Fuel-Flexible Gasification-Combustion Technology for Production of H_2 and Sequestration-Ready CO_2

Final Technical Report

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ABSTRACT

In the near future, the nation will continue to rely on fossil fuels for electricity, transportation, and chemicals. It is necessary to improve both the process efficiency and environmental impact of fossil fuel utilization including greenhouse gas management. GE Global Research (GEGR) investigated an innovative fuel-flexible Unmixed Fuel Processor (UFP) technology with potential to produce H_2, power, and sequestration-ready CO_2 from coal and other solid fuels. The UFP technology offers the long-term potential for reduced cost, increased process efficiency relative to conventional gasification and combustion systems, and near-zero pollutant emissions. GE was awarded a contract from U.S. DOE NETL to investigate and develop the UFP technology. Work started on the Phase I program in October 2000 and on the Phase II effort in April 2005.

In the UFP technology, coal, water and air are simultaneously converted into (1) hydrogen rich stream that can be utilized in fuel cells or turbines, (2) CO_2 rich stream for sequestration, and (3) high temperature/pressure vitiated air stream to produce electricity in a gas turbine expander. The process produces near-zero emissions with an estimated efficiency higher than Integrated Gasification Combined Cycle (IGCC) process with conventional CO_2 separation. The Phase I R&D program established the chemical feasibility of the major reactions of the integrated UFP technology through lab-, bench- and pilot-scale testing. A risk analysis session was carried out at the end of Phase I effort to identify the major risks in the UFP technology and a plan was developed to mitigate these risks in the Phase II of the program.

The Phase II effort focused on three high-risk areas: economics, lifetime of solids used in the UFP process, and product gas quality for turbines (or the impact of impurities in the coal on the overall system). The economic analysis included estimating the capital cost as well as the costs of hydrogen and electricity for a full-scale UFP plant. These costs were benchmarked with IGCC polygen plants with similar level of CO_2 capture. Based on the promising economic analysis comparison results (performed with the help from WorleyParsons), GE recommended a “Go” decision in April 2006 to continue the experimental investigation of the UFP technology to address the remaining risks i.e. solids lifetime and the impact of impurities in the coal on overall system. Solids attrition and lifetime risk was addressed via bench-scale experiments that monitor solids performance over time and by assessing materials interactions at operating conditions. The product gas under the third reactor (high-temperature vitiated air) operating conditions was evaluated to assess the concentration of particulates, pollutants and other impurities relative to the specifications required for gas turbine feed streams. During this investigation, agglomeration of solids used in the UFP process was identified as a serious risk that impacts the lifetime of the solids and in turn feasibility of the UFP technology. The main causes of the soilds agglomeration were the combination of oxygen transfer material (OTM) reduction at temperatures ~1000ºC and interaction between OTM and CO_2 absorbing material (CAM) at high operating temperatures (>1200ºC).

At the end of phase II, in March 2008, GEGR recommended a “No-go” decision for taking the UFP technology to the next level of development, i.e. development of a 3-5 MW prototype

system, at this time. GEGR further recommended focused materials development research programs on improving the performance and lifetime of solids materials used in UFP or chemical looping technologies. The scale-up activities would be recommended only after mitigating the risks involved with the agglomeration and overall lifetime of the solids.

This is the final report for the phase II of the DOE-funded Vision 21 program entitled "Fuel-Flexible Gasification-Combustion Technology for Production of H_2 and Sequestration-Ready CO_2" (DOE Award No. DE-FC26-00NT40974). The report focuses on the major accomplishments and lessons learned in analyzing the risks of the novel UFP technology during Phase II of the DOE program.

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EXECUTIVE SUMMARY

GE Global Research (GEGR) investigated an innovative fuel-flexible Unmixed Fuel Processor (UFP) technology with potential to produce H_2, power, and sequestration-ready CO_2 from coal and other solid fuels. The UFP technology offers the long-term potential for reduced cost, increased process efficiency relative to conventional gasification and combustion systems, and near-zero pollutant emissions.

GE was awarded a contract from U.S. DOE NETL to develop the UFP technology. Work started on the Phase I program in October 2000 and on the Phase II effort in April 2005. The Phase I R&D program established the chemical feasibility of the major reactions of the integrated UFP technology through lab-, bench- and pilot-scale testing. A risk analysis session was carried out at the end of Phase I effort to identify the major risks in the UFP technology and a plan was developed to mitigate these risks in the Phase II of the program.

The Phase II effort focused on three high-risk areas: economics, lifetime of the solids used in the UFP process, and product gas quality for turbines (or the impact of impurities in the coal on the overall system). This final report summarizes the phase II program accomplishments and recommended future work.

The major accomplishments and lessons learned during the program are listed below.

Systems and economic analysis of UFP:

GEGR worked with WorleyParsons to develop detailed estimates of UFP plant costs to assess the commercialization potential of the technology and guide future development efforts. An apples-to-apples economic comparison was made between the UFP technology and the conventional IGCC-polygen technology with similar process parameters including the level of CO_2 capture.

- The economic analysis comparison of the UFP technology with the conventional IGCC-polygen technology performed with today's understanding suggests that the UFP technology may have cost advantages over IGCC-polygen technology with CO_2 capture. The analysis suggests that the capital cost for the UFP technology may be lower than the IGCC-polygen technology by ~10%. The potential lower cost of UFP technology can be attributed to the following two factors:

    1. UFP technology does not require the air separation unit (ASU) to separate O_2 from air, and,

    2. UFP technology captures CO_2 inherently at high temperature and pressure resulting in lower compression costs

- The baseline cost of hydrogen product from the UFP process was estimated to be ~10% lower than the IGCC-polygen technology. However, the technical assumptions such as

conversion, yield, solids lifetime and impact of coal impurities, going into the economic analysis, need to be validated experimentally.

- The solids lifetime and in turn the annual cost of the solids used in the process was identified as the main parameter influencing the economic feasibility of the UFP technology.

The task to establish the economic feasibility of the UFP technology was completed and the results were communicated to DOE in a program review meeting on April 12, 2006. Based on this economic analysis comparison completed with the help of WorleyParsons, GE recommended a “Go” decision to evaluate the technical feasibility of the UFP technology experimentally.

Experimental evaluation of UFP technology:

The UFP technology was evaluated using a bench-scale and a pilot-scale experimental system during the Phase II of the program.

- The pilot-scale system designed and fabricated during the Phase I of the program was upgraded to improve its reliability and experiments were carried out using a single reactor. Although successful, these experimental evaluations during year 2006 revealed that the smaller bench-scale experimental system was better suited to evaluate and mitigate the risks of solids lifetime and impact of coal impurities as compared to the larger pilot-scale system. The experimental results further revealed that the major technical risks should be mitigated before carrying out extensive pilot-scale testing. Based on experimental results and analysis in 2006, GEGR recommended a revised plan for the remaining part of the Phase II investigation in 2007. GE and DOE leadership approved the revised experimental plan in December 2006. In year 2007, the bench-scale system was used to carry out the evaluation and mitigation of the major UFP risks: solids lifetime and impact of coal impurities.

- The bench scale UFP reactor was also upgraded to have multiple coal injections and to operate at high temperatures required for UFP process. The upgrade improved the injection reliability and the system was capable of performing multiple sequential coal injections into fluidized bed reactor for studying the rates of important gasification steps such as devolatilization, char formation and gasification occurring in reactor 1 (R1). The system was also upgraded with a ceramic reactor to investigate the UFP reactions and solids interactions in the temperature range of 1000-1300ºC that reactor 2 (R2) and reactor 3 (R3) are expected to operate at.

Impact of impurities such as sulfur in the coal on the UFP process:

- The impact of impurities in the coal on the UFP process was predicted through controlled experiments using the upgraded bench-scale reactor. The experiments were focused on understanding the fate of sulfur containing species in the coal. The sulfur species in the coal can interact irreversibly with the solid material used in the UFP process or can be emitted as H_2S from R1 and R2, or, can come out as SO_2 from R3. The interaction of sulfur with the solids would impact the lifetime of the solids. The H_2S coming out from R1 and R2 can be removed by cooling these process streams and then capturing sulfur using commercial processes such as Selexol (costs were accounted for in the economic analysis). Handling and clean-up of SO_2 coming out of R3 would be challenging as this stream directly enters in a gas turbine expander to generate electricity. The sulfur content in R3 stream would influence the gas turbine expander cost and reliability. Further, SO_2 in the R3 stream would be diluted with air resulting in higher clean-up costs because of the high flow rate of the total stream. Therefore, it would be desirable to optimize the UFP process conditions in such way that the amount of SO_2 in R3 is minimized. The fate of sulfur in the UFP process was investigated by measuring the concentration of SO_2 in the product gas coming out in simulated R3 conditions in the bench-scale reactor. It was predicted that the SO_2 concentration in the R3 exhaust might be a strong function of the total sulfur content in the coal. When a low rank coal such as PRB coal with very low sulfur content is used in the UFP process the SO_2 concentration in the exhaust may be similar to that of an IGCC plant. However, for coals with higher sulfur content the SO_2 in the exhaust gas can be much higher than that of an IGCC plant, indicating the need for additional sulfur clean-up process on the R3 exhaust stream. The cost impact of additional sulfur clean-up processes on the overall cost of the UFP process needs to be analyzed.

Lifetime of the solids material used in the UFP technology:

- Solid lifetime was evaluated by studying solid materials attritions and agglomeration under the UFP conditions in the bench-scale reactor. Physical attritions of both CAM and OTM were observed. Although the attrition index was moderate under the testing conditions, particle size for the bed materials was reduced after physical attrition tests. Also, decomposition of the CAM accelerated its physical attrition. Reaction between the OTM and CAM was predicted with material thermodynamics and was confirmed with the experimental works.

- It was found that the lifetime of the solid is one of the key technical risks and the cost and technical feasibility of UFP are critically dependent on the materials performance and durability. Agglomeration of solid materials was one of the main concerns of the solid lifetime. Numbers of causes to agglomeration were tested and analyzed. The main causes of agglomeration were the combination of OTM reduction and high temperatures exposure. At moderate temperatures, say 1000ºC, the reduction of OTM caused the surface morphology/composition to change and intensified the interaction between CAM and OTM, which resulted in bed materials agglomeration. Heat-treatment at 1000ºC in the absence of OTM reduction wouldn't cause the bed agglomeration. However, at higher temperatures (>1200ºC), significant chemical interactions were predicted between OTM and CAM, and thus the agglomeration can occur even in the absence of OTM reduction.

At the end of this study the team concluded that the solids agglomeration risk needs to be mitigated via focused research programs for the UFP and other chemical looping technologies using coal as a fuel to be commercially viable.

Technology status and recommendations:

At the end of phase II, in March 2008, GEGR recommended a “No-go” decision for taking the UFP technology to the next level of development, i.e. development of a 3-5 MW prototype system, at this time. GEGR further recommended focused materials development research programs on improving the performance and lifetime of solids materials used in UFP or chemical looping technologies. The scale-up activities would be recommended only after mitigating the risks involved with the agglomeration and overall lifetime of the solids. A final review meeting with DOE was held on March 6, 2008.

1 INTRODUCTION

Projections of increased demands for energy worldwide, coupled with increasing environmental concerns have given rise to the need for innovative technologies for coal-based energy plants. Incremental improvements in existing plants will likely fall short of meeting future capacity and environmental needs. The objective of this Phase II research and development program was to further investigate GE's novel Unmixed Fuel Processor (UFP) technology, which includes quantifying the economic benefits and characterizing the technical risks associated with solids attrition/lifetime and product gas quality through experimental evaluation at both bench- and pilot-scales, as well as through engineering and modeling efforts.

The UFP technology is a new concept with the long-range potential for energy efficient, near-zero pollution conversion of coal into separate streams of hydrogen, sequestration-ready CO_2, and vitiated air. It has the potential to meet the DOE's future energy plant objectives of efficiently and economically producing energy and hydrogen from coal with utilization of opportunity feedstocks.

GE Global Research was the primary contractor for the UFP program under a contract from U.S. DOE NETL (Contract No. DE-FC26-00NT40974). This project integrated bench- and pilot-scale studies with process and economic modeling to investigate the UFP technology. The remainder of this section presents the objectives, concept, and main tasks of the UFP program.

1.1 Objectives

The primary objectives of the UFP program were to:

- Establish the economic feasibility and competitiveness of the UFP technology. Estimate capital cost and cost of hydrogen and electricity for a UFP plant and compare these costs with IGCC-Polygen with CO_2 capture technology costs. A "Go" decision to investigate the technical feasibility of the UFP technology was recommended based on the results of economic feasibility analysis.
- Quantify and assess the attrition, lifetime and performance of solid materials through bench-scale attrition testing and pilot-scale testing.
- Investigate the quality of the third-reactor product stream fed to the gas turbine; characterize the particulate, pollutant and other impurity concentrations in the stream and gauge the need for gas cleanup prior to feeding to the gas turbine.

Updates in the program schedule based on results obtained:

By the end of the first quarter in 2006, the task to establish the economic feasibility of the UFP technology was completed and the results were communicated to DOE in a program review meeting on April 12, 2006. An apples-to-apples economic comparison was made between the UFP technology and the conventional IGCC-polygen technology with similar process parameters. Based on this economic analysis comparison completed with the help of WorleyParsons, GE recommended a "Go" decision to evaluate the technical feasibility of the UFP technology experimentally. The highest technology risk elements such as solids lifetime and impact of impurities in the coal were investigated using the bench scale experimental system and the upgraded single pilot scale reactor in 2006. The results of the bench scale and single reactor testing and the test plan for 2007 were reviewed with DOE in December 2006.

Although successful, these 2006 experimental evaluations revealed that the smaller bench-scale experimental system is better suited to evaluate and mitigate the risks of solids lifetime and impact of coal impurities as compared to the larger pilot-scale system. The experimental results further revealed that the major technical risks should be mitigated before carrying out extensive pilot-scale testing. Based on experimental results and analysis in 2006, GE Global Research recommended a revised plan for the remaining part of the Phase II investigation. GE and DOE leadership approved the revised experimental plan in December 2006.

During the year 2007, bench-scale experimental system was upgraded and used to address the risk issues associated with UFP technology: solids lifetime and impact of coal impurities. In order to investigate the UFP technology risks in detail and to cover the final review meeting, GE requested a no-cost extension to the program until March 2008. A final review meeting with DOE was held on March 6, 2008.

Impact on the existing work statement:

The revised plan in 2007 did not change the deliverables or the budget of the current contract. The UFP technology risks was evaluated and a future plan and a Go/No-Go decision was communicated to DOE in March 2008. The impact of the revised plan on the main tasks in the work statement is summarized below:

Task 1 – Economic analysis and systems analysis: No impact, completed.

Task 2 – Attrition/lifetime testing: No impact, completed using bench-scale system.

Task 3 – Pilot plant baseline testing & contaminant fractionation: No impact, completed using single pilot-scale reactor.

Task 4 – Parametric testing: Bench-scale system was used instead of the pilot-scale system to identify optimum operating conditions to maximize the solids lifetime and minimize the impact of coal impurities.

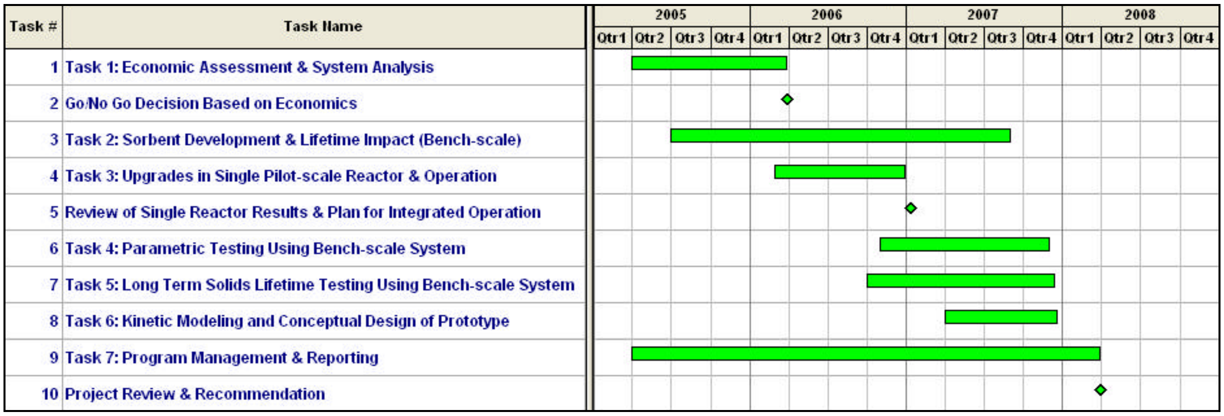
Task 5 – Long term testing: Lifetime testing of the solids was carried out using the bench-scale system. Long term testing will not be needed until the agglomeration risk is mitigated.

Task 6 – Kinetic modeling and conceptual design of prototype: The prototype design cannot be initiated before the lifetime risks of solid lifetime are mitigated. The impact of solids lifetime was evaluated in Task 1.

Task 7 – Program management and reporting: No impact, completed.

The revised UFP program tasks and schedules are summarized in Table 1.

Table 1-1 Main tasks and schedules for Phase II UFP program



Task #	Task Name	2005				2006				2007				2008			
		Qtr1	Qtr2	Qtr3	Qtr4	Qtr1	Qtr2	Qtr3	Qtr4	Qtr1	Qtr2	Qtr3	Qtr4	Qtr1	Qtr2	Qtr3	Qtr4
1	Task 1: Economic Assessment & System Analysis		🟩	🟩	🟩	🟩											
2	Go/No Go Decision Based on Economics					◆											
3	Task 2: Sorbent Development & Lifetime Impact (Bench-scale)			🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩					
4	Task 3: Upgrades in Single Pilot-scale Reactor & Operation					🟩	🟩	🟩	🟩								
5	Review of Single Reactor Results & Plan for Integrated Operation									◆							
6	Task 4: Parametric Testing Using Bench-scale System								🟩	🟩	🟩	🟩	🟩				
7	Task 5: Long Term Solids Lifetime Testing Using Bench-scale System								🟩	🟩	🟩	🟩	🟩				
8	Task 6: Kinetic Modeling and Conceptual Design of Prototype										🟩	🟩	🟩				
9	Task 7: Program Management & Reporting		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩			
10	Project Review & Recommendation													◆			

1.2 Technology Concept

The UFP technology makes use of three circulating fluidized bed reactors containing CO_2 absorbing material (CAM) and oxygen transfer material (OTM), as shown in Figure 1. CAM is a sorbent that absorbs CO_2 to form CAM-CO_2. OTM is a metal oxide, which can be oxidized to form OTM-O. A mixture of the bed materials is present in each reactor, and the bed materials undergo a variety of transformations and reactions as they move from one reactor to another. Each reactor serves a different key purpose: gasification, CO_2 release, or oxidation.

The first reactor from the left (R1) is the site of initial coal gasification. Coal fed to R1 is partially gasified with steam, producing H_2, CO and CO_2. Conditions in R1 facilitate CO_2 absorption by the CAM (CAM + CO_2 → CAM-CO_2). The reduction in gas-phase CO_2 concentration shifts the equilibrium of the water-gas shift reaction to deplete CO from the gas phase ($CO + H_2O \rightarrow H_2 + CO_2$). The removal of both CO and CO_2 from R1 results in an H_2-rich product stream suitable for use in liquefaction, fuel cells, or turbines after further treatment. The circulation of bed materials provides a continuous supply of fresh CAM from the second reactor (R2) and transfers spent CAM to R2 for regeneration.

The middle or the second reactor is the location of CO_2 release from spent CAM (CAM-CO_2 + heat → CAM + CO_2). The CAM is regenerated as the hot bed material transferred from the third reactor from the left (R3) enters R2, increasing the bed temperature to the level required for CO_2

release. This CO_2 release generates a CO_2-rich product stream suitable for sequestration upon further treatment. In addition, char present in the bed materials transferred from R1 is gasified in R2. The oxidized OTM transferred from R3 is reduced as it provides the oxygen needed to oxidize CO to CO_2 and H_2 to H_2O ($OTM\text{-}O + CO \rightarrow 2OTM + CO_2$ or $OTM\text{-}O + H_2 \rightarrow 2OTM + H_2O$).

The OTM is oxidized in R3 ($2OTM + \frac{1}{2} O_2 \rightarrow OTM\text{-}O + heat$). Air fed to R3 re-oxidizes the OTM via a highly exothermic reaction that consumes most of the oxygen in the air feed. Thus, R3 produces high-temperature, high-pressure oxygen-depleted (vitiated) air for a gas turbine expander as well as generating heat that is transferred to R1 and R2 via solids transfer.

Reactor 2 exchanges bed materials with both R1 and R3 (there is no direct R1-R3 transfer), allowing for the regeneration and recirculation of both the CAM and the OTM. CAM absorbs CO_2 in R1 and releases it in R2. OTM is oxidized in R3 and reduced in R2. In the experimental systems, the ash and bed materials will be removed from the system periodically and replaced with fresh bed materials. The impact of ash and other contaminants on the solids and other components was evaluated in the Phase II of the program.

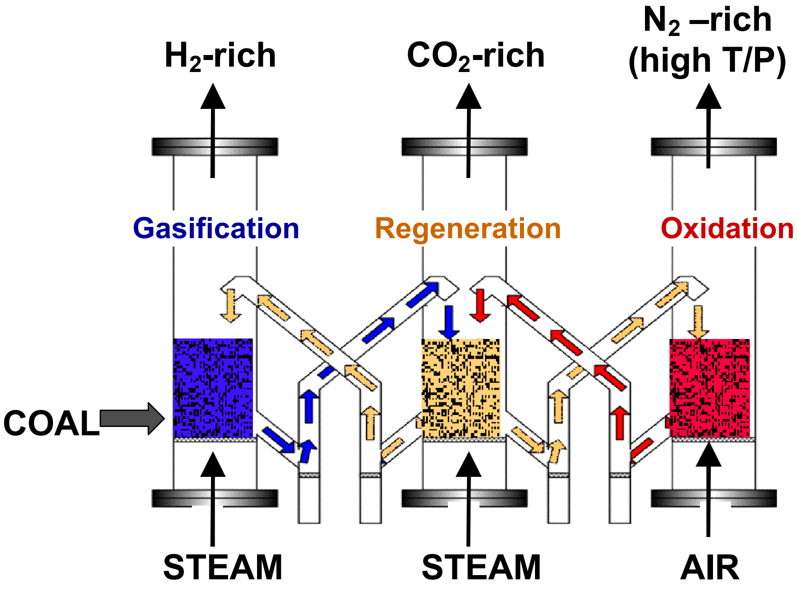


Figure 1-1 Conceptual design of the UFP technology.

2 EXPERIMENTAL

2.1 Economic Analysis

One of the objectives of this program was to reduce the technical and economic risks associated with a commercial full-scale UFP-based energy plant. GE Global Research worked with WorleyParsons to develop detailed estimates of UFP plant costs to assess the commercialization potential of the technology and guide future development efforts. The economic analysis was been focused on the following areas:

- Scale-up analysis of an UFP-based Polygen process to commercial scale using Aspen/Gate-cycle software.
- Preliminary design of commercial size reactors and auxiliary unit operations for CAPEX estimate.
- CAPEX and O&M cost estimates for UFP & IGCC polygen technologies.
- Calculation of cost of electricity (COE) and cost of hydrogen (COH).

Scale-up tools were developed for the conceptual design of an UFP-based full-scale system combined with power-island. Aspen software was used to develop material and energy balances for fully integrated power generation systems. MathCad and TechPlot software was used to scale up the UFP system from pilot-scale to commercial-scale with detailed reactor designs and equipment specifications, which provide the basis for economic analysis of the commercial-scale three-reactor UFP system. The scale-up information was provided to WorleyParsons to carry out an independent assessment of cost of the UFP technology. WorleyParsons reviewed the UFP information and provided the capital cost estimates for a full-scale UFP process combined with a power-island. WorleyParsons also provided capital cost estimates for IGCC and IGCC polygen system with CO_2 separation. Based on the capital cost and material and energy balance provided by Worley Parsons, cost of hydrogen and electricity were calculated for the UFP and IGCC technologies.

2.1.1 UFP System Analysis

In order for WorleyParsons to carry out the economic analysis of the UFP technology, the existing pilot-scale UFP system model was scaled up to commercial size, which included developing estimates of reactor sizes, construction materials and auxiliary equipment designs. Scale-up and equipment design requires detailed UFP system analysis to provide inputs to the reactor design, fluidization calculations and for Worley Parsons' CAPEX estimates.

Commercial-scale UFP system analysis was performed using Aspen software. Figure 2-1 shows a simplified process flow diagram developed using Aspen software. This Aspen analysis was scaled up to account for commercial scale power generation using dual 7FA turbines.

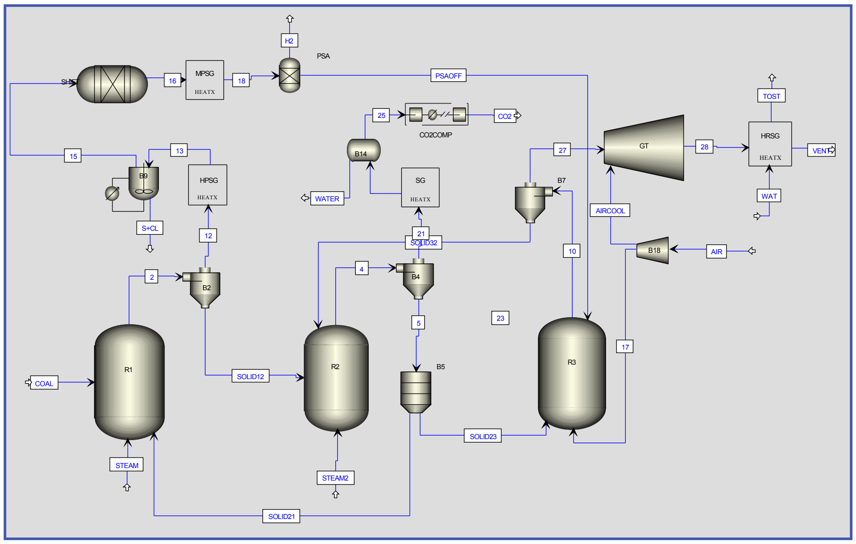


Figure 2-1 UFP process flow diagram

2.1.2 UFP Reactor Design and Scale-up Using Fluidization Modeling

The commercial scale UFP reactor system design was divided into three phases: (1) Fluidization calculations (2) Fluidization regime mapping/reactor type selection and (3) Reactor geometry optimizations. The following design criteria and resources were considered during these three design phases:

- Fluidization conditions and flow regimes
- Engineering estimations and “rule of thumbs”
- Literature and commercial scale application information, and
- Kinetic limitations

2.1.3 Fluidization Calculations

During detailed fluidization calculations, solid and gas flow rates, operating conditions, and gas-solid compositions were provided based on Aspen UFP system analysis results. For any given fluidized bed geometry (internal diameter, D and aspect ratio, L_{mf}/D), a series of fluidization condition parameters were calculated including the minimum fluidization velocity u_{mf} and maximum reactor aspect ratio $(L_{mf}/D)_{max,}$ bed void fraction, total reactor height, mass of the bed, solid residence time, superficial gas velocity, etc. By iteratively calculating the fluidization conditions for a series of bed dimensions, a fluidization design map was developed for each reactor.

2.1.4 Scale-up of UFP Process: Reactor Design Optimizations

The scale-up calculation was focused on optimizing the reactor designs of the commercial scale UFP process for the economic analysis. Sensitivity analysis was performed for the geometry of each of the three reactors as a function of the particle size of the CAM & OTM material. These calculations and analysis provided crucial information for the optimization of reactor designs to achieve the desirable fluidization conditions as well as the optimal solid separation approaches.

2.1.5 Peripheral Equipment Cost Estimations

Based on the optimal reactor geometries for the UFP system, the following equipments were also designed and their cost was estimated:

- Refractory materials for each reactor
- Reactor metal shell material
- Solid transfer legs, and
- Cyclones and filtration units

The list of equipment specifications along with the UFP process flow diagram were completed and submitted to WorleyParsons for cost estimations.

2.1.6 Capital Cost Estimation & Systems Analysis by Worley Parsons

WorleyParsons carried out systems analysis for a conventional IGCC process, IGCC polygen system with CO_2 capture and the UFP process. WorleyParsons used GateCycle software for power-island analysis. GE simulated the chemical processes using Aspen Plus. WorleyParsons estimated the capital cost for the above technologies using their cost database for the IGCC processes and the scale-up information about the UFP technology provided by GE.

2.1.7 Cost of Hydrogen and Electricity estimation

GE calculated the costs of hydrogen and electricity using an economic analysis model based on DOE's H2A model.

2.2 Pilot-scale System

The pilot-scale system was assembled in Phase I of the program. The assembled pilot reactors are shown in Figure 2-2 while the P&ID of the pilot-scale system is shown in Figure 2-3. The system was composed of three interconnected circulating fluidized bed reactors designed to operate at temperatures between 700°C to 1100°C. Superheated steam, at 400°C and compressed process air were fed through five sets of heating tube coils, each set encased in a 45-kW electric furnace, which then exited from the top of each furnace to the UFP reactors. The interconnected reactor system was composed of three vessels: Reactor 1 (R1), Reactor 2 (R2), and Reactor 3 (R3) where bed material circulated throughout the vessels through a series of interconnected ducts (solids-transfer legs). Products generated included H_2, CO_2, N_2 and traces of CO, SO_2, CH_4 and others. A small fraction of the product streams was analyzed and discharged while the balance was released into an emissions process-control unit.

Figure 2-2 Assembled pilot reactors on the stands

During the initial experiments, the reduction-oxidation chemistry of OTM was validated under the coal feeding conditions. The pilot-scale experimental system designed in the Phase I of this program was operated for the first time for extended period and several limitations of the current design were identified during the operation. The pilot-scale system was then upgraded to overcome some of the observed limitations. The major upgrades needed mainly included a robust auxiliary heating system to maintain required operating temperatures and continuous removal of ash from the reactors. The system design was also tested for the mechanical stresses under the desired operated conditions.

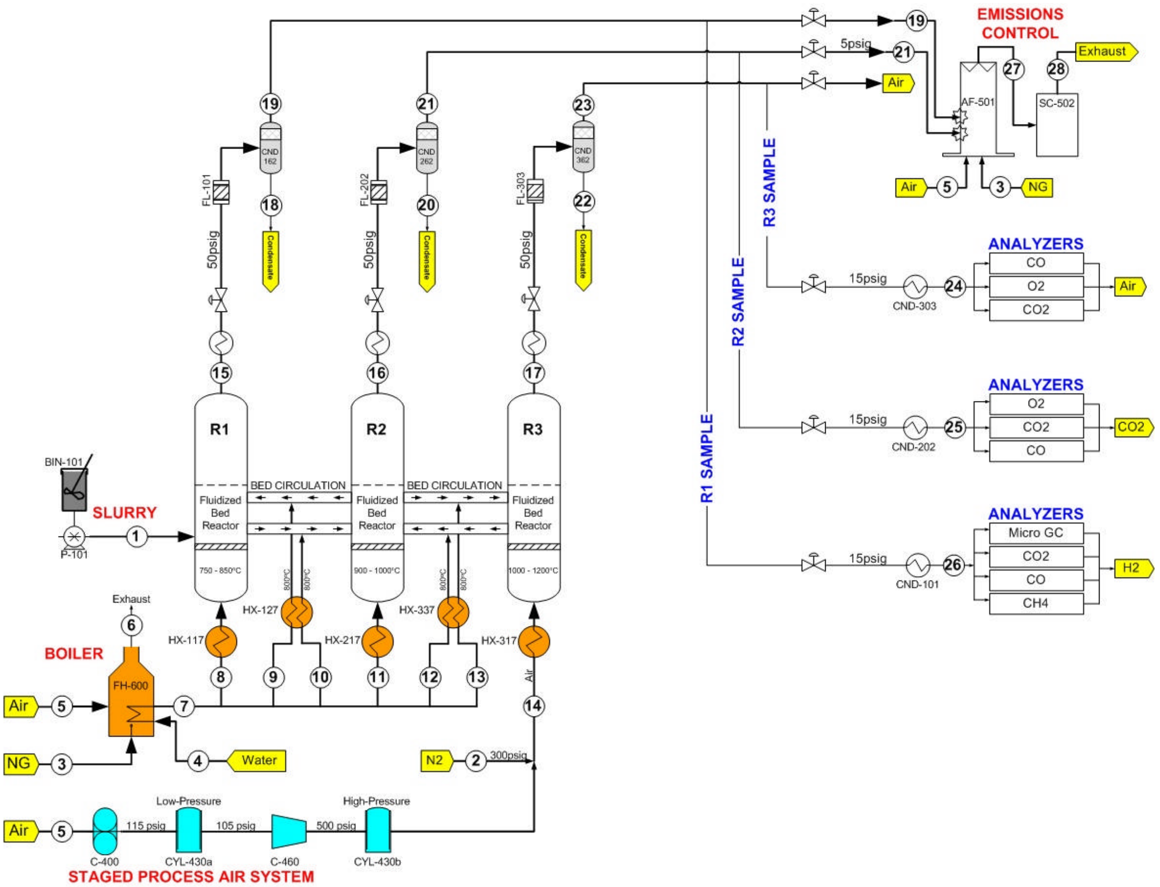


Figure 2-3 P&ID of the pilot scale system

2.3 Bench-Scale Reactor

In addition to the pilot-scale system, a bench-scale reactor was extensively used for experiments in the current phase of the program. The system, shown in Figure 2-4, consisted of a tubular reactor, a high temperature furnace, a gas feeding system, a steam generator, a coal feeder, product gas analyzers, and a data acquisition system. The product gas exiting the reactor passed through a condenser to remove steam before it could condense in the backpressure regulator that maintained reactor pressure. A set of continuous emission monitors (CEMs) was used to measure the concentration of the dry gas. This included monitoring for CO, CO_2, H_2, SO_2, O_2 and CH_4. A gas chromatograph (GC) was also used intermittently to measure these gases as well as others such as H_2S.

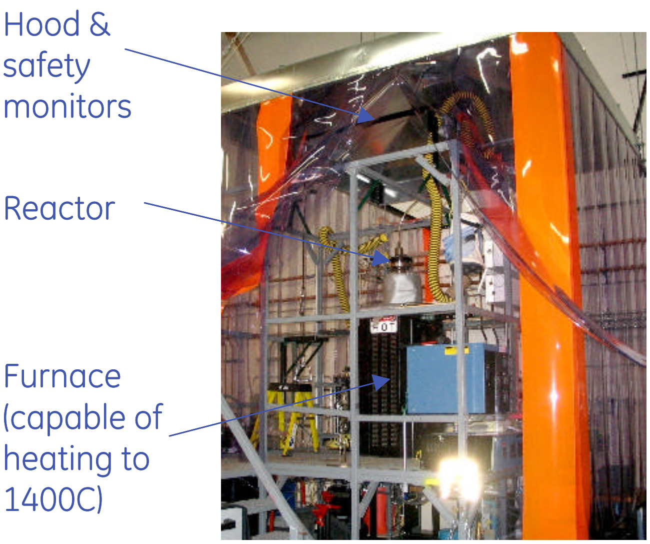


Figure 2-4 Bench-scale reactor

A Labview™ FieldPoint™ data acquisition system was programmed to collect temperature, pressure, flow rate and concentration data and record it for later analysis, as well as to display the data for the benefit of system operators. The program displayed real-time data and a graphical history of measurement values. Data collected was formatted for compatibility with calculation templates to facilitate rapid data analysis. Figure 2-5 is the process and instrumentation diagram for the bench-scale system. All thermocouples, pressure transducers and flow measurement devices, and CMEs were connected to the data acquisition system.

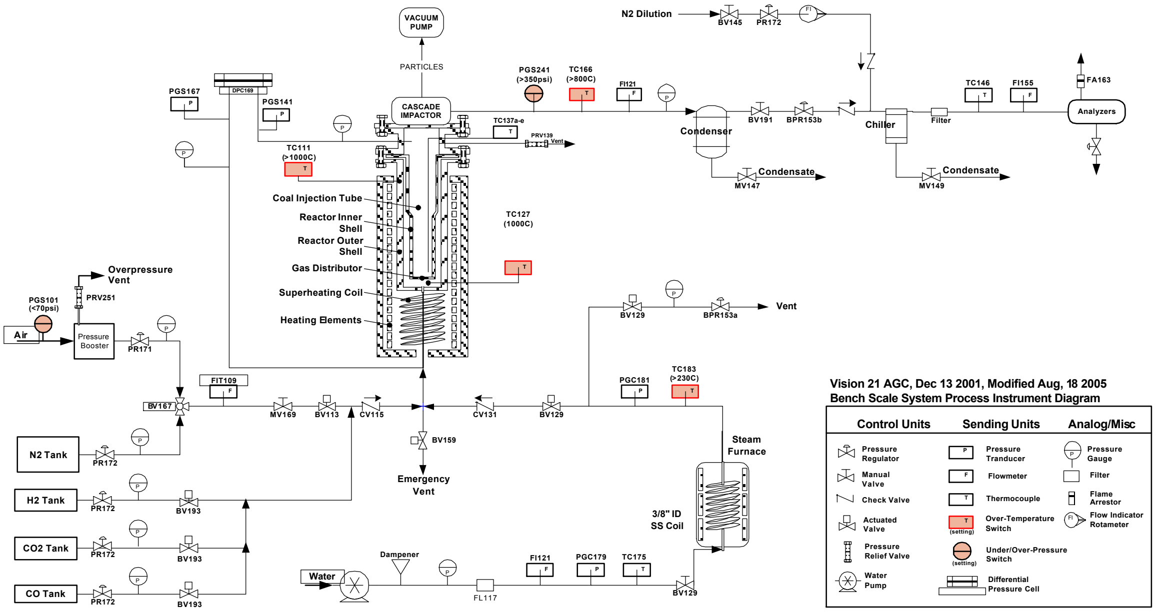


Figure 2-5 Process and instrumentation diagram for the bench-scale reactor

2.4 Solid Material Lifetime

The properties and performance of the solid materials used are crucial to the overall UFP technology. CAM is a sorbent that absorbs CO_2 to form CAM-CO_2. OTM is a metal oxide, which can be oxidized to form OTM-O. The mixture of the bed materials undergoes a variety of transformations and reactions as they move from one reactor to another during the process. In addition to the low cost and fast reaction kinetics (CO_2 absorption and desorption for CAM and redox for OTM) requirements, the lifetime of the solid materials must be evaluated to assess the risks associated with the overall technology. The main focus of this task was thus to

- Evaluate solids (CAM & OTM material) attrition and extrapolate results to a commercial size plant
- Evaluate lifetime of solids to obtain deactivation profiles as a function of number of cycles.

2.4.1 Physical Attrition

The main sources of physical attrition of CAM & OTM can be categorized in:

- High velocity impact, which is generally caused by high velocity jets within the fluidized bed causing particle entrainment.
- Low velocity impact, which is caused by particle-to-particle contact and within a bubble media. The fluidization linear velocity and the mass of the bed itself are the main contributors for this category.
- Particle-wall impacts: These become negligible at large scale commercial reactors. The critical factor is the ratio of the mean particle size to the reactor diameter ($d_p/D_{reactor}$).
- Other sources: auxiliary units or components in the fluidized bed processing plant also create additional attrition. Examples are attrition inside cyclone units, and attrition in riser and solids return legs in circulating fluidized beds.

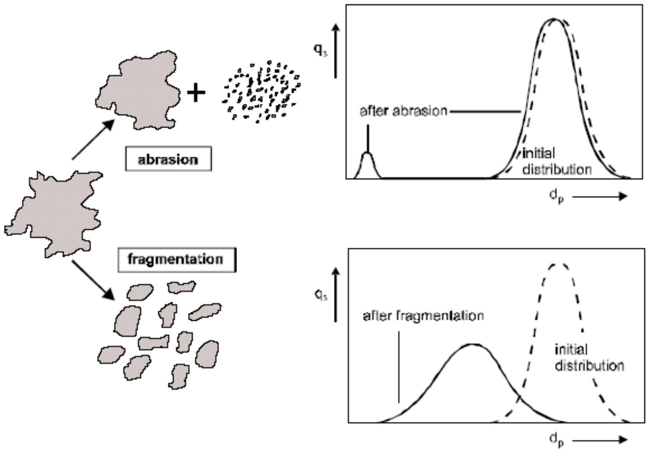


Figure 2-6 Particle distribution as result of attrition

Regardless of the nature of the source, attrition typically results in two basic categories of particle distribution: by abrasion and/or by fragmentation. From abrasion, very fine particles are created; and from fragmentation, individual particles are typically larger. These two types will generate narrow and wide particle size distributions, respectively, as illustrated Figure 2-6. Methods of evaluating attrition are scarce and mostly empirical. In the case of fluidized beds, the attrition testing techniques typically do not account for attrition within the bed, i.e., particles resulting from attrition that remain in the bed. Attrition levels are measured in respect to the particles that leave the bed by entrainment.

There are industry-accepted standard methods to evaluate attrition levels. The catalyst industry primarily utilizes ASTM D-5757 (1995 and 2000) for evaluating samples for attrition properties (equipment in the figure next). Research Triangle Institute (RTI) performed these tests for various CAM & OTM materials. These tests employ a bed fluidized by air jet to create inter-particle collisions. The response of such test is given in terms of material weight loss during at 1 and a 5 hour test period. The limitation of this apparatus is that it uses standard conditions of flow, temperature and pressure, and therefore, it is suitable for material screening only. It will not determined attrition level at specific fluidized bed absolute conditions, although it will determine attrition relative to two or more different materials, which in turn can be used to estimate attrition at the process condition.

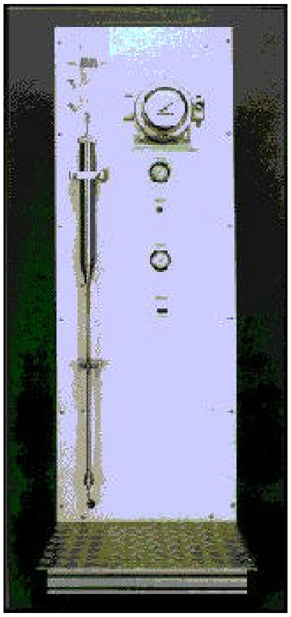


Figure 2-7 ASTM D5757 apparatus

The objective of the physical attrition task was to determine particle attrition levels at the commercial scale operation. Several solid CAM & OTM materials of interest were obtained as summarized in **Table 2-1**.

Table 2-1 Examples of CO_2 sorbent and oxygen transfer materials

Material	Description
1 Material 1	CO_2 sorbent
2 Material 2	CO_2 sorbent
3 Material 3	CO_2 sorbent
4 Material 4	Oxygen-transfer material
5 Material 5	Oxygen-transfer material

A methodology was developed to estimate the physical attrition of sorbents used in the UFP process. This method encompassed a combination of ASTM attrition measurements and fluidized bed bench-scale testing. It is illustrated in **Figure 2-8**.

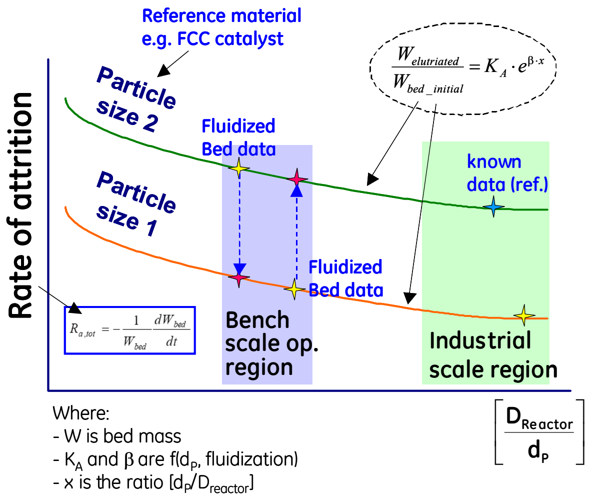


Figure 2-8 Illustration of the method to evaluate physical attrition and extrapolate to commercial scale operation

With this test, data can be obtained on relative physical attrition comparing the materials in question and a standard characterized material, in this case a FCC catalyst. The attrition index (AI) is calculated from:

$$\frac{\boldsymbol{WeightLoss\%}_{5-hour} - \boldsymbol{WeightLoss\%}_{1-hour}}{4}.$$

Once AI is known for each one of the candidate materials listed above, the relative AI is determined. This is the ratio between the AI of the material (particle 1 in the plot) over the AI of the standard reference (particle 2). Upon testing each material, including the standard in the fluidized bed bench-scale, one data point in the plot will be determined (yellow stars), which named FBAI (fluidized bed attrition index). Because it is impractical to change the diameter of the fluidized bed reactor, only one experimental point can be obtained for each particle. The concept of the relative AI will be used to determine a 2nd data point for each particle curve, by multiplying the FBAI by the relative AI, for instance:

$$\boldsymbol{FBAI}_{particle-2} \times \left(\frac{\boldsymbol{AI}_{particle-1}}{\boldsymbol{AI}_{particle-2}}\right)_{ASTM-data} \Rightarrow \boldsymbol{FBAI}_{particle-1}$$

Where $FBAI_{particle-2}$ is the yellow start data-point on the particle 2 curve and $FBAI_{particle-1}$ is red star data-point on the particle 1 curve, both taken at the same ratio $D_{reactor}$-to-d_p from Figure 2-8. The $FBAI_{particle-2}$ in this case is a calculated point at constant $D_{reactor}$-to-d_p. This methodology assumes that:

- The relative attrition ratio between particles remains a constant, independent of the nature of the particle; and
- The attrition decay curves are parallel to each other, and asymptotic.

These two assumptions are reasonable according to the literature reviewed. The level of attrition at a commercial scale system was determined at the point of the asymptote. For the reference material, since the attrition levels are known at industrial scale, it was used to validate the methodology. This flow down chart illustrates the method to extrapolate attrition levels to industrial scale, including validation.

2.4.2 Chemical Attrition

A furnace apparatus was constructed where attrition due to chemical reactions can be characterized. A schematic of the apparatus is shown in Figure 2-9. The apparatus was used to investigate the CAM as well as the OTM. Nitrogen was fed into mass flow meter (MFM)1. Input gas (oxygen or CO_2) was fed through mass flow controller (MFC)1. The gas mixture (oxygen or $CO_2 + N_2$) was fed into the furnace. In the absence of absorption or desorption, the gas flow through the outlet (MFC2) equals the sum of MFM1 and MFC1. If gas is being adsorbed, additional nitrogen is drawn from MFM1 to compensate gas flows. If gas is being desorbed, the flow from MFM1 is diminished. The respective flows are monitored via computer interface. Consequently, a plot of dm/dt vs t is a measure of adsorption or desorption events.

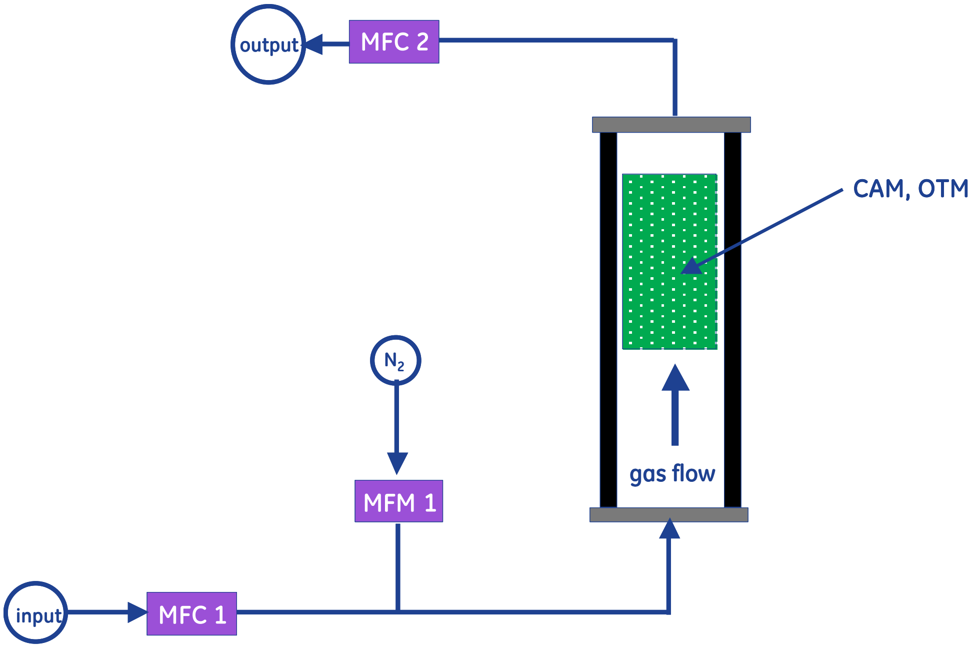


Figure 2-9 Schematic of chemical attrition apparatus

The anticipated output from these experiments was two-fold. First, degradation of the absorption/desorption properties was monitored over multiple cycles. Second, XRD, SEM, BET, etc were used to analyze changes in particle morphology and composition.

2.4.3 Solid Materials Agglomeration

Agglomeration of solid particles used in the UFP process was identified as the major parameter controlling the life of the OTM and CAM materials. Agglomeration of solid particles was observed in the bench-scale and in the pilot-scale experimental systems, resulting into defluidization and loss of activity of the agglomerated material. The possible causes for the agglomeration behavior include: (1) interaction of low-melting-point ash compounds in the coal with the CAM and/or OTM materials, (2) formation of low-melting species such as $CAM(OH)_2$, and eutectic compound between CAM and $CAM(OH)_2$, (3) interaction of OTM with coal and syngas, and (4) interaction between OTM and CAM materials. The degree of agglomeration may also be influenced by the operating conditions, such as temperature, pressure, gas compositions and fluidization velocity. To analyze the root causes of the bed materials agglomeration, both offline tests and bench reactor gasification tests in conjunction with the characterization were conducted.

2.4.3.1 Offline heat treatment

Offline thermal heat treatments of bed materials were carried out in a box furnace in stagnant air to evaluate the material interaction characteristics. Offline thermal heat treatment tests of varied bed materials with addition of NaOH, coal ash, and coal were also conducted to examine the material interaction characteristics and their associations with the agglomeration issues.

2.4.3.2 Bench reactor

Gasification tests were conducted in the bench-scale fluidized bed reactor (Figure 2-5). The experiments included coal gasification, petcoke gasification with steam and CO_2, and a few blank runs without gasification.

2.4.3.3 Characterization

Both fresh bed materials and used bed materials were characterized with XRD/XRF for compositions and SEM/EMPA for the microstructures and interactions.

2.5 Impact of Impurities in the Coal on the UFP Process

The impurities in the coal can be classified in two broad categories. The solid impurities contain ash and inorganic material and the gaseous impurities contain sulfur, chlorine, ammonia, mercury etc. For the success of the UFP technology, a major fraction of these impurities needs to be removed from R1 and R2. The output of R3 needs to be free of these impurities, as it would be sent to a gas turbine expander to produce electricity.

In the current phase of the program, fate of the impurities in the UFP process was investigated via bench scale reactors. The concentration of SO_2 in the product gases under the R3 conditions was measured and compared to the gas turbine specs. The solids (OTM and CAM) were also analyzed to assess the poisoning effect of sulfur.

In addition, coal washing experiments were carried out at room temperature to investigate the possibility of removing ash and sulfur from coal prior to gasification. To screen the potential washing solvents, preliminary screening tests were carried out. Solvents used in the preliminary tests were selected not only by the chemical properties, but also by the price, availability and the potential for commercialization. The ash content, sulfur level and detailed ash compositions were analyzed.

3 RESULTS AND DISCUSSION

3.1 Economic Analysis

GE Global Research worked with WorleyParsons to develop detailed estimates of UFP plant costs to assess the commercialization potential of the technology and guide future development efforts.

In order for WorleyParsons to carry out the economic analysis of the UFP technology, the pilot-scale UFP system model was scaled up to commercial size, which included developing estimates of reactor sizes, construction materials and auxiliary equipment designs. Scale-up and equipment design requires detailed UFP system analysis to provide inputs to the reactor design, fluidization calculations and for Worley Parsons' CAPEX estimates.

Commercial-scale UFP system analysis was performed using Aspen software. This Aspen analysis was scaled up to account for commercial scale power generation using dual 7FA turbines.

The commercial scale UFP reactor system design was divided into three phases: (1) Fluidization calculations (2) Fluidization regime mapping/reactor type selection and (3) Reactor geometry optimizations. The following design criteria and resources were considered during these three design phases:

- Fluidization conditions and flow regimes
- Engineering estimations and "rule of thumbs"
- Literature and commercial scale application information, and
- Kinetic limitations.

Scale-up tools were developed for the conceptual design of an UFP-based full-scale system combined with power-island. Aspen software was used to develop material and energy balances for fully integrated power generation systems. MathCad and TechPlot software was used to scale up the UFP system from pilot-scale to commercial-scale with detailed reactor designs and equipment specifications, which provided the basis for economic analysis of the commercial-scale three-reactor UFP system. The scale-up information was provided to WorleyParsons to carry out an independent assessment of cost of the UFP technology. WorleyParsons reviewed the UFP information and provided the capital cost estimates for a full scale UFP process combined with a power-island. Worley Parsons also provided capital cost estimates for IGCC and IGCC polygen system with CO_2 separation. Based on the capital cost and material and energy balance provided by Worley Parsons, cost of hydrogen and electricity were calculated for the UFP and IGCC technologies.

3.1.1 Fluidization Calculations

Fluidization calculations were performed while estimating the size of commercial UFP reactors based on the systems analysis. Figure 3-1 shows the fluidization design map calculated for R1. For a given reactor design point on the map, its Y-axis represents the internal diameter, D, and the X-axis represents the reactor aspect ratio, L_{mf}/D. In this fluidization design map, the red contour represents the total length of the reactor, the blue contour represents the solid residence time, and the yellow contour represents the fluidization parameter u/u_{mf}.

As shown in Figure 3-1, the fluidization design space can be bounded by the slugging flow conditions. The maximum superficial gas velocity to prevent slugging was calculated, which in turn sets a lower bound on the reactor diameter – the Y-axis. Similarly, a maximum aspect ratio, L_{mf}/D, to prevent slugging can be calculated, which sets the boundary for the X-axis.

The fluidization design map provides a visual means of correlating reactor geometry with fluidization conditions. Based on fluidization theories, engineering estimations and rules of thumb, a desired fluidized bed operation region is identified on the fluidization design map that corresponds to a set of feasible solutions in terms of the reactor dimensions.

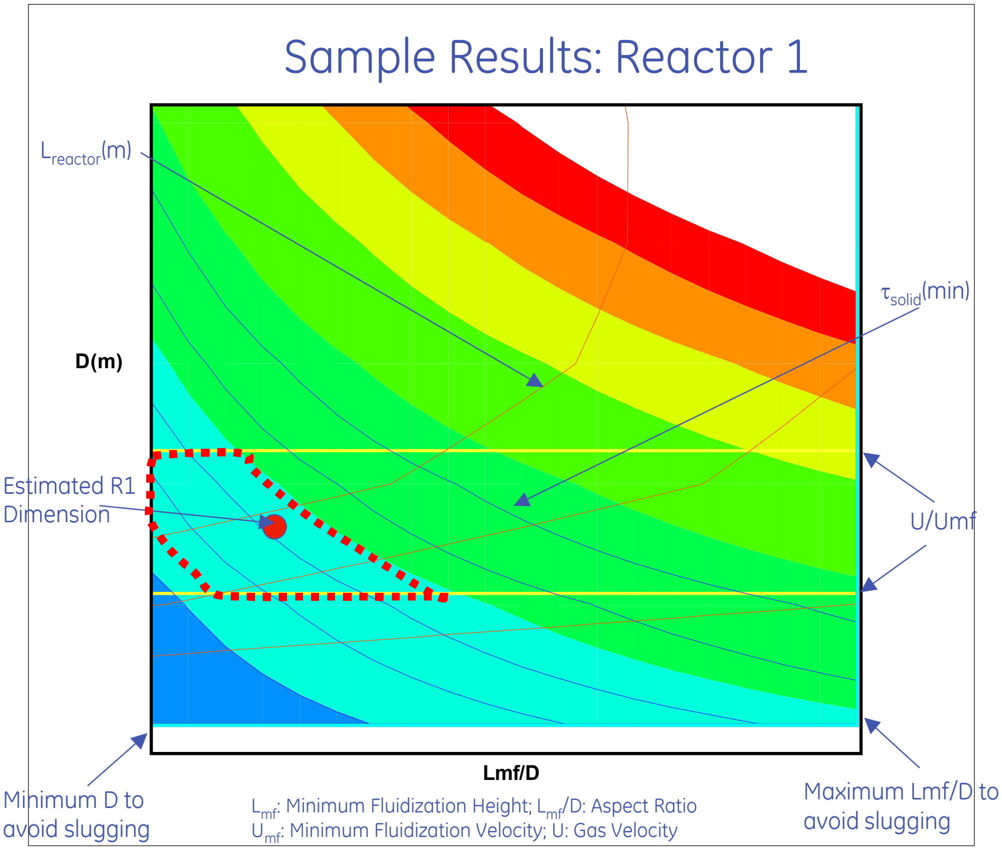


Figure 3-1 Fluidization design map for Reactor 1

3.1.2 Fluidization Regime Mapping/Reactor Type Selection

The reactor types and fluidization regimes are primarily dictated by the solid and gas flow rates and solid residence time required for the chemical reactions. Bench scale experiments and technical literature results indicated that the kinetics for the gasifier (R1) and regenerator (R2) required residence times much longer than that of the oxidization reactor (R3).

When assuming bubbling fluidized bed for R1 and R2, these residence time requirements can be met fairly well with reasonable reactor size and bed loading. However, a bubbling fluidized bed design for R3 would result in a very large reactor size and an unnecessarily long residence time of solid materials. Instead, a transport reactor design was found out to be suitable for this reactor.

Figure 3-2 shows a qualitative design map comparison for R3 between bubbling bed design and transport bed design. A bubbling bed design requires twice the number of reactor trains as that of the transport bed reactor. Additionally, each fluidized bed reactor would also require the internal diameter to be several times larger than the transport bed.

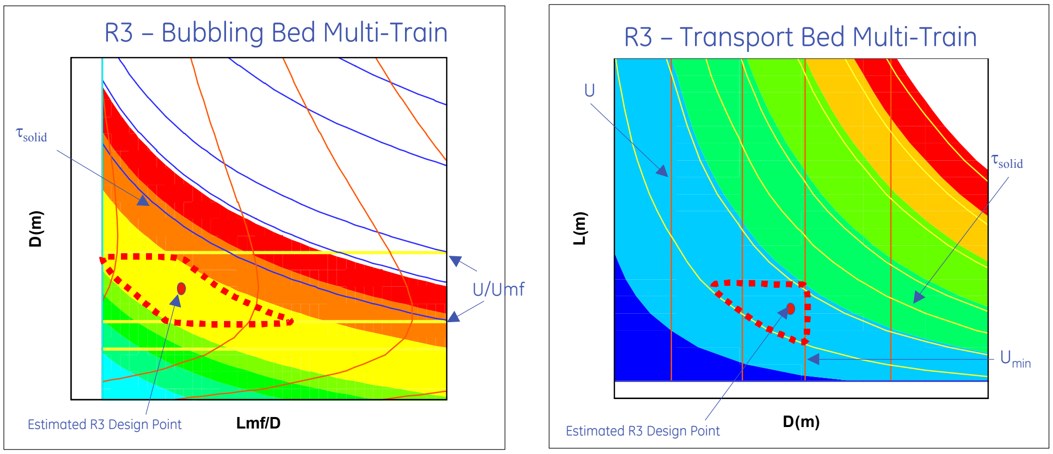


Figure 3-2 Reactor type comparison for oxidization reactor

Through the use of fluidization design maps, it can be concluded that the gasifier and regenerator reactors should both be designed as bubbling fluidized beds while the oxidation reactor should be designed as a transport reactor. The general fluidization flow regime diagram by Kunii and Levenspiel, as shown in Figure 3-3, was also used to confirm the selected reactor types and benchmark results against other commercial applications.

3.1.3 Reactor Geometry Optimization

The last phase in the scale-up reactor design was to use fluidization theory, engineering estimates, and kinetic limitations to identify a feasible fluidization design space and eventually pinpoint the optimal reactor design.

As a rule of thumb, the optimal operation condition for a bubbling fluidized bed requires the u/u_{mf} ratio to be between 2 and 3. This condition poses an upper bound and a lower bound on the design space for R1, which can then be translated to a maximum and a minimum reactor diameter on the design map.

Preliminary kinetics provides limitations on the residence time, which can be used to further narrow down the design space horizontally. As shown in Figure 3-2, the bench scale experiments and technical literature provided kinetic information for setting the left and right boundaries using residence time.

Finally, as shown in Figure 3-2, the region bounded by red dashed lines represents the optimal reactor geometries for reactor 1. Similarly, the optimal reactor design space was identified all other reactors. The mid point in these design spaces was picked for each reactor as the final reactor geometry design for economic analysis purpose.

Fluidization Analysis – Flow Regime Mapping

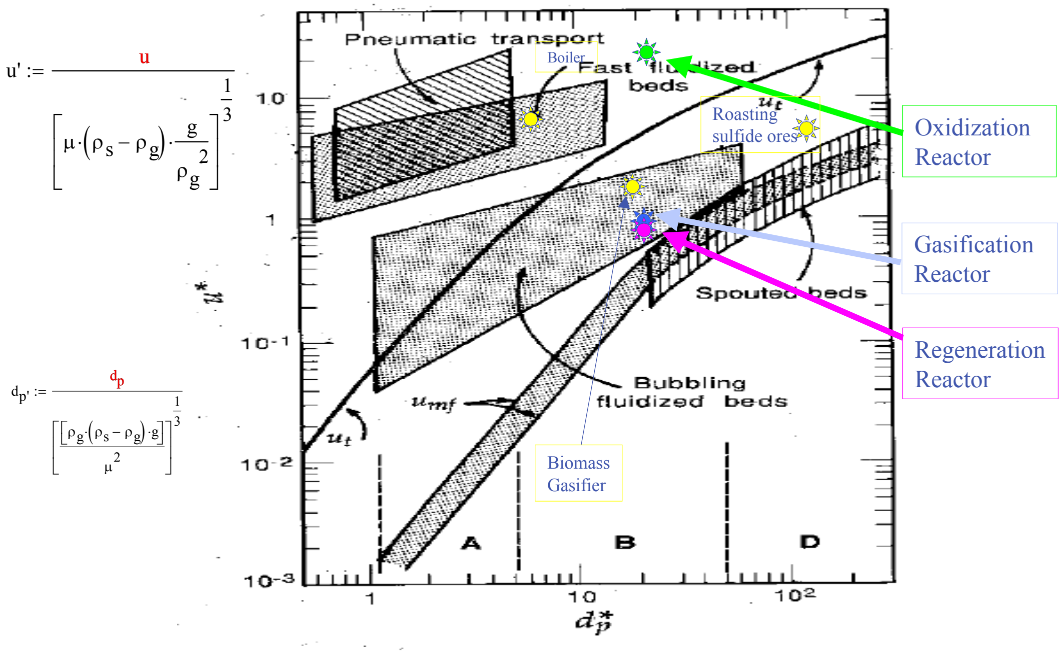


Figure 3-3 Fluidization flow regime analysis

3.1.4 Reactor Scale-up for Capital Cost Estimate

The size of the UFP reactors for a commercial scale plant was estimated. The scale-up was performed in such way that the UFP process can be integrated with two 7-FA gas turbine expanders. For any given fluidized bed geometry (internal diameter D and aspect ratio Lmf/D), important data characterizing the fluidization conditions was calculated including the minimum fluidization velocity (umf) and maximum reactor aspect ratio (Lmf /D)max, bed void fraction, total reactor height, mass of the bed, solid residence time, superficial gas velocity, etc.

Further fluidization calculation was carried out to study the effect of particle sizes of the CAM & OTM material on reactor geometries. Generally, smaller particles require lower fluidization gas velocity and higher transport disengagement height to prevent particle entrainment.

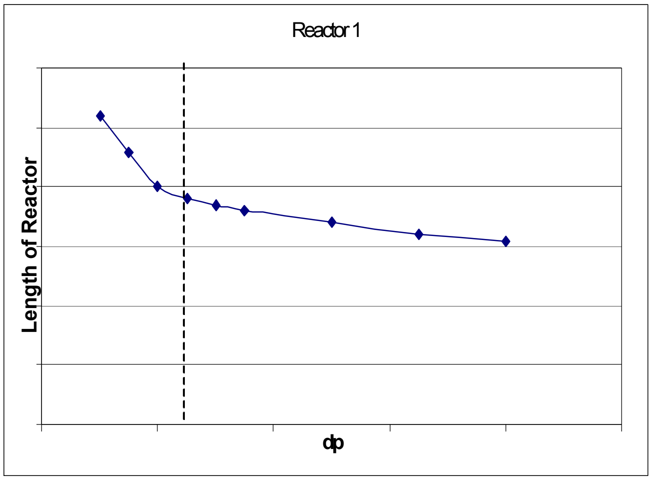


Figure 3-4 Reactor length required for different particle sizes

Figure 3-4 shows various particle sizes of solids in R1 and their corresponding reactor lengths that are required to prevent particles from being conveyed out of the fluidized bed. As the particle size decreases, the required transport disengagement height increases, resulting in an increase in the total reactor height. After a critical height of reactor, the decrease in particle size would result in much faster increase in the total reactor height required and thus a significant increase in the capital cost of the reactor vessel. At this point, the height of the reactor will only allow particles smaller than the critical particle size to escape from the reactor, which can then be collected using a cyclone and re-injected back to the reactor. Therefore, the critical reactor length was chosen as optimal design point.

3.1.5 Auxiliary Equipment Cost Estimations

Once the reactor dimensions were finalized, detailed designs & cost estimations for the auxiliary equipment were carried out including refractory, reactor vessels, solid transfer ducts and solid separation equipments.

Typical refractory and metal shell materials were selected for the UFP reactors. Pressure vessel shell thickness and reactor heat transfer (Figure 3-5) calculations were performed for each reactor to determine the thickness of each layer of materials to satisfy both the temperature and the pressure requirement of the reactors according to the ASME codes.

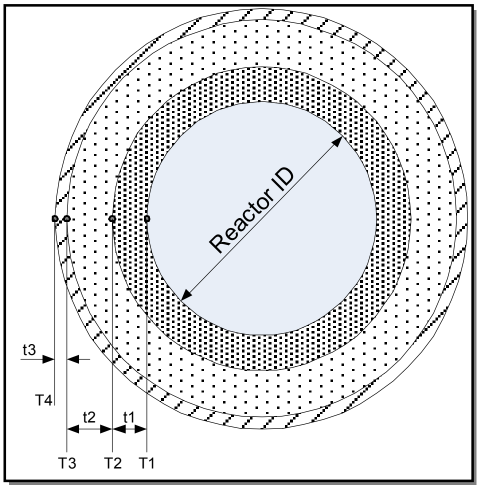


Figure 3-5 Refractory and shell thickness estimation

Designs for solid transfer ducts were also estimated. According to the different temperature and pressure requirements for each solid transfer ducts, their corresponding refractory and shell materials and thicknesses were also estimated.

Fluidization calculation results were used when determining the solid separation equipments for the UFP processes. Gas and entrained solid flow rates were sent to outside vendors of gas/solid separation units for estimation of cyclone sizes and costs. Based on the vendor feedback, it was determined that one cyclone per reactor was sufficient for R1 and R2. Three to four cyclones would be required for R3 due to its high solid flow rate. Final costs were estimated based on these configurations and unit cost estimations provided by outside vendors. WorleyParsons used this information for the final economic analysis of the UFP technology.

3.1.6 Capital Cost and Cost of Hydrogen and Electricity Estimate and Comparison

The economic viability of the proposed UFP process for producing hydrogen depends on recovering process energy as electricity. The electricity is sold to add to the positive cash flow in the overall plant economic analysis. The DOE H2A Excel model for calculating the required selling price of hydrogen accommodates this as “by-product Electricity” and allows the entry of a selling price of electricity. Since the value of the electricity and hydrogen streams are of the same order of magnitude, the selection of the selling price of electricity is extremely important in determining the price of hydrogen. The following describes an approach that uses the H_2A model to first calculate a selling price of electricity for an electricity only plant and then uses this value to calculate the selling price of hydrogen for hydrogen and electricity plant.

The integration of the UFP process into power generation plant can be viewed as similar to replacing the gasification process in an Integrated Gasification Combined Cycle (IGCC) plant that has been modified to produce hydrogen from a portion of the syngas product. In order to obtain a set of consistent set of equipment cost numbers WorleyParsons was contracted to calculate total installed equipment costs and performance estimates for three main plant configurations.

The first configuration, Case 1, is for a typical GE Texaco IGCC quench system that produces only electricity. Case 2 is for a system where the coal handling and gasification streams have been increased in capacity to allow a portion of the syngas stream to be diverted to a shift reactor to produce hydrogen. In Case 3, the gasifiers are replaced with the UFP process and the power generation equipment is modified to accept the hot exhaust stream. Since one of the attributes of the UFP process is the presence of a CO_2 rich stream, which is favorable for CO_2 separation, Cases 2s and 3s were analyzed which included equipment to separate and compress CO_2.

The inputs to H_2A model were adjusted for Case 1 for a hypothetical H_2 production plant with a capacity 1 kg/day. Using 1 kg/day, the inputs for coal feed rate and by-product electricity, which were entered per unit of H_2 production, were simply the plant daily capacities. By entering a very small value for the required selling price of hydrogen on the H_2A Cash flow Analysis sheet ($1E-7 was used), the selling price of electricity can be adjusted so that the net present value of the cash flow streams is zero. This same approach is normally used to generate the required selling Price of hydrogen. This selling price of electricity, calculated for Case 1, was then used, along with same financial assumptions, to calculate a cost of hydrogen for the other equipment configuration cases.

The cost of hydrogen and electricity were estimated for IGCC-polygen and UFP technology in an apples-to-apples comparison for a case of >85% CO_2 capture using the capital cost information provided by WorleyParsons. The CAPEX analysis generally had +/-30% accuracy.

Figure 3-5 shows the comparison of capital cost of UFP technology and the IGCC-polygen technology. The two technologies were compared at the same process parameters of:

- H_2 production rate (~62 MMscfd =150,000 kg/day)
- CO_2 capture (~85% and a base case at 35%)
- Gas turbine equipment (equivalent of 2 trains of 7FA GE gas turbine).

WorleyParsons used contingency factors of 15% for the IGCC-polygen technology and 25% for the UFP technology because of the novelty of the UFP technology.

The analysis suggests that the capital cost for the UFP technology may be lower than the IGCC-polygen technology by ~10%. The potential lower cost of UFP technology can be attributed to the following two factors:

- UFP technology does not require the air separation unit (ASU) to separate O_2 from air. ASU costs account for ~10% of the total capital cost. In the UFP technology OTM was used to capture O_2 from air.
- IGCC-polygen technology requires the low temperature CO_2 capture using chemical or physical absorption. Low temperature CO_2 capture using conventional methods is capital and energy intensive. UFP technology uses CAM to capture CO_2 inherently at high temperature and pressure. Further UFP technology reduces the CO_2 compression load as the separated CO_2 is obtained at the system pressure as compared to low pressure CO_2 recovery using conventional solvent based processes.

Thus the capital costs for the UFP technology seem promising based on this economic analysis. However, the technical assumptions going into the economic analysis need to be verified experimentally. This experimental verification using the pilot and bench scale experimental systems was identified to be the focus the remaining phase of the program.

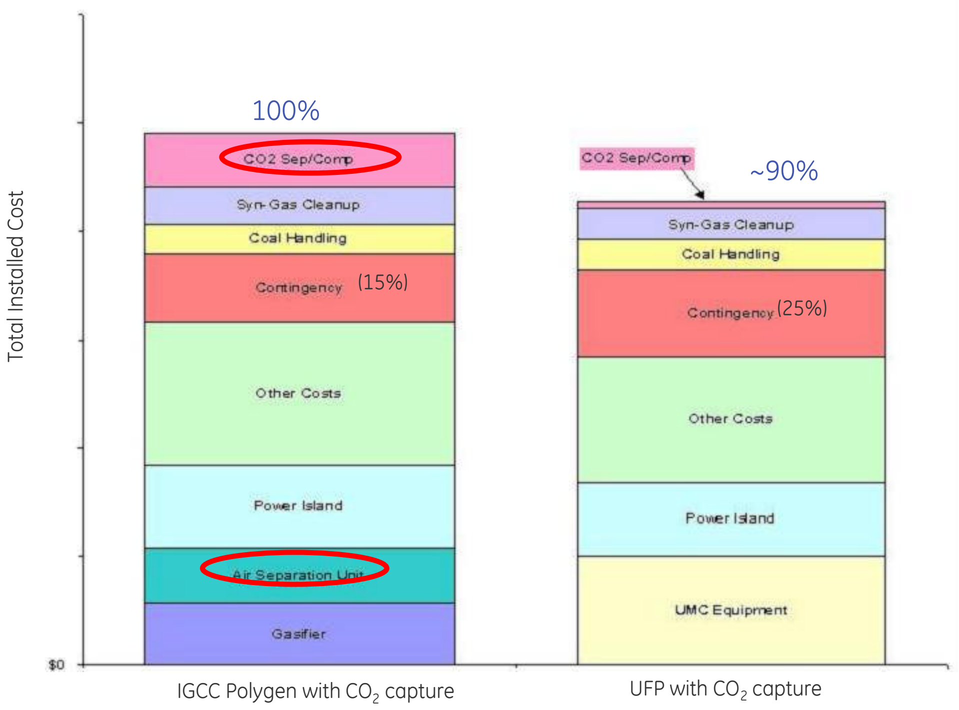


Figure 3-6 Capital cost comparison between IGCC-polygen and UFP technologies

The cost of hydrogen (COH) was calculated from the capital cost and process analysis information received from WorleyParsons. For this comparative analysis the cost of electricity was kept constant for both the cases and the entire cost for CO_2 separation was added into the COH. A sensitivity analysis was performed to understand the effect of important parameters such as solids lifetime on the COH (Figure 3-7). This analysis was conservative and assumed that the entire mixture of OTM & CAM needed to be replaced if one of the solids was deactivated. However, it is expected that the OTM would have a longer lifetime than CAM and can be reused after separating it from the deactivated CAM.

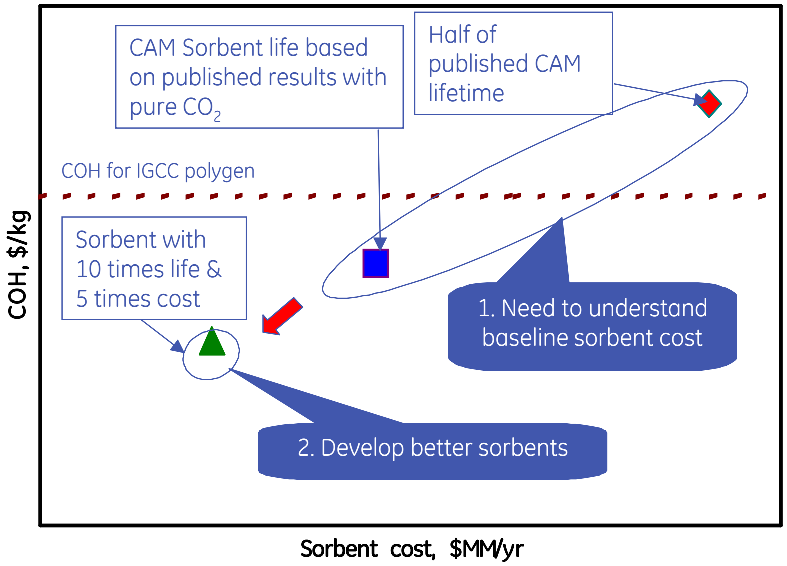


Figure 3-7 Effect of sorbent/solids cost on the cost of hydrogen

The horizontal dotted line in Figure 3-7 represents the estimated COH for the IGCC-polygen technology. The baseline sorbent/solids cost for the UFP technology was estimated from the lifetime for the CAM (~100 CO_2 adsorption/desorption cycles) reported in the literature. The analysis suggested that the baseline COH, represented by the 'blue' colored point in the Figure 3-7, may be lower than the COH for the IGCC-polygen technology by ~10%. Development of advanced sorbents with better lifetime would reduce the COH for the UFP technology further as shown by the 'green' colored point in the Figure 3-7. However, the lifetimes of the CAM sorbents reported in the literature are typically studied under pure CO_2 environment and not under the coal gasification environment where the syngas consists of small quantities of impurities such as sulfur, chlorine, ammonia and ash. These impurities may interact with the solids and reduce their lifetime. The 'red' colored point in the Figure 3-7 shows one example where the solids lifetime was assumed only half of the typical lifetime reported in the literature. In this case, the COH for UFP technology is higher than the COH for the IGCC-polygen technology.

Thus, the cost of the solids is very important in determining the cost competitiveness of the UFP technology. In the current program, the lifetime of the sorbents was investigated under coal gasification conditions in the presence of impurities.

The above cost analysis results were communicated to DOE during April 2006. Following up on the action items from this economic analysis review meeting, the possible impact of following changes in the process parameters was also investigated:

- CO_2 capture (90% instead of 85%)
- Gas turbine equipment (equivalent of 2 trains of GE 7FB gas turbine instead of GE 7FA).

Most of the economic analyses were compared at two CO_2 capture levels 35% and 85%. The costs for these two capture levels varied for the two technologies but the overall trend of lower costs for UFP remained the same. Increasing the CO_2 capture level to 90% would result in additional cost for both the technologies, but the conclusions based on the comparison would remain the same.

The economic evaluations of the IGCC-polygen cases used the GE 7FA gas turbine as the foundation of the power generation block. The analyses of UFP cycles have assumed that a compressor and turbo expander would be built that would have specifications similar to those of the 7FA. Recent designs for IGCC plants have specified the use of the upgraded GE 7FB for the combustion turbine and it was decided to explore the implications of using the 7FB specifications for the UFP and IGCC cases.

Improvements in materials and aerodynamic design allow the 7FB to operate at a higher compressor ratio and a higher firing temperature than the 7FA. The result is a system with 6% greater power with 2% improvement in heat rate. Table 3-1 shows a comparison of the most important cycle parameters in a natural gas fired combined cycle (NGCC) plant with the two turbines.

Table 3-1 Comparison of 2 GE 7FA vs GE 7FB gas turbines in NGCC plants

Turbine Model	**Net Cycle Power[1] (MW)**	**Net Cycle LHV Heat Rate[1] (BTU/kW-hr)**
PG7241(7FA)	530	6040
PG7251(7FB)	563	5940

A detailed analysis was not performed for either the IGCC-polygen or UFP systems with the 7FB power generation block, however the trends can be expected to be the same as those shown for the NGCC plant comparison. Greater electrical output and lower heat rate for both IGCC-polygen and UFP would lower the costs of electricity and hydrogen for all systems. The operating pressure of the UFP would need to be increased to match the 18.5 to 1 compression ratio and the Reactor 3 conditions would need to be optimized to get similar power as that from a GE 7FA frame machine. The 7FB is a higher capacity machine compared to the 7FA, and therefore the unit operations need to be scaled up accordingly resulting in slightly higher capital cost. Thus, the capital cost and efficiency would increase slightly for both technologies but the overall trend in the cost of hydrogen and electricity would remain similar for this economic analysis comparison with +/-30% accuracy.

Thus, changing the process parameters slightly would not change the conclusions drawn from the economic analysis comparison of UFP and IGCC-polygen technologies based on today's knowledge.

3.1.7 Summary

Fluidization analysis indicates that, assuming all reactors are bubbling beds, the UFP system would require large reactors. Based on the technical literature as well as existing commercial scale applications, such large reactors would incur considerable increase in capital cost and tremendous technical challenges in terms of material and constructions. A more realistic and economic approach is to divide the UFP system into multi-train reactor systems that are within commercially available vessel sizes of similar applications.

Furthermore, according to different gas-solid flow rates, R1 and R2 are designed as bubbling fluidized bed while R3 is designed as a transport reactor. The sizes and fluidization conditions of each reactor were also calculated. These reactor designs provided the quantitative basis for the economic analysis of the UFP system viability.

The economic analysis comparison of the UFP technology with the conventional IGCC-polygen technology performed with today's understanding suggests that the UFP technology may have cost advantages over IGCC-polygen technology. However, the technical assumptions such as conversion, yield, solids lifetime and impact of coal impurities, going into the economic analysis, need to be validated experimentally.

3.2 Experimental Evaluation of UFP Using Pilot-Scale System

3.2.1 Pilot-scale Baseline Testing

Experimental results were obtained for the preliminary assessment of the OTM oxidation-reduction using one of the three reactors. The other reactors were kept off-line because of issues related to auxiliary heating and solid transfer.

Oxidation-reduction of OTM is one of the key technology components in the UFP process. In the third reactor, air oxidizes OTM in an exothermic reaction. This stage provides the heat required for the endothermic reactions occurring in the first and second reactors and also produces a high temperature vitiated air stream for power generation. The oxidized OTM is transferred into the second reactor where it is reduced by the syngas generated by steam gasification of char. This oxidation-reduction chemistry of OTM was validated using single reactor operation).

The reactor was pre-heated typically to > 800°C before introducing steam and coal for OTM reduction. Pre-heating consisted of a two-stage process. First, the bed was fluidized with air at 700°C that brought the bed temperature to 550°C. Second, after reaching 550°C, propane was fed directly into the bed and was auto-ignited with the hot air raising the reactor temperature to typically ~ 800°C.

The reactor feed gas was cycled between steam for the reduction of OTM and air for the oxidation of OTM process. The OTM reduction reaction was started after the fluidized bed was preheated and maintained at ~800°C for ~2-3 hours. The auxiliary propane heating was then shutoff prior to the reduction stage in order to avoid mixing of propane combustion products with the reduction products. With the auxiliary propane heating shutoff the fluidized bed temperature dropped to ~725°C. With the steam flow stabilized at 48 lbs/hr, coal slurry (~45% coal by weight in water) was introduced. During this process the reactor temperature dropped quickly stabilizing at ~670°C. This drop in temperature could be the effect from the following reactions occurring in the reactor:

- Endothermic steam gasification of coal to produce CO and H_2
- Reduction of OTM material with CO and H_2 to produce CO_2 and steam
- Latent heat loss due to water content in coal slurry

The generation of a high CO_2 concentration stream demonstrated reduction of OTM material. During the first 2 min of coal gasification, in the presence of a metal oxide (MO_x), CO_2 was the major detectable product diluted by the lingering air from the preheating mode as shown in Figure 3-8. CO_2 was produced from coal via the following main reactions

$$\text{Coal} + H_2O = CO + H_2 \text{ (endothermic)}$$

$$CO + MO_x = CO_2 + MO_{x-1}$$

$$H_2 + MO_x = H_2O + MO_{x-1}$$

Coal reacted with steam to produce CO and H_2 in the endothermic steam gasification reaction. These gasification products further reacted with the oxidized OTM to produce CO_2 and steam. The relatively quick temperature drop is an indication that the active part of OTM was being reduced during this period, which was followed by a stable temperature indicating all of the active OTM was reduced. In a UFP based plant, simultaneous operation of all three reactors would provide a constant fresh supply of OTM coming from the Reactor-3. This fresh material would provide additional heat, and thus the reactor temperature would be maintained steady. The reduction process was terminated after 5 minutes by shutting off the coal feed followed by cycling of the feed gas from steam to air.

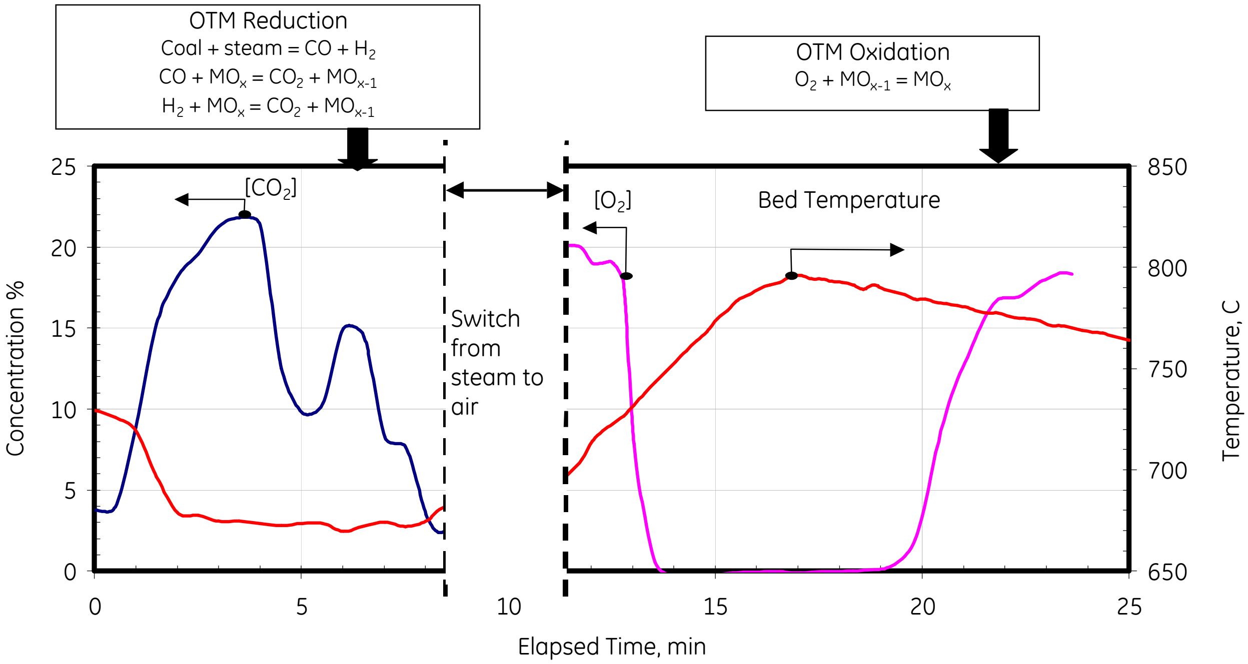


Figure 3-8 Oxidation-reduction chemistry of OTM material

During oxidation of OTM, the reactor temperature increased from 670°C to 800°C within ~10min. The oxidation process was initiated by switching the feed gas from steam to air, as to simulate reactor 3 conditions. Oxygen from air was consumed by the OTM in this process and no O_2 was detected in the product stream for first few min as shown in the Figure 3-8. During this period the temperature of the bed was increased from 670°C to 800°C. The temperature rise is caused by the exothermicity of the oxidation reaction from the reduced OTM.

$$O_2 + MO_{x-1} = MO_x$$

As the temperature began to drop from 800°C oxygen began to appear in the products stream. The rise in the O_2 concentration and the corresponding decrease in the bed temperature suggest complete oxidation of the OTM material in the fluidized bed. In a simultaneous bed-circulating operation, reactor 2 would provide a constant supply of reduced OTM.

Thus, the reduction-oxidation cycle for the OTM was validated using single reactor pilot-scale operation at near atmospheric pressure and at moderate temperatures (<900°C). During these initial experiments, several limitations of the current pilot-scale system were identified especially related to auxiliary heating and coal slurry feeding. Agglomeration of the OTM, most likely due to melting of alkali metals in the ash, was also observed during the cyclic experiments.

The effect of ash on the UFP performance was investigated. Figure 3-9 is a DTA analysis of ash resulting from the combustion of Utah coal. As shown in the plot, the glass transition temperature (T_g) was estimated to be in the range of 575°C based on the endothermic and exothermic peaks measured for the heating and cooling cycle, respectively. With a T_g of 575°C, it is anticipated that the ash could play a role in binding particles within the fluidized bed together, particularly in R2 and R3. The concern here is that changes in the CAM and OTM morphology would change the fluidization properties as well as increase the risk of cross-reaction. Consequently, mitigation steps will need to be adopted that remove ash before it is transferred from R1. Due to the considerable difference in particle size between the CAM/OTM and the ash, mechanical means can be particularly effective.

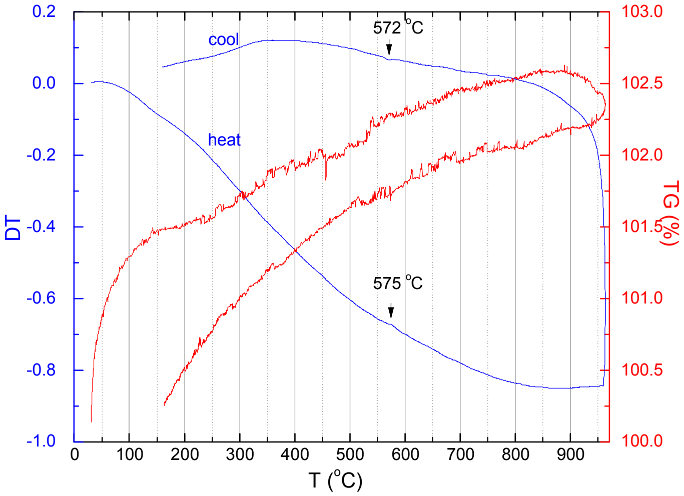


Figure 3-9 DTA plot for Utah coal ash

3.2.2 Pilot System Upgrades

During the baseline pilot system tests, several system limitations were observed. To overcome the limitations, major upgrades were carried out including a robust auxiliary heating system to maintain required operating temperatures, continuous removal of ash from the reactors, structural reinforcement pads to reduce the mechanical and thermal stresses, and high temperature materials upgrade for the gas preheater.

3.2.2.1 Reinforcement of reactor supports

At various stages of the shakedown process, the reactors were often removed for diagnosing and repairs. This caused high cyclic stress concentrations on the reactor shell around the structural support members. A thorough inspection revealed undesired deformations along the reactor outer wall around the supporting members. In parallel, computer stress analysis, in ANSYS, predicted similar behavior. The high stress areas (red and orange color) on the reactor shells around the current structural support pads are shown in Figure 3-10 as predicted by the ANSYS model. Based on this analysis it was concluded that adding reinforcement pads would reduce the mechanical and structural stresses on the reactor.

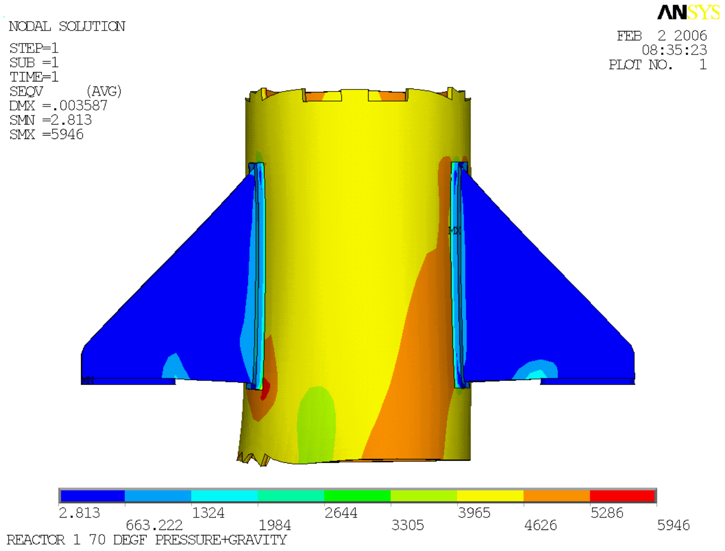


Figure 3-10 ANSYS stress analysis results

The support legs on the reactor were then redesigned based on the ANSYS analysis. This new design accounted for thermal stresses and the unbalanced plug loads caused by the solids-transport legs of the reactor**.** Figure 3-11 shows the improved design of the reactor supports.

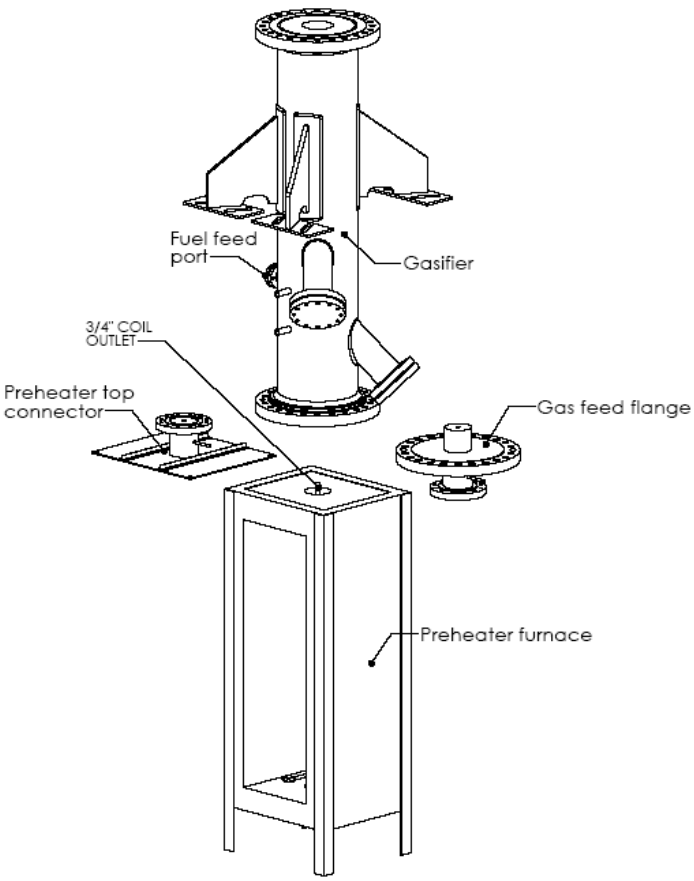


Figure 3-11 Upgrades in the single pilot scale reactor

*3.2.2.2 **Reactor auxiliary heater***

Reaching the reactor target temperature of ~1000°C was one of the major challenges during operation due to the large heat losses. Various auxiliary heating methods were identified, analyzed and compared to meet the technical requirements of the current design. A custom designed immersion-type electric cartridge heater was identified as the best option. Technical requirements for this heater were derived from thermal analysis results and actual experimental performance data. The selected cartridge heater was able to provide 6.9 kW of heat at 1000°C directly into the fluidized bed reactor.

*3.2.2.3 **Reactor gas pre-heater***

Based on baseline operating experimental results it was concluded that some reactor internal components needed to operate at >700°C in order to achieve the desired operating conditions in the reactor. The existing reactant gas pre-heater was retrofitted for an increase in operational temperature. This was achieved by replacing the internal heating tube-coils made out of stainless steel with an adequate high-temperature material, INCONEL600. This upgrade increased the heater operational temperature to 800°C, an increase of 200°C from the previous design.

3.2.2.4 High-temperature gas distributor plate

An improved gas distributor plate design was developed to address the frequent plugging encountered during prior experimental investigation. The revised distributor plate was based on a novel design retrofitted for high-temperature use. This design reduced the direct contact between bed material and distributor nozzles. The material of construction was upgraded to INCONEL600.

3.2.2.5 Gas pre-heater high-temperature connector

The reactor bottom section gas feed was retrofitted to address the heat losses previously observed. These upgrades were composed of a set of refractory-lined flange pipe assemblies connecting the output of the gas pre-heater and the reactor bottom.

3.2.3 Pilot-scale Reactor Performance Results

The upgraded single pilot-scale reactor was used to investigate the UFP technology with focus on avoiding agglomeration of solids. A summary of the main upgrades performed and the lessons learned from the operation are shown in Figure 3-12. Some of the upgrades were successful while some others were partially successful.

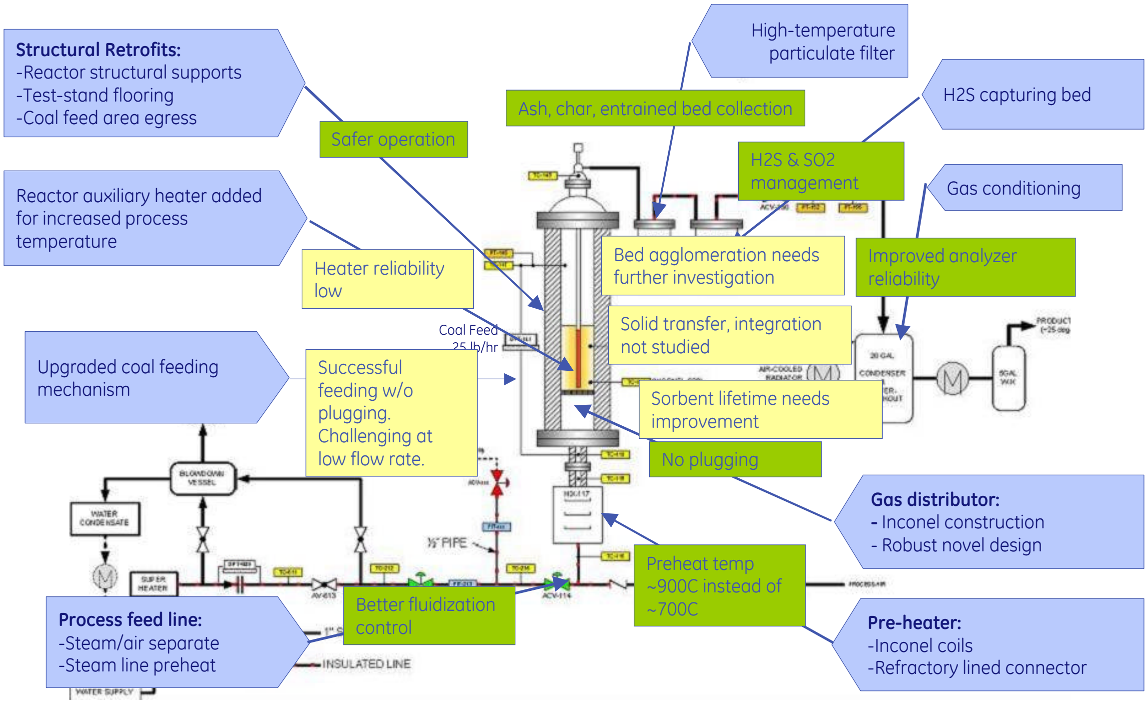


Figure 3-12 Summary of upgrades performed in the pilot-scale system and lessons learned

Overall, the upgrades improved the reliability of the reactor significantly. The duration of experimental tests was extended from 30 minutes to an average of 3 hours, and the time required for loading unloading of the bed material was reduced by 50%. Upgrades to the reactor inlet and outlet had a successful impact in the reduction of overall heat losses. As a result, reactor heat-up time was reduced and the duration of gasification experiments was extended.

The upgraded gas distributor plate assembly helped improve fluidization robustness. Prior to the upgrades agglomerates formed around the nozzles, eventually plugging the gas distributor. Reliability of the distributor plate was a major issue during the operation of the system resulting in 1-2 weeks of downtime after each plugging. The upgraded gas distributor was operated successfully for more than 180 hours. During this period, it was exposed to extreme conditions (>1,000°C, >100 in-H_2O pressure drop, reducing/oxidizing environments) and has remained relatively unaffected. Tests demonstrate that agglomerates no longer block the nozzles allowing continued operation under the presence of agglomeration. The robust nozzle design also provided an improved distribution of the gas.

Operation of the coal slurry feed system was greatly improved. Start-up reliability was increased to 90%. This is mainly due to the addition of a recycle stream and the injection of a purging gas along the reactor internal coal feed line. Structural upgrades, aimed to improve safety, were successfully implemented. No mechanical failures were observed on the structural supports. The control of the fluidization and the switching between steam and air flows were also improved to minimize disturbance in the fluidized bed during the flow transition. Figure 3-13 shows the effects on ΔP as the feed gas stream was switched from air to steam. The deviation during this gas switch was relatively small, less than +/- 5%. This gas switching process was performed reliably through the use of PID control loops developed in LabView. Reliability of control instrumentation was also improved; downtime was reduced by 80%.

Modifications to the reactor outlet and the addition of a high-temperature filter nearly eliminated entrained particles from reaching downstream control instrumentation. Installation of a sorbent directly downstream of the filter helped reduce H_2S to less than 2,000 ppm.

The Pilot Scale reactor was operated for approximately 70 hrs compared to 8 hrs before the upgrades. During this time 9 experiments were performed; the results are summarized in Table 3-2.

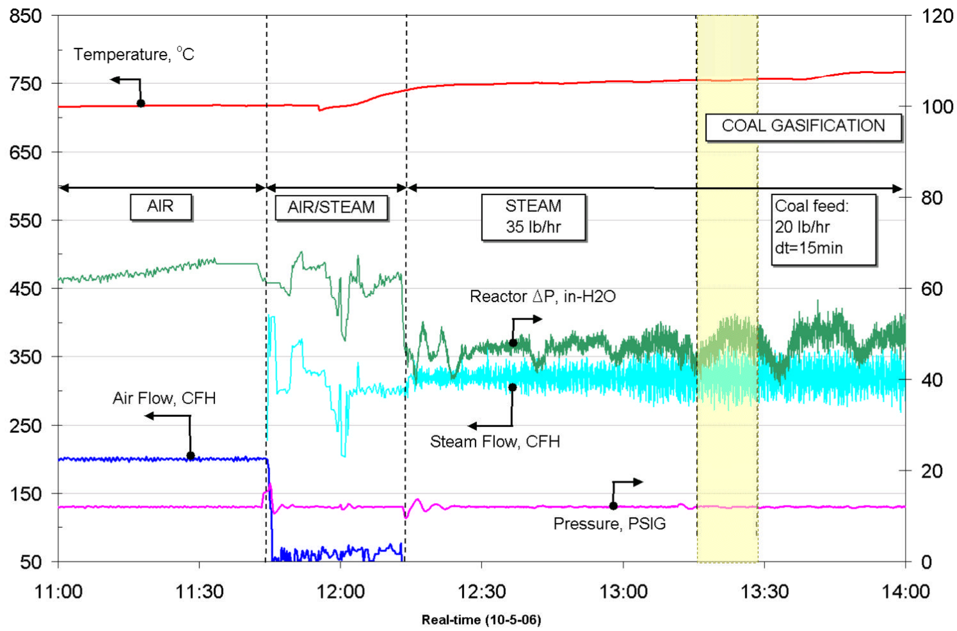


Figure 3-13 Fluidization gas-switch from air to steam effects on reactor differential pressure

Table 3-2 UFP pilot-scale results summary table

EXPERIMENTAL RUN DESCRIPTION	NOTES (pictures available on server)
Reactor performance baseline: Observe process-gas condenser performance and response	Baseline operational limits were determined. Successful continous operation with either steam, air or both at the same time.
Coal slurry start-up: Observe filter and desulfurizer performance and functionality **Reactor bed analysis - baseline:** Remove and collect bed samples, send samples for analysis. **Agglomeration & yields at R1 conditions:** Vary OTM / CAM ratio (50%-90%), temperature (650-800C), flow rates.	Fast fluidization, large amount of entrained material collected from filter and pre-filter
	Low-flow fluidization run, large amount of entrained material collected (mainly coal). Layered caking observed in pre-filter
	Low-flow fluidization run, small amount of solids obseved in filter housing. Fine solid particles (layered) was observed in pre-filter housing. Overall successful coal injection. Negligible products observed.
	Continue low fluidization run to attempt to maximize coal residence time in reactor. Reactor temperature dropped considerably subsequent to feeding coal slurry. Negligible products observed.
	Excellent run (with aux-heating), good gasification data, no large agglomerates observed, 98% bed recovery
Shakedown of internal heater: Allows temperatures >800C in the reactor	Heater sent back to vendor on 11/20 for repairs returned onsite on 11/27. Heater failure on 12/08, returned to vendor for repairs
Agglomeration & yields at R1 followed by R2 conditions: Vary OTM / CAM ratio (50%-90%), temperature (650-1000C), flow rates.	Unable to calcine dolomite
Agglomeration at R1 followed by R3 conditions: Vary OTM / CAM ratio (50%-90%), temperature (650-1200C), flow rates.	Good run (with aux-heating), included R3-conditions -reached 1100C. Inspection of reactor revealed a large agglomerate formed on the refractory liner, around the propane feeding probe. Sample collected, ~3.5lb, a small sample was sent out for analysis, a coal sample was also sent out. Reactor core cleaned. Dist-plate in great cond.
	Improved temperature uniformity throughout bed material, good overall run. Repeatable concentrations as 11/20. Subsequent internal reactor inspection reveal two formation growths on refractory wall. The larger formation was dark gray and grainy in apperance. Second formation was light beige and also gainy in appearance. This test was performed with a fresh (new iron oxide) bed material will be used.
	PRB coal used (all other exp's used Utah coal) to investigate lower ash-content-coal effects on bed agglomeration. Successful coal gasification at 800C was accomplished, but duration was shortened to 15min due to an excessive temperature drop. Subsequent Reactor-3 conditions generated a 50C increase. No agglomerates were observed.

3.2.4 Fluidization effects on solids agglomeration

The agglomeration of solids issue was investigated using the single pilot-scale reactor. Based on the literature and previous results, the main reason for agglomeration of solid material in the fluidized bed was thought to be the low melting ash compounds in the coal. The alkali metals and other low melting components in the ash tend to soften and agglomerate the solid particles under the coal gasification condition. Experiments were carried out to investigate if the ash particles smaller than the coal particles can be entrained out of the reactor under fast fluidizing conditions before they melt. Four experiments were performed at superficial velocities ranging from 0.2-0.5 m/s under R1 conditions. At the conclusion of each experiment, the bed material was collected and inspected for agglomeration. Entrained samples were collected from the downstream filter and reactor outlet cavity.

Fast fluidization at 0.5 m/s superficial velocity resulted in coal entrainment of greater than 90%. Subsequent collection and inspection of the OTM/CAM bed mixture revealed no agglomerates. Although fast fluidization minimized agglomeration, this also reduced the overall coal conversion. Small agglomerates were observed at low-fluidization conditions of 0.2 m/s. In addition, coal entrainment was observed at less than 25%. Subsequent inspection of the OTM/CAM bed mixture revealed small 1"x 2" agglomerates. Thus, these preliminary experiments demonstrated that fast fluidization could minimize the agglomeration of solids in the reactor. Optimum fluidization conditions for each reactor need to be determined to minimize agglomeration and at the same time maximize the extent of desired reaction in that reactor.

The agglomeration was also studied in the simulated R3 conditions by first preheating the reactor to 950^{o}C. The fluidizing gas stream was then switched from air to steam and allowed to stabilize for 10 minutes. During this time a small amount of nitrogen was fed to monitor and flush any undesired non-condensable in the reactor. The coal slurry was then fed; this marked the start of the gasification step, or R1 conditions. After 1 hr of gasification, the reactor was purged with nitrogen. Finally, the nitrogen stream (fluidizing gas) was then switched to air to achieve R3 conditions. During this step, the temperature was closely monitored to not exceed the reactor specifications. This step (R3 conditions) concluded when the reactor output oxygen concentration equaled the input concentration, or approximately 21%. The entire process is shown in Figure 3-14. Under these conditions, the reactor temperature reached 1,100^{o}C. This is an increase of 360^{o}C from R1 temperature. Subsequent recovery of the bed mixture revealed large agglomerates (10% of the entire weight of the bed material) attached to the refractory wall.

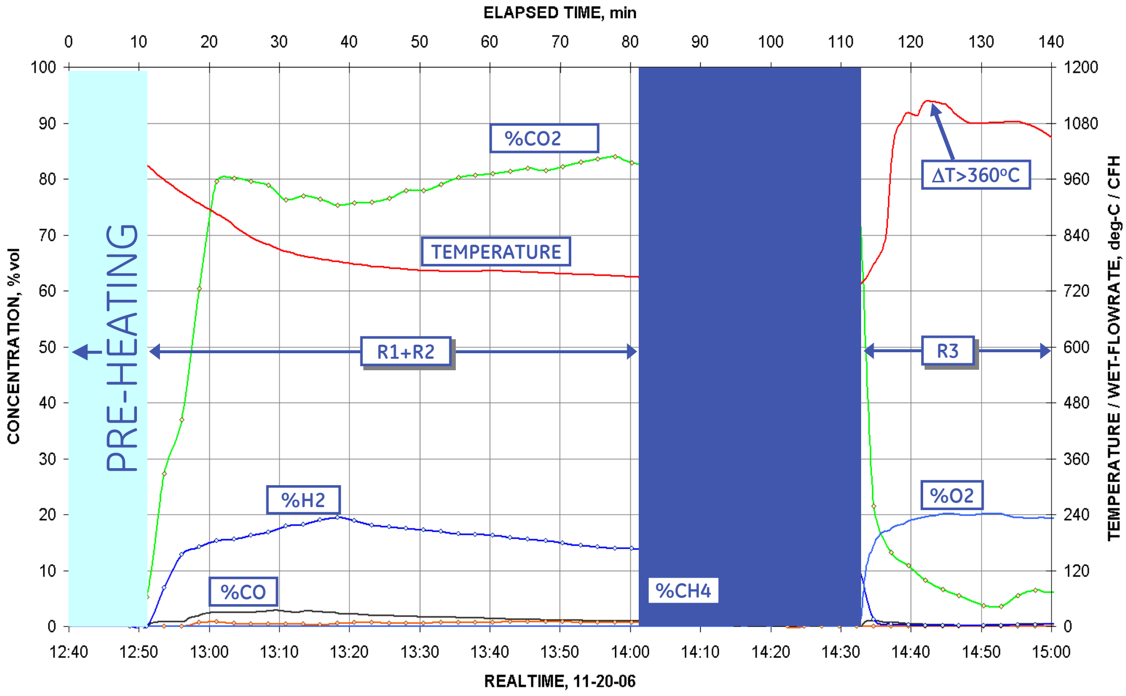


Figure 3-14 Typical reactor performance at various stages: preheating, R1 and R3 conditions

Figure 3-15 shows the relative location of where the agglomerates were found and actual pictures of the reactor core and agglomerate samples. Subsequent lab analysis shows their composition to be mostly OTM. The agglomerates were formed near the port for the auxiliary fuel used during the start-up of the experiment. The preliminary conclusion was that the agglomerates were formed because of a local hot spot in the reactor during either preheating step or the oxidation step simulating R3 conditions.

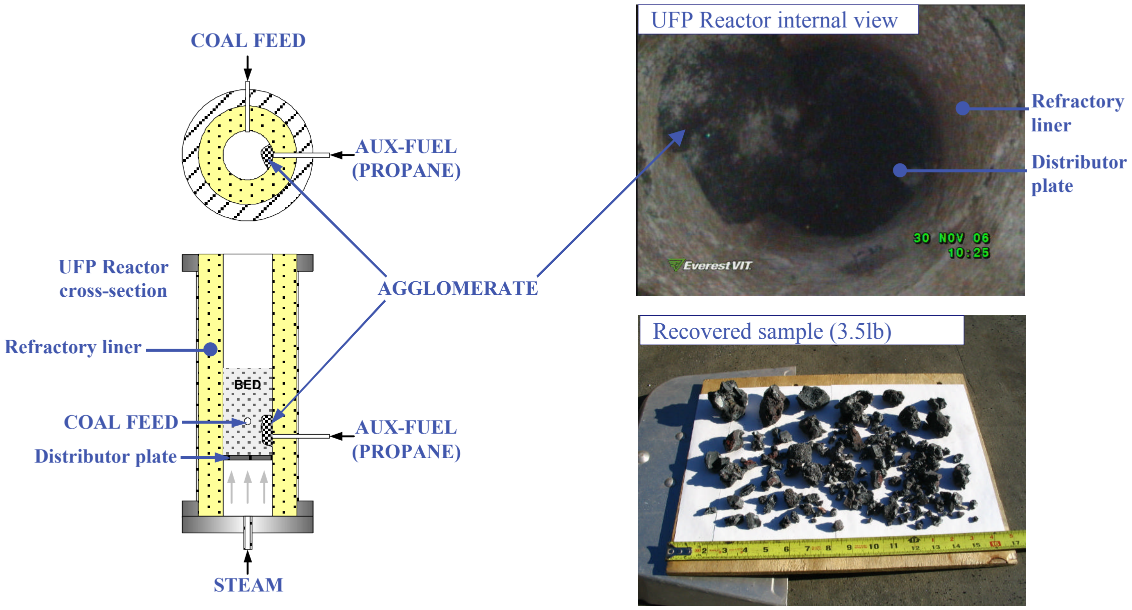


Figure 3-15 Relative location of agglomerate in reactor and actual pictures

3.2.5 Limitations of the Pilot-scale Reactor and Recommendation

The upgraded single pilot-scale reactor was used to investigate the bed agglomeration risk in the UFP technology. Some of the upgrades described in the previous section were successful; however, it was clear that the pilot-scale system was not the suitable tool to investigate and mitigate the technical risks associated with the novel UFP technology. Maintaining the reactor temperature above 850°C reliably over long periods was still a challenge, making it difficult to investigate the solid lifetime under R2 & R3 conditions. The initial plan to mitigate this risk was to use a custom-made auxiliary electric cartridge heater. However, this unit proved to be unreliable as the auxiliary heating unit had frequent internal thermocouple failures above 900°C. Further, the current reactors were not certified to operate under pressure, thus enabling the operation only up to 15 psig. The major UFP technical risks such as agglomeration of solids, lifetime of bed material and the impact of coal impurities on the process can be investigated using the bench scale system in a much more controlled environment compared to the pilot-scale system.

Based on experimental results and analysis in 2006 GE Global Research recommended a revised plan for the remaining part of the Phase II investigation. According to this plan the bench-scale system were to be used to carry out the evaluation and mitigation of the major UFP risks, solids lifetime and impact of coal impurities. The results obtained with the Pilot scale experimental system and the revised plan was communicated to DOE in December 2006.

3.3 Experimental Evaluation of UFP Technology using Upgraded Bench Scale Reactor

The bench scale reactor system was upgraded in 2007 in order to investigate the major risks associated with the UFP technology. The main upgrades and their effects are described in the following section.

3.3.1 Multiple Coal Injections

Various engineering upgrades were performed for the coal injection system. The ability to inject coal in the high temperature reactor allowed the investigation of devolatilization stage during coal gasification, as the devolatilization of coal is an important chemical reaction occurring in the R1. Coal undergoes devolatilization reaction to produce char and gaseous products including CO, H_2, CH_4 and other hydrocarbons. The upgrades have improved the injection reliability and the system was capable of performing multiple sequential injections into fluidized bed reactor. The initial coal injection result is shown in Figure 3-16. Each time 10g coal was injected to the reactor in a 5-minute interval while the gas composition was continuously monitored. After each injection, the reactor temperature dropped about ~40ºC and then slowly recovered. Four injections were successfully conducted while the fifth injection was aborted because the injection probe was clogged, which was contributed to the disruption of the purge gas flow.

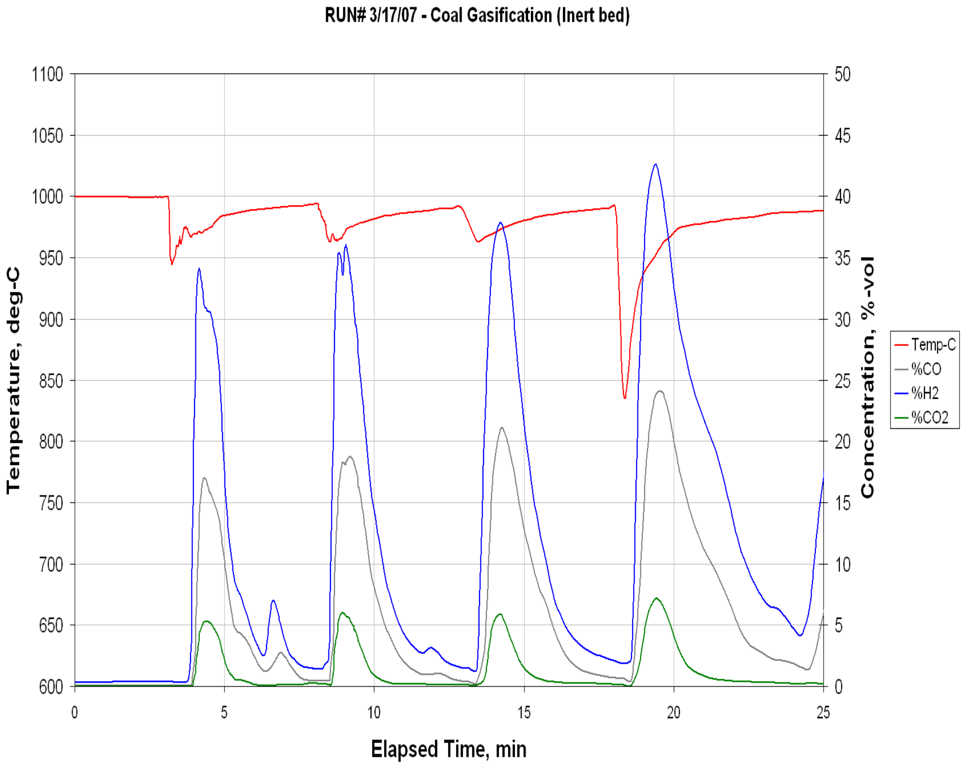


Figure 3-16 Multiple coal injections

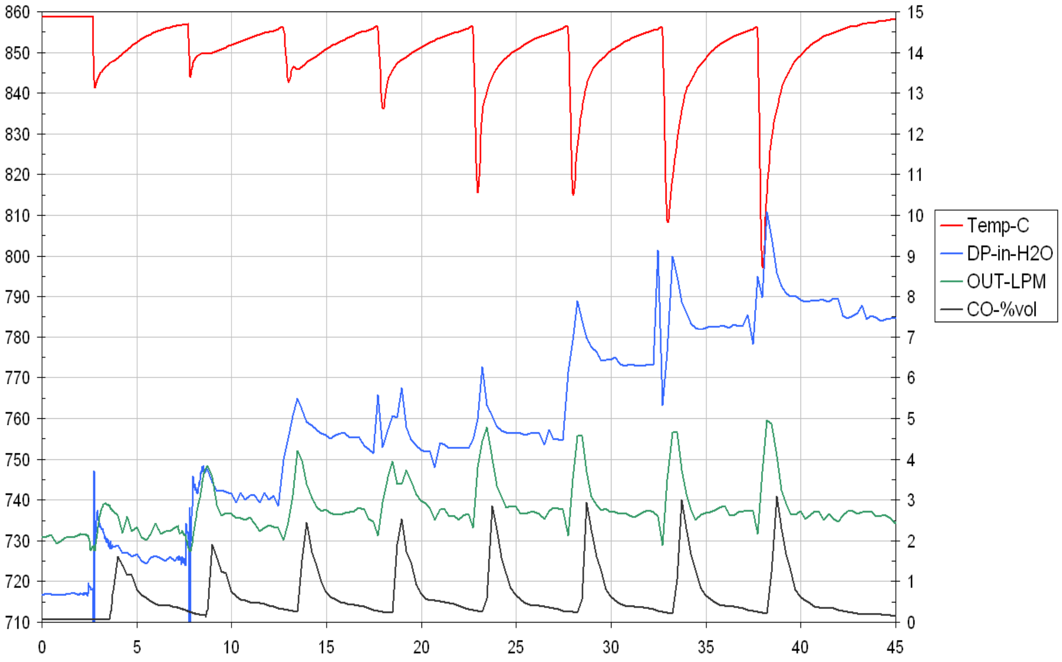


Figure 3-17 Eight sequential coal injections in petcoke char preparation

The injection capability was also tested with petcoke char preparation. As shown Figure 3-17, eight injections were performed. The pressure drop increases observed were probably related to the char accumulation in the downstream filter. The petcoke char was used to investigate the impact of ash content in the coal feed on the lifetime of the solids materials in the UFP process.

3.3.2 High Temperature Operation

A limitation of the bench-scale fluidized bed reactor was that it could be operated only up to 1000°C as the material of construction of the reactor was a high temperature metal alloy and the reactor was heated externally with a electric furnace. It was very important to investigate the UFP reactions and solids interactions in the temperature range of 1000-1300°C as R2 and R3 are expected to operate at these high temperatures. To do so, the bench-scale reactor was modified. The modification mainly included changing the material of construction of the reactor from metal to ceramic material.

The high temperature reactor was designed as a ceramic tube reactor with metal caps at both ends to provide the seals as well as the feed-through connections. The ceramic materials considered for the reactors were high purity Al_2O_3 and SiC. The materials selection was mainly based on mechanical strength, thermal expansion coefficient, thermal conductivity, and availability. The end caps were universal tube seals. Since the end caps provided seals with Viton fluoroelastomer, one of design criteria is to maintain the seal temperature below 200ºC.

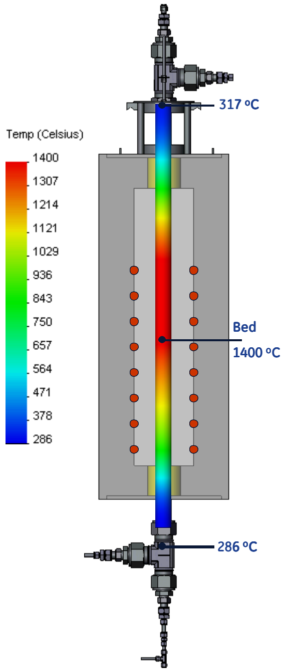


Figure 3-18 Thermal analysis of the high temperature reactor

To estimate the temperature profile of the reactor, thermal analysis using COSMOS software simulation was conducted and the result was shown in Figure 3-18. The bed that composed of a 1.75" internal diameter and 4' long cylinder located at the center of the tube was set to 1400ºC and various heat-transfer coefficients were used along the tube to account for the gas flow effects. The simulation indicated inlet (bottom end cap) temperature of ~286ºC and outlet (top end cap) temperature of ~317ºC at planned flow conditions with a 5' alumina tube.

To reduce the temperature at both end cap seals, longer ceramic tubes (6') were used and the heating elements for the top zone of the furnace were also disabled. A high temperature reactor with 6' alumina tube was assembled and tested as shown in Figure 3-19. Most of the initial tests were conducted with fluidization configuration in the temperature range of 800-1200ºC. During these tests, the end cap seals temperature was no than more 100ºC. Even in a shakedown test at higher temperature of 1300ºC, the seal temperature was ~150ºC.

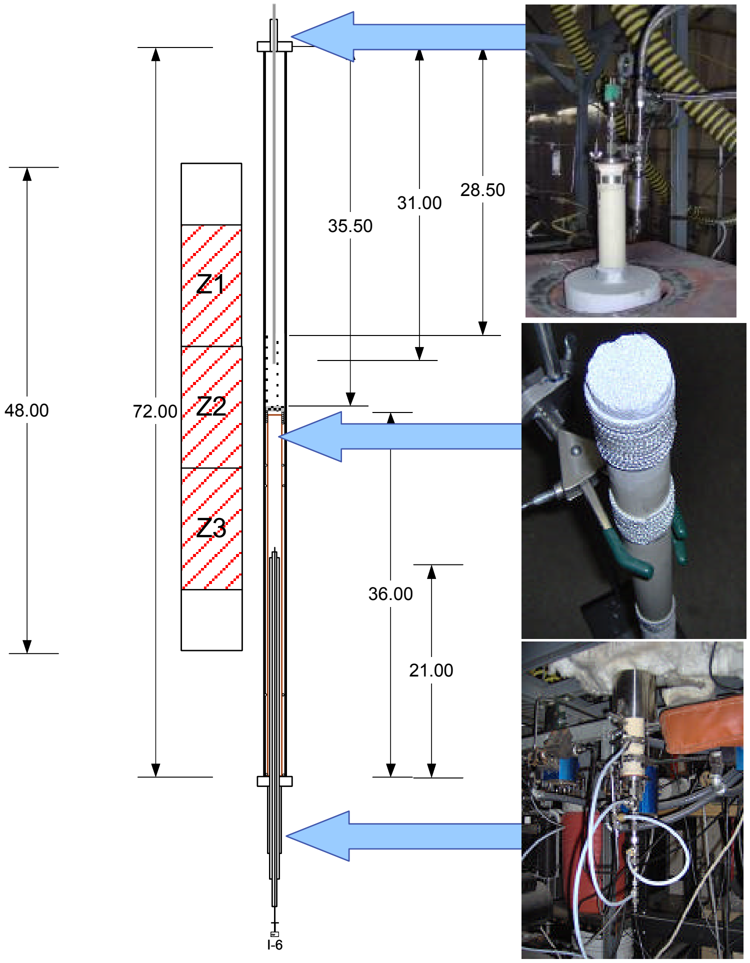


Figure 3-19 High temperature reactor assembled with 6' alumina tube

Several tests were conducted with upgraded high temperature reactor. For example, Figure 3-20 showed the gasification kinetics obtained at 1100ºC from the ceramic reactor comparing with that obtained at 1000ºC from the metal reactor. As expected, increasing the gasification temperature significantly increased the reaction kinetics. Most of the high temperature tests, however, were carried out for the solid materials life assessment as described in the next section.

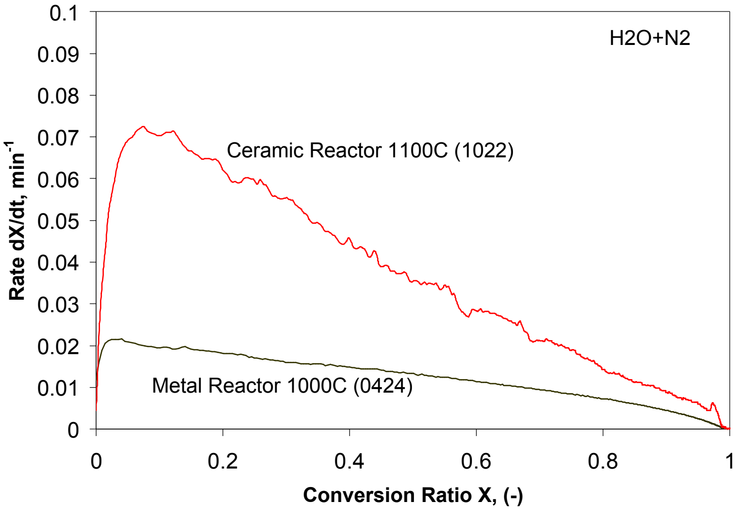


Figure 3-20 Coal gasification kinetics at 1000ºC and 1100ºC

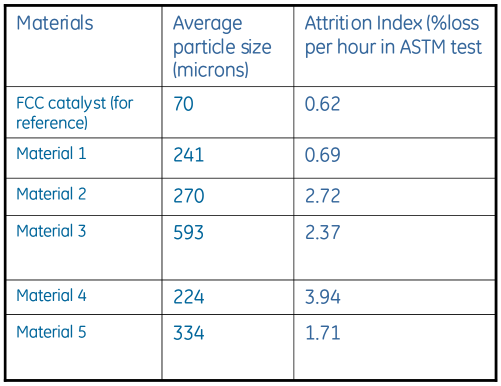
3.4 Solids Life Assessment

The economic analysis of the UFP process indicated that the cost of the solids material used in the UFP technology is the critical parameter in determining the feasibility of the process. Various mechanism affecting the lifetime of the solids were investigated including physical attrition, chemical attrition and agglomerations. The agglomeration of the solids was identified as the most critical and rate determining mechanism affecting the lifetime of the solids and in turn the cost of the UFP technology. The agglomeration issue and its impact on the UFP technology was further investigated in detail. The following section describes the results obtained during the investigation of solids lifetime.

3.4.1 Physical Attrition

To determine particle attrition levels, several solid CAM & OTM materials of interest were obtained as summarized in Table 2-1. Below are results of the AIs from ASTM measurements and the mean particle size performed at RTI.

Table 3-3 Physical attrition measurement results



Materials	Average particle size (microns)	Attrition Index (%loss per hour in ASTM test
FCC catalyst (for reference)	70	0.62
Material 1	241	0.69
Material 2	270	2.72
Material 3	593	2.37
Material 4	224	3.94
Material 5	334	1.71

The average particle size of the standard material is typically 65-70 micron and those of the candidate materials are considerably larger. With that in mind, it is reasonable to conclude that:

- Material 1 was significantly more attrition resistant than material 2
- Materials 1 had strong attrition resistance, potentially as good as the reference material
- Material 4, with mean particle size ~200 µm, was probably less attrition resistant than material 5, with mean particle size ~300 µm.

Again, it is important to clarify that these AIs are useful for comparison only, and cannot be extrapolated to attrition level at several hours under operation (>> 5 h). Another remark on the ASTM results is that one does not know the extent of particle size effect on the results at this point. Generally attrition increases with the square of particle size. However, it is unclear whether this generalization applies to different materials. Assuming this assumption is true, all candidate materials seem to be attrition resistant in comparison to standards. For true comparison, targeted materials should be first made in the size range of 65-70 µm and then retested.

Experiments were also carried out to investigate the physical attrition of the sorbents in a bench scale fluidized bed reactor. OTM (50g) or CAM (30g) was fluidized with N_2 at various temperatures in the range of 700-900^{o}C at near atmospheric pressure for 4h. After the experiments, bed material left in the reactor was collected and the weight loss was measured. Then the sample was analyzed to determine the particle size distribution before/after the physical attrition test.

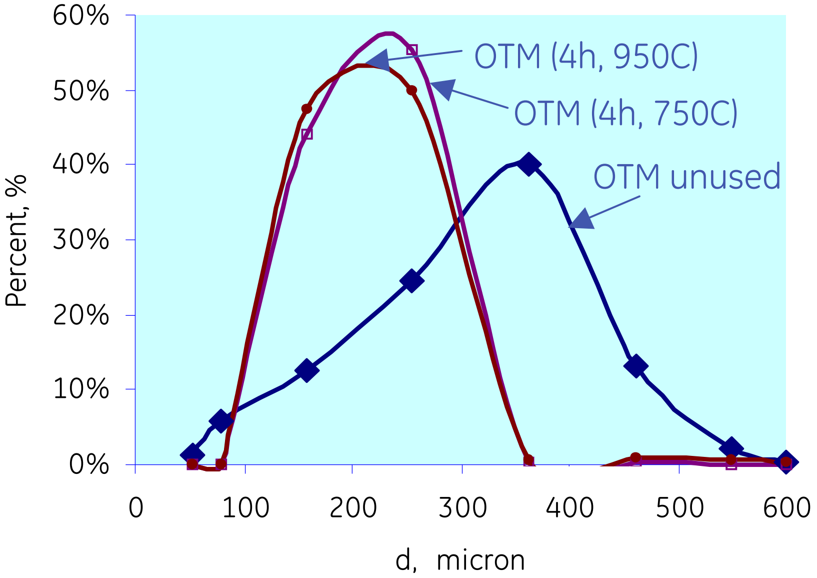


Figure 3-21 Effect of physical attrition on the particle size distribution (OTM)

Figure 3-21 shows the particle size distribution of OTM before and after the physical attrition experiments for 4 hours in the bench scale system. The physical attrition tests were carried out under ambient pressure at two different temperatures: 750°C and 950°C. It was observed that at both temperatures, the averaged particle diameter decreased after 4 hours of fluidization, probably due to fragmentation. Fines smaller than ~100µ were removed from the reactor by entrainment in the gas flow. The amount of bed material lost by entrainment after 4 hours was <2% by weight. Furthermore, there was no significant difference between two particle size distributions at the two temperatures studied. The effect of the temperature on the OTM physical attrition was negligible.

The effect of the physical attrition on the CAM particle size distribution is shown in Figure 3-22. The operating conditions were similar as those of OTM tests. At 750°C, the particle size distribution of the CAM did not vary much from that of the unused CAM after 4 hours of continuous fluidization. After the 950°C experiment, the average particle size of the CAM decreased. In addition, the portion of 100-200µ diameter particles also increased during the 950°C experiment indicating abrasion of CAM under these conditions. The physical attrition analysis of the CAM is much more complex than that of the OTM because of the decomposition of CAM especially at 950°C. Decomposition of CAM also indicated a loss in the overall weight of the fluidized bed as the CO_2 adsorbed in the CAM was removed from the reactor. The bed loss of the CAM was negligible after accounting for the released CO_2 gas.

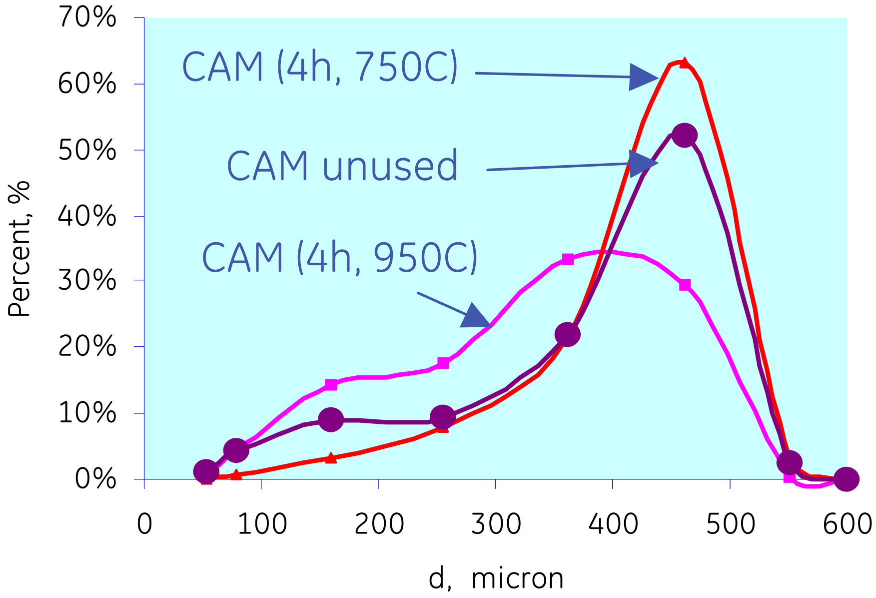


Figure 3-22 Effect of physical attrition on the particle size distribution (CAM)

3.4.2 Chemical Attrition

Testing protocol was developed whereby the attrition of the CAM & OTM particles resulting from chemical cycling can be studied. Specifically, the test was intended to measure the degradation of absorption/desorption performance for the CAM and OTM materials with time. An example of such a test is shown in Figure 3-23 for a commercial CAM material. In this test, the temperature was cycled in a manner to simulate material moving between R1, R2, and R3, respectively. Absorption and desorption events are shown by the positive and negative peaks in the CO_2 flow. Based on the area under these respective curves, the magnitude of absorption/desorption can be quantified. Although long-term testing is by no means complete, preliminary results show:

- Desorption of CO_2 occurs rapidly at temperatures in excess of 925 °C.
- Absorption is more complex. It begins quite rapidly at 925°C, but tapers off dramatically after only partial carbonation. The reaction then proceeds slowly with no perceptible completion after the 3-hour soak.
- Qualitatively, commercial material shows no significant degradation following 10 cycles (not shown).

Clearly, performance is strongly related to both composition and morphology. Consequently, determination of the efficacy of any one composition requires multiple tests from varying suppliers.

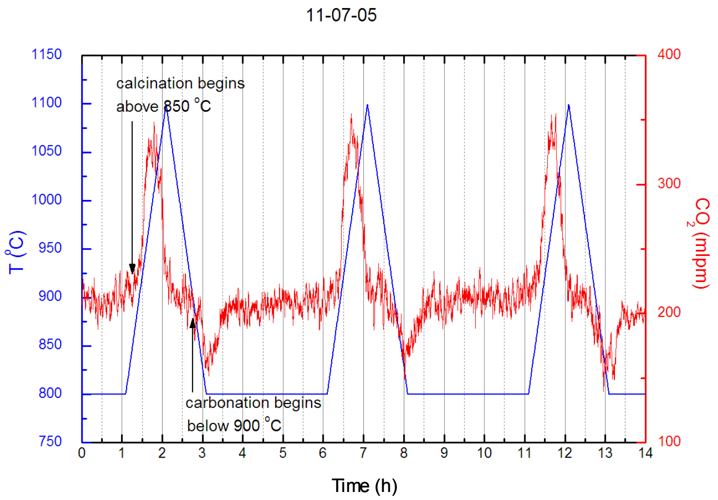


Figure 3-23 Chemical attrition test for commercially-available CAM material

Reactivity between the various chemical species is of considerable risk. Thermodynamic studies were taken to offer insight into the potential reactivity of the sorbents, furnace lining, coal slag, etc. These analyses were entirely thermodynamic in nature; these reactions may be kinetically limited depending on the nature of the interaction. Nonetheless, an understanding of the nature of these interactions was important to gaining a better understanding of materials interactions. TDATA© version 4.74 was used to analyze the equilibrium composition in the 3-reactor UMC design. Of note was the fact that considerable reactivity between the OTM and CAM is predicted. This was also confirmed with the experimental work. Heat treatments were performed where CAM and OTM mixtures were fired at 1000, 1100, and 1150°C for duration of 1h. The resultant x-ray diffraction patterns are shown in Figure 3-24. The reactivity was significant, as predicted by the thermodynamic model. The kinetics of these reactions under the actual operating conditions needs to be determined because the materials are maintained in a fluidized state, the average time the particles are in contact is quite low as compared to the heat treatments described here. Therefore, more detailed analyses are required where the extent of reactivity can be measured under fluidized bed conditions.

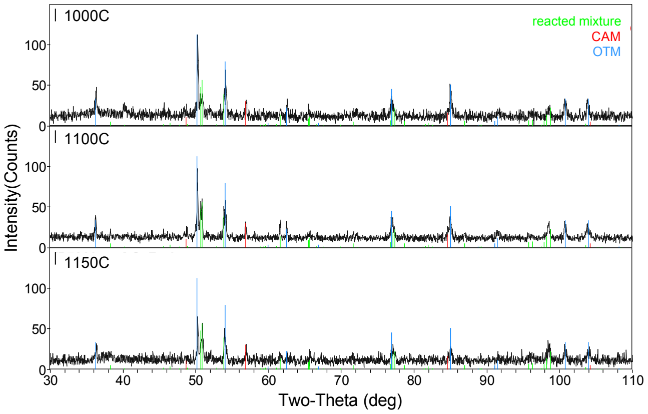


Figure 3-24 X-ray diffraction pattern of CAM/OTM mixtures treated at different temperatures

3.4.3 Solid Materials Agglomeration

Agglomeration of solid particles used in the UFP process was identified as the major parameter controlling the life of the OTM and CAM materials. The possible causes for the agglomeration behavior include: (1) interaction of low-melting-point ash compounds in the coal with the CAM and/or OTM materials, (2) formation of low-melting species such as $CAM(OH)_2$, and eutectic compound between CAM and $CAM(OH)_2$, (3) interaction of OTM with coal and syngas, and (4) interaction between OTM and CAM materials.

Experiments were designed to understand the causes of the solid agglomeration. These have been done through (1) bench-scale reactor at < 1000ºC (2) offline tests, and (3) high temperature tests.

3.4.3.1 Bench-scale Reactor Test at < 1000ºC

The thought process and the design of experiments with the bench-scale reactor to understand the reason behind the solids agglomeration are summarized in Figure 3-25. Several decision points were made through the process based on bed materials agglomeration analyses. The green lines in the figure link the experiments conducted and the red lines link the experiments considered as unnecessary based on the experimental results after the decision points.

In coal gasification experiments at 1000°C with various bed material combinations (CAM+OTM, CAM+Alumina, OTM+Alumina), no agglomeration was observed with the CAM+Alumina bed composition. The results suggested that ash interaction with CAM+Alumina mixture might be insignificant to cause the bed material agglomeration. They also suggested that the formation of $CAM(OH)_2$ and its eutectics with CAM would be unlikely under the testing conditions or even if it occurs it would not cause significant agglomeration. On the side, whenever OTM was present in the bed materials (either OTM+CAM or OTM+Alumina mixtures), heavy bed agglomeration was observed as shown in Figure 3-26, suggesting that OTM might be associated with the main cause of the agglomeration.

To understand the root cause for agglomeration, the OTM+CAM bed material was further tested under petcoke gasification conditions. It turned out that the bed material was heavily agglomerated even though the petcoke has little or no ash species. Although this result couldn't rule out the possibility of ash as the cause to the agglomeration, it concluded that other factors, such as OTM-CAM interaction, OTM interaction with coal could be the main causes. To verify this, the CAM+OTM mixture was exposed to a mixture of CO_2 and steam in the reactor. No agglomeration was observed. This again indicated that formation of $CAM(OH)_2$ and its eutectic compound with CAM was not significant under the testing conditions. It also suggested that the interaction between OTM and CAM under the non-reducing environment might be insignificant to cause the agglomeration observed. Further, the bed materials were exposed to a syngas mixture (CO, CO_2, H_2, H_2O, and N_2) to simulate the coal gasification environment; and the bed materials agglomerated after the exposure. This result clearly demonstrated that reducing atmosphere of the gasification environment alone could have caused significant agglomeration of the bed materials. Gasification with graphite was not performed, however, it was anticipated that the bed would be agglomerated even though the graphite is ash-free. Under the oxidation-reduction conditions, it was believed that the reduction of the OTM caused the surface morphology/composition to change, which in return resulted in self-adhesion and intensified the interaction with CAM. The later was confirmed with SEM analysis on the agglomerated bed materials that showed an OTM–rich zone on the surface of the CAM materials, indicating the reaction between the OTM and CAM in the gasification environment as shown in Figure 3-27.

The results based on the experiments in the bench-scale reactor indicate that,

- Reduction of OTM under the gasification conditions was the major cause to the bed materials agglomeration
- Interaction of CAM and OTM was also evident
- Ash could cause the agglomeration, but the effect was less significant in comparison with OTM reduction
- Formation of the $CAM(OH)_2$ and eutectic compound between CAM and $CAM(OH)_2$ was also insignificant.

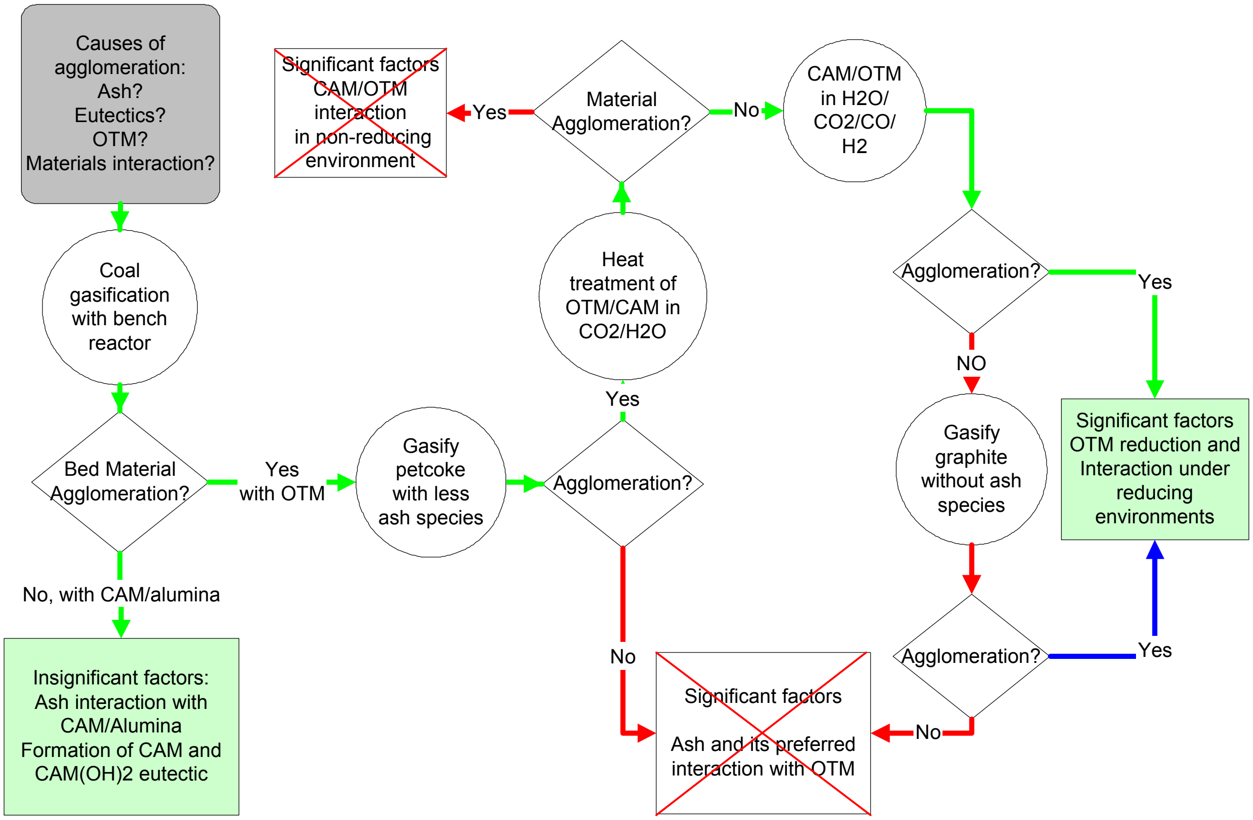


Figure 3-25 Thought process and design of experiments with the bench reactor to diagnose the causes of bed materials agglomeration

Figure 3-26 OTM/CAM bed materials after gasification run showing agglomeration

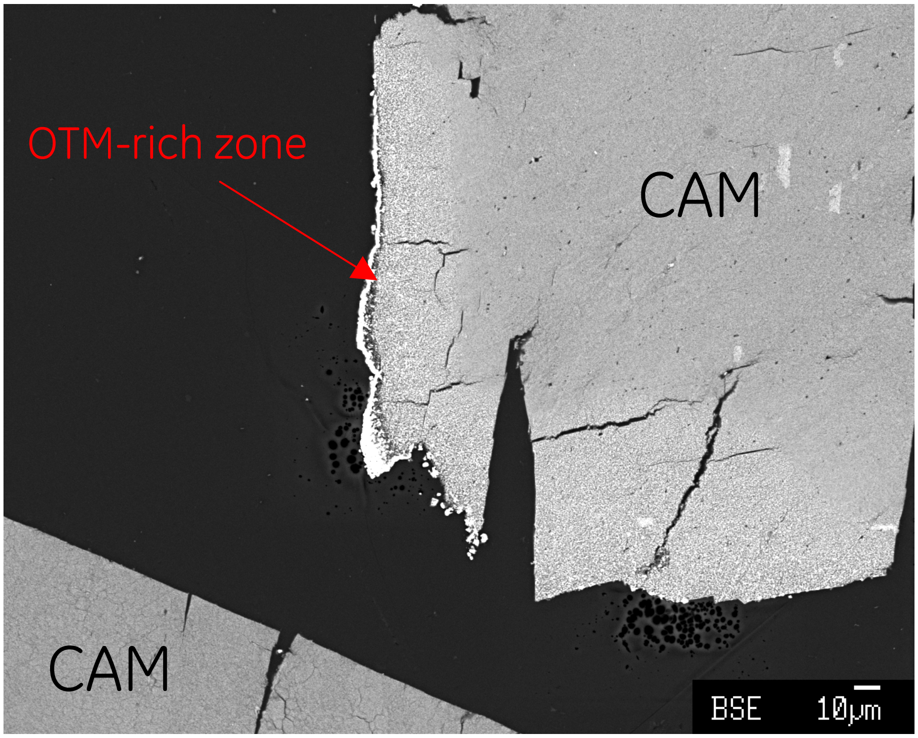


Figure 3-27 SEM analysis of the broken agglomeration, showing OTM-rich zone on the CAM particle surfaces

The design of experiment demonstrated that reducing atmosphere of the gasification environment alone could have caused significant agglomeration of the bed materials and it was found that reduction of the OTM was the major cause of the bed material agglomeration. Given the Redox nature of the OTM, it was believed that the reduction of the OTM caused the surface morphology/composition change, which in return resulted in self-adhesion and intensified the interaction with CAM. To further verify this, the bed materials exposed to coal gasification and those exposed to CO_2 and steam were characterized comparatively.

Shown in Figure 3-28 is a backscattering image from SEM analysis on sample 20070524, which has been used in a blank run with H_2O/CO_2 feed at 1000°C for 2 hours. The dark particles are CAM, where some cracks were evident after calcination at 1000°C. The bright particles are OTM, which appears to be relatively dense. Some impurities were also observed in the OTM. Since the materials were tested in the bench reactor at 1000°C with CO_2/H_2O feed but without coal, the OTM wasn't reduced. No interactions were observed between OTM and CAM.

In comparison, strong interactions were observed when CAM and OTM were used in fluidized bed for gasification at 1000°C. Shown in Figure 3-29 is a backscattering image of CAM and OTM after test. Reaction zones are clearly visible on the margins of both CAM and OTM materials. OMT-rich reaction zone was observed on the CAM particles. For the OTM particles, porous reaction zone was also evident. The interaction between OTM and CAM causing the bed materials agglomeration can be better seen from Figure 3-30, where OTM and CAM particles were stuck together with the reaction zone.

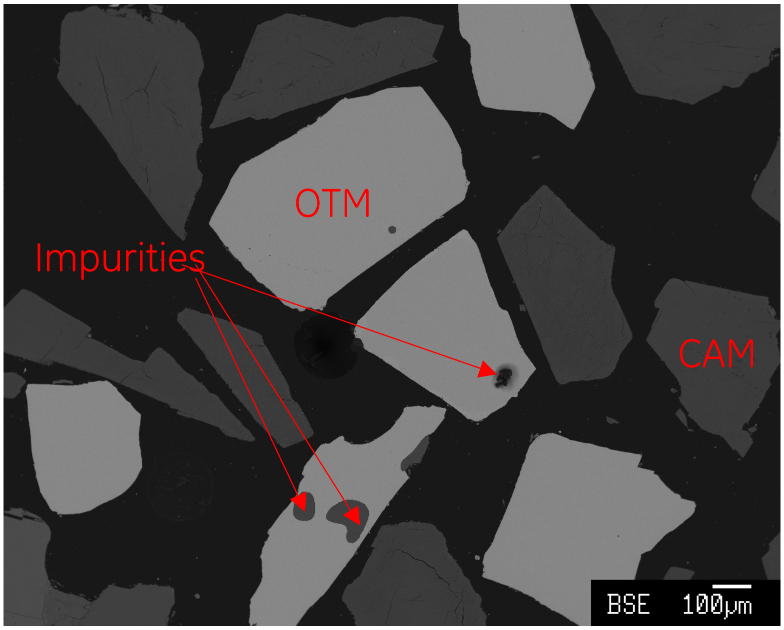


Figure 3-28 SEM image of OTM and CAM after being exposed to H_2O and CO_2 at 1000°C in the bench reactor without coal gasification

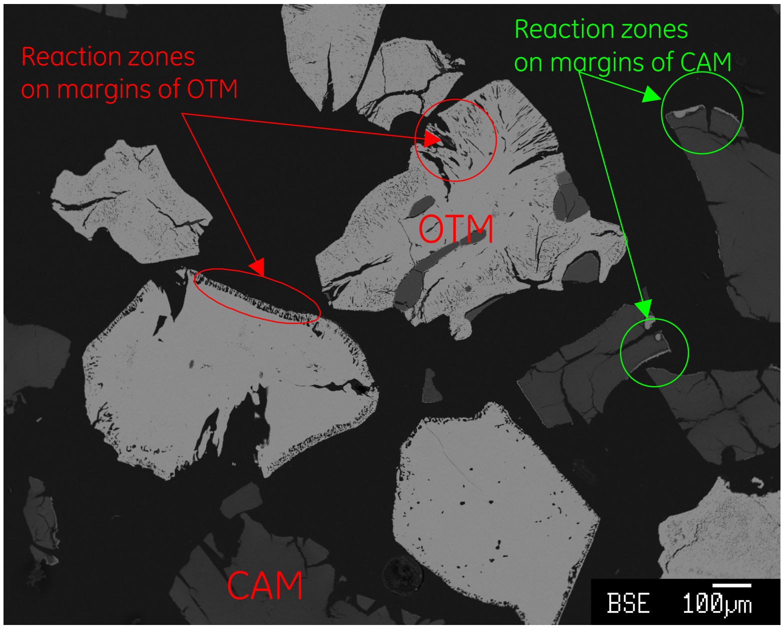


Figure 3-29 SEM image of OTM and CAM after being exposed to H_2O and CO_2 at 1000°C in the bench reactor with coal gasification

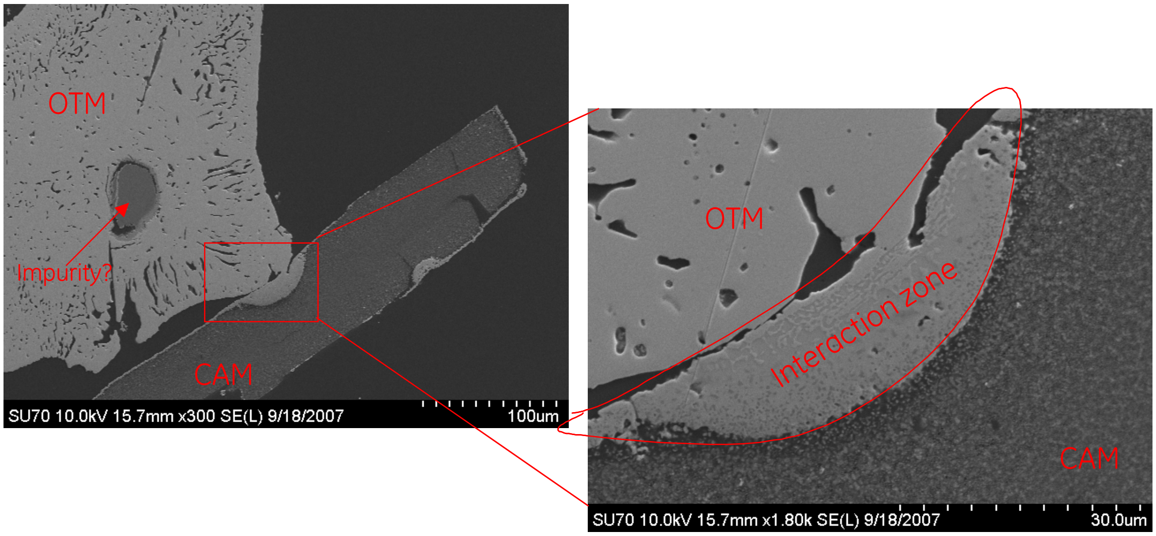


Figure 3-30 SEM images showing the interactions between OTM and CAM

3.4.3.2 Offline tests

Alkali species in coal ash, such as sodium and potassium, can form low melting-point compounds, thus causing stickiness at the surface because of their ability to modify the glass network. To examine the influence of these species on solids agglomeration, small amount of

NaOH was dosed on to the bed material through a water solution. After heat treatment in air at 1000°C for 2 hours, the results are summarized in Table 3-4. It can be seen that no agglomeration was formed when the OTM+CAM mixture was treated with water only. However, when NaOH was added, heavy agglomerates were formed with the OTM; moderate agglomerates were formed with the OTM+CAM mixture, and light agglomerates were formed with the CAM. It is worth to mention that even small amount of NaOH addition (0.2 wt%) can cause heavy agglomeration of OTM. This is probably resulted from the reactions of sodium species with OTM and the impurity phase (quartz) in the OTM raw materials.

Table 3-4 Experiment summary with NaOH addition to varied bed materials

CAM, g	OTM, g	NaOH, g	Agglomeration Status
40	40	0*	No agglomeration
40	40	0.48	Heavy, stuck in crucible
0	80	0.48	Heavy and hard, fused together and stuck in crucible
80	0	0.48	Light, loosely packed, some stuck to crucible wall
40	40	0.16	Moderate, loosely packed
0	80	0.16	Heavy and hard, fused together and stuck in crucible
80	0	0.16	Very light, very easy to break
*Only treated with water			

In parallel, the influence of ash addition on agglomeration was also tested. In one test, ~0.8 g coal ash was mixed with 20 g OTM and 20 g CAM, no agglomeration was observed after heat treatment in air for 2 hours at 1000°C. In the other test, 20 g OTM and 20 g CAM mixture was loaded on top of ~1 g coal ash resulting in minor agglomeration after heat treatment and the agglomerated particles were very easy to break. Although inconclusive, these results indicated that the influence of ash could be negligible under the testing conditions.

In the bench-scale reactor tests, the results indicated that the agglomerates were directly linked to the OTM materials and the main cause was the reducing environment. To verify this further, varied amount of coal was mixed with OTM, CAM, and Alumina and those samples were heat-treated at 1000°C for 2 hour in stagnant air. The results showed in Table 3-5 indicate that the amount of OTM agglomeration was proportional to the amount of coal added. No OTM agglomeration was observed in the absence of coal addition. No agglomeration was observed when CAM was mixed with coal. Only very light agglomeration was formed when alumina was mixed with coal. Although the cause to the light agglomeration of alumina was not clear at this moment, it is suspected that it may be related to the impurities in the raw materials.

Table 3-5 Offline heat treatment summary with coal addition

CAM, g	OTM, g	Alumina, g	Coal, g	Agglomeration Status
0	40	0	4	Heavy, all agglomerated together
0	40	0	1	Heavy, bottom half agglomerated together
0	40	0	0	No
40	0	0	4	No
0	0	40	4	Very light and easy to break

3.4.3.3 High temperature tests

The purpose of the high temperature test was to assess the solid life during their exposure to the high temperatures in R2 and R3 reactor conditions. As indicated in the chemical attrition section, OTM and CAM are expected to react with each other at high temperatures. Such reactions could cause the bed materials agglomeration, subsequent defluidization, and loss of the bed material activity.

Heat treatment of CAM, OTM and mixture of CAM and OTM were carried out in air. At 1200ºC, only light agglomerations were formed when heat–treating OTM and CAM separately. The light agglomeration was probably due to the partial materials sintering at high temperature and influence of impurities such as silica. However, heat-treating the mixture of CAM and OTM at 1200ºC for 2 hrs caused heavy agglomeration of the mixture. Since the heat treatment was conducted in stagnant air without fluidization, the contact time between materials was relatively long. It was expected that the contact time between particles would be reduced under fluidization conditions, thus the reaction could be diminished. To test this, bed materials was heat-treated at 1200ºC under fluidization conditions in the upgraded high temperature reactor. Surprisingly, the whole bed was agglomerated after such treatment, indicating that the interactions between CAM and OTM were significant at high temperature and the agglomeration would cause defluidization and eventually clog the reactor.

In summary, solids agglomeration was one of the main concerns for the solid lifetime. The main causes to the solids agglomeration were combination of OTM reduction and high exposure temperatures. At moderate temperatures, say 1000ºC, the reduction of OTM caused the surface morphology/composition change and intensified the interaction between CAM and OTM, which resulted in bed materials agglomeration. Heat-treatment at 1000ºC in the absence of OTM reduction wouldn't cause the bed agglomeration. However, at higher temperatures (>1200ºC), the high temperature itself would cause significant chemical interaction between OTM and CAM, and resulting in solid agglomeration even in the absence of OTM reduction.

3.4.3.4 OTM modification and development

To reduce the agglomeration tendency of OTM, during the last quarter of the experimental program the efforts were focused on exploring:

- OTM morphology modification
- Composite formation with inert bed materials, and
- New OTMs exploration

The baseline OTM that had been used is in the angular and rectangular prism shape. The sharp corners can intensify the particle stickiness. Particles with spheroid shape may help reduce the possible contact area and stickiness. To evaluate an OTM with same composition but with round shapes, both offline heat treatment and bench scale reactor gasification tests were conducted. The results indicated that the morphology modification only marginally reduced the OTM agglomeration.

Another approach to reduce the agglomeration tendency is to form composite with inert bed materials. The composite can decrease the direct contact areas between OTM and it can potentially improve the attrition resistance. Several OTM composites were synthesized in the lab. XRD analysis indicated the desired OTM phase and inert material. SEM observation showed composite particles consisting of sub-micron mixtures of OTM and the inert material. The inert phase on the OTM particle surface is expected to be effective in increasing agglomeration resistance of the composite materials. Off-line test was conducted to check the agglomeration behavior of the composite made and to compare with that of baseline OTM particles. After heat treatment with coal, baseline OTM particles exhibited agglomeration, while no agglomeration was observed with the composite. In another offline heat treatment with significant amount of coal, only light agglomeration was observed with the composite while, the baseline OTM heavily agglomerated. Although the new materials sets were promising, the analyses on oxygen transfer capability and redox characteristics of the composite OTM and validation tests with the fluidization reactor were not conducted due to program time constraints. The material development of OTM should be explored in future research projects.

3.4.4 Impact of CO_2 Recycle on Coal Gasification

Out of various forms of solid-attritions, agglomeration of solids seems to be the most critical technical risk that can affect the lifetime of the solids. Agglomeration may happen due to low-temperature melting ash compounds in the coal and due to low-temperature melting hydrated form of CAM. Using CO_2 to partially replace steam for fluidization in the reactor 2 in the UFP process can reduce the formation of hydrated form of CAM. Using recycled CO_2 for fluidization can also increase the overall efficiency by reducing the steam requirement for the UFP process. The study of CO_2 recycle impact on gasification and the overall UFP process was initiated and the effect of CO_2 on the slowest step in gasification, gasification of char with steam, was studied.

In the baseline tests, the nitrogen-steam mixture was used as the gasification agent and alumina was used as inert bed material. Char was loaded in batch mode in the reactor. Tests were conducted under the ambient pressure and at 950°C (temperature similar to reactor 2 in the UFP process). Figure 3-31 shows the char conversion as function of time on stream with same partial pressure CO_2 (Test 1), steam (Test 2) and steam/CO_2 mixture (Test 3: the partial pressure of steam is same as that in Test 2, while the partial pressure of CO_2 is 1/6 of that in Test 1) as the gasification agent. It was observed that the conversion of char with steam was much higher than that with CO_2 under the operating conditions in the present experiment. Furthermore, when steam/CO_2 mixture was used as the gasification agent, a significant increase in the conversion was observed. Based on these preliminary experiments, CO_2 seems to have a positive impact on char conversion under the fluidizing bed conditions.

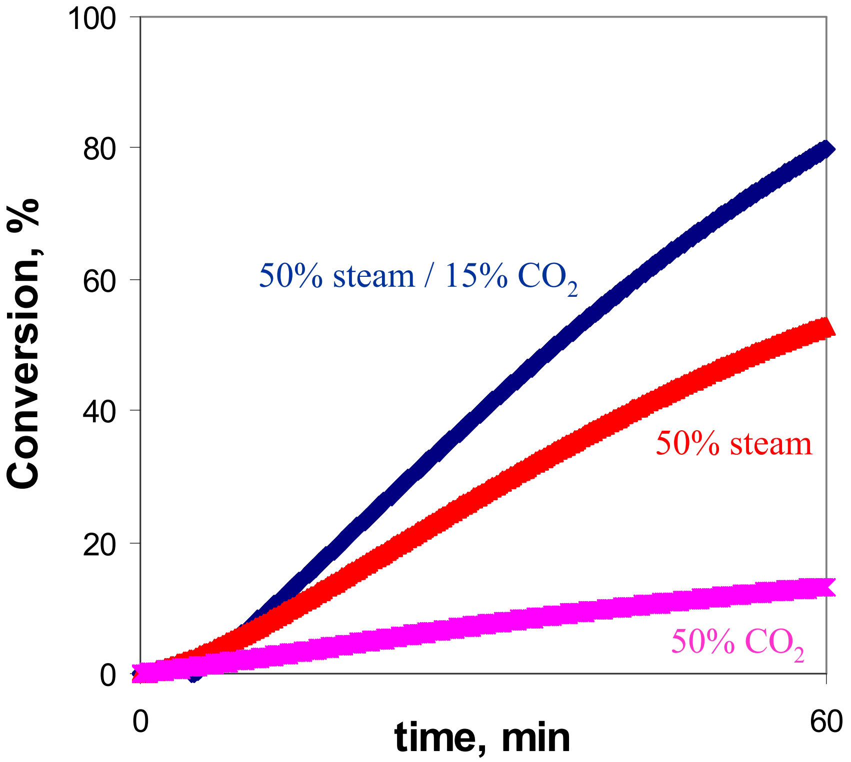


Figure 3-31 Positive impact of CO_2 addition on char conversion

3.5 Impact of Impurities in the Coal

3.5.1 Sulfur Tracking in Bench Scale Fluidized Bed Reactor

When coal is used as fuel in the power industry, it is of importance to manage the sulfur emission in the process. In the UFP process the sulfur content in the coal can be released as H_2S during the gasification process from R1 and R2 or as SO_2 during the oxidation process from R3. The sulfur emissions coming out from R1 can be treated in the conventional syngas clean-up unit operations. The sulfur content released from R2 can be sent for sequestration along with CO_2. However, the sulfur emission from R3 needs to be minimized, as it would be detrimental to the downstream power island equipments. Further, the output of R3 is expected to go directly to a gas turbine expander without any cooling in order to get high efficiency. However, technologies to clean up SO_2 at >1200ºC is not available. Thus, it is important to minimize the emission of sulfur from the R3 of the UFP process.

The bench-scale experimental system was used to track sulfur in the UFP process. The bench scale reactor containing mixture of CAM, OTM and coal was cycled through operating conditions simulating R1, R2 and R3 conditions respectively. The product gas concentrations including SO_2 were monitored during the experiments.

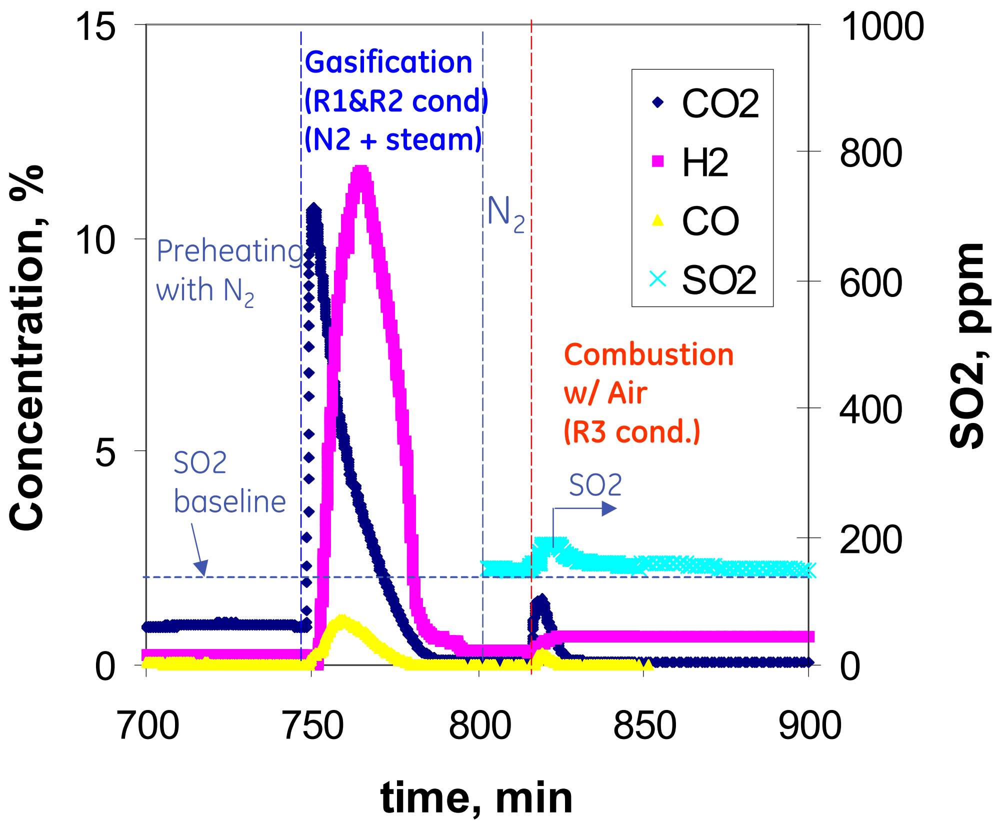


Figure 3-32 Sulfur tracking: CAM and OTM

The coal was preheated in N_2 and gasified with steam (simulating R1 & R2 condition) at 1000°C. After gasification, air was injected into the system and oxidation process was initiated (R3 condition). The sulfur (SO_2) emissions were monitored using an infrared gas analyzer while the CO_2, H_2 and CO in the product were also monitored. Figure 3-32 shows the sulfur tracking results obtained on the bench scale fluidized bed reactor. It was shown that although most of the sulfur is removed during the gasification, a small peak of SO_2, representing about 5% of the total sulfur content in the coal feed, was observed when the oxidation process began.

The individual effects of CAM and OTM on the predicted SO_2 emission were also studied. Figure 3-33 shows the effect of CAM and OTM on the SO_2 concentration in the combustion product, respectively. It was found that with the presence of CAM, no SO_2 peak was observed during R3 simulation, which means that most of the sulfur in the coal was released during the gasification process as H_2S or was captured on the CAM. However, in the absence of CAM but presence of OTM, a peak of SO_2 was observed.

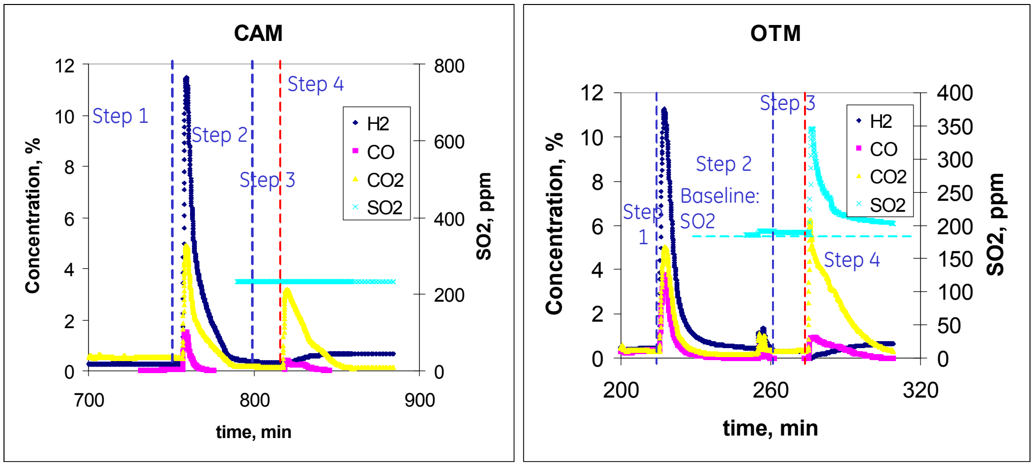


Figure 3-33: Effects of CAM and OTM on sulfur emission under simulated R3 condition. Step 1: Preheating with N_2, Step 2: Gasification (R1& R2 Cond.) (N_2 + Steam), Step 3: N_2, Step 4: Combustion with Air (R3 Cond.)

To further investigate the effect of CAM and OTM on the sulfur emissions during the gasification/oxidation in a bench scale fluidized bed reactor, a two-factor, full factorial DOE matrix was carried out as shown in Table 3-6 and the product gas concentrations including SO_2 were monitored during the experiments.

Table 3-6 DOE for effect of CAM and OTM on sulfur emission

StdOrder	RunOrder	Blocks	CAM	OTM	CAM, g	OTM, g
5	1	1	2	2	100	100
7	2	1	3	1	200	0
6	3	1	2	3	100	200
4	4	1	2	1	100	0
3	5	1	1	3	0	200
2	6	1	1	2	0	100
9	7	1	3	3	200	200
8	8	1	3	2	200	100
1	9	1	1	1	0	0

In the experiments, fixed amount of coal was gasified with steam while the bed was loaded with varied amount of CAM and OTM materials (R1 & R2 condition) at 1000^{o}C. After gasification, air was injected into the system and oxidation process was initiated (R3 condition). The sulfur (SO_2) emission from devolatilization, gasification, and oxidation was monitored using an infrared gas analyzer while the CO_2, H_2 and CO in the product were also monitored. The portion of the sulfur emitted from the oxidation period was then calculated. In all the tests, more than 95% carbon conversion was observed under the gasification conditions.

The percentage of sulfur in the feed coal emitted under the oxidation reactor R3 is shown in Figure 3-34. It was observed that with the increase of CAM concentration in the bed material, the sulfur emitted from oxidation process decreased. Furthermore, with the CAM and OTM presence in the bed material, the sulfur emission under the R3 condition is lower than 4% of the total sulfur in the coal feed.

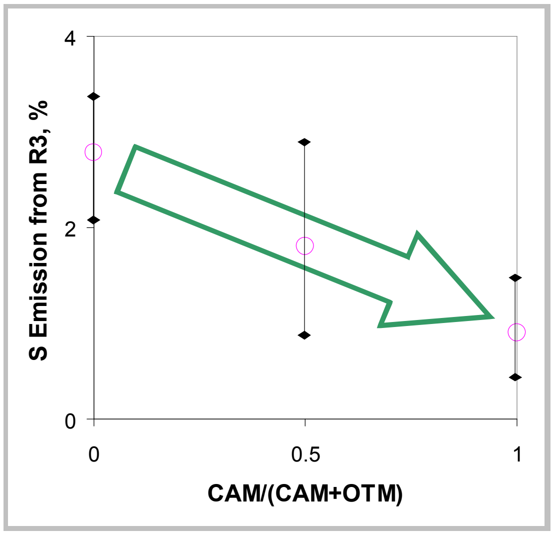


Figure 3-34 Sulfur emission from oxidation (R3) process as a % of total sulfur in the coal feed

Based on the result, an Aspen simulation was performed to estimate the SO_2 level in the R3 product in an integrated UFP plant. It was predicted that SO_2 level may vary from 3 to 25 ppm in the R3 product, depending on different sulfur content in coal. The predicted SO_2 concentration in the R3 exhaust for various types of coals is shown in Figure 3-35. In the IGCC process irrespective of the type of the coal the syngas is cleaned up to have <20 ppm sulfur before entering the gas turbine expander. The SO_2 concentration expected from the exhaust of a conventional IGCC plant is also plotted on Figure 3-35. For the UFP system, it was predicted that the SO_2 concentration in the R3 exhaust might be a strong function of the total sulfur content in the coal. When a low rank coal such as PRB coal with very low sulfur content is used in the UFP process the SO_2 concentration in the exhaust may be similar to that of a conventional IGCC plant. However, for coals with higher sulfur content the SO_2 in the exhaust gas can be much higher than that of a conventional IGCC plant, indicating the need for additional sulfur clean-up process on the exhaust stream. The cost impact of additional sulfur clean-up processes on the overall cost of the UFP process needs to be analyzed.

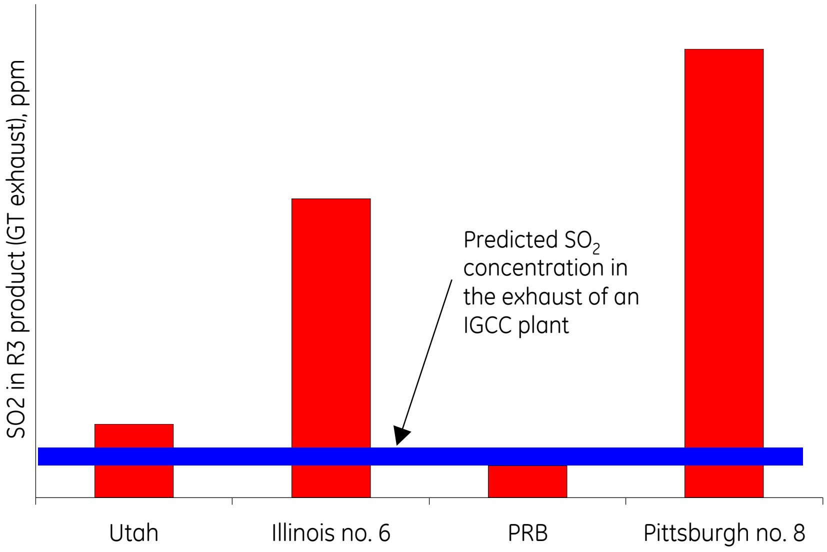


Figure 3-35 Predicted concentration of SO_2 from R3 exhaust for various coals and comparison with SO_2 concentrations in an IGCC-exhaust

3.5.2 Coal Deashing and Desulfuring

The alkali metals in the ash are expected to have a link with the agglomeration of the solids as reported in the previous section. Experiments were carried out to investigate the possibility of removing ash from the coal prior to gasification. Partial or complete removal of ash may result in reduction of agglomeration of the solids in the UFP process. The effectiveness of this washing procedure on the overall sulfur content in the coal was monitored during these experiments. Partial removal of sulfur prior to gasification can reduce the load on the sulfur capture unit after the gasifier resulting in potential reduction in the cost of the coal gasification based power plants. Air floating and jigging methods have been used for coal deashing for many years. These methods generate a huge amount of wastewater during the process. Therefore, it is important to develop alternative coal pre-treating method that is more environment-friendly.

The effort started with screening the effectiveness of different solvents for coal deashing/desulfurization. The results are shown in Figure 3-36. Among all the deashing solvent candidates, solvent 4 showed the best deashing results with a 30% reduction of ash. Solvents 3, 6 and 7 also showed significant deashing effect in the preliminary tests. Solvent 5 shows the best desulfurization results but the ash content increased after treatments. Based on the preliminary results, the price, and the availability of the solvents, solvents 6 and 7 are selected for further deashing/desulfuring investigation even though they showed less degree of ash and sulfur removal than other solvents.

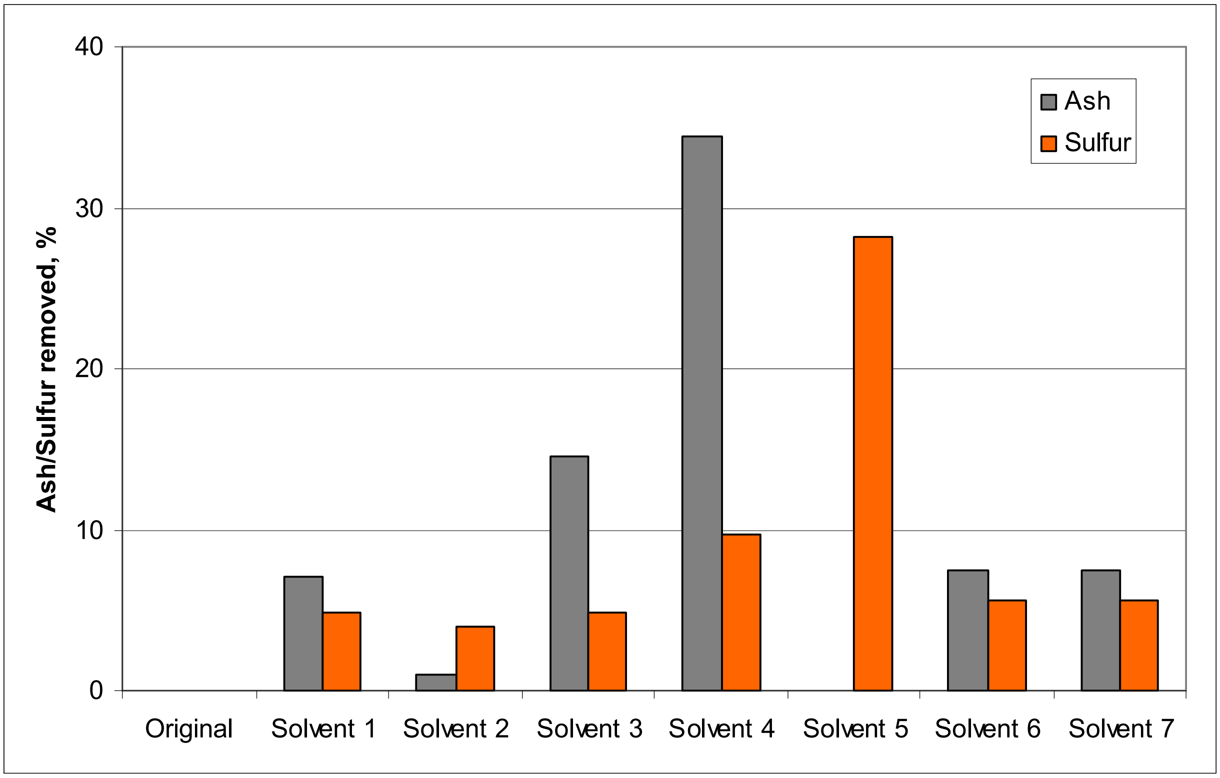


Figure 3-36 Preliminary deashing/desulfurization results

The deashing/desulfuring test results with selected solvent for PRB coal are shown in Figure 3-37. The tests were performed under varied operating conditions (coal/solvent ratio, floating time, rinsing). As can be seen, the sulfur and ash content in the PRB coal can be reduced by 15 ~ 20% within a reasonable operating range. For further operating condition optimization, continuous operation will be necessary.

Figure 3-38 shows the detailed mineral reduction using solvent floating method. It is found that the reduction of Na_2O is the most significant (reduced by 40 ~ 50%) while CaO and Al_2O_3 can be reduced by 10 ~ 15%. The significant removal of low meting point Na_2O may help reduce the agglomeration of coal/ash during gasification process.

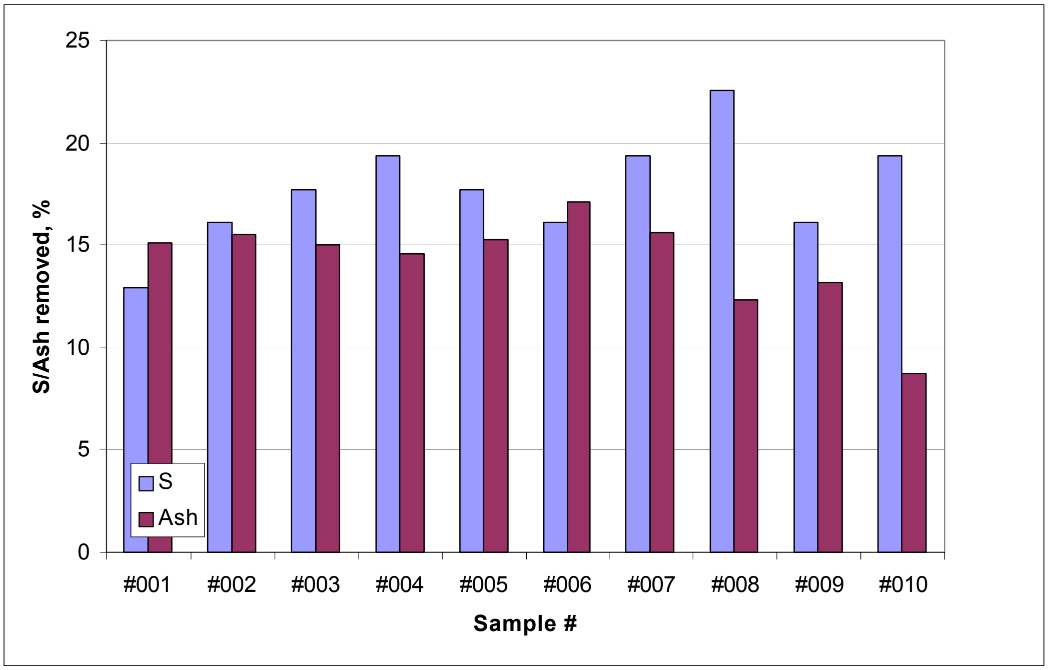


Figure 3-37 Deashing/desulfuring results for PRB coal

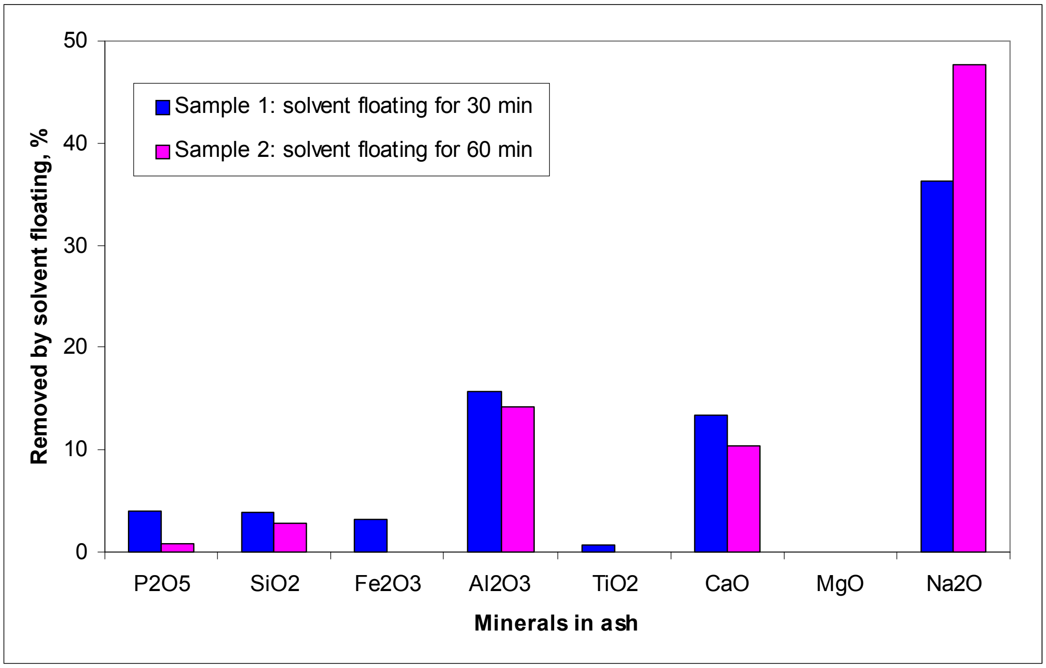


Figure 3-38 Minerals removed with solvent floating method

The reproducibility of the solvent floating deashing/desulfuring is investigated with Illinois no. 6 coal. The result is shown in Figure 3-39. It is shown that the difference between two replicates was less than 1%, suggesting a good repeatability of the floating method.

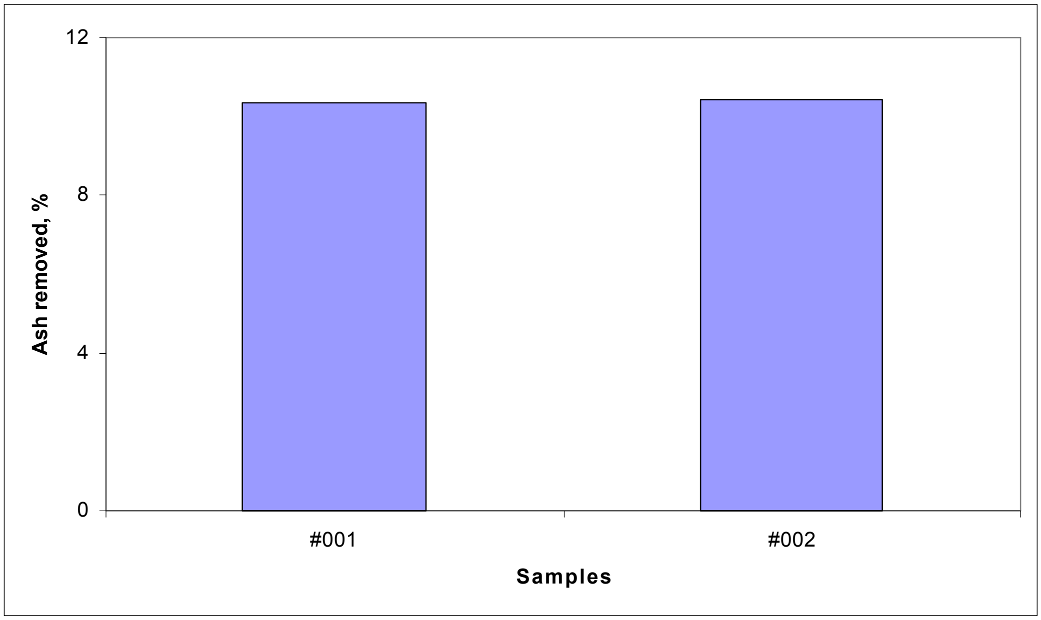


Figure 3-39 Repeatability of deashing/desulfuring method

3.5.3 Analysis of Stream Cleanup Needs for the UFP process

One of the concerns that arise when developing a process for the production of fuels and other side gaseous streams is whether the fuel streams will contain contaminants in such high enough concentrations that may need to undergo extensive cleaning before use. In the case of UFP, the production of three different gaseous streams from coal, a hydrogen-rich (R1), a CO_2-rich (R2), and a vitiated air stream (R3), represents a range of purification needs for the streams produced so that they can meet the requirements of each of the applications, namely H_2 for chemical production (R1), CO_2 for sequestration (R2), and vitiated air for power generation (R3).

A study was initiated to assess the potential need for cleanup of coal-derived contaminants that may be present in each of these fuel streams described above and to identify the technologies and costs associated with.

Figure 3-40 is the schematic of the UFP process showing the three streams produced. Stream R2, the CO_2-rich stream, was selected for the initial cleanup analysis as there is currently a great deal of interest on the quality of CO_2 streams required for enhanced oil recovery (EOR) and for injection in saline aquifers. Also shown in Figure 3-40 is a schematic of the rough conditioning and cleaning that may be necessary to use the R2 stream for these two applications.

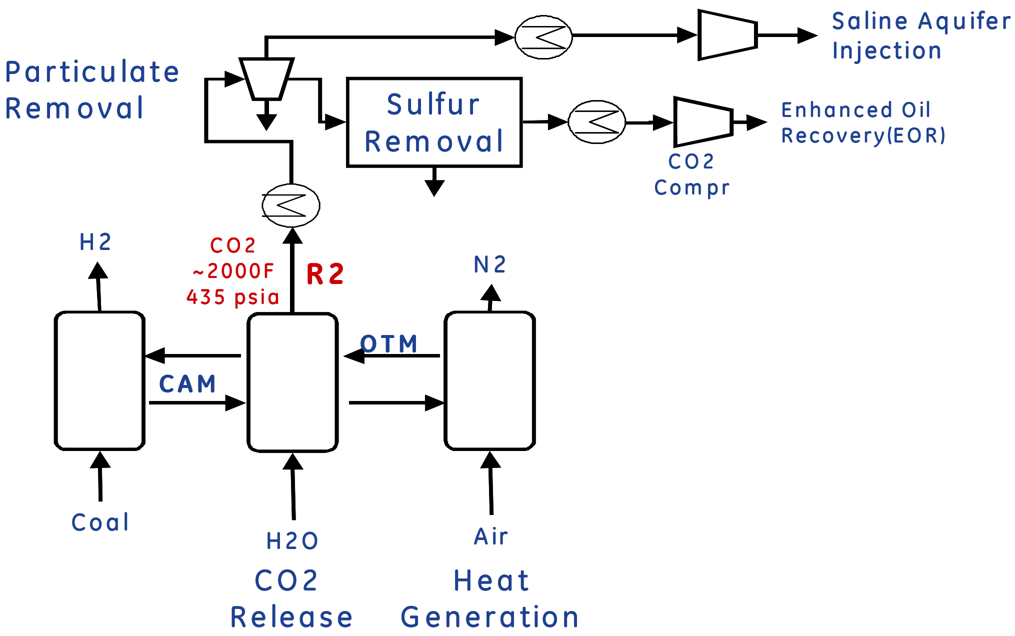


Figure 3-40 A schematic of rough conditioning and cleaning for R2 stream

Recent studies on the quality of CO_2 streams have uncovered that there is a wide range of the suggested values for the acceptable residual levels of the contaminants. Table 3-7 shows some of the suggested contaminant concentrations remaining in CO_2-rich streams for EOR. As can be seen, CO_2 purity is greater than 95 mol% with allowable levels of contaminants relatively low (as ppm or single-digit percentages). The purity level is required by the need to compress the CO_2 to supercritical pressures during EOR injection. The presence of water and other contaminants can significantly increase this minimum pressure required to achieve the supercritical state of CO_2 (thus increasing pumping costs). In addition, the contaminants may decrease the effectiveness of the supercritical CO_2 to displace oil from geological strata, thus reducing the oil recovery yield per unit mass of CO_2 injected.

Table 3-7 Allowable concentrations of various components in CO_2-rich streams for EOR

Component	Case 1	Case 2	Case 3
CO_2, mol%	>95%	>96%	>95%
N_2, ppm	<40,000	<6,000	<40,000
CH_4, mol%	<5%	<2%	<5%
H_2S, ppm	<1061	<10,000	<200
O_2, ppm	<7.5	<100	<10
H_2O, ppm	<641	<2	<480
Reference	IPCC, 2005	Dakota Gasification Co.	Kinder Morgan, 2006

For pipeline transport, it is suggested that the H_2S concentration be less than 10-200 ppm for safety reasons. If the stream is being ultimately used for injection in aquifers, the allowable H_2S concentration can be relaxed to less than 2 mol%.

For the purification of the R2 stream (CO_2-rich) in the UFP, we can envision that at least one or two different technologies will be required to bring the gas to minimum specifications. First of all, particulate matter will need to be removed to protect the CO_2 compression equipment from wear. Since the UFP already has a cyclone system to recirculate the sorbent around the R2 solids closed loop, a polishing filter or secondary cyclone may only be the necessary technology to ensure dust-free operation at the compressor inlet. Second, H_2S must be reduced below acceptable levels to maintain EOR efficiency. It is likely that the particulate removal system will control the sulfur levels from carryover sulfided sorbent. Third, the H_2O concentration will have to be reduced to ppm levels if EOR is contemplated. Condensation or permeation technologies will likely work in this case. Consequently, as a minimum two technologies, fine particulate removal and water removal will probably be needed for CO_2 purification for EOR.

The costing of additional equipment needed for clean-up of R2 and R3 streams should be carried out once the solids lifetime risk is mitigated. Such analysis can be performed with the help of a software like Icarus Process Evaluator^{TM} (IPE). For example, IPE software has been used in the past for other chemical process cost estimation involving particulate matter removal and dry sorbent desulfurization technologies. Figure 3-41 shows an example of the relative magnitude of the capital cost (CAPEX) line items associated with typical dry sorbent contaminant removal. These line items are: purchased equipment, installation labor, and bulks costs (piping, civil, steel, instrumentation, electrical, insulation and paint). The same methodology can be employed in the assessment of suitable technologies applicable for purification of product fuel streams in the UFP process.

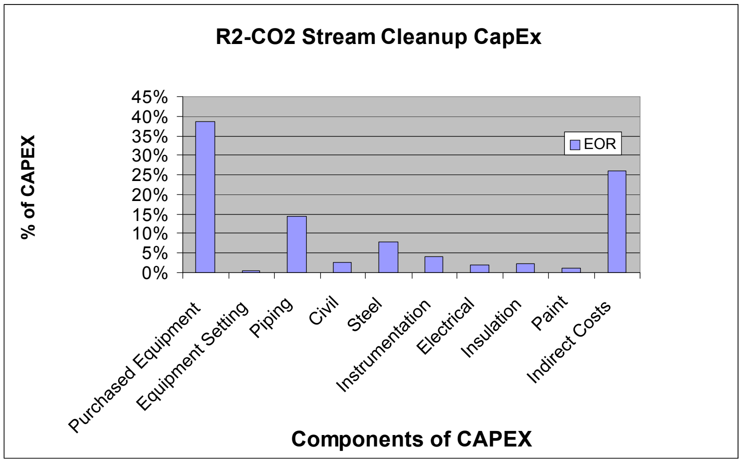


Figure 3-41 Example of relative capital cost components for the purification of fuel streams

4 TECHNOLOGY DEVELOPMENT/RECOMMENDATIONS

The Phase II effort of the DOE funded project focused on three high-risk areas: economics, solids attrition and lifetime, and product gas quality for turbines (or the impact of impurities in the coal on the overall system). Significant progress was made in understanding these risks and their impact on the feasibility of the UFP technology. The conceptual system design and economic analysis were conducted to establish the economic feasibility and competitiveness of the UFP technology. Cost of the hydrogen production and cost of electricity were estimated through the capital cost and O&M cost analyses. The economic analysis comparison of the UFP technology with the conventional IGCC-polygen technology performed with today's understanding suggests that the UFP technology may have cost advantages over IGCC-polygen technology. However, the technical assumptions such as conversion, yield, sorbent lifetime and impact of coal impurities, going into the economic analysis, need to be validated experimentally.

The impact of sulfur impurity in the coal feedstock on the overall UFP process was analyzed through bench-scale experiments and analysis. It was predicted that the SO_2 concentration in the R3 exhaust might be a strong function of the total sulfur content in the coal. When a low rank coal such as PRB coal with very low sulfur content is used in the UFP process the predicted SO_2 concentration in the exhaust may be similar to that of a conventional IGCC plant. However, for coals with higher sulfur content the predicted concentration of SO_2 in the exhaust gas can be much higher than that of an IGCC plant, indicating a need for additional sulfur clean-up process on the exhaust stream. The cost impact of additional sulfur clean-up processes on the overall cost of the UFP process needs to be analyzed.

Solid lifetime was assessed based on deactivation mechanisms such as physical attrition, chemical attrition, and solid agglomeration. It was found that the lifetime of the solid is one of key technical barriers as cost and technical feasibility are critically dependent on the materials performance and durability. Solids agglomeration was one of the main concerns for the solids lifetime and cost. The main causes to the bed materials agglomeration were combination of OTM reduction and high exposure temperatures. At moderate temperatures, say 1000ºC, the reduction of OTM caused the surface morphology/composition change and intensified the interaction between CAM and OTM, which resulted in bed materials agglomeration. Heat-treatment at 1000ºC in the absence of OTM reduction wouldn't cause the bed agglomeration. However, at higher temperatures (>1200ºC), significant chemical reactions between OTM and CAM, and thus the agglomeration can occur even in the absence of OTM reduction.

Based on the above results as described in section 3 of this report, at the end of phase II, GE recommended a "No-go" decision on taking the UFP technology to the next level of development, i.e. development of a prototype system. GE further recommended focused materials development research programs on improving the performance and lifetime of solids materials used in UFP or chemical looping technologies. A final review meeting with DOE was held on March 6, 2008.

Following recommendations were made for the future technology development.

- Further evaluation of the CAM and OTM: As the most important basic elements of the system, their performance, cost and reliability determine the overall system feasibility and the techno-economic competitiveness. Throughout the current phase of the program, solid agglomeration was identified as the most important challenge in the technology development. Thermodynamic analysis indicated the baseline OTM and CAM would interact at higher temperatures, and liquid phases were likely to form at temperatures ~1200ºC. Reduction of OTM under gasification conditions made it easier for the reaction and liquid phases formation. Reviewing phase diagrams suggests a narrow, but probable operating window in terms of the composition and temperature. Such windows can be used as the initial system operation boundaries if the baseline OTM and CAM are to be used

- Development of the CAM and OTM: The operating windows with the baseline CAM and OTM are likely to be narrow and will limit the system design and optimization space. Development of high performance bed materials can not only address the lifetime issues but also provide system design flexibility. The development of the CAM and OTM can be achieved with material composition and structure engineering and new composition exploration. The development of CAM and OTM can also be synergized with syngas clean up technologies and CO2 removal technologies from coal based power generation systems.

- Novel system design: The solid handling, energy and mass balance are critical to the economic feasibility and competitiveness of the technology. The solid circulation conditions, reactor temperatures, and mechanisms of heat and oxygen transfer determine the system cost, efficiency, and reliability. They will also provide the top down requirements on the solid materials. Any innovated system designs to minimize the solid circulation and lower the operating temperatures without compromises on reaction kinetics will improve the solid lifetime, thus the technology feasibility.

5 CONCLUSIONS

During the "Fuel-Flexible Gasification-Combustion Technology for Production of H_2 and Sequestration-Ready CO_2" program the major risks associated with the UFP technology were investigated and their impact on the feasibility of this novel technology was analyzed. The economic analysis comparison of the UFP technology with the conventional IGCC-polygen technology performed with today's understanding suggested that the UFP technology may have cost advantages over IGCC-polygen technology. The analysis suggested that the capital cost for the UFP technology may be lower than the IGCC-polygen technology by ~10%. The baseline cost of hydrogen of the UFP was estimated ~10% lower than the IGCC-polygen technology. The potential lower cost of UFP technology can be attributed to the following two factors: (1) UFP technology does not require the air separation unit (ASU) to separate O_2 from air and (2) UFP technology captures CO_2 inherently at high temperature and pressure.

The technology feasibility was demonstrated through baseline operation and parametric operation with the pilot-scale system. Although the pilot system operation provided the first hand experience with the novel technology concept, challenges still remained, such as the auxiliary heating and solid circulation at the pilot system level. Lifetime of solids and the impact of coal impurities on the process were investigated using the upgraded bench scale system in a much more controlled environment.

The impact of the sulfur impurity in the coal on the UFP process was investigated. The predictions based on bench-scale results indicated that the SO_2 concentration in the R3 exhaust would be a strong function of the total sulfur content in the coal. When a low rank coal such as PRB coal with very low sulfur content is used in the UFP process the SO_2 concentration in the exhaust may be similar to that of a conventonal IGCC plant. However, for coals with higher sulfur content the SO_2 in the exhaust gas can be much higher than that of an IGCC plant, indicating a need for additional sulfur clean-up process on the exhaust stream. The cost impact of additional sulfur clean-up processes on the overall cost of the UFP process has to be analyzed.

Solid lifetime was assessed on physical attrition, chemical attrition, and solid agglomeration investigation. Physical attritions of both CAM and OTM have been observed. Although the attrition index was moderate under the testing conditions, particle size for the bed materials was reduced after physical attrition, most likely due to fragmentation. Also, decomposition of the CAM accelerated its physical attrition. Reaction between the OTM and CAM was predicted with material thermodynamics and was observed from experiments. It was found that the lifetime of the solid was one of the key technical barriers as cost and technical feasibility were critically dependent on the materials performance and durability. Bed materials agglomeration was one of the main concerns of the solid lifetime. The main causes of the bed materials agglomeration were the combination of OTM reduction and high exposure temperatures. At moderate temperatures, say 1000ºC, the reduction of OTM caused the surface morphology/composition change and intensified the interaction between CAM and OTM, which resulted in bed materials agglomeration. Heat-treatment at 1000ºC in the absence of OTM reduction wouldn't cause the bed agglomeration. However, at higher temperatures (>1200ºC), significant chemical interactions between OTM and CAM, and thus the agglomeration can occur even in the absence of OTM reduction.

At the end of phase II, in March 2008, GEGR recommended a "No-go" decision for taking the UFP technology to the next level of development, i.e. development of a 3-5 MW prototype system, at this time. GEGR further recommended focused materials development research programs on improving the performance and lifetime of solids materials used in UFP or chemical looping technologies. The scale-up activities would be recommended only after mitigating the risks involved with the agglomeration and overall lifetime of the solids. A final review meeting with DOE was held on March 6, 2008.

6 PUBLICATIONS AND PRESENTATIONS

Team members have presented the UFP concept and progress on UFP and other gasification technologies development at several conferences. These presentations and their subsequent publication in conference proceedings have generated interest in the UFP technology and helped in raising awareness of the DOE's technology development program. The selected presentations are listed below.

- Parag Kulkarni, Zhe Cui, Raul Subia, JieGuan, Vladimir Zamansky, Kelly Fletcher "Unmixed Fuel Processing (UFP): Potential Long Term Technology for Production of H_2 and Electricity from Coal with CO_2 Capture," *24th International Pittsburgh Coal Conference,* Johannesburg, South Africa, September 12, 2007.
- Parag P. Kulkarni, Raul Subia, Wei Wei, Zhe Cui, Vladimir Zamansky, Roger Shisler, Tom McNulty, George Rizeq and Greg Gillette, "Advanced Unmixed Combustion/Gasification: Potential Long Term Technology for Production of H_2 and Electricity from Coal with CO_2 Capture," *23rd International Pittsburgh Coal Conference*, Pittsburgh, PA, September 28, 2006.
- A. Frydman, G. Rizeq, J. West, R. Subia, P. Kulkarni, and V. Zamansky, "Modeling of Unmixed Fuel Processor for Production of Hydrogen from Coal," *National Hydrogen Association 15th Annual U.S. Hydrogen Conference*, Los Angeles, CA, April 26-29, 2004.
- George Rizeq, Arnaldo Frydman, Raul Subia, Janice West, Vladimir Zamansky and Kamalendu Das, "Unmixed Fuel Processor: Pilot-Scale System Design and Initial Experimental Results,*" The 29th International Technical Conference on Coal Utilization & Fuel Systems (Clearwater 2004*), Clearwater, FL, April 18-22, 2004
- George Rizeq, Raul Subia, Arnaldo Frydman, Janice West, Vladimir Zamansky, and Kamalendu Das, "Unmixed Fuel Processor for Production of H_2, Power, and Sequestration-Ready CO_2," *Twelfth International Conference on Coal Science (ICCS)*, Cairns, Queensland, Australia, November 2-6, 2003.
- George Rizeq, Arnaldo Frydman, Janice West, Raul Subia, Vladimir Zamansky, and Kamalendu Das, "Advanced Gasification-Combustion Technology for Production of Hydrogen, Power and Sequestration-Ready CO_2", *Gasification Technologies 2003*, San Francisco, CA, October 12-15, 2003.
- George Rizeq, Raul Subia, Arnaldo Frydman, Janice West, Vladimir Zamansky, and Kamalendo Das, "Development of Unmixed Fuel Processor for Production of H_2, Electricity, and Sequestration-Ready CO_2," *Twentieth Annual International Pittsburgh Coal Conference*, Pittsburgh, PA, September 15-19, 2003.
- George Rizeq, Raul Subia, Janice West, Arnaldo Frydman, Vladimir Zamansky, and Kamalendu Das, "Advanced Gasification-Combustion: Bench-Scale Parametric Study." *19th Annual International Pittsburgh Coal Conference*, Pittsburgh, PA, Sept 23-27, 2002.

- George Rizeq, Vladimir Zamansky, Vitali Lissianski, Loc Ho, Bruce Springsteen, Lucky Benedict, Thomas Miles, Valentino Tiangco, and Rajesh Kapoor, "Gasification-Combustion Technology for Utilization of Waste Renewable Fuels," *Bioenergy 2002: Bioenergy for the Environment*, Boise, Idaho, September 22- 26, 2002.

- Zamansky, V.M., Advanced Gasification-Combustion Technology for Production of H_2, Power and Sequestration-Ready CO_2, Invited Lecture at the Advanced Clean Coal Technology Workshop, Tokyo, Japan, September 2002.

- Lissianski, V., Zamansky, V., and Rizeq, G. "Integration of Direct Combustion with Gasification for Reduction of NO_x Emissions," presented and published in the proceedings of the *29th Symposium (International) on Combustion*, Hokkaido University, Sapporo, Japan, July 21-26, 2002.

- George Rizeq, Janice West, Arnaldo Frydman, Raul Subia, and Vladimir Zamansky, Poster entitled: "Advanced Gasification-Combustion Technology for Utilization of Coal Energy with Zero Pollution." *29th International Symposium on Combustion*, Sapporo, Japan, July 22-26, 2002.

- George Rizeq, Janice West, Raul Subia, Arnaldo Frydman, Vladimir Zamansky, and Kamalendu Das, "Advanced-Gasification Combustion: Bench-Scale System Design and Experimental Results," *27th International Technical Conference on Coal Utilization & Fuel Systems (Clearwater 2002)*, Clearwater, FL, March 4-7, 2002.

- R. George Rizeq, Ravi Kumar, Janice West, Vladimir Zamansky, and Kamalendu Das, "Advanced Gasification-Combustion Technology for Production of H_2, Power, and Sequestration," *18th Annual International Pittsburgh Coal Conference*, Newcastle, New South Wales, Australia, December 4-7, 2001.

- George Rizeq, Janice West, Arnaldo Frydman, Raul Subia, Ravi Kumar, Vladimir Zamansky and Kamalendu Das, "Fuel-Flexible Gasification-Combustion Technology for Production of Hydrogen and Sequestration-Ready Carbon Dioxide," *Vision 21 Program Review Meeting,* NETL, Morgantown, WV, November 6-7, 2001.

- R. George Rizeq, Richard K. Lyon, Janice West, Vladimir M. Zamansky and Kamalendu Das, "AGC Technology for Converting Coal to Pure H_2 and Sequestration-Ready CO_2," *11th International Conference on Coal Science* (ICCS), San Francisco, CA (Sept 30-Oct 5, 2001). NOTE: This conference was cancelled, but a proceedings volume was published.

- R. George Rizeq, Richard K. Lyon, Vladimir M. Zamansky, and Kamalendu Das, "Fuel-Flexible AGC Technology for Production of H_2, Power, and Sequestration-Ready CO_2," *26th International Technical Conference on Coal Utilization & Fuel Systems* (Clearwater Conference 2001), Clearwater, FL, March 5-8, 2001.

7 LIST OF ACRONYMS AND ABBREVIATIONS

ASME	American Society of Mechanical Engineers
ASU	Air Separation Unit
CAM	CO_2 Absorber Material
CEMS	Continuous Emissions Monitoring System
CTQ	Critical to Quality
DFSS	Design for Six Sigma
GC	Gas Chromatograph
GEGR	General Electric Global Research
GHSV	Gas Hourly Space Velocity
HRSG	Heat Recovery Steam Generator
IGCC	Integrated Gasification Combined Cycle
NETL	National Energy Technology Laboratory
OTM	Oxygen Transfer Material
OTM-O	Oxidized OTM
OTM-R	Reduced OTM
PSA	Pressure Swing Adsorber
P&ID	Process and Instrumentation Diagram
PID	Proportional Integral Derivative (controller)
R1	Reactor 1
R2	Reactor 2
R3	Reactor 3
SIU-C	Southern Illinois University – Carbondale
TGA	ThermoGravimetric Analyzer
UFP	Unmixed Fuel Processor
U.S. DOE	United States Department of Energy