
Phenol	320	88	80		
o-Cresol	30	ND	100		
p,m cresol	180	17	90		
Di- and Tri-Methylphenol	70	ND	100		

NOTE: ND = not detected.

Figure 3. **Effluent Ammonia Concentration Versus pH**

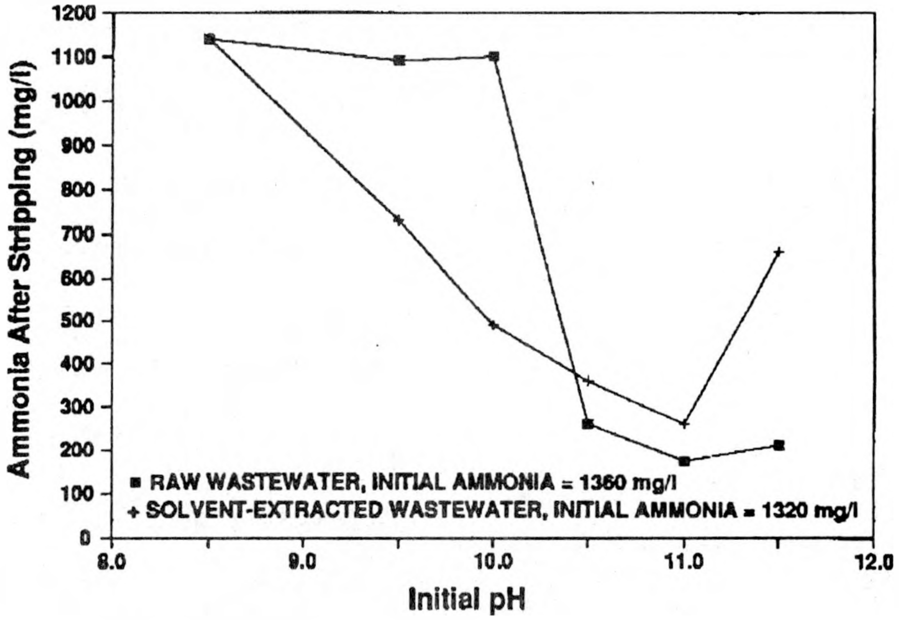
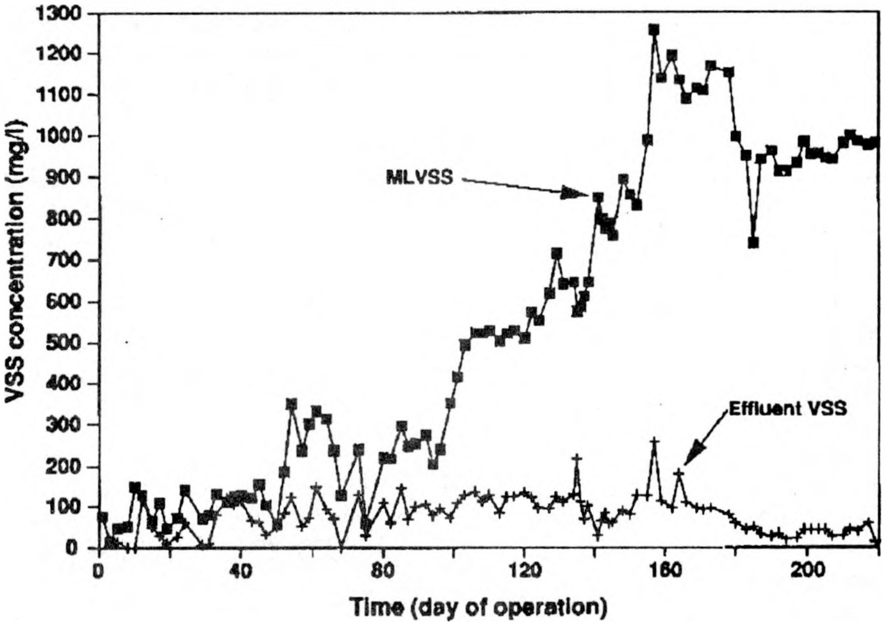


Figure 4. **Mixed Liquor VSS and Effluent VSS Concentrations**



chemical oxygen demand (COD) was reduced to only 1,500 mg/l. A high concentration of biorefractory organics remains in the KILnGAS wastewater following biotreatment. Addition of powdered carbon to the reactor did not significantly reduce the COD concentration.

Table 5. **KILnGAS Activated Sludge Operating Parameters**

HRT	1.6 days
SRT	23 days
F/M	0.28 lb BOD_5lb MLVSS/d
MLVSS	980 mg/l

Table 6. **KILnGAS Activated Sludge Treatment Performance**

	Influent Concentration (mg/l)	Effluent Concentration (mg/l)	Removal Efficiency (percent)
BOD_5	560	15	97
COD	3,000	1,500	50
Ammonia	150	127	15
Cyanide	14	9	36
Phenols (4AAP)	>100	1.6	98
Phenol	92	<0.005	100

Ammonia removal by nitrification was not achieved in the biological reactors. The small reduction in ammonia across the system could be accounted for entirely by the nutrient requirements for the growth of biological solids. Nitrate and nitrite were not detected in the effluent. Addition of powdered carbon and a second stage reactor did not produce nitrification.

Very high removal rates for phenolics were achieved. Total phenols (by 4AAP analysis) were 1.6 mg/l. Total phenols before biological treatment were estimated to be greater than 100 mg/l.

Overall, the activated sludge process performed very well with the pretreated KILnGAS wastewater. The biological character was healthy, the MLVSS increased to target levels and exhibited good settling behavior, and BOD_5 removal efficiencies were very high. However, further reductions of ammonia and COD would likely be required prior to discharge of this wastewater.

AMMONIA AND COD REMOVAL

To reduce ammonia and COD, the activated sludge effluent was processed through granular activated carbon (GAC) and clinoptilolite ion exchange resin. COD was reduced to 600 mg/l at contact times of 20 to 60 minutes and carbon loadings of 0.05 to 0.1 gram of COD per gram of carbon. Ammonia was reduced to 1 mg/l by ion exchange with clinoptilolite media with contact times of 20 minutes and processing through 40 bed volumes.

COOLING TOWER

Solvent-extracted and steam-stripped wastewater was treated in a bench-scale cooling tower to simulate a zero discharge reuse treatment system. The makeup rate to the bench-scale system was 6 liters per day.

The operating conditions and performance of the reuse cooling tower are summarized in Tables 7 and 8. The cooling tower was operated at 4.4 cycles of concentration and a steady bacteria count of 3 to 8 million per milliliter was reached after 60 days of operation. There was

Table 7. **KILnGAS Cooling Tower Operating Parameters**

Cycles of Concentration	4.4
Hydraulic Application Rate	1.75 liters/min/m^3
Organic Application Rate	0.22 kg/m^3/d
Bacterial Count	5 x 10^6/ml
pH	8.5
Corrosion in Packing	
304 stainless steel	0.77 mil/yr
Carbon steel	9.58 mils/yr
Loss in CT Exhaust	
Ammonia	90+ percent
Phenol	2 percent

minimal fouling of the packing over the trial. The predominant microbe in the system was Arthrobacter.

Table 8. **Average KILnGAS Cooling Tower Treatment Efficiences**

Constituent	Mean Makeup Concentration (mg/l)	Mean Blowdown Concentration (mg/l)	Removal (percent)
BOD$_5$	632	666	76
COD	2,970	9,885	24
Ammonia (total)	143	51	93
Nitrate	5	ND	100
Cyanide (total)	14	44	29
Phenolics (total)	97	ND	100
Chloride	1,068	4,466	1.8
TDS	5,778	25,054	-3.0
Sodium	1,453	6,406	0.2

Note: ND = not detected by gas chromatography.

High removal efficiencies of BOD$_5$ and phenol were achieved in the cooling tower. As with the activated sludge biological system, a high concentration of biorefractory organics, as measured by COD, remained in the blowdown. Removal of ammonia was attributed entirely to air stripping as there was no nitrate in the blowdown, and cooling tower exhaust measurements balanced with the loss of ammonia from the recirculating water. There was minimal loss of phenol in the exhaust gas and phenol was reduced to nondetectable levels in the blowdown.

High corrosion rates occurred with the carbon steel coupons uniformly across the surface. The stainless steel coupons had relatively low corrosion rates, but localized pitting was apparent. The localized pitting was likely caused by the chloride content of the KILnGAS wastewater.

TEXACO TREATABILITY TESTING

The Texaco gasifier is an oxygen-blown, slagging, entrained-flow unit that operates at about 600 psig. The 1,000-ton-per-day, commercial-scale unit has been operated at the Cool Water IGCC plant in Daggett, California, since 1984. Four waste streams were sampled at this plant when operating on SUFCO coal: gray water and ammonia condensate (gas liquor streams) and the SCOT and Selexol condensates (sulfur removal and recovery wastewaters). The characteristics are shown in Table 9.

STEAM STRIPPING

Steam stripping of the Texaco wastewaters was necessary to reduce ammonia concentrations prior to further treatment by activated sludge.

When mixed together, the gray water and ammonia condensates had a high potential for scaling, so these waste streams were steam stripped separately. Caustic addition was necessary only for the gray water to reduce the ammonia concentrations to near 100 mg/l. The results of the steam stripping process are summarized in Table 9 along with the characterization data.

BIOLOGICAL TREATMENT

Two biological processes were tested for treating the Texaco wastewater: rotating biological contactors (RBCs) and activated sludge. The RBCs never attained a viable population of attached biomass and had significant scaling of the media. They were found to be ineffective in treating the wastewater at the conditions that were run during the testing period.

The activated sludge system, on the other hand, achieved very high removal efficiencies. A healthy biological population was maintained in the reactors, although a high concentration of inert material also formed in the reactor, as shown by the mixed liquor solids concentration in Figure 5. Operating parameters and treatment performance are shown in Tables 10 and 11.

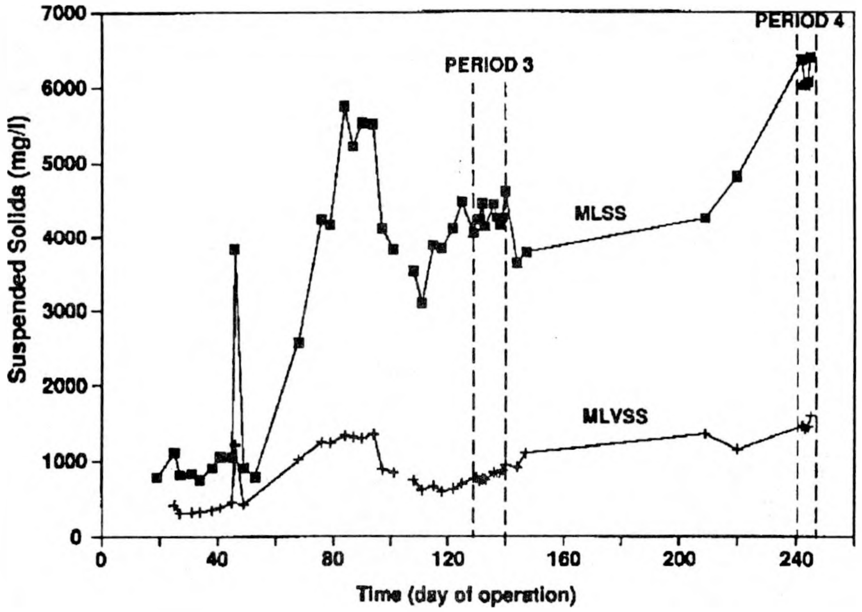
The BOD was reduced to less than 10 mg/l. Nitrification of the wastewater occurred after a long acclimation to the activated sludge process. Figure 6 shows effluent ammonia, nitrate, and

Table 9. **TEXACO Wastewater Characteristics**

	Raw Wastewater				
	Gray Water	**Ammonia Condensate**	**SCOT Condensate**	**Selexol Condensate**	**Combined Product After Steam Stripping**
Percent of Total Flow	61.9	27.5	10.3	0.28	
pH	9.0	8.9	8.2	8.2	8.5
Ammonia	721	13,600	3,330	6,820	115
COD	677	160	852	17,200	500
BOD	—	116	1,014	3,487	270
Cyanide	6	36	25	302	3
Phenol	<0.02	<0.02	<0.02	<0.02	ND
Sulfide	ND	170	64	3,250	ND

NOTE: ND = not detected.

Figure 5. **Mixed Liquor Suspended Solids Versus Time**



nitrite concentrations over time. Full nitrification was achieved after day 200 as indicated by the increase in nitrate concentration and the full removal of ammonia and nitrite.

***Table 10.* TEXACO Activated Sludge Operating Parameters**

HRT	0.6 day
SRT	22 days
F/M	0.57 lb BOD/lb MLVSS/d
MLVSS	820 mg/l

***Table 11.* TEXACO Activated Sludge Treatment Performance**

	Influent (mg/l)	Effluent (mg/l)	Removal Efficiency (percent)
BOD_5	268	7	97
COD	496	117	76
Ammonia	114	5	96
Cyanide	3	3	0
Formic Acid	1,390	6	99
Thiocyanate	7	0.1	99

COOLING TOWER

Biodegradation was also tested using a cooling tower for the Texaco wastewater. Initial operation of the system at three cycles of concentration resulted in serious scaling of the media and all components of the system. This scaling was predictable from the chemistry of the wastewater. Following this initial period, the pH of the recirculation water was lowered and controlled to between 6.5 and 7.2 and operated at three cycles of concentration with no scale buildup for the remainder of the trial. The average cooling tower operating parameters and performance over the trial are shown in Tables 12 and 13.

Very high efficiencies of organics removal were achieved with greater than 99 percent for BOD_5 and formate. The high concentration of COD shows that some biorefractory compounds do remain in the Texaco wastewater.

Ammonia removal in the cooling tower was approximately 30 percent. Exhaust testing showed virtually all of the ammonia was removed by stripping. Since the pH was maintained at 7, the removal of ammonia by stripping was much lower than that for the KILnGAS cooling tower, which was operated at pH 8.5.

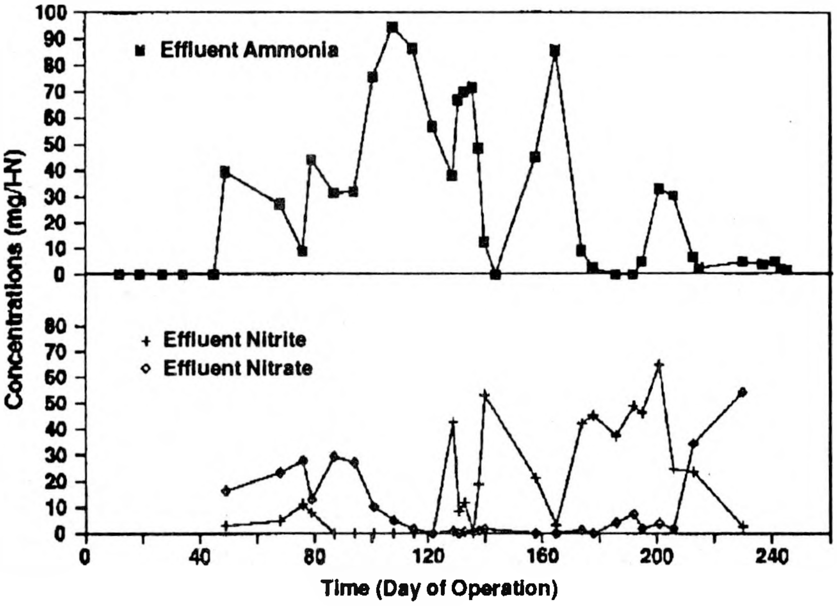
***Table 12.* TEXACO Cooling Tower Operating Parameters**

Cycles of Concentration	3.2
Hydraulic Application Rate	liters/min/m^3
Organic Application Rate	0.07 kg/m^3/d
Bacterial Count	2 x 10^7/ml
pH	6.5 to 7.2
Sulfuric Acid Dose	43 meq/l
Corrosion in Packing	
304 stainless steel	mils/yr
Carbon steel	mils/yr
Loss in CT Exhaust	
Ammonia	10 percent
Formate	0 percent

***Table 13.* Average TEXACO Cooling Tower Treatment Efficiences**

Parameter/ Constituent	Mean Makeup Concentration (mg/l)	Mean Blowdown Concentration (mg/l)	Removal (percent)
pH	8.6	6.8	—
TDS	1,120	8,400	(-150)
BOD_5	341	14	99
COD	691	456	78
Ammonia (total)	590	1,260	29
Nitrate	1.3	2.1	—
Cyanide (total)	26	5.4	33
Formate	2,220	2.4	>99
Chloride	136	449	—
Sodium	195	612	0.1

Figure 6. **Effluent Ammonia, Nitrate and Nitrite Concentrations Versus Time**



Even with the operation at a pH of 7 and three cycles of concentration, some scale was present on the packing at the end of the trial. This scale was much less than during the first period of the trial and did not affect the performance of the system.

Stainless steel, carbon steel, and sulfate-resistant concrete coupons were placed in the cooling tower basin and packing for the test run. Corrosion rates for the stainless steel were low, at less than 0.10 mil per year (mpy) in each test location. Pitting was not evident. The corrosion experienced by the carbon steel was low to moderate in the basin (3.31 mpy) and moderate to high in the packing (7.69 mpy). The carbon steel coupons exhibited general corrosion over the entire surface. The metal coupons had a continuous layer of inorganic scale over the entire surface of each coupon, which could reduce the corrosion rates.

The concrete coupons from the Texaco cooling tower lost 3.6 percent and 4.1 percent of the original coupon weight from the packing and basin test locations, respectively. These relatively high concrete weight losses over the 59-day test run may be attributable to the high sulfate levels in the recirculating wastewater stream. Although all test coupons exhibited the same amount of scale accumulation, the metal coupons seem to have been protected from corrosion while the concrete coupons were attacked at a high rate.

CONCLUSIONS

1. Treatment of the coal gasification condensate (gas liquor) and the sulfur removal and recovery wastewaters is an important environmental consideration for IGCC power plants. These are wastewaters that are not found in conventional coal-fired power plants and for which there is little commercial treatment experience.

2. Effective biological treatment of gasification condensates can be obtained in activated sludge treatment systems or reuse cooling towers with adequate pretreatment and process control.

3. Further processing in addition to biological treatment may be required for IGCC wastewaters to meet discharge standards for some parameters.

REFERENCES

1. Electric Power Research Institute. Proceedings: Sixth Annual EPRI Contractors' Conference on Coal Gasification. EPRI AP-5343-SR. October 1987. Palo Alto, California.
2. Electric Power Research Institute. Treatability Testing of KILnGAS and Texaco Coal Gasification Wastewaters. EPRI AP-5893, Project 2526-1. July 1988. Prepared by CH2M HILL and Energy and Mineral Research Center.
3. U.S. Department of Energy. The Pipeline Gas Demonstration Plant. Contract No. EF-77-C-01-2542. Prepared by Conoco.

"ANAROBIC BIOLOGICAL TESTABILITY OF SYNTHETIC FUELS WASTEWATER"

BY: STEVE HRUDEY
UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA, CANADA

ANAEROBIC BIOLOGICAL TREATMENT OF SYNTHETIC FUEL WASTEWATERS

Steve E. Hrudey[1] and Phillip M. Fedorak[2]

[1]Department of Civil Engineering
[2]Department of Microbiology
University of Alberta
Edmonton, Alberta, Canada T6G 2G7

ABSTRACT

Anaerobic biological treatment has been used for decades for the digestion of organic sludges from municipal sewage. Anaerobic methods have also been used for many years for specific food industry wastes such as those from meat and poultry processing. The many advantages of anaerobic processes for waste treatment (i.e. lower energy demands, high organic loading capability and low sludge generation rate) have only been seriously considered for synthetic fuel industry wastewaters in the past several years.

The major organic components of synthetic fuel industry wastewaters, such as phenol, have been shown to be readily degradable by anaerobic biological systems. Because anaerobic systems are not limited in their organic loading by aeration capacity considerations which limit aerobic biological systems, anaerobic systems are well suited to high strength wastes. However, anaerobic biological systems are also subject to inhibition by various wastewater components. The complexity of synthetic fuel wastewaters (e.g. coal conversion wastewaters) makes inhibition by trace organic substances a major concern. Research has demonstrated the need for dealing with inhibition problems by means such as solvent extraction pre-treatment and activated carbon adsorption. Findings to date suggest that with appropriate pre-treatment methods, anaerobic biological systems may provide feasible and cost effective treatment of a substantial portion of the organic loading found in synthetic fuels wastewaters.

INTRODUCTION

Anaerobic biodegradation is a natural phenomenon which can occur spontaneously when facultative micro-organisms (those which can function with or without oxygen) deplete the immediate environment of dissolved oxygen during the process of aerobic biodegradation. If conditions are suitable, strict anaerobic bacteria convert complex organic molecules to simple organic acids and ultimately to methane. Because this process can occur quite readily under natural conditions, it was recognized very early as a process for achieving stabilization of domestic sanitary wastes.

As domestic waste treatment has developed during this century anaerobic degradation has most commonly been applied to the stabilization of organic solids (either settled directly from sewage in primary treatment or produced as excess biomass which grows on the dissolved and colloidal organic matter removed in secondary biological treatment). Because the anaerobic process occurs readily with domestic sewage solids, the process was used for many years with very little research to determine what factors control process performance. Consequently, when the process did occasionally fail, little was known about what may have caused the problem or what could be done to recover or improve performance. As a result, the anaerobic biological process developed a reputation as being unpredictable and unstable.

In the past 20 to 30 years, considerably more research has been done on the anaerobic biodegradation process. Much of the early research documented the role of specific chemical substances in inhibiting the process. These findings along with the prior uncertainty about anaerobic process stability combined to make anaerobic biological processes seem to be a poor choice for industrial waste treatment.

The past 10 to 15 years has focused considerable attention on energy conservation and process economics for industrial waste treatment. This emphasis has caused renewed interest in the anaerobic biological process because of some of its inherent advantages over aerobic biological treatment. The most notable potential advantages are:

1. a capability to process very high strength wastes which would be difficult to handle with aerobic processes because of oxygen transfer limitations,

2. a potentially lower net energy budget because a functional system produces methane as a byproduct and there is no need to supply aeration,

3. a lower net yield of microbial biomass (excess sludge) which reduces the quantities of biological sludge which must be ultimately processed and disposed.

These factors will all be important to varying degrees for various wastes, but the reduction in quantities of waste sludge requiring disposal is usually a major beneficial factor. Speece (1983) summarized a typical comparison between aerobic and anaerobic biological treatment in Table 1.

Clearly, anaerobic treatment warrants consideration relative to aerobic treatment for any given industrial waste. The advantages of anaerobic treatment have led to considerable process research over the past decade with dramatic improvements in process utility and capability demonstrated. To date, most of the advances which have reached large pilot or full scale application have been in the food processing industries. Extremely efficient, high-rate waste conversion to methane has been achieved. In the food industries, inadequate waste biodegradability and/or the presence of inhibitory substances in the wastes have been a minor concern. However, applications to synthetic fuel wastewaters must deal with these two issues.

Table 1. Comparison of Anaerobic and Aerobic Biotechnology per Tonne of Chemical Oxygen Demand Degraded (after Speece, 1983)

Process Factor	Anaerobic	Aerobic
Electricity Used	neglible	1100 kWh
Methane Produced	1.1 x 10^7 BTU	none
Net Biomass (Sludge) Yield	20 - 150 kg	400 - 600 kg

SYNTHETIC FUEL WASTEWATER TREATABILITY

Phenolic Components

The wastewaters from synthetic fuels processes generally exhibit a high organic strength composed of a complex mixture of organic compounds. Neufeld (1984) presented a comprehensive overview of wastewater characteristics. Major components include phenolics and aliphatic acids. Only the latter had been widely recognized as effective substrates for anaerobic processess.

Phenolics may comprise 70 to 80% of total organic carbon in synthetic fuel wastewaters. Phenol had been mistakenly regarded in the environmental engineering field as being resistant to anaerobic biodegradation despite the pioneering research of Tarvin and Buswell (1934) which observed phenol as a transient intermediate in the anaerobic degradation of tyrosine. There were also early Polish reports of successful anaerobic degradation of phenolic compounds (Chmielowski et al. 1965) and of phenolic wastewaters (Chmielowski and Kusznik 1966). More recently Healy and Young (1978) demonstrated stoichiometric conversion of phenol and catechol to methane and carbon dioxide. With the expanding interest in anaerobic processes there has been a proliferation of research on the anaerobic biodegradation of phenolic substrates (Fedorak and Hrudey 1988a).

The various phenolics exhibit different degrees of anaerobic treatability. In relatively short term (45 d) batch cultures Fedorak and Hrudey (1984) found that of a series of phenolics (phenol, cresols and dimethyl phenols), only phenol and p-cresol were converted to methane. Subsequent investigations (Fedorak and Hrudey 1985) found that m-cresol was also degradable to methane, but less readily than p-cresol and phenol. These findings were consistent with those of Boyd et al. (1983).

Differences in degradation pathways for different phenolics are also suggested. Balba and Evans (1980) proposed an anaerobic pathway for phenol metabolism by ring cleavage and Young and Rivera (1985) demonstated that p-cresol was metabolized to phenol prior to mineralization. However, Roberts et al. (1987) found that the methyl carbon of p-cresol was mainly (92%) oxidized to carbon dioxide while the methyl carbon of m-cresol was mainly (87%) converted to methane.

Prepared Phenolic Wastewaters

Successful continuous laboratory-scale anaerobic treatment of wastewaters prepared with nutrient solutions and pure phenolic compounds has been demonstrated in several cases. Khan et al. (1981) treated phenol concentrations of 200 to 1,000 mg/L in a three-stage anaerobic activated carbon filter with intermediate effluent recycle. Khan et al. (1982) compared anthracite with activated carbon in anaerobic filters treating phenol and found the activated carbon to be superior. Suidan et al. (1981a, 1981b) studied a prepared wastewater containing phenol, o-cresol and catechol using a similar methodology. Phenol and catechol were readily degraded with methane production . o-Cresol was removed only by adsorption and it eventually broke through when the carbon was saturated. Wang et al. (1986) demonstrated 99.9% phenol removal in an anaerobic activated carbon reactor receiving phenol feed concentrations up to 2864 mg/L. Kim et al. (1986) demonstrated that anaerobic activated carbon filters bioregenerated the adsorption capacity of the activated carbon.

Suidan et al. (1983a) studied a two stage anaerobic filter on a complex prepared wastewater designed to simulate coal conversion wastewater. The first stage consisted of polypropylene berl saddles and the second stage consisted of granular activated carbon. The first stage provided relatively insignificant treatment with only 7.6% phenol removal compared with 99.8% in the activated carbon stage. Suidan et al. (1983b) coupled this process train with an activated sludge nitrification system to achieve excellent overall treatment of a prepared coal gasification wastewater.

Authentic Phenolic Wastewaters

Khan et al. (1982) treated a phenolic aircraft paint-stripping wastewater using a granular activated carbon column for an anaerobic reactor. The wastewater had to be nutrient-supplemented and diluted to about 500 mg/L of phenol and 1460 mg/L of COD. Their system achieved 82% phenol removal and 90% COD removal while actively producing methane.

Cross et al. (1982) treated a coal gasification wastewater with a 2 stage anaerobic filter (first stage packed with Raschig rings, second with granular activated carbon). The raw wastewater contained 5600 mg/L of phenol and a COD of 26,900 mg/L and was diluted to 10% V/V prior to treatment. At a loading rate of 2.5 kg COD / m^3, COD removals were near 80% and phenol and cresol removals exceeded 90 and 99% respectively. The system actively produced methane.

Suidan et al. (1983) treated coal gasification wastewater in an expanded bed activated carbon filter. They demonstrated the utility of activated carbon at enhancing the anaerobic conversion of phenol to methane (reduction from 207 mg/L influent to 0.08 mg/L in the effluent) while providing adsorptive removal of nondegradable o-cresol and the dimethylphenols. Extraction of the activated carbon after 302 d of operation confirmed the enhanced adsorption of the higher molecular weight but non-degradable dimethylphenols.

Ossio and Fox (1980) studied laboratory scale treatment of oil shale retort process wastewaters. Although no phenolic composition data was presented, this waste would be expected to contain substantial quantities of phenolics. Wastewater COD concentrations ranged from 9440 to 29,000 mg/L. Following ammonia stripping at pH 11, neutralization with carbon dioxide and nutrient addition (calcium, magnesium and phosphorus) the anaerobic digestor was able to achieve a 65 to 75% COD and 90% BOD_5 removal.

Umfleet (1981) studied the treatability of a coal gasification wastewater using a patented fixed film anaerobic process. The wastewater which contained phenolics totalling 4,900 mg/L was judged to be untreatable even at dilutions down to 5 to 7% by volume.

Fedorak and Hrudey (1985) studied the batch anaerobic treatability of phenolic condensates from an H-Coal conversion demonstration plant. The wastewater had a COD of 21,100 mg/L and total phenolics (phenol, cresols and dimethylphenols) of about 7500 mg/L. Batch treatment was only possible at large dilutions with successful treatment yielding methane achieved at concentrations less than 6% V/V, whereas concentrations of 8 and 10% V/V were found to be inhibitory. The inhibition was attributed to ether-extractable components.

Studies of the dynamics of phenolic degradation, at concentrations of a few hundred mg/L, by semi-continuous cultures showed that process failure was indicated when m-cresol degradation began to fail (Fedorak and Hrudey, 1986a). This was followed closely by p-cresol failure and ultimately failure of phenol degradation.

Britz et al. (1988) studied the nutrient requirements for anaerobic biological treatment of wastewater from the Fischer-Tropsch Sasol coal to oil process. They found minimum phosphate and nitrogen requirements of 8 mg/L PO_4-P and 45 mg/L TKN respectively. Fedorak and Hrudey (1986b) found that anaerobic cultures converting phenol and p-cresol to methane apparently required a source of carbon dioxide (bicarbonate) in addition to sources of nitrogen and phosphorus. Nutrient solutions containing B vitamins and trace metals were not required.

Dealing with Inhibition of Anaerobic Processes

Assessment of Inhibitors

Blum et al. (1986) studied a variety of constituents reported in coal conversion wastewaters for their biodegradability and their inhibition of acetate conversion to methane. Of the components tested, the only ones causing inhibition at concentrations expected in coal conversion wastewaters were phenol , resorcinol, catechol, o-cresol, 2,3-dimethylphenol and 4-ethylphenol.

Fedorak et al. (1986) studied the role of cyanide inhibition on the anaerobic biodegradation of several phenolics (phenol, m-cresol, p-cresol, catechol and hydroquinone). Methanogens were found to be more sensitive to cyanide than phenolic degrading bacteria. The effect of cyanide inhibition of phenolic degradation in batch cultures was caused by the buildup of the endproducts of non-methanogenic fermentation (e.g. acetate). However, semi-continuous cultures were able to adapt to 5 mg/L of cyanide and produce methane at the same rate as a cyanide-free control. Subsequent studies (Fedorak and Hrudey 1988b) with semi-continuous phenol-degrading anaerobic cultures have demonstrated an ability for methanogenic consortia to detoxify total cyanide concentrations of 30 mg/L.

Solvent Extraction

Kindzierski et al. (1988a) evaluated pH control for di-isopropyl ether extraction pretreatment of coal conversion wastewater. Batch anaerobic cultures operated on wastewater extracted at different pH and corresponding phenolic levels indicated no substantial inhibition. Kindzierski et al. (1988b) used this experience to design anaerobic semi-continuous treatment of undiluted coal conversion wastewater. Phenol strength was brought to treatable levels by extracting at pH levels from 8.5 to 9. Complete phenol removal with methane production was demonstrated.

Activated Carbon Intervention

Wang et al. (1984) studied the performance of an anaerobic activated carbon filter receiving a nutrient medium containing indole, quinoline and methylquinoline. Effective anaerobic treatment with methane production was achieved until inhibitory methylquinoline exceeded the carbon adsorption capacity and broke through.

Reducing inhibitory effects with activated carbon was studied by Fedorak et al. (1985). This work with H-Coal wastewater demonstrated that addition of activated carbon to batch cultures substantially reduced acclimation times and allowed batch phenolic concentrations up to 900 mg/L to be treated with conversion to methane. Harper et al. (1983) also demonstrated a beneficial role for activated carbon in treating gasification wastewater from the the Grand Forks Energy Technology Center.

Pfeffer and Suidan (1985) demonstrated that the expanded bed activated carbon filter could anaerobically treat a full strength coal gasification wastewater (about 4400 mg/L total phenolics) with methane production, provided that carbon was regularly replaced. They arbitrarily choose a replacement rate of 10% per week which gave 0.38 g of COD removed per g of carbon replaced. With this adjustment, excellent phenolic removals were achieved. Fox et al. (1988) and Suidan et al. (1987) achieved high levels of treatment on a synthetic coal conversion wastewater until o-cresol levels in reactors reached about 50 mg/L. At such times, replacement of 10% of the carbon allowed the system to recover.

Edeline et al (1986) studied anaerobic treatment of coke plant wastewater in a two stage filter. They experienced a series of failures until they incorporated activated carbon into the first stage. They found they could treat a steady state influent concentration of 1,250 mg/L of phenol in the presence of 400 mg/L of thiocyanate. The latter was undegraded by the process.

Gardner et al. (1988) reported the use of an expanded bed, granular activated carbon reactor for refinery sour water stripper bottoms. They achieved COD removals of 83 to 91% when treating full strength waste. By comparison, filters operated with non-activated carbon failed because of inhibition problems. They also concluded that regular carbon replacement would be necessary to maintain process performance.

CONCLUSIONS

Considerable knowledge has been gained in the past 10 years on the capability of anaerobic biological systems for industrial waste treatment. Phenolic waste degradation, in particular, is subject to rapidly emerging knowledge. Full scale application of anaerobic process technology to synthetic fuels wastewaters will likely require the use of:

- some pretreatment to control total phenolic concentrations,
- activated carbon support media in anaerobic filters,
- regular replacement of activated carbon media to avoid break through of inhibitors, and
- some polishing treatment to convert the anaerobic effluent to discharge standards.

With appropriate development, anaerobic biotechnology offers considerable promise for cost effective treatment of the complex high strength wastewaters which can be expected from the synthetic fuels industry.

REFERENCES

Balba, M.T. and Evans, W.C. (1980). The anaerobic dissimilation of benzoate by *Pseudomonas aeruginosa* coupled with *Desulfovibrio vulgaris* with sulphate as a terminal electron acceptor. *Biochem. Soc. Trans.* **8**, 624-625.

Blum, D.J., Hergneroeder, R. Parkin, G.F. and Speece, R.E. (1986). Anaerobic treatment of coal conversion wastewater constituents: biodegradability and toxicity. *J. Water Pollut Control Fed.* **58**, 122-131.

Boyd. S.A. , Shelton, D.R. , Berry, D., and Tiedje, J.M. (1983). Anaerobic biodegradation of phenolic compounds in digested sludge. *Appl. Environ. Microbiol.* **46**, 50-54.

Britz, T.J., Noeth, C. and Lategan, P.M. (1988). Nitrogen and phosphate requirements for the anaerobic digestion of a petrochemical effluent. *Water Res.* **22**, 163-169.

Chmielowski, J., Grossman, A. and Labuzek, S. (1965). Biochemical degradation of some phenols during methane fermentations. *Zesz. Nauk. Politech. Slaska., Inz., Sanit.* (Pol.), **8**, 97-122.

Chmielowski, J, and Kusznik, W. (1966). Preliminary trials on the methane fermentation of some phenolic wastewaters. *Zesz. Nauk. Politech. Slaska., Inz., Sanit.* (Pol.), **9**, 123-144.

Cross, W.H., Chian, E.S.K., Pohland, F.G., Harper, S., Kharkar, S., and Lu, F. (1982). Anaerobic biological treatment of coal gasifier effluent. *Biotechnol. Bioeng. Symp.* No. **12**, J. Wiley & Sons, New York, 349-363.

Edeline, F., Lambert, G. and Fatticcioni, H. (1986). Anaerobic treatment of coke plant waste water. *Process Biochem.* **21**, 2, 58-60.

Fedorak, P.M. and Hrudey, S.E. (1984) The effects of phenol and some alkyl phenolics on batch anaerobic methanogenesis. *Water Res.* **18**, 361-367.

Fedorak, P.M. and Hrudey, S.E. (1985). Batch anaerobic methanogenesis of phenolic coal conversion wastewater. *Water Sci. Technol.* **17**, 143-154.

Fedorak, P.M. and Hrudey, S.E. (1986a). Anaerobic treatment of phenolic coal conversion wastewater in semi-continuous cultures. *Water Res.* **20**, 113-122.

Fedorak, P.M. and Hrudey, S.E. (1986b). Nutrient requirements for the methanogenic degradation of phenol and p-cresol in anerobic draw and feed cultures. *Water Res.* **20**, 929-933.

Fedorak, P.M. and Hrudey, S.E. (1988a). Anaerobic degradation of phenolic compounds with application to treatment of industrial wastewaters. In: Biotechnology Applied to Environmental Problems: A. Bioenvironmental Systems. Ed. Wise, D.L. CRC Press, Boca Raton, Florida, In press.

Fedorak, P.M. and Hrudey, S.E. (1988b) Cyanide transformation in anaerobic phenol-degrading methanogenic cultures. *Water Sci. Technol.* In press.

Fedorak, P.M., Knettig, E. and Hrudey, S.E. (1985). The effects of activated carbon on the methanogenic degradation of phenolics in H-Coal wastewater. *Environ. Technol. Lett.* **6**, 181-187.

Fedorak, P.M., Roberts, D.J. and Hrudey, S.E. (1986). The effects of cyanide on the methanogenic degradation of phenolic compounds. *Water Res.* **20**, 1315-1320.

Fox, P., Suidan, M.T. and Pfeffer, J.T. (1988). Anaerobic treatment of a biologically inhibitory wastewater. *J. Water Pollut. Control Fed.* **60**, 86-92.

Gardner, D.A., Suidan, M.T. and Kobayashi, H. (1988). Role of GAC surface activity and particle size during fluidized bed anaerobic treatment of sour water stripper bottoms. *J. Water Pollut. Control Fed.* **60**, 505-513.

Harper, S.R., Cross, W.H., Pohland, F.G. and E.S.K. Chian. (1983). Adsorption-enhanced biogasification of coal conversion wastewater. *Biotechnol Bioeng. Symp.* **13**, J. Wiley & Sons, New York, 401-420.

Healy, J.B. and Young, L.Y. (1978). Catechol and phenol degradation by a methanogenic population of bacteria. *Appl. Environ. Microbiol.* **35**, 216-218.

Khan, K.A., Suidan, M.T. and Cross, W.H. (1981). Anaerobic activated carbon filter for the treatment of phenol-bearing wastewater. *J. Water Pollut. Control Fed.* **53**, 1519-1532.

Khan, K.A., Suidan, M.T. and Cross, W.H. (1982). Role of surface active media in anaerobic filters. *J. Environ. Eng. Div. Am. Soc. Civ. Eng.* **108**, 269-285.

Kim, B.R., Chian, E.S.K., Cross, W.H. and Cheng, S.S. (1986). Adsorption, desorption and bioregeneration in an anaerobic granular activated carbon reactor for the removal of phenol. *J .Water Pollut. Control Fed.* **58**, 35-40.

Kindzierski, W.B., Hrudey, S.E. and Fedorak, P.M. (1988a) Solvent extraction and anaerobic biological treatment of a high strength phenolic wastewater. *Proc. CSCE-ASCE National Conf. Environ. Eng.* Vancouver, In Press.

Kindzierski, W.B., Hrudey, S.E. and Fedorak, P.M. (1988b) Anaerobic semi-continuous treatment of solvent-extracted, undiluted coal conversion wastewater. Summer Nat. Meeting A.I.Ch.E., Denver.

Neufeld, R.D. (1984). The treatment of wastes from the synthetic fuels industry. In: *Surveys in Industrial Wastewater Treatment.* **2** (Ed. Barnes, D., Forster, C. and S.E. Hrudey) Longmans, London, 65-129.

Ossio, E. and Fox, P. (1980). Anaerobic biological treatment of in-situ retort water. Lawrence Berkeley Laboratory publ. no. LBL-10481. University of California, 47pp.

Pfeffer, J.T. and Suidan, M.T. (1985). Anaerobic-aerobic process for treating coal gasification wastewater. Presented at Industrial Wastes Symposium, 58th Conference, Water Pollution Control Federation. Kansas City.

Roberts, D.J., Fedorak, P.M. and Hrudey, S.E. (1987). Comparison of the fates of the methyl carbons of m-cresol and p-cresol in methanogenic consortia. *Can. J. Microbiol.* **33**, 335-338.

Speece, R.E. (1983) Anaerobic biotechnology for industrial wastewater treatment. *Environ. Sci. Technol.* **17**, 416a-427a

Suidan, M.T., Cross, W.H., Fong, M. and Calvert, J.W. (1981a). Anaerobic carbon filter for degradation of phenols. *Environ. Eng. Div., Am Soc. Civ. Eng.,* **107**, 563-579.

Suidan, M.T., Cross, W.H., Khan, K.A. and Fong, M. (1981b). Treatment of phenol and substituted phenols with an anaerobic activated carbon filter. In: Chemistry in Water Reuse. **2**, Ed. by W.J. Cooper, Ann Arbor Sci. , 509-520.

Suidan, M.T., Strubler, C.E., Kao, S.W. and Pfeffer, J.T. (1983a). Treatment of coal gasification wastewater with anaerobic filter technology. *J. Water Pollut. Control Fed.* , **55**, 1263-1270.

Suidan, M.T., Siekerka, G.L., Kao, S.W. and Pfeffer, J.T. (1983b). Anaerobic filters for the treatment of coal gasification wastewater. *Biotechnol. Bioeng.* **25**, 1581-1596.

Suidan, M.T., Fox, P. and Pfeffer, J.T. (1987). Anaerobic treatment of coal gasification wastewater. *Water Sci. Technol.* **19**, 229-236.

Tarvin, D. and Buswell, A.M. (1934). The methane fermentation of organic acids and carbohydrates. *J. Am. Chem. Soc.* **56**, 1751.

Umfleet, R.A. (1981). Evaluation of the treatability of coal gasification waste by the Celrobic process. Rep. DOE/PL/30189-1. Pittsburgh Energy Technology Center, NTIS Publ. DE82-010099.

Young, L.Y. and Rivera, M.D. 1985. Methanogenic degradation of four phenolic compounds. *Water Res.* **19**, 1325-1332.

Wang, Y.-T., Suidan, M.T. and Pfeffer, J.T. (1984). Anaerobic activated carbon filter for the degradation of polycyclic N-aromatic compounds. *J. Water Pollut. Control Fed.* , **56**, 1247-1253.

Wang, Y.-T., Suidan, M.T. and Rittman, B.E. (1986). Anaerobic treatment of phenol by an expanded-bed reactor. *J. Water Pollut. Control Fed.* , **58**, 227-233.

Dr. Steve E. Hrudey is a Professor of Environmental Engineering, at the University of Alberta. He has been engaged in teaching, research and consulting in industrial and hazardous waste management for 18 years. He currently serves as Chairman of the Toxic and Hazardous Wastes Management Committee of the Canadian Society for Civil Engineering and is a member of the Editorial Advisory Board for the journals, *Environmental Technology Letters* (London) and *Hazardous Wastes and Hazardous Materials* (New York).

AUTHORS' INDEX

AUTHORS' INDEX (CONTINUED)