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INTEGRATION REPORT FOR SRC-I POST-BASELINE ENVIRONMENTAL R&D

By
A. F. Yen

Work Performed Under Contract No. AC05-78OR03054

International Coal Refining Company
Allentown, Pennsylvania

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Prepared by

A. F. Yen

INTERNATIONAL COAL REFINING COMPANY
P.O. Box 2752
Allentown, Pennsylvania 18001

for the

UNITED STATES DEPARTMENT OF ENERGY
Office of Solvent-Refined Coal Products
under Contract DE-AC05-78-OR-03054

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ABSTRACT

The Baseline Design for the wastewater treatment/reuse and solid-waste handling and disposal systems for the SRC-I Demonstration Plant was completed in 1982. Because of the ambitious construction schedule contemplated at that time, the design was not based on comprehensive design data. Consequently, since submission of the Baseline, ICRC has been generating experimental data to confirm and/or refine the Baseline Design. This report integrates all the environmental research and development (R&D) data generated during that period by many different R&D programs.

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EXECUTIVE SUMMARY

To reduce America's dependence on imported petroleum, the U.S. Department of Energy contracted with International Coal Refining Co. (ICRC) to build a solvent-refined coal (SRC-I) demonstration plant in Newman, Kentucky. One major goal of the plant was to demonstrate the environmental acceptability of the SRC-I process. In the course of pursuing that goal, DOE and ICRC reached two key milestones: (1) publication of a Final Environmental Impact Statement (FEIS) in 1981 and (2) completion of the SRC-I Baseline Design in 1982.

Because of the ambitious construction schedule contemplated at that time, the Baseline Design for the off-sites facilities, including the wastewater treatment and reuse (zero discharge) and solid-waste handling and disposal systems, was formulated without solid laboratory data. Therefore, after the Baseline, considerable R&D work was subcontracted, focusing on development of information that would confirm and/or refine the Baseline Design.

The post-Baseline R&D effort consisted of four interrelated tasks:

- Data base expansion
- Phenol recovery evaluation
- Zero-discharge evaluation
- Integration of the results

Generally, the objective of data-base expansion was to generate information on wastewater treatment to confirm the Baseline Design or to alter it slightly, without any radical changes. In contrast, the objective of phenol recovery evaluation was to assess the possibility of adding a step to remove phenols from certain phenolics-laden sour-water streams, which is a major change. The zero-discharge evaluation concentrated on unit processes associated with wastewater recycle, which suffered from much technical uncertainty. The results of the tasks had to be integrated, which was the objective of the last task and the subject of this report.

In summary, the post-Baseline environmental R&D work resulted in the following significant findings:

- Although the concept of the Baseline Design is basically sound, it would require modification to make it reliable and operable.
- A wastewater treatment system with phenol recovery is technically superior and more cost-effective than the Baseline Design scheme, which does not have phenol recovery. Phenol recovery is highly recommended.
- Laboratory work has shown that phenol recovery is feasible for SRC-I wastewater. As expected, it substantially reduced organic volatilization during ammonia/sulfide stripping, which could have serious repercussions on the Claus sulfur recovery operation. Phenol recovery was found to reduce the organic loading on downstream treatment systems by two-thirds, and to dampen loading fluctuations. Phenol recovery was also found to eliminate the need for continuous high doses of powdered activated carbon (PAC), thereby substantially affecting plant operating costs.
- With phenol recovery, and subsequent treatment, the system's effluent can comply with all the estimated effluent qualities published in the FEIS, and the anticipated effluent limits projected from final or proposed regulations for petroleum-refining and coke-making industries with a wide margin. The effluent would not significantly impact the Green River water quality under the worst conceivable scenario. In many respects, the effluent is superior to the river quality.
- Limited aquatic ecotoxicity data generated by the post-Baseline R&D programs, although by no means conclusive, suggest that the fully treated wastewater is not unsuitable for discharge.
- The zero-discharge evaluation has indicated that the Baseline Design zero-discharge scheme requires some modifications to be technically workable. Results of the limited R&D suggest that

zero discharge, after revisions, would be technically feasible. But the R&D data, which was limited by a lack of sufficient wastewater for testing, is not definitive; more work is needed.

- The zero-discharge equipment incurs substantial cost penalties. With zero discharge, the total capital cost for wastewater treatment/reuse and solid-waste handling/disposal systems is $70 million, of which $30 million is for zero discharge. The operating cost for the entire system is $18 million per year, half of which is attributable to the zero-discharge equipment.
- Because of the cost penalties, and unaddressed uncertainties associated with zero discharge, and because of the good quality of the fully treated wastewater, effluent discharge is an option to zero discharge that warrants further evaluation.

I. INTRODUCTION

A. BACKGROUND

To reduce America's dependence on imported petroleum, the U.S. Department of Energy (DOE) contracted with International Coal Refining Company (ICRC), a partnership between Air Products and Chemicals, Inc. and Wheelabrator-Frye, Inc., to design a Solvent-Refined Coal (SRC-I) Demonstration Plant. The plant, planned for construction in Newman, Kentucky, was designed to convert 6,000 tons/day of high-sulfur, high-ash bituminous coal (Ky #9) to a variety of clean-burning solid and liquid fuels.

One major goal of the SRC-I project was to show that the Demonstration Plant could be environmentally safe. In the course of pursuing that goal, DOE and ICRC reached two key milestones:

1. Publication of the Final Environmental Impact Statement (FEIS) in July 1981[1]
2. Completion of the Baseline Design for the wastewater treatment/reuse system and solid-waste handling/disposal facility in April 1982[2]

As required by the National Environmental Policy Act, an environmental impact statement must be prepared for all major federal projects; SRC-I was no exception. The SRC-I FEIS identifies the potential environmental impacts that the project could impose on the environment and delineates mitigation measures to reduce the impact to an acceptable level. One major mitigation measure is to treat the SRC-I wastewater with advanced treatment methods, including primary, secondary (biological), and tertiary steps.

The FEIS also states that the treated wastewater will be recycled to an evaporative cooling tower, to avoid discharge of any liquid effluent most of the time. However, ICRC realized that the zero-discharge equipment would not function all the time; therefore, provisions were made to discharge the treated wastewater part of the time. This FEIS concept has been fully incorporated in the Baseline Design.

As the name implies, the Baseline Design is a design package that establishes a data base from which future refinements and improvements to the plant design can be made. Individual Baseline Designs were prepared for each area in the SRC-I Demonstration Plant, including the off-sites area that encompasses the wastewater treatment/reuse and solid-waste disposal facilities.

The Baseline Design was prepared under an ambitious time schedule. The time pressure was particularly intense for the off-sites area, because it had to integrate with other upstream waste-generating areas, and its design could not be fully initiated until the upstream areas were fairly complete. Hence, the Baseline Design for the off-sites area was carried out in the last stage. With a fixed deadline for the Project Baseline, any slippage of schedule by the upstream process areas exacerbated the time pressure on the off-sites Baseline.

Because of the time constraints, the Baseline Design for the off-sites facilities did not have a good data base from which a firm design could be established, nor did it have the full benefit of environmental R&D data. Much of the design was based on preliminary results of the ongoing R&D programs and literature values, which did not specifically pertain to the SRC-I process.

Despite these limitations, however, the Baseline Design did serve its intended purpose, i.e., to establish the basis for future refinements. Following completion of the Baseline, ICRC conducted further environmental R&D to refine the design. This report describes the work done during that post-Baseline period. However, before the refinements are discussed, the major wastewater streams that must be treated as well as the treatment facilities are reviewed.

B. MAJOR WASTEWATER STREAMS

The SRC-I wastewater treatment system is designed to treat the following major wastewaters:

1. Ammonia/sulfide water stripper (ASWS) bottoms (441 gpm)
2. Gesellschaft für Kohle-Technologie (GKT) gasifier washwater blowdown (184 gpm)
3. DEA brine/SO_2 scrubber purge (12 gpm)
4. Stretford purge (5 gpm)
5. Cooling tower blowdown (360 gpm)
6. SRC/coal storage runoff (variable)
7. Contaminated runoff from curbed process areas (variable)
8. Sanitary waste (70 gpm)
9. Miscellaneous wastes

A more complete inventory of wastewater streams is included in Figure 1.

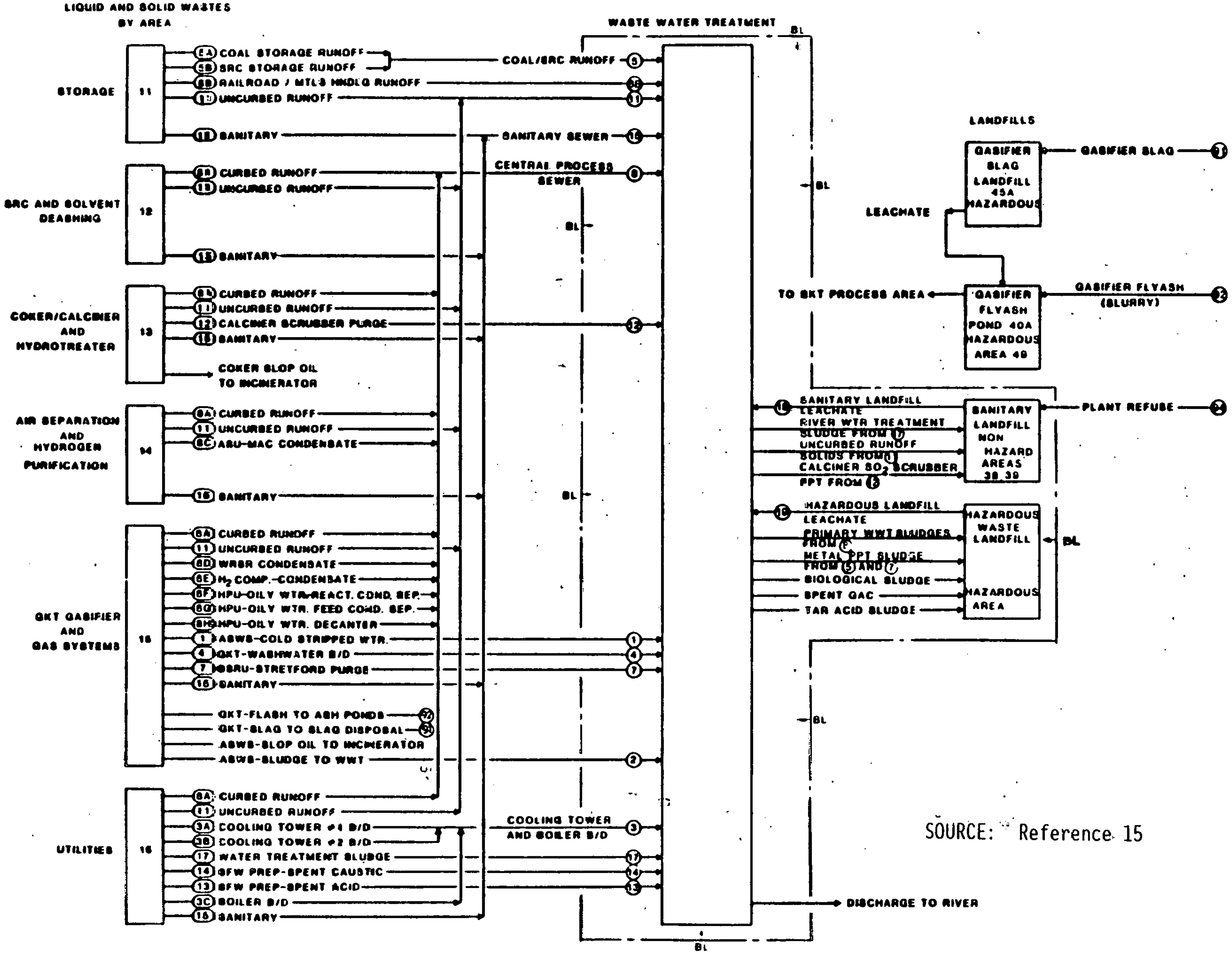
The ASWS bottoms (or cold stripped water) is a combined stream of heavily contaminated process condensates from all process areas, including SRC processing, coking/calcining, and expanded-bed hydrocracking. The process condensates are laden with ammonia, hydrogen sulfide, and organics, including phenolics. The combined stream is steam-stripped to remove ammonia and hydrogen sulfide in a stripper located outside of the off-sites area.

GKT washwater blowdown originates in the gasification area. The dust-laden hot syngas from the gasifier must be cooled and cleaned with water. The water is also used to sluice the dust and transport it to the ash ponds, where the dust is permanently disposed. Although most of the water is recycled, it must be purged to control the salt buildup. The major contaminants in this stream are a large concentration of chlorides, and a relatively low level of cyanides, thiocyanates, and ammonia. Few organics are present in this stream.

The diethanolamine (DEA) brine is produced during cleaning of fuel gas that is contaminated with acid gases, such as CO_2 and H_2S, and hydrogen chloride. The acid gases are removed by Selexol and DEA, and the hydrogen chloride is removed by scrubbing with caustic. The DEA brine is the spent caustic solution, and it contains much sodium bicarbonate and carbonate. Because of the $NaHCO_3$ and Na_2CO_3, the DEA brine is sent to the SO_2 scrubber, which treats the flue gas from the calciner. The purge from the scrubber, which contains sodium sulfate, bisulfite, and sulfite, goes to wastewater treatment.

Figure 1

Liquid and Solid Waste Stream Inventory



SOURCE: Reference 15

Stretford purge comes from the Beavon-Stretford sulfur removal unit (BSRU), which is part of the sulfur recovery unit. The BSRU employs vanadium-salt-bearing Stretford solution to oxidize the residual H_2S in the Claus sulfur removal unit tail gas to elemental sulfur. One major contaminant in the Stretford purge is, therefore, vanadium.

Cooling tower blowdown is a large stream containing all the impurities present in the makeup water, which consists of river water and recycled treated wastewater. Chemicals are added to control corrosion, scaling, fouling, and biological growth in the cooling system. No chromate cooling water treatment chemicals will be used.

Runoffs from the SRC and coal storage areas are combined. They will be contaminated mostly by the impurities in the coal, predominately iron, heavy metals, and dissolved solids. The composition and flow of the SRC/coal pile runoff will be highly variable, changing with the amount of rainfall and time.

The runoff from the curbed process areas will also vary significantly in flow and composition. Because all major process equipment is located in the curbed areas, the runoff can potentially be contaminated with process solvent, slop oil, and the like. Some process solvents contain known or suspected mutagens or carcinogens. Also, any equipment ruptures and leaks could have severe repercussions for the wastewater treatment system. Therefore, this stream must be handled with due precaution.

Sanitary waste is collected from sources scattered throughout the plant. Because of the large area that the sewer must cover, the sanitary wastewater will be collected by the same sewer network that collects the contaminated process area runoff, to minimize piping costs.

In addition to these waste streams, the SRC-I plant also generates miscellaneous wastes, such as boiler blowdown, spent regenerants from the demineralizers of the boiler feedwater treatment system, and compressor condensates. These streams are relatively insignificant in comparison to the other wastes, but they will be treated as the other streams.

C. DESCRIPTION OF THE BASELINE DESIGN

The Baseline Design was prepared by Rust Engineering of Birmingham, Alabama, the contractor for the utilities and off-sites area. The design can be divided into three sections:

- Wastewater treatment
- Wastewater reuse (or zero discharge)
- Solid waste handling and disposal (H/D)

Rust separated the wastewaters into two groups--strong wastes and weak wastes--and treated them differently. Figure 2A illustrates the first section, and Figure 2B depicts the second and third sections.

1. Wastewater Treatment

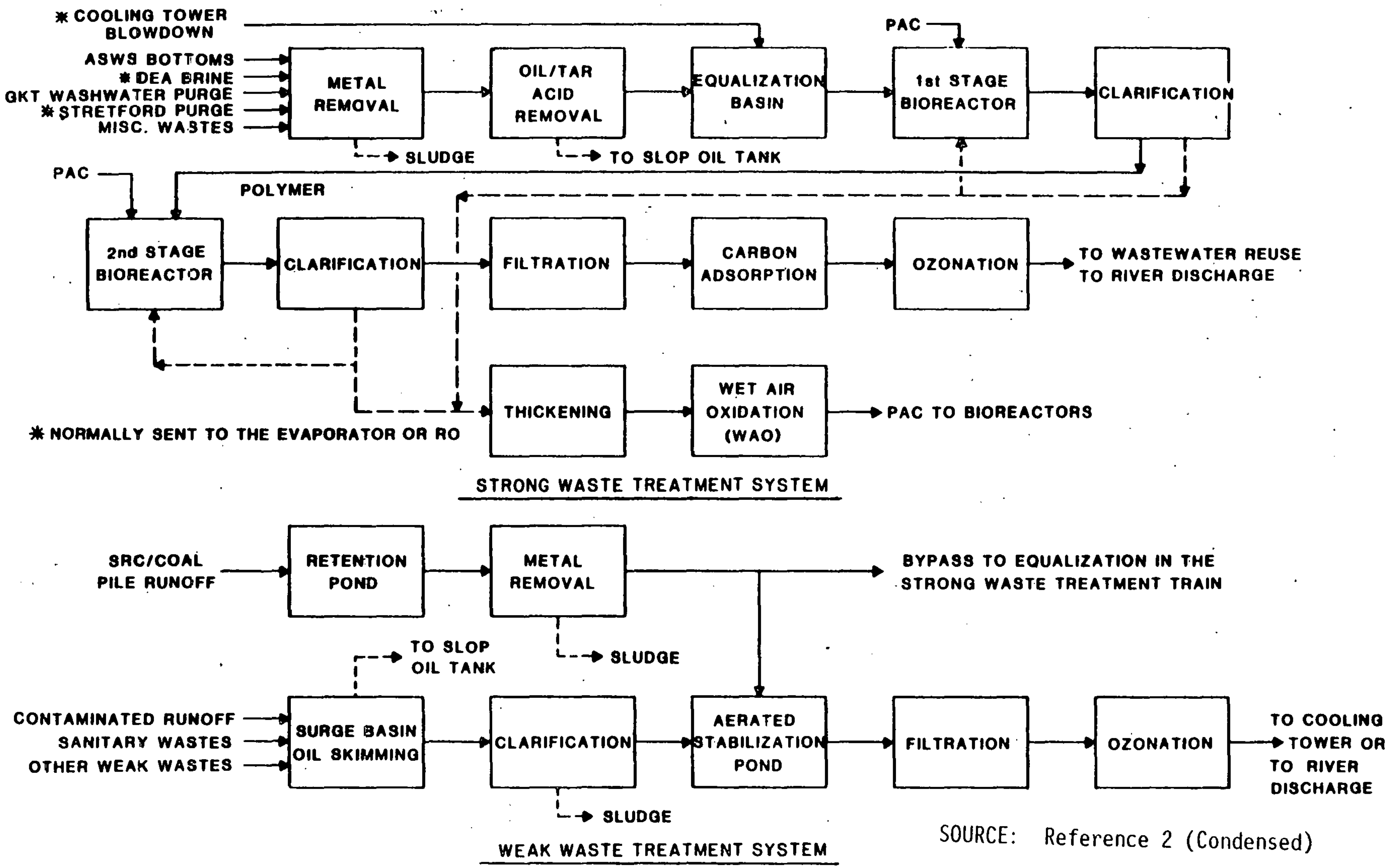
a. Strong-Waste Treatment. The strong-waste treatment system consists of primary, secondary, and tertiary treatment. Primary treatment comprises metal removal and oil/tar acid removal steps treating ASWS bottoms, DEA brine/SO_2 scrubber purge, GKT washwater blowdown, and other miscellaneous streams. The cooling tower blowdown, the DEA brine/SO_2 scrubber purge, and Stretford purge are also treated by the strong-waste treatment system when the zero-discharge system is not functional. When it is functional, these streams are sent to that system directly.

Metals are removed by precipitation with lime. Oil, emulsions, and tar acids are removed by acidification and coagulation. Tar acids are a class of complex, unidentified organic compounds that form precipitates at a low pH. Because the wastewater has a high buffering capacity, the acidification requires a large quantity of sulfuric acid. A large amount of lime is also needed to neutralize the wastewater after tar acid removal. After neutralization, the wastewater enters an equalization basin where it mixes with other streams such as filter backwash. The wastewater is then withdrawn from the equalization basin and fed to the biological treatment system.

Biological treatment (secondary treatment) is the heart of the wastewater treatment system, removing most of the organics. It consists of two bioreactors in series, each with its own clarifier. Each bio-

Figure 2A

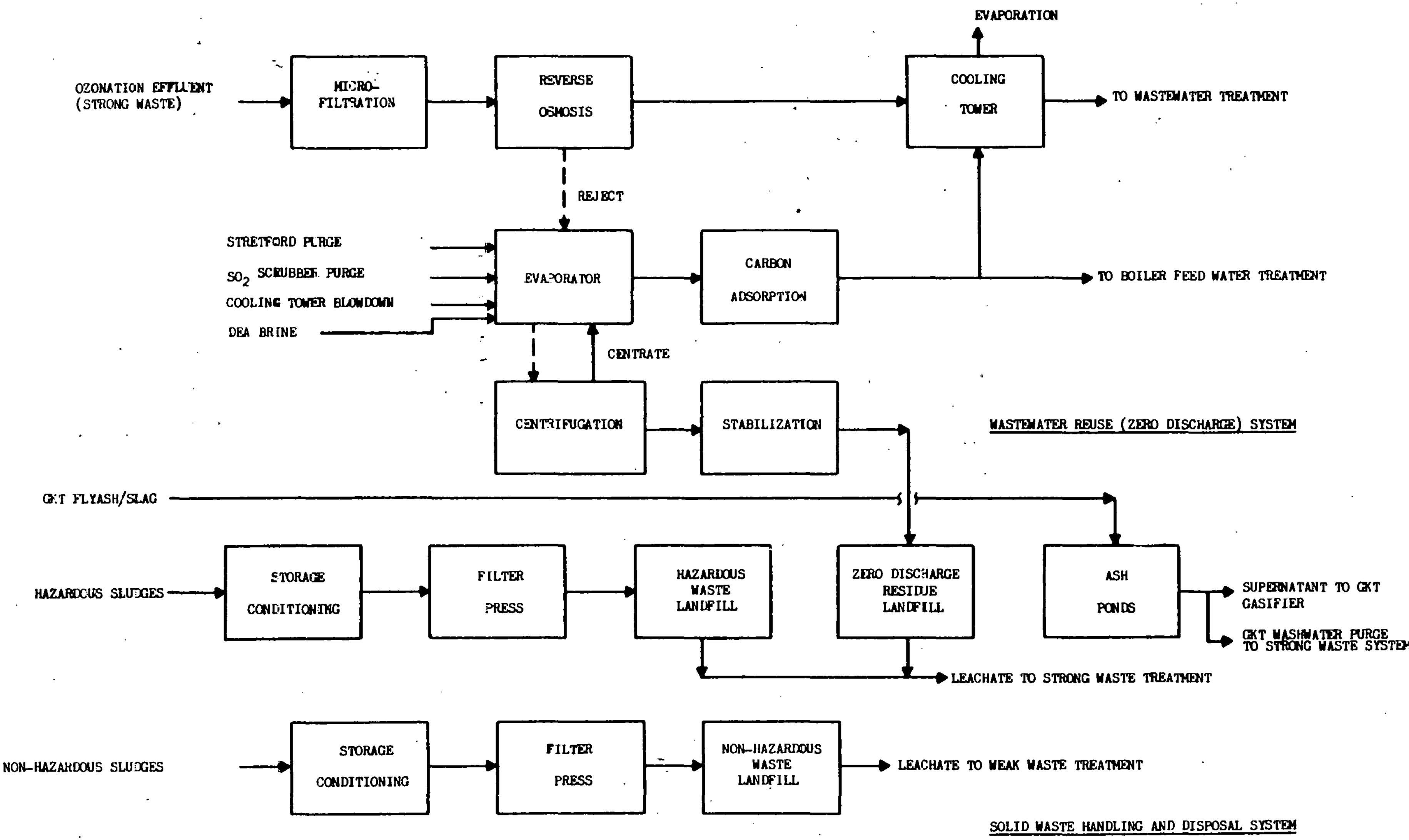
Baseline Design Wastewater Treatment



SOURCE: Reference 2 (Condensed)

Figure 2B

Baseline Design Wastewater Reuse and Sludge Disposal



SOURCE: Reference 2 (Condensed)

reactor has a 2.5-day nominal hydraulic residence time. High doses of powdered activated carbon (PAC), about 7,000 mg/L of feed, are constantly added to each bioreactor. Because of the high PAC consumption rate and its high cost, the PAC to be wasted along with the biomass will be regenerated by wet air oxidation (WAO). For the Baseline Design, the sizings for the bioreactor, clarifiers, and WAO were not based on firm R&D data.

The effluent from biological treatment is further polished during tertiary treatment, which consists of filtration, granular activated carbon (GAC) adsorption, and ozonation. Again, the sizes of those units were not based on experimental data because data were unavailable when the Baseline Design was in progress. The ozonated effluent is sent to the wastewater reuse system when the plant is in the zero-discharge mode, or discharged into the Green River when the plant is in the discharge mode.

b. Weak-Waste Treatment. The weak-waste treatment system is intended to handle lightly contaminated streams, predominately runoffs. Because the flow and composition of the runoffs are highly variable, the water is held in a retention pond. After retention, the SRC- and coal-pile runoff is treated to remove metals and then sent to the aerated stabilization pond for organic removal. Also sent to the aerated stabilization pond are runoff and washdown from the process areas where most of the process equipment and vessels are located. Sanitary waste and other weak process wastes, such as filter backwash from river water treatment, are also treated along with the contaminated runoff. The effluent from the stabilizing pond will be filtered and ozonated before being used as cooling tower makeup or discharged into the river.

2. Wastewater Reuse (Zero Discharge)

Figure 2B shows the major unit processes in the zero-discharge system. Wastewater reuse consists of microfiltration, reverse osmosis (RO), evaporation, and stabilization of zero-discharge residue. The cooling system, although, strictly speaking, not part of the off-sites facilities, is an integral component of the reuse system because the treated wastewater is eventually used as cooling tower makeup water.

Microfiltration is intended to protect the RO. RO removes most of the inorganic contaminants that could be detrimental and concentrates them into relatively small brine streams. The evaporator further concentrates the brine streams and, in the process, disposes of Stretford purge, DEA brine/SO_2 scrubber purge, and cooling tower blowdown. The slurry from the evaporator is centrifuged, and the cake is stabilized before being landfilled. The stabilization involves mixing in additives such as lime, cement, and pozzolans to convert the highly soluble zero-discharge residue into a nonpermeable monolithic mass.

3. Solid-Waste Handling and Disposal

The SRC-I Demonstration Plant produces a number of solid wastes, the most significant being the gasifier fly ash and slag, which are the most voluminous, and the solid wastes produced during wastewater treatment and reuse.

Figure 2B illustrates the solid-waste handling and disposal system. The fly ash is transported from the gasifier by sluicing, and the slag is removed by truck to the ash ponds. The stabilized zero-discharge residue is landfilled in a site designated for that use. The other solid wastes are stored, conditioned, and then dewatered in a filter press. Hazardous and nonhazardous wastes are handled separately, and disposed of in segregated landfills. The leachate from all landfills is returned to an upstream process for treatment.

The Baseline Design for the solid-waste handling and disposal facility was also preliminary. Estimates for sludge quantity were crude, properties of the sludge were not well-defined, and the design data were not fully available.

D. OBJECTIVES OF POST-BASELINE ENVIRONMENTAL RESEARCH AND DEVELOPMENT (R&D)

The Baseline Design uses the most advanced, commercially available wastewater treatment technology. However, many issues had to be resolved and uncertainties addressed before a final design could be adopted. The following questions required answers:

- How do wastewater characteristics vary with time?
- Is the sizing of the unit processes too conservative or too optimistic?
- Will the technology, which has been demonstrated for other wastes such as those from petroleum refining, work on SRC-I wastes?
- Is there a better process configuration than the Baseline Design?
- Are there more cost-effective, technically reliable processes for organic removal than biological methods? Would phenol extraction be satisfactory and/or of value?
- Will zero discharge work?
- What is the quality of the treated plant effluent? Is zero discharge necessary?

Addressing those issues and uncertainties was the main goal of post-Baseline environmental R&D. The primary objective was to generate data that could eventually lead to confirmation or refinement of the Baseline Design as much as possible. Alternative processes that might be technically superior to and/or more cost-effective than the Baseline Design were also to be evaluated within time and budgetary constraints. Obviously, some issues could not be fully addressed in the laboratory; only a full-scale demonstration plant that has been on stream for a long period can provide all the answers.

The secondary objective of the post-Baseline environmental R&D was to expand the data base for pollution control of synthetic fuels in general, and of direct coal liquefaction in particular. ICRC and DOE hoped that comparison of the SRC-I data with results from other coal-processing waste treatment systems would reveal some general trends.

E. SPECIFIC TASKS OF POST-BASELINE R&D

To achieve its objectives, the environmental R&D was divided into four specific tasks:

- Data base expansion
- Phenol recovery evaluation
- Zero-discharge evaluation
- Integration of results

1. Data Base Expansion

This task dealt specifically with the Baseline wastewater treatment scheme. It was intended to evaluate the Baseline Design *per se*; it did not assess alternative process schemes that are radically different from the Baseline Design or the zero-discharge system of the Baseline Design.

Experimental data were generated to confirm or refine the Baseline wastewater treatment system. The experimental work focused on the following areas:

- Variation of wastewater characteristics with time, process variables, and operating conditions
- Better alternatives for tar acid removal than that shown in the Baseline
- Minimum hydraulic residence time required for the bioreactors, and the need for powdered activated carbon
- Experimental confirmation of other unit processes chosen in the Baseline Design, including biological solids separation, filtration, carbon adsorption, ozonation, and vanadium removal.

Solid-waste handling and dewatering was also part of the post-Baseline R&D program, but work was not initiated until late 1983.

More specific issues are identified and addressed individually in Chapter II, entitled "Data Base Expansion."

2. Phenol Recovery Evaluation

The combined wastewater flow of the 6,000-tpd SRC-I Demonstration Plant under dry weather conditions is about 1,160 gpm. Of the total flow, about 400 gpm is heavily contaminated process condensates, laden with high concentrations of phenolics.

Early in the preliminary design phase of the project (Phase I), a tradeoff study performed by the Ralph M. Parsons Company of Pasadena, California and Rust Engineering showed that the added costs of removing phenols from certain process condensates could not offset the value of the recovered phenolics and the savings for wastewater treatment. In addition, the tight construction schedule contemplated at that time prohibited substantial design changes, and laboratory work had indicated that wastewater treatment without phenol recovery was technically feasible. Therefore, phenol recovery was not incorporated in the Design Baseline.

However, subsequent laboratory work completed immediately after the Baseline indicated that phenol recovery could improve the operation and stability of downstream processes, including the ammonia/sulfide water stripper, Claus sulfur recovery unit, and the wastewater treatment/reuse system. Because the improvements appeared to be significant and the construction schedule was delayed indefinitely due to funding cutbacks, assessment of phenol extraction was included in the post-Baseline program.

ICRC anticipated that phenol extraction could:

1. Reduce the amount of hydrocarbons in the overhead from the ammonia/sulfide water stripping unit.
2. Buffer the bioreactors from unexpected phenolic concentration fluctuations in major sour-water streams. Much of the uncertainty stems from the lack of representative wastewater samples.
3. Possibily eliminate the tar acid precipitation process and its consequent chemical usage, sludge production, and dissolved solids burden in the wastewater.
4. Improve biological treatment by way of smaller and more stable organic loadings, smaller bioreactors, lower aeration power, lower sludge volume, reduction or elimination of powdered activated carbon addition, more stable nitrification, and reduction in effluent nonbiodegradable organics.

5. Improve tertiary treatment by reducing granulated activated carbon consumption and ozone because the effluent from the bioreactor would be of better quality.
6. Reduce the toxicity of the final effluent.

Evaluation of phenol extraction entailed the following steps:

- Determining distribution coefficients of the phenolics in solvents used in commercial phenol recovery processes, which would indicate whether recovering phenols from SRC-I wastewater is technically feasible.
- Screening two commercially proven processes (Lurgi and Chem-Pro) using data from the above step and information produced by the vendors, and selecting one to assess further for impacts on downstream processes
- Evaluating impacts of phenol recovery on downstream processes
- Performing economic trade-off studies

Experimental work needed to evaluate the impact of phenol recovery on downstream processes focused on the following areas:

- Loss of volatile organic compounds during stripping
- Efficiency of tar acid removal
- Effects on biological oxidation and subsequent tertiary treatment
- Impact on powdered activated carbon addition and regeneration
- Effects on the quality of the fully treated wastewater

3. Zero-Discharge Evaluation

Zero discharge consists of four unit processes: reverse osmosis, evaporation, solid-waste stabilization, and recycle of most of the water to a cooling system. Zero discharge is costly and none of the unit processes is well-proven, particularly for synthetic fuel wastes. Because of the high cost and technical uncertainty, more data and further evaluation were required.

Experimental data were generated to either confirm or refine the Baseline Design. Specifically, the R&D programs entailed the following objectives:

- Experimentally determine efficacy of the pretreatment envisioned in the Baseline Design for the feed to the RO unit
- Test RO membranes using limited wastewater samples available
- Conduct an evaporator study
- Evaluate alternative stabilization processes by laboratory studies using synthetic wastes

Concurrently with the above efforts, alternatives to zero discharge, i.e., partial discharge and total discharge, were assessed. Partial discharge recycles the highly contaminated treated wastewater streams and discharges lightly contaminated water. This alternative could reduce costs considerably without unacceptably impacting river water quality. Evaluation began with an update of the material balance for the entire plant, including the water balance. ICRC expected that the updated material balance might identify areas where wastewater generation could be minimized and where partial discharge could be used. Total discharge is a viable option only if the treated wastewater does not significantly degrade river quality. Data on the treated effluent were needed to prove that.

The composition of the major contaminants in the treated effluent can be determined through chemical analyses and material balances; however, speciation of trace contaminants is complex and expensive. Thus, to determine effluent quality in the most practical way, analyses were used in conjunction with an aquatic bioassay study to indicate the suitability of the treated effluent for discharge.

4. Integration of All Post-Baseline Environmental R&D Programs

Because the R&D programs were so diverse, they had to be performed by many contractors at scattered locations. Yet, all of the programs were interrelated. The purpose of this task was to integrate the results generated from all the post-Baseline environmental R&D. This report is the product of that task.

II. DATA BASE EXPANSION

This chapter highlights specific areas of uncertainty associated with the wastewater treatment section of the Baseline Design, and results of certain post-Baseline R&D programs conducted to minimize the uncertainty.

A. SPECIFIC ISSUES IN THE BASELINE DESIGN

1. Variation of Raw Wastewater Characteristics

Little information on the variablity of wastewaters was available when the Baseline Design was developed. To determine how wastewater characteristics vary with time and with operating variables in an operating plant, ICRC contracted with Catalytic, Inc. in Philadelphia, Pennsylvania to conduct a comprehensive sampling program from May 1 to July 31, 1982 at the SRC-I pilot plant in Wilsonville, Alabama (nominal coal throughput of 6 tons/day).

Various wastewater sources and points throughout the wastewater treatment facilities at the Wilsonville plant were sampled and statistical analyses were performed between May 1 and July 31. Historic data that had been collected prior to the sampling period (February 1979 to December 1981) were also included in the statistical analysis. The final report entitled "Wilsonville Wastewater Sampling Program," dated October 1983, detailed the results.[3]

The Wilsonville pilot plant does not have all the wastewater streams that the 6,000-tpd SRC-I Demonstration Plant would have. However, it does generate samples that resemble the two most significant streams in the demonstration plant: the SRC and expanded-bed hydrocracker (EBH) sour waters. A combination of these two streams represents more than 80% of total sour water flow and organic load in the demonstration plant. The corresponding streams at Wilsonville are effluents from vessel V-105 of the SRC process unit and vessel V-1080 of the hydrotreater unit (HTU). Because the HTU was installed much later than the SRC process unit, most data available are from V-105. As a result, most statistical analyses to determine variations in characteristics were performed on that stream.

The historic data (1979-81) show that the concentrations and mass flow rates of total organic carbon (TOC), chemical oxygen demand (COD), NH_3, H_2S, and phenolics in V-105 have log-normal distribution. The concentrations can be summarized as follows:[3]

Parameter	50 percentile (mg/L)	90 percentile (mg/L)
TOC	13,100	37,900
COD	53,000	76,000
NH_3	10,400	17,100
H_2S	7,200	14,200
Phenolics	2,590	4,170

With few exceptions, the 1982 data fell between these 50 and 90 percentile values for each parameter.

The data for V-1080 collected during the two-month sampling period in 1982 show that this sample contains less TOC and phenolics than the V-105 sample, but the ammonia and hydrogen sulfide are comparable. The 50 percentile TOC and phenolics concentrations for V-1080 were 1,866 and 920 mg/L, and the 90 percentile values were 2,330 and 1,800 mg/L, respectively. For ammonia, the 50 percentile value was 12,520 mg/L, and the 90 percentile value was 14,300 mg/L; the respective values for H_2S were 8,000 and 17,500 mg/L.

The Wilsonville data demonstrated that the two most contaminated sour water streams vary in their makeup. The variability is not atypical for coal processing waste. The Baseline Design, which has considerable equalization capacity, should be able to handle the variation.

2. Metal Removal from ASWS Bottoms and GKT Washwater Blowdown

The Baseline Design removes metals from the ASWS bottoms, which include all sour waters that have been steam-stripped, and the GKT washwater blowdown. Various R&D studies[3-5] have shown that toxic metal concentrations in these streams are insignificant, and will not inhibit biological treatment or cause noncompliance with the river water quality standards. Hence, the metal removal step for these streams can be eliminated.

3. Tar Acid Removal before Biological Treatment

Because tar acids inhibit biological treatment, they must be removed.[5] Tar acids are a class of complex organic compounds that precipitate at an acidic pH. The Baseline Design includes provisions to remove tar acid by acidification. However, acidification requires a large quantity of sulfuric acid. Furthermore, after acidification, the wastewater must be neutralized with lime before undergoing biological treatment.

The amount of sulfuric acid needed to lower the wastewater pH to about 3, assuming that the ASWS effectively removes all of the ammonia and sulfide, is 115 mequiv/L. For a 400 gal/min sour-water flow, the acid consumption rate would be about 1,840 gal/day or 28,200 lb of 66° Be sulfuric acid per day.

The consumption rate of base is also great. Experimental data show that 27 mequiv/L of lime is needed to neutralize the acidic wastewater after tar acid removal. For a 400-gpm wastewater flow, the lime usage rate is 6,545 lb/day of dry quicklime (56 wt % as CaO).

In addition to the heavy chemical consumption, tar acid removal also produces large quantities of solid wastes. Experimental data show that about 9 to 9.5 g of tar acid/L (dry basis) was precipitated by acidification of steam-stripped sour water.[6] The corresponding volume was between 70 and 180 mL of sludge/L of wastewater. For a 400-gpm sour-water stream, the production of tar acid sludge would be 43,300 to 45,700 lb/day (dry basis), or 5,400 to 14,000 ft^3/day. Tar acid precipitates are a sticky, greasy solid waste and are difficult to handle.

Tar acid removal also adds many dissolved minerals to the wastewater. When the wastewater (after full treatment) is recycled, the salt must be purged to avoid buildup in the cooling system. Therefore, the salts eventually become a solid waste when zero discharge is practiced. The amount of zero-discharge residue associated with tar acid removal can be approximated by assuming the sludge is calcium sulfate. The 28,200 lb/day of 66° Be sulfuric acid is equivalent to slightly more than 39,000 lb/day of calcium sulfate, on a dry basis. Assuming the $CaSO_4$ could be evaporated to 50 wt %, the volume of the $CaSO_4$ sludge would be close to 900 ft^3/day.

Because of the problems associated with tar acid removal by sulfuric acid addition, attempts were made to use carbon dioxide, which will not add minerals to the wastewater.[6] The attempts were partially successful. CO_2 lowered the pH of the wastewater to 6.5, and removed a significant amount of tar acid. However, CO_2 was unable to reduce the pH to 2.5-3.0, which is required for complete tar acid removal. In order to reduce the pH to that range, a pressurized CO_2 dissolution system would probably be needed. Without the pressurized system, CO_2 could be used, but only in conjunction with H_2SO_4, which would reduce the acid requirements. However, no further attempts were made to pursue the CO_2 study because phenol extraction, as discussed later, seemed to reduce and sometimes completely eliminate tar acids.

4. Bioreactor Design

Biological oxidation is the heart of the SRC-I wastewater treatment system and hydraulic retention time (HRT) is a key design parameter. The Baseline Design provided an HRT of 2.5 days for both first- and second-stage bioreactors, with the combined HRT being 5 days. The capability to continuously add powdered activated carbon (PAC) at a high dose was also incorporated. The R&D data indicate that the Baseline bioreactor design is basically sound. However, refinements can be made.

The data show that, with continuous high-dose PAC, only a single-stage bioreactor is required. The second-stage bioreactor did not significantly enhance biooxidation. In fact, because of almost complete removal in the first-stage bioreactor, the second-stage bioreactor was so lightly loaded that the biological solids underwent endogenous respiration, their concentrations were very low, and they did not separate and thicken as well as the first-stage solids. Hence, solid separation in the second stage is a problem.

The R&D data also suggest that a combined HRT of 5 days should be adequate. The laboratory data showed that 3.5 days is sufficient under steady-state conditions. Thus, the combined HRT of 5 days used in the Baseline Design seems reasonable; it provides a safety margin.

The data also confirmed that a continuous high dosage of PAC (enough to maintain a concentration of 4,500 to 7,500 mg/L of the mixed liquor) is required to produce acceptable quality effluent. Without PAC, even a two-stage bioreactor configuration with a much longer HRT could not produce an effluent of comparable quality. The following is a comparison of systems with and without PAC.[4,5]

	With PAC[4]	Without PAC[5]
No. of stages	One	Two
HRT (days)	3.5	3.0/4.2
Solids residence time (SRT) (days)	40	18/30
Effluent composition (mg/L unless noted otherwise)		
COD	262 ± 102	648 ± 163**
TOC	218 ± 73	289 ± 34
Phenolics	0.07 ± 0.02	0.016
NH_3-N	6.5 ± 5	74 ± 26
NO_2^-/NO_3^--N	150 ± 29*	122 ± 12
SCN	7.2 ± 7.1	12.8
CN	1.3 ± 0.8	0.14
Color (APHA units)	200 ± 400	5,000 ± 1,000**

*Based on HRT = 4.45 days; data obtained from a separate study.[5]
**Based on HRT = 3.0/3.0 days; data obtained from a separate study.[4]

The single-stage PAC configuration was significantly better than the two-stage non-PAC system in terms of COD, TOC, color, and ammonia removal. Although the limited data show the two-stage system is better than single-stage for phenolics, SCN, and CN, the differences are not significant.

5. Powdered Activated Carbon Regeneration

The continuous high dose of PAC required for the Baseline Design necessitates regeneration. The nominal consumption rate of PAC is estimated to be more than 10,000 lb/day; without regeneration, the cost would be exorbitant. Assuming that PAC costs 25¢/lb, and that the plant is operating 330 days/year, the annual carbon replacement cost would be $825,000, and this does not include costs for landfill. Therefore, the economics justify regeneration.

The Baseline Design uses wet air oxidation (WAO) to regenerate PAC. However, WAO has been demonstrated only on a laboratory scale, and testing on coal liquefaction wastes is limited. Originally, testing of WAO was scheduled as one of the post-Baseline activities. However, the phenol extraction evaluation showed that a continuous high dose of PAC was not necessary when certain sour waters were extracted; also, the costs of phenol extraction were more than offset by savings in other affected areas. Therefore, since phenol extraction was highly recommended, evaluation of WAO became unnecessary. A subsequent section details the results of the phenol extraction evaluation.

6. Biological Solids Separation

Effective separation of the biomass is essential to successful operation of the biological treatment system. The Baseline Design did not have a good basis for sizing the clarifiers for the bioreactors. Sizing of a clarifier is controlled by two factors: the settling rate, which is measured by zone settling velocity (ZSV), and the thickening rate, which is indicated by limiting flux.

The separation data generated during the post-Baseline period for the first-stage bioreactor with PAC are presented in Table 1.[5] Assuming the total amount of mixed-liquor suspended solids (TMLSS), including PAC, is about 14,000 mg/L, the ZSV would be about 5 ft/hr and the maximum clarifier overflow rate would be 900 gpd/ft^2. For a wastewater flow of 1,000 gpm, the minimum size of the clarifier would be 45 ft in diameter, if the settling rate controls the clarifier sizing. The sizing based on the settling rate must also be checked against thickening. Figure 3 shows a flux curve generated from the data in Table 1.

Table 1

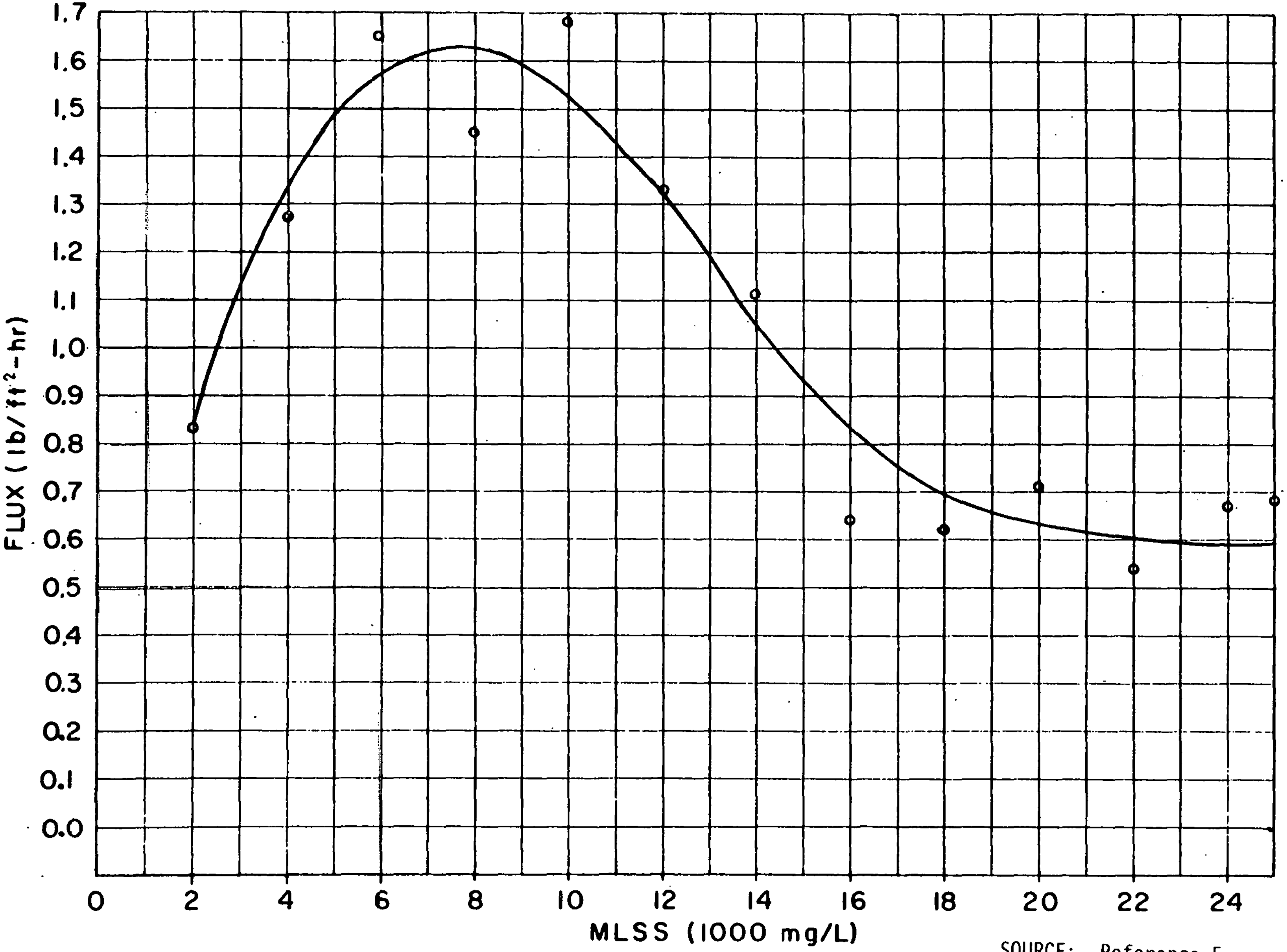
Settling and Thickening of Biological Solids First-Stage Bioreactor with PAC

TMLSS (mg/L)	ZSV (ft/hr)	Flux (lb/ft^2-hr)
2,000	25	0.83
4,000	19	1.27
6,000	17	1.65
8,000	11	1.45
10,000	10	1.68
12,000	6.7	1.33
14,000	5	1.18
16,000	2.4	0.64
18,000	2.1	0.62
20,000	2	0.71
22,000	1.5	0.54
24,000	1.7	0.67
25,000	1.6	0.68

SOURCE: Reference 5

Figure 3

Flux Curve for First Bioreactor with PAC



SOURCE: Reference 5

This curve suggests that the limiting flux is about 1.7 lb/ ft^2-hr if a clarifier underflow concentration of 3 wt % is desired. The diameter based on thickening would be 72 ft. Therefore, thickening controls the clarifier size. In terms of overflow rate, the 72-ft clarifier yields 354 gpd/ft^2. The overflow rate used for the Baseline Design was 400 gpd/ft^2, which is too high if thickening is also considered.

Furthermore, as discussed previously, the R&D data showed that the second-stage bioreactor had poor settling properties. Generally, the ZSVs and flux were an order of magnitude less than those of the first-stage bioreactor (see Table 2). The data for the flux are also much more scattered; no clear pattern emerged (Figure 4). The poor biological separation characteristics further negate the need for a second-stage bioreactor when PAC is used.

7. Post-Biological Tar Acid Removal

The Baseline Design does not include a post-biological tar acid removal step. However, the treatability studies[4] showed that, despite prebiological tar acid removal, some tar acid continued to drop out after biological treatment. These studies demonstrated that tar acid could be removed by acidifying the wastewater to pH 2.5 with sulfuric acid. The step is a repetition of the prebiological tar acid precipitation step, except that the amount of sulfuric acid required would be smaller.

Post-biological tar acid removal should be included in the Baseline Design because it accomplishes two objectives. First, it reduces the organic load to the granular carbon adsorption step, which is an expensive process. Second, it removes the foulant from the feed to the reverse osmosis unit, which is extremely sensitive to fouling. However, post-biological tar acid removal exacerbates the problems associated with prebiological tar acid removal.

8. Coagulation before Tertiary Treatment

Chemical coagulants and doses were not evaluated for the Baseline Design. A single nonspecified polymer is added to the second-stage bioeffluent, which is then mixed in a flocculation tank and sent to the

Table 2

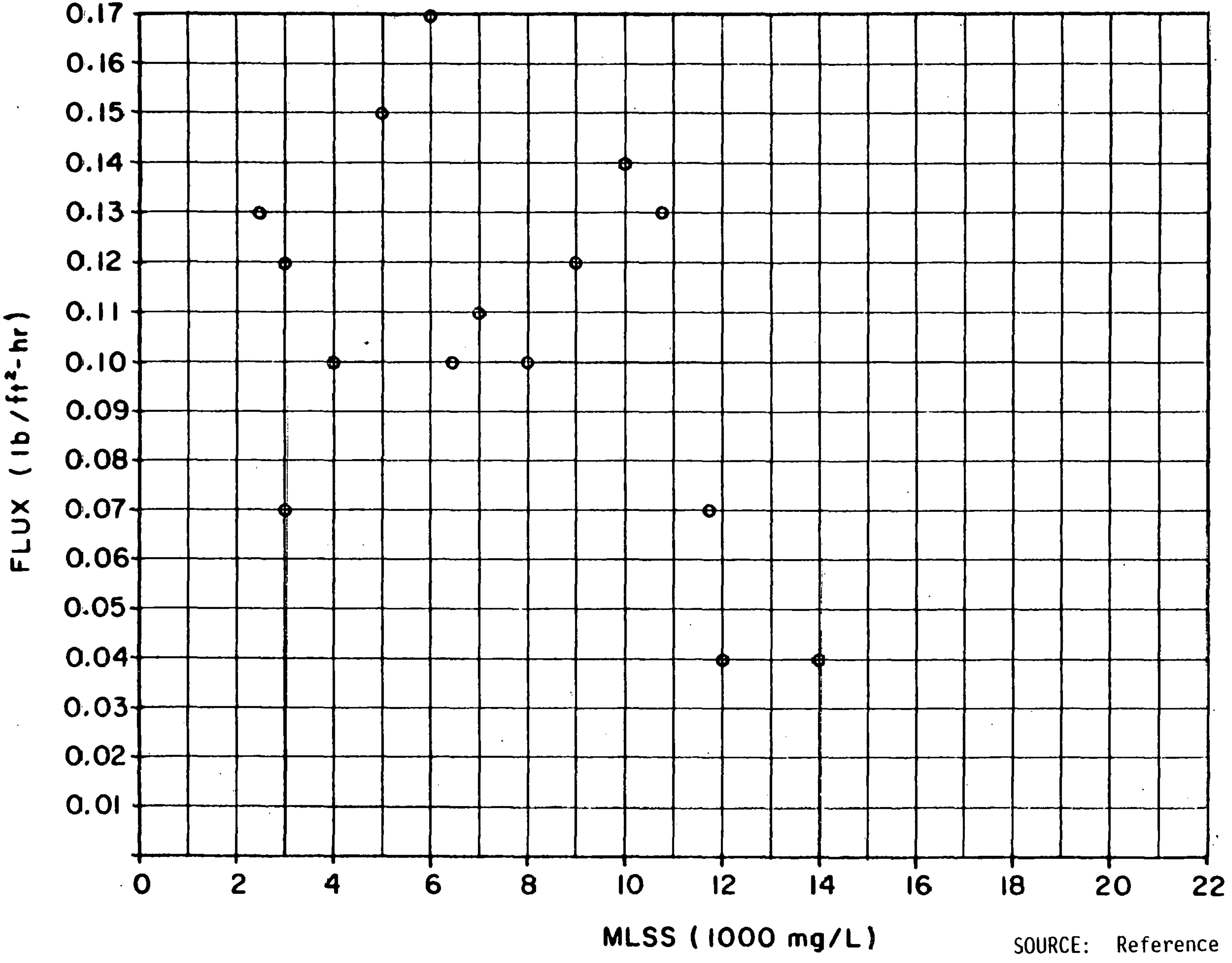
Settling and Thickening of Biological Solids
Second-Stage Bioreactor with PAC

TMLSS (mg/L)	ZSV (ft/hr)	Flux (lb/ft^2-hr)
2,500	3	0.13
3,000	2.5	0.12
3,000	1.4	0.07
4,000	1.5	0.10
5,000	1.8	0.15
6,000	1.7	0.17
6,450	0.94	0.10
7,000	0.95	0.11
8,000	0.75	0.10
9,00	0.83	0.12
10,000	0.88	0.14
10,800	0.72	0.13
11,820	0.38	0.07
12,000	0.19	0.04
14,000	0.17	0.04

SOURCE: Reference 5

Figure 4

Flux Curve for Second-Stage Bioreactor with PAC



SOURCE: Reference 5

biological clarifier. However, laboratory testing during the treatability studies[4] demonstrated that a two-coagulant system produced better settling characteristics.

The bioreactor effluent still contains considerable amounts of nondegradable organics which can be removed by the granular activated carbon (GAC) downstream. However, GAC is an expensive process, so there was incentive to find more cost-effective alternatives to reduce the organics level. Screening tests examined ferric chloride, ferric sulfate, alum, and lime, with and without polymer addition to aid in settling. Results were evaluated on the basis of zeta potential, floc size, floc strength, floc settleability, and supernatant clarity. Ferric chloride and ferric sulfate both appeared to produce equivalent results at the same dose. The chloride salt was selected because sulfate concentrations were already high from sulfuric acid addition during the tar acid removal step. High sulfate concentrations would cause problems in the zero-discharge system. The optimum dose was established as 800 mg/L (as $FeCl_3 \cdot 6H_2O$). Lime was then added to adjust the pH to about 7.0. An anionic polymer, Magnifloc 835-A, at a dose of 0.5 mg/L, was found to aid in flocculation and to improve clarity.

9. Filtration

A filter loading rate of 2 gpm/ft^2 was used in the Baseline Design, but the filter medium was not specified. Laboratory tests were conducted using the same loading rate in a 1-in.-diameter column, with 36 in. of mixed media:

Media	Depth (in.)	Effective size (mm)	Uniformity coefficient
Anthrafilt	18	1.20-1.50	1.6-1.7
Fine sand	12	0.46-0.48	1.5
Coarse sand	3	0.61-0.80	1.5
Gravel	3	32-64	-
	36		

As stated above, coagulation was very effective in removing suspended solids (down to about 4 mg/L), and no pressure drop was observed after a 4-hr test run at the same rate. Although filtration would not be necessary were this effluent quality always achievable from coagulation, it should be included in the design to protect the downstream carbon columns from plugging should high solids be encountered.

10. Granular Activated Carbon (GAC) Adsorption

Sizings in the Baseline Design were based on hydraulic loading rate: 4 gpm/ft^2 at peak flow. A post-Baseline R&D study[7] conducted carbon-isotherm and column-breakthrough tests. The isotherm tests showed that Calgon FS-400 was the most effective of several types screened. The data for TOC fit the Freundlich model well (correlation coefficient = 0.937) and yielded the following relationship:

$$q_1 = 0.00017C_1^{1.52}$$

where q_1 is milligrams of TOC adsorbed per gram of carbon and C_1 is TOC concentration in the wastewater. The maximum theoretical capacity is 76 mg of TOC/g of carbon.

For color, the data yielded the following with a correlation coefficient of 0.972:

$$q_2 = 0.012C_2^{0.66}$$

where q_2 is the number of APHA units adsorbed per gram of carbon. The maximum theoretical capacity is 1,260 units/g of carbon.

The column breakthrough test targeted an effluent TOC of 13 mg/L, which is the maximum ambient concentration in the river. The influent concentration was 44 mg/L. Under those conditions, the column data developed the following relationship:

$$t = 2.56(D - 38)$$

where t is service time in hours and D is bed depth in centimeters. The critical depth is 38 cm. The minimum empty bed contact time (EBCT) was found to be 18.5 min.

11. Ozonation

Ozonation was originally intended for disinfection and for removal of trace contaminants in the carbon column effluent. Disinfection is required because the sanitary waste is transported from sources to the wastewater treatment system via the same pipeline carrying process wastes. Using the same pipeline saves money. Since the effectiveness of ozonation for disinfection has been demonstrated, the post-Baseline R&D did not include disinfection tests. Instead, the work focused on the removal of trace contaminants.

The R&D data[7] show that ozonation removed little TOC. The benefit of ozonation was primarily for COD removal. Without ozonation, the target COD of 150 mg/L could not be met. However, aquatic ecotoxicity tests,[8] which will be discussed in detail, showed that ozonation actually increased toxicity to certain aquatic life. This problem will also be further addressed in Chapter III entitled Phenol Recovery Evaluation. Phenol extraction of certain sour waters eliminates the problem.

12. Vanadium Removal

The Baseline Design treats the Stretford purge in the metal removal unit along with other strong wastes (Figure 2A) when the evaporator is shut down. When the evaporator is functional, this stream is evaporated, and the vanadium is stabilized along with zero-discharge residues.

Combining the Stretford purge with other strong wastes might complicate the vanadium removal step because the organics could interfere with the precipitation of the vanadium. The laboratory data on vanadium precipitation did show that, in the presence of organics, the vanadium removal required a much higher pH and a higher chemical dosage than that needed without the organics.[9] Although the mechanism of organic/vanadium interaction is not known, it is hypothesized that organics chelate the vanadium and form an organometallic complex that remains in solution.

The optimal condition established for vanadium precipitation by testing an actual Stretford purge obtained from an oil refinery is a combination of controlling the pH at about 10 and adding $FeSO_4$ at an Fe:V molar ratio of 4.9. This dosage was about 20 times the stoichiometric amount based on FeV_4O_9 and 10 times that based on $Fe(VO_3)_2$. The oil refinery waste contained 41,700 mg/L of BOD, and 493 mg/L of TOC. The required dosage observed for a synthetic waste with few organics was much lower: 9.12 times based on FeV_4O_9 and 2.74 times based on $Fe(VO_3)_2$. The optimal pH for the synthetic waste was also much lower--8.2.[10] Thus, the presence of organics apparently affected the optimal conditions for vanadium precipitation.

The vanadium removal efficiency achievable was about 92%. This will be acceptable for the SRC-I Demonstration Plant. After being mixed with other non-vanadium-bearing streams, the residual vanadium in the 5-gpm Stretford purge would be reduced to much less than 1 mg/L in the 1,159-gpm (dry weather flow) plant effluent. The concentration in the receiving water (the Green River) would be 1/150 less, which is considered acceptable because the 96-hr median tolerance limit on fish ranges from 4.8 to 55 mg/L.

The vanadium sludge settles very slowly; the observed zone settling velocity (ZSV) was about 1 ft/hr,[9] which is equivalent to 180 gpd/ft^2. The sludge was thickened to 5.7 wt % in 2 hr. Despite the low ZSV, the residual suspended solids in the supernatant totaled only 7 mg/L.

The oxidation state of vanadium affected its removal, and aeration inhibited vanadium removal. To minimize the effect of aeration, the Stretford purge should be removed from the Beavon-Stretford unit before regeneration, which is accomplished by aeration.

Aeration failed to reduce the COD (69,500 mg/L) substantially. The Stretford purge would increase the COD in the feed to biological treatment by about 10%. Because the COD could not be removed significantly by aeration, ozonation will be the method for COD reduction.

13. SO_2 Scrubber Purge

This stream contains a large quantity of reduced sulfur compounds. Under normal operating conditions, the stream will have 350 lb/hr of Na_2SO_3, 231 lb/hr of $NaHSO_3$, 79 lb/hr of Na_2SO_4, and 2 lb/hr of NaHS.

All of these sulfur compounds except Na_2SO_4 have oxygen demand. The calculated oxygen demand is 81 lb/hr.

The Baseline Design employs evaporation to treat this stream when the zero-discharge system is operational, and uses the strong-waste treatment train to dispose of this stream when the plant is in the discharge mode. A post-Baseline study[11] has indicated that sending the purge directly to the evaporator will be a problem. Sulfite and bisulfite will decompose in the evaporator to SO_2, which is corrosive. Therefore, sulfite and bisulfite have to be oxidized to sulfate. After oxidation, the wastewater should be precipitated with lime to remove sulfate so that the scaling potential can be minimized.

B. REVISED BASELINE DESIGN--A MARGINAL ALTERNATIVE SCHEME

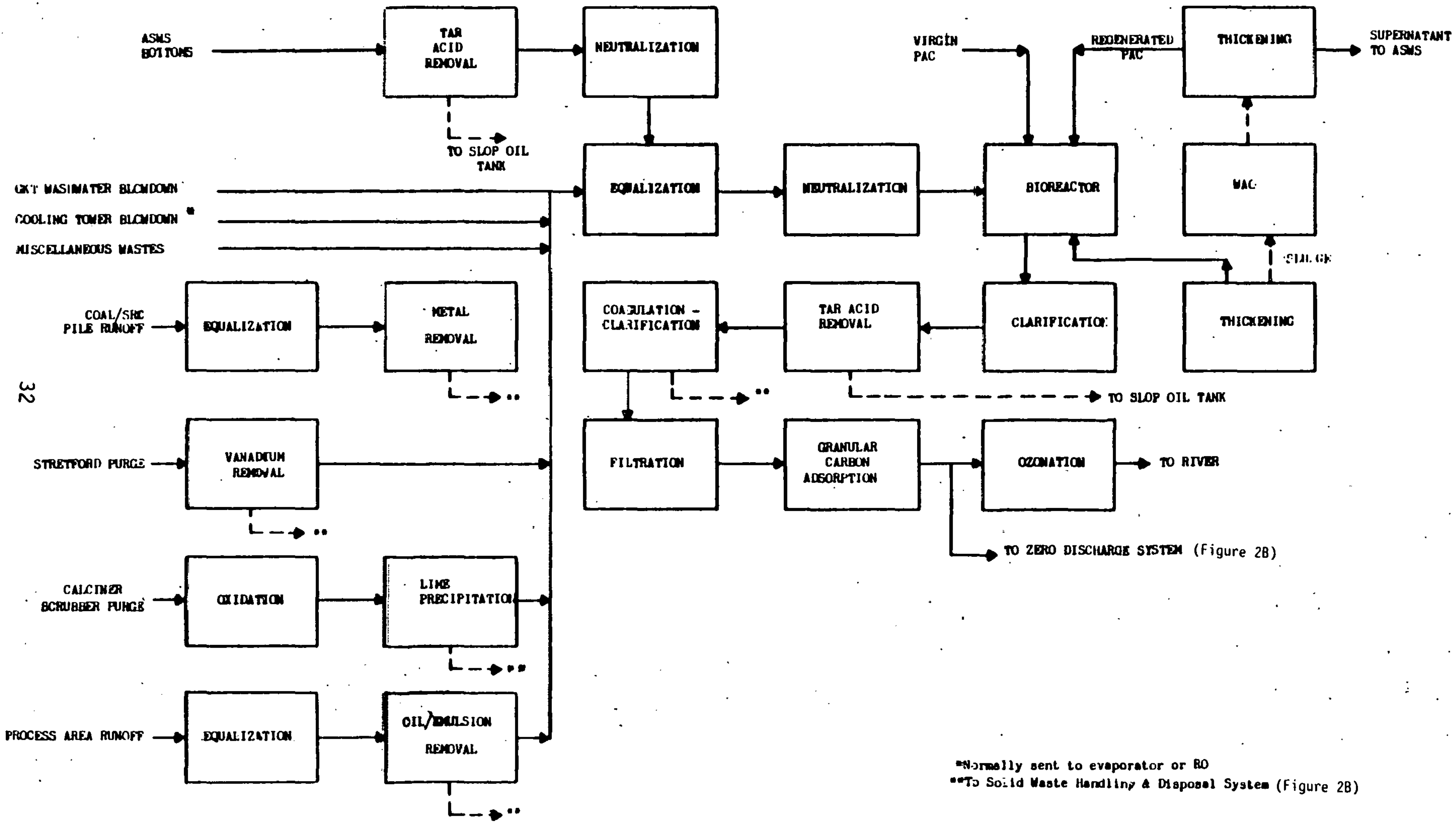
This section presents a revised Baseline Design incorporating the changes described in the preceding section. Note that the revised Baseline Design detailed in this section is not a recommended system. The only purpose of this revision was to derive a firm basis from which tradeoff studies of phenol extraction could be made. Phenol extraction of certain sour waters will have an impact on the wastewater treatment and solid-waste disposal facilities. The tradeoff studies compared the facilities with and without phenol extraction on the basis of this revised Baseline Design, not the Rust Baseline Design.

Figure 5 depicts the revised Baseline Design. Unlike the original Baseline Design, the ASWS bottoms in the revised design are sent to tar acid removal (TAR) without being treated for metal removal. After TAR, the wastewater is neutralized before being sent to the equalization basin, where it is comingled with other wastes.

Also sent to equalization is GKT washwater blowdown. Cooling tower blowdown is also sent there when the plant is in the discharge mode. In the zero-discharge mode, the cooling tower blowdown can be directly treated in the RO or evaporator in the zero-discharge section. Likewise, the Stretford purge is sent to the evaporator directly in the zero-discharge mode. In the discharge mode the Stretford purge is

Figure 5

Revised Baseline Design (Wastewater Treatment Only)



*Normally sent to evaporator or RO

**To Solid Waste Handling & Disposal System (Figure 2B) treated separately with lime and $FeSO_4$ before being mixed with other streams.

Coal/SRC storage runoff is equalized and then treated for metal removal. Unlike the original Baseline Design, this stream is mixed with other "strong" wastes and treated together. The same holds true for the runoff from the curbed process areas. After oil/emulsion removal, that too is mixed with other "strong" wastes. The joint treatment will ensure that any contamination of the runoff by toxic materials leaked from the process vessels can be treated by the same advanced treatment processes intended to handle heavily contaminated wastes. The SO_2 scrubber purge is oxidized to convert bisulfite and sulfite to sulfate, followed by lime precipitation to remove $CaSO_4$.

After equalization, the combined wastewater undergoes final pH adjustment before entering the biological treatment unit, consisting of a single-stage bioreactor with provisions to add high-dose PAC continuously. The bioreactor will have an HRT of 5 days.

The PAC wasted routinely, along with the biological solids, will be regenerated by wet air oxidation. The regenerated PAC is stored and then recycled to the bioreactor. The supernatant, which contains a significant amount of organics and ammonia, can be returned to the ASWS and eventually treated biologically.

As in the original Baseline Design, the clarified bioreactor effluent goes through post-biological tar acid removal, followed by coagulation/clarification, filtration, and carbon adsorption. The effluent from carbon adsorption is ozonated if the treated wastewater is to be discharged into the Green River. If the wastewater is to be recycled, it will go to the zero-discharge system, as shown in Figure 2B.

Even though the revised Baseline Design is a refinement of the Baseline Design, there are still underlying disadvantages that are inherent to a scheme without phenol extraction. As will be discussed in the next section in detail, phenol extraction can eliminate these disadvantages.

III. PHENOL RECOVERY EVALUATION

A. INTRODUCTION

As discussed previously, phenol recovery was not incorporated in the Baseline Design, primarily due to the tight construction schedule contemplated at that time. However, subsequent laboratory work suggested that phenol recovery would offer many potential advantages, and, as a result, phenol recovery evaluation became a major area for the post-Baseline R&D program.

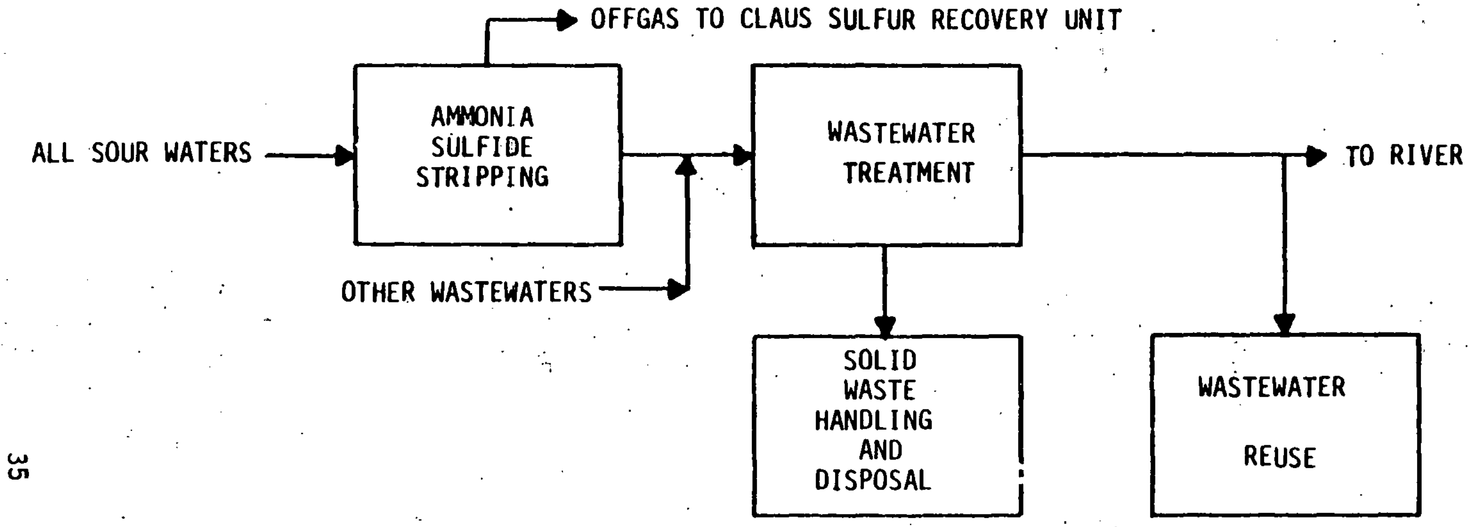
Figure 6 shows the two schemes that were compared. The scheme without phenol extraction consists of four basic blocks: ammonia/sulfide stripping, wastewater treatment, wastewater reuse (zero discharge), and solid-waste handling and disposal. The wastewater treatment block comprises the unit processes in Figure 5; the solid-waste handling and disposal and the wastewater reuse blocks contain all of the unit processes shown in Figure 2B. The scheme with phenol recovery contains the same four blocks, as well as phenol recovery. The individual unit processes contained in the wastewater treatment blocks for the two schemes are similar, but not necessarily identical. More about this will be discussed later.

The objective of the evaluation was to determine the technical and economic benefits of extracting phenolics from certain sour-water streams. To accomplish that objective, it was necessary to assess (1) the technical feasibility of phenol recovery itself, (2) the impact of phenol extraction on the downstream unit processes and final effluent quality, and (3) the economic tradeoffs.

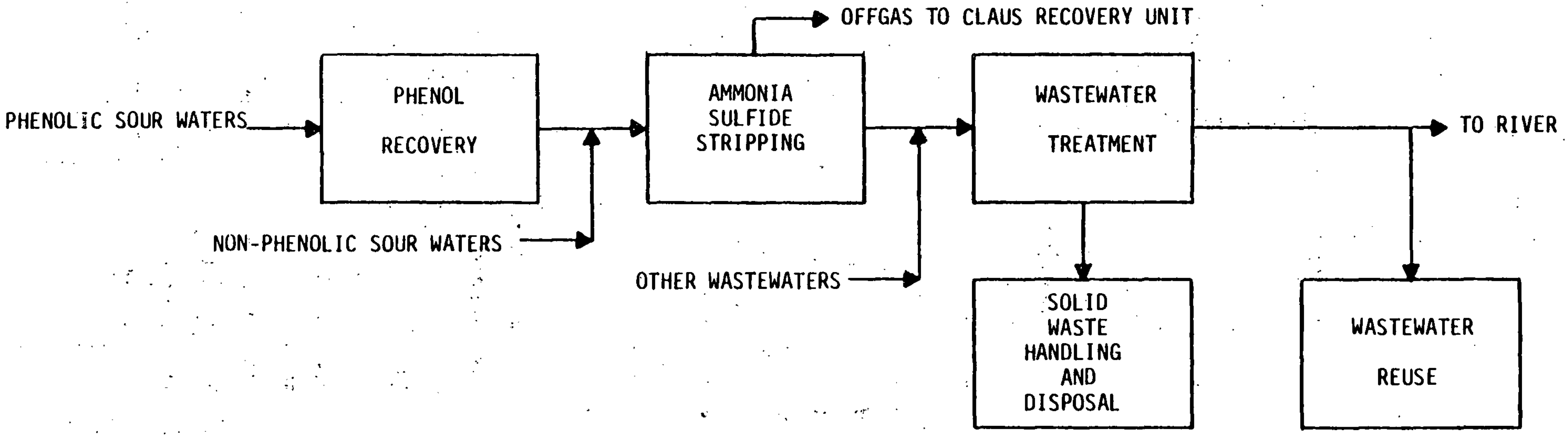
Evaluation of the technical feasibility of phenol recovery itself was carried out in several steps. The first step involved solvent screening. Using batchwise extraction, three solvents were tested, and distribution coefficients for phenolics were determined. A large distribution coefficient would indicate that the solvent could effectively remove the phenolics from the wastewater. If the screening tests showed that the solvents were effective, the next step to be carried out

Figure 6

Two Alternative Wastewater Treatment Schemes



ALTERNATIVE I: WITHOUT PHENOL RECOVERY



ALTERNATIVE II: WITH PHENOL RECOVERY

would be comparing the two commercially available processes marketed by Lurgi and Chem-Pro, and selecting one for more in-depth evaluation. The in-depth evaluation would entail (a) extraction of phenolics from the wastewater using a continuous-flow column, (b) stripping of the solvent from the raffinate, (c) solvent regeneration, and (d) recovering the phenolics from the rich solvent.

Once the technical feasibility of phenol recovery was proven, the impact of phenol recovery on the downstream processes had to be assessed. The assessment involved ammonia/sulfide water stripping (ASWS), tar acid removal (TAR) before biooxidation, biooxidation, and subsequent tertiary treatment (post-biological TAR, coagulation, filtration, granular activated carbon adsorption, and ozonation), as well as the zero-discharge process.

Finally, economic tradeoffs had to be made. Phenol recovery increases the cost, but this is offset by savings in the downstream treatment processes. The objective of the tradeoffs was to determine if phenol recovery provided a net saving in capital and operating costs.

The results of the phenol recovery evaluation are discussed in the following sections.

B. TECHNICAL FEASIBILITY OF PHENOL EXTRACTION

1. Solvent Screening

A series of batchwise laboratory experiments was carried out by R. G. Luthy of Carnegie-Mellon University.[6] As the first step in the evaluation, the raw wastewater was characterized. The results are reproduced in Table 3. The water is highly alkaline, with high sulfide and ammonia concentrations, and heavily contaminated with organic material. Samples from this supply of wastewater were then subjected to batch extraction with three candidate solvents selected from the literature: diisopropyl ether (DIPE), n-butyl acetate (NBA), and methyl isobutyl ketone (MIBK).

Solvent extraction results are reported in Table 4. Based on the phenolic content of the raw water, reduction in phenolics varied from 88 to 99% depending on the solvent and the solvent-to-wastewater ratio. At one volume of solvent to five volumes of wastewater, phenolic removal

Table 3

SRC Ft. Lewis Process Water/Raw Water Sample Characterization for Phenol Extraction Study (mg/L)

COD (as received)	74,800[a]
(after expelling S^{2-})[b]	31,200[a]
TOC	9,600
Phenolics[c]	8,000[a]
Alkalinity (as $CaCO_3$)	67,700
pH (units)	9.1
Phenol[d]	5,720
Aniline[d]	150
Pyridine[d]	23

[a] Average of two analyses.
[b] Acidified and purged with nitrogen for sulfide removal.
[c] 4AAP procedure (Standard Methods).
[d] By gas chromatography.

SOURCE: Reference 6

Table 4

Summary of Results of Solvent Extraction Screening Tests [Average of Duplicate Samples (mg/L)]

Solvent		Solvent/water ratio (vol.)			
		0.2	0.6	1.0	Blank[a]
DIPE	TOC[b]	4,400	4,170	3,570	89
	COD[b]	16,200	13,900	13,200	295
	Phenolics[c]	975	435	290	
	Organic-N	64	60	61	
NBA	TOC[b]	3,450	2,860	2,550	83
	COD[b]	10,520	8,380	7,935	205
	Phenolics[c]	643	240	154	
	Organic-N	60	60	62	
MIBK	TOC[b]	3,250	2,920	2,770	100
	COD[b]	9,840	8,950	8,510	220
	Phenolics[c]	480	175	107	
	Organic-N	68	76	73	

[a] Clean water saturated with solvent.

[b] Samples acidified and purged with nitrogn for sulfide and residual solvent removal.

[c] 4AAP procedure (Standard Methods).

SOURCE: Reference 6

efficiencies were 94% for MIBK, 92% for NBA, and 88% for DIPE, all for a single extraction. There was almost no change observed in the organic nitrogen levels from those reported for the raw water. TOC reductions varied from a minimum of 54% to a maximum of 70%.

From these results, distribution coefficients were calculated for the phenolics as follows: DIPE, 27; NBA, 56; and MIBK, 76. The distribution coefficient is defined as the ratio of the weight fraction of phenolics in the solvent to the weight fraction of phenolics in the aqueous phase (the higher the value the better).

The effect of pH on the distribution coefficient was also examined using another set of experiments with NBA as the solvent. Reducing the pH of the wastewater would be expected to increase the distribution coefficient because a smaller fraction of the phenolics would be ionized in the aqueous phase. Indeed, it was found that the distribution coefficient increased from 56 to 81, as pH decreased from that of raw water (9.1) to 6.2. The pK_a for phenol is 9.98. Therefore, most of the increase in the distribution coefficient occurs as the pH is lowered to the range of 8.5.

In a later series of experiments, Luthy characterized and extracted a sample of Wilsonville hydrotreater unit water at several pHs using DIPE and NBA in separatory funnels. The raw water characterization and extraction results are given in Table 5. Compared to the SRC process water (Table 3), Wilsonville hydrotreater unit wastewater is weaker. Results of the extractions again show a substantial reduction in the phenolic content of the wastewater, similar to the reduction indicated in Table 4 for the SRC water extractions. As expected, decreasing the pH improved phenolics recovery.

Note that for the NBA extractions part of the COD and TOC remaining in the extracted samples is attributable to the presence of residual solvent. Heating and purging of the samples in preparation for TOC/COD determinations was apparently much more effective in removing residual solvent in the DIPE-extracted samples, because of DIPE's higher volatility.

As part of their biological treatment studies, Catalytic initially pretreated some Ft. Lewis SRC-I wastewater by double extraction with

Table 5

Wilsonville Hydrotreater Unit Water Sample Characterization and Extraction Results

Raw wastewater (mg/L)	
TOC	2,400
COD	29,000
COD[a]	3,900
Alkalinity	47,000
Phenolics	1,770 (4AAP method)
Phenol	980
pH (units)	9.8

After extraction[a]

pH	COD[a]	DIPE TOC	Phenolics	COD[b]	NBA TOC	Phenolics
9.8	1,355	290	305	2,000	465	215
7.5				1,220	310	127
7.0	985	211	165	1,020	286	101
6.5				1,090	280	95
5.0	965	240	132	1,050	248	86
Blank water solvent	114	37		1,300	380	

[a] Two extractions at a solvent/water ratio of 0.2.
[b] Sample pH-adjusted, heated, and purged with N_2.

SOURCE: Reference 6

fresh MIBK at a solvent-to-wastewater ratio of 0.094 per extraction.[4] They noted a reduction in TOC of from 10,280 to 6,200 mg/L, while phenol was reduced from 5,000 to about 155 mg/L. Luthy's data (Table 5) show more TOC removal and better phenol removal, but at twice the solvent-to-wastewater ratio.

In summary, the Luthy data provide a strong indication that solvent extraction could be an attractive treatment process for SRC condensates. Phenolics can easily be extracted to low levels, while TOC can be reduced to one-third of its initial value.

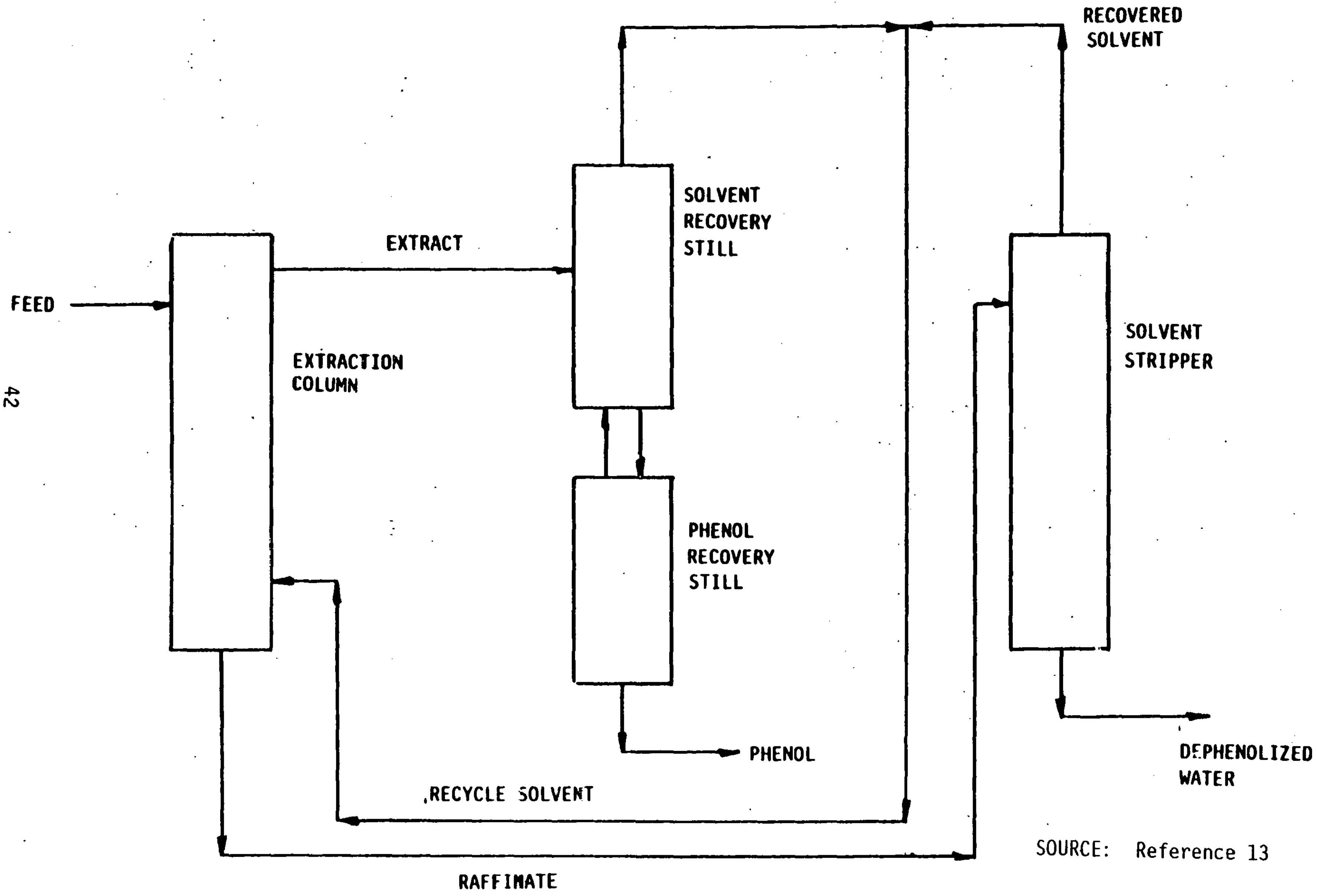
2. Selection of Commercial Phenol Extraction Technology

The Lummus Company of Bloomfield, New Jersey prepared a technical and economic comparison of two phenol recovery processes: Lurgi's Phenosolvan process and the Chem-Pro Corporation process. Both processes use solvent extraction to recover phenol, but equipment and solvents differ. Phenosolvan is a well-established process, whereas the Chem-Pro process has limited commercial-scale experience. However, the Chem-Pro process could reduce the phenols concentration in the wastewater stream to a lower level at nearly half the capital cost and the same (if not lower) operating costs compared to the Phenosolvan process. Therefore, Lummus recommended the Chem-Pro process.[12]

A schematic process flow diagram of the Chem-Pro process is shown in Figure 7. The untreated wastewater containing phenolic compounds is contacted with a countercurrent stream of solvent as the water descends through the reciprocating-plate type of extractor. The dephenolated water (raffinate) leaving the bottom of the extractor is sent to the stripping column, in which the residual solvent is recovered using steam. The extract, containing the phenols dissolved in solvent, is then pumped to the solvent recovery still. The solvent is recovered as an overhead product and recycled. Crude phenol is pumped from the bottom of the solvent recovery still to the phenol recovery still, where it is purified by distilling under vacuum. The phenol is pumped from the bottom of the phenol recovery still to storage. The recovered phenol consists of a variety of phenolic species. Because of its heterogeneity, and also because of the relatively small quantities involved, the phenol will be incinerated as a plant fuel.

Figure 7

Chem-Pro Phenol Recovery Process



SOURCE: Reference 13

3. In-Depth Laboratory Evaluation at Chem-Pro

Chem-Pro performed laboratory experiments to simulate the process discussed above.[13] The results are discussed in three parts: (a) the solvent extraction process itself; (b) solvent recovery; and (c) solvent regeneration.

a. Solvent Extraction--Laboratory Column. Chem-Pro Corporation was to determine the operating variables required to extract phenols from SRC-I process condensate using a semicontinuous flow column and Chem-Pro's proprietary solvent. The target concentration for total phenolics (phenolics by the 4AAP method plus resorcinol) was 100 to 125 ppm.

The results, including feedwater analyses, are summarized in Table 6. The feed analyses for the Chem-Pro work indicate an average of 6,300 mg/L phenolics (by the 4AAP method) in the wastewater, compared to an average value of 8,000 mg/L found by Luthy (Table 3). Luthy also found higher ammonia levels than Chem-Pro. Resorcinol levels in the Chem-Pro feed were measured at 1,100 ppm by Luthy and Chem-Pro.

As data in Table 6 show, the extraction column was quite capable of consistently reducing phenolics (4AAP) from about 6,000 to below 10 mg/L, with little effect on ammonia and hydrogen sulfide concentrations. Resorcinol concentrations were reduced from 1,100 to between 2 and 190 ppm. During the study, solvent-to-feed ratios varied in the range of 0.084 to 0.20. The column had approximately 4.5 theoretical stages.

For most of the runs the total phenol concentrations [phenolics (4AAP) plus resorcinol] were well below the desired level of 100 to 120 ppm because of higher than necessary solvent-to-feed ratios. Very conservative values were used for the solvent-to-feed ratios in most of the runs because of concerns about resorcinol extraction. Relative to other phenolic compounds, resorcinol has a low distribution coefficient and it would place a lower limit on the solvent-to-feed ratio.

As the table indicates, resorcinol was indeed relatively more difficult to extract than the other phenolics. Although the resorcinol concentrations in the raffinate correlate reasonably well with solvent-to-feed ratios ($r = -0.83$), the total phenolics (4AAP) are apparently reduced to such low levels that variations in concentration are due to

Table 6

Summary of Feed and Raffinate for Chem-Pro Corporation Extraction Columns[a]

Run no.	Solvent/feed ratio	Total phenolics (ppm)[b]	Resorcinol (ppm)[c]	H_2S (ppm)	NH_3 (ppm)
		Column optimization runs (1-in. column)			
Feed		6,800	1,100	12,000	10,900
4	0.13	6.8	20	10,500	11,000
8	0.20	6.2	9.0	11,500	13,100
10	0.10	4.6	190	12,000	10,900
11	0.084	2.0	190	12,000	12,600
13	0.20	2.0	3.0	9,900	14,000
14	0.13	2.0	22.0	10,500	15,000
15	0.20	2.0	2.0	10,000	14,000
		Production runs (2-in. column)[d]			
Feed		5,800	1,100	11,000	12,200
16	0.2	7.0	4.0	10,000	12,000
17	0.2	2.0	3.0	9,500	17,000
18	0.22 (ave.)	2.0	4.0	10,100	14,500

[a] 125 to 175 strokes per min.
[b] 4AAP method (Standard Methods); does not include resorcinol.
[c] High-pressure liquid chromatography.
[d] To generate samples for Catalytic's biooxidation work.

SOURCE: Reference 13

random experimental errors and therefore show no correlation to solvent-to-feed ratios.

Performance of the extraction column did not appear to be affected by nonphenolic constituents, including other organic materials, dissolved salts, and dissolved gases (NH_3, H_2S, and CO_2).

Overall, the Chem-Pro work supports the conclusion that continuous solvent extraction (at least the extraction phase) of phenolic materials from SRC-I wastewater is technically feasible. Their work indicates that a countercurrent column operating at a solvent-to-feed ratio of about 0.13 or slightly lower can maintain total phenolics plus resorcinol at less than 100 ppm.

b. Stripping Solvent from Raffinate. The next step in the feasibility evaluation of phenol extraction was for Chem-Pro to examine the removal of solvent from the extractor raffinate stream. The goal was to steam strip the solvent from a concentration of about 2.4% in the raffinate down to 25 ppm, without removing the hydrogen sulfide and ammonia. Stripping was performed in a 3-in. diameter column containing 9 ft of packing (about 15 theoretical stages).

During the early testing, a white solid appeared in the overhead condensate about 2 hr after operation started. The solids clogged valves, vents, and the condenser surface making it necessary to stop the tests. The composition of the solids was not determined, but they were speculated to be a salt of ammonia and hydrogen sulfide. The only effective method of eliminating the problem proved to be reducing the steam rate.

Table 7 gives the average composition of the raffinate feed to the stripper and summarizes the results of the stripping process. The average hydrogen sulfide and ammonia concentrations in the stripper feed were 10,100 and 15,000 ppm, respectively. During the period when solids appeared in the overhead condensate, most of the ammonia and hydrogen sulfide did not appear in the stripper bottoms. After the steam rate was reduced, the solids disappeared and ammonia levels in the stripper bottoms approached the levels in the feed. However, because hydrogen sulfide is more volatile than ammonia, most of the hydrogen sulfide was stripped along with the solvent. The overhead from the solvent stripper

Table 7

Steam Stripping of Extractor Raffinate (Stripper Feed and Bottoms Composition)

Run ID	H_2S (ppm)	NH_3 (ppm)	Solvent (ppm)
Feed (avg)	10,100	15,000	2.4%
	Solids in stripper condensate		
1/18	1,500	5,800	1
1/18	2,500	2,500	1
1/19	1,700	1,900	4
2/1	1,800	9,300	220
2/3	3,400	4,600	280
2/9	1,400	6,300	260
	No solids, lower steam rate		
2/16	1,500	8,100	7.6
2/17	1,500	13,000	5.8
2/18	1,900	14,000	6.6
2/22	3,000	14,000	490[a]
2/23	2,300	10,200	74[a]

[a] Presumably caused by temperature upsets.

SOURCE: Reference 13

can be condensed to remove the hydrogen, which can then be sent to the sulfur recovery unit.

These results indicate that stripping solvent from the extracted wastewater to a level of less than 25 ppm while keeping ammonia in solution is feasible. However, hydrogen sulfide is also stripped along with the solvent, but it can be removed as uncondensed gas leaving the stripper overhead condenser.

c. Solvent Regeneration/Phenol Separation. The final phase of Chem-Pro's extraction work was to examine solvent and phenol recovery by distillation. In this two-step distillation process, the extract stream (about 4% phenolics) from the extraction column is first distilled to recover the solvent as an overhead stream. The column bottoms, rich in phenolics, are sent to another distillation column, operating at low pressure, where the phenolics are further concentrated in the bottoms. The overhead stream from the second column would have a phenolics concentration similar to that in the extract stream and would be mixed with the first-stage distillation feed in the actual process. The primary purpose of the second column is to reduce the phenolic boiling point so that lower pressure steam may be used in the reboiler.

Feed, bottoms, and overhead compositions for the first-stage distillation are provided in Table 8. Overhead phenolics from the first column were found to be on the order of 1.4%; however, due to possible analytical errors during measurement of the o-cresol portion of the phenolics, the actual phenolics concentration in the overheads is suspected to be much lower than indicated. The overhead solvent concentration was more than 98%. Bottoms were 70% solvent, somewhat higher than the desired value of 50. However, this concentration can vary over a considerable range without much effect on the overall process. Hydrogen sulfide in the feed did not show up in the overhead or the bottoms. It was apparently lost via the overhead condenser vent.

Feed, bottoms, and overhead compositions of the second-stage distillation are also given in Table 8. Column overheads contained about 97% solvent and 3% phenolics, while the bottoms held less than 1% solvent. Apparent analytical errors in bottoms analysis leave about 20% of the bottoms composition unaccounted for.

Table 8

Solvent Regeneration/Phenol Recovery Distillation
(wt % Except as Noted)

	Solvent	Water	Phenolics[a]	Others	H_2S (ppm)	NH_3 (ppm)
	Solvent recovery (first column)					
Overhead	98+	1.8	1.4		24	2
Bottoms (ave.)	71	0.070	31	3.2	9.7	12
Feed (ave.)			4.5		3,200	120
	Phenol recovery					
Overhead (ave.)	97		2.9		39	1
Bottoms (ave.)	0.93		71	8.3	7	1
Feed (ave.)	71		31		9.7	12

[a] Defined here simply as the sum of phenol, o-cresol, m- and p-cresol, and resorcinol. This is not the same as 4AAP analysis for phenolics.

SOURCE: Reference 13

Overall, the solvent recovery process operated without unusual difficulties. Solvent was regenerated at better than 98% purity with the by-product phenolics stream containing less than 1% solvent. The recovered phenol was rather heterogeneous; it contained a wide variety of phenolic species. Therefore, it has limited market value as a product. The current disposition plan is to use it in the plant as a supplemental fuel.

In summary, Chem-Pro's work demonstrated that phenol recovery for the SRC-I wastewater was technically feasible. The post-Baseline R&D program was continued, and the assessment of the effects of phenol recovery on downstream processes was subsequently conducted.

C. AMMONIA/SULFIDE WATER STRIPPING

Chem-Pro Corporation, as an extension of its work on extraction, examined the feasibility of stripping the dephenolated water produced in the extraction process.[13] The primary purpose of ammonia/sulfide stripping at Chem-Pro was to produce water for the work performed at Catalytic. Catalytic, in their bioreactor pretreatment work, also produced limited data on stripping of both extracted and raw Ft. Lewis SRC-I process condensate.[4] Finally, Luthy and Campbell examined in the laboratory the effects of steam-stripping on the quantity of organic material in the overhead gases produced by stripping of both solvent-extracted water and raw wastewater.[6]

1. Stripping of Dephenolated Wastewater by Chem-Pro

Dephenolated wastewater produced by solvent extraction was to be steam-stripped to remove ammonia and hydrogen sulfide to levels below 200 and 1 ppm, respectively.

Prior to producing large quantities of stripped water for Catalytic, Chem-Pro initiated a two-phase optimization study to determine the optimal operating parameters. In the first phase (A), 9 ft of packing was used, while in the second phase (B), packing depth was increased to 11 ft. To force the fixed ammonia from the ionized to the free state for stripping, caustic was added at a point 3 ft above the bottom of the packing.

Phase A runs, used to establish proper operating conditions, were carried out at two feed rates, each with and without caustic addition. Since the steam rate was held constant, changing the feed rate was equivalent to changing the steam-to-feed ratio. The results in Table 9 show that neither the hydrogen sulfide nor the ammonia goals were achieved. The bottoms hydrogen sulfide concentration averaged about 3.5 ppm, with apparently only random variations with a change in feed rate (i.e., different steam-to-feed ratios) and caustic addition (as indicated by the pH changes in the bottoms). However, the ammonia concentrations did respond, as would be expected. As the feed rate was decreased (i.e., steam-to-feed ratios increased), the ammonia concentration fell. Addition of caustic to reduce the ionized fraction of ammonia increased the stripping efficiency.

For Phase B, the feed point to the column was changed to effectively increase packing depth by 2 to 11 ft, and the caustic concentration was reduced. Results are given in Table 9. This time, the ammonia concentration was reduced below the target level of 200 ppm. However, the hydrogen sulfide concentration in the bottoms increased by a factor of two to three. This was expected considering the higher pH at which the Phase B runs were made. The un-ionized (i.e., strippable) fraction of hydrogen sulfide and ammonia dissolved in the water is a function of pH. At lower average pHs, such as in the Phase A runs, a much larger fraction of the hydrogen sulfide is not ionized while more ammonia is in the ionic state. Conversely, at higher pHs as in the Phase B runs, a larger fraction of the ammonia is on the average not ionized, while there is little free hydrogen sulfide.

Following the evaluation work done under Phases A and B, nine more drums of dephenolated wastewater were stripped for the bioreactor studies. Because of time constraints, further optimization work was discontinued and the remaining dephenolated water was processed at a pH of 9 at the highest feed rate. The main composition of the nine drums of treated water is presented at the bottom of Table 9, including final phenol levels. This latter data is a summary of the results of the combined extraction/stripping process work done by Chem-Pro.

Table 9

Ammonia/Hydrogen Sulfide Stripping of Extracted (and Solvent Stripped) Wastewater by Chem-Pro Corp.

Date	Feed rate (mL/min)	pH	Stripper bottoms (ppm) H_2S	NH_3	Solvent
		Phase A (optimization)			
2/3	300	5.52	3.3	750	<1
2/4	300	7.79	2.7	300	<1
2/3	500	5.72	2.2	820	<1
2/4	500	7.77	4.3	540	<1
2/4	Composite	9.12	4.9	580	<1
		Phase B (optimization)			
2/24	Feed	10.22	2,300	10,200	74
2/24	300	9.22	7.0	32	<1
2/24	450	8.86	13.0	93	<1
2/24	600	8.90	16.0	140	<1
2/24	600	11.57	16.0	94	<1

Production runs (averages for 9 drums)

pH	9.02 ± 0.23
Total phenol	2.5 ± 2.2
Resorcinol	<1
Solvent	5.4 ± 9.9 (contains suspect high single analysis)
H_2S	10.5 ± 9.9
NH_3	351 ± 101

SOURCE: Reference 13

In none of the stripper runs was hydrogen sulfide ever reduced below the target value of 1 ppm; also, ammonia was reduced below 200 ppm only during Phase B. Production runs resulted in average hydrogen sulfide and ammonia concentrations of 100 and 351 ppm. The high average ammonia concentration is surprising, since Phase B runs were consistently below 200 ppm. The variation in caustic feed rates may have been at least partly responsible.

2. Stripping of Extracted and Process Wastewaters by Catalytic

Because of time constraints, while Chem-Pro's work was ongoing, Catalytic proceeded to prepare feed for the bioreactor study by batch-extracting raw Ft. Lewis process condensate with the Chem-Pro solvent, followed by a two-step steam-stripping process. Raw wastewater was also steam-stripped. The stripping process used two bench-scale continuously operated packed columns. The first column removed sulfide and the second stripped ammonia. After the first column, the pH of the wastewater had been reduced to 8.5, down from 9.5 in the feed. Prior to the second pass pH was adjusted to 11.5 with lime,

Results of the extraction and stripping pretreatment steps are summarized below. All concentrations are in mg/L.

	TOC	NH_3-N	Sulfide	Phenolics
Raw water (feed)	10,280	18,350	46,000	5,000
Extracted (run 56)	6,200	16,534	26,600	45
Extracted/stripped (ave)	2,800	208	<1	44
Stripped only	4,800	180	<1	2,570

As the data indicate, the two-step stripping process was quite effective in removing sulfide and ammonia.

3. Organic Material in Stripper Overhead

One advantage of placing the extraction step ahead of ammonia/hydrogen sulfide stripping is that the quantity of hydrocarbons leaving with the stripper overheads that are sent to sulfur recovery can be reduced. Claus sulfur recovery plants usually operate at high enough temperatures to combust hydrocarbons to water vapor and carbon dioxide. However, incomplete combustion and cracking of some of the heavier aliphatics and aromatics that may end up in the feed to the sulfur recovery unit can cause deactivation of the catalyst by deposition of carbonaceous materials.

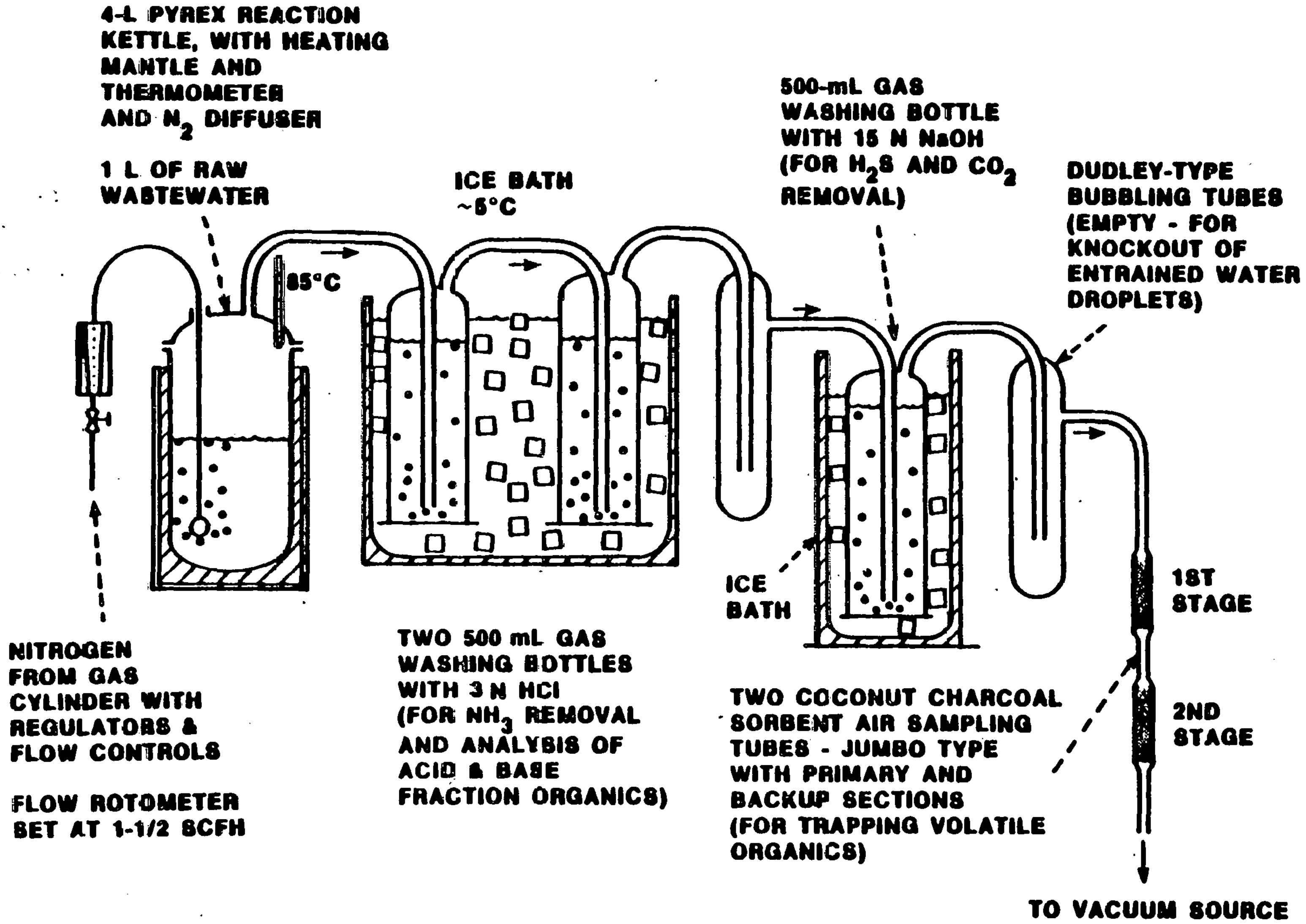
Luthy and Campbell[6] examined the effects of stripping on the amount of organic material volatilized from Ft. Lewis SRC-I process condensate and solvent-extracted condensate. One-liter samples of raw and extracted water were tested with the apparatus illustrated in Figure 8. The samples were stripped for 6 hr with an exit gas temperature of 85°C. A nitrogen purge and vacuum were used to draw off-gases through a scrubbing train and charcoal sorbent columns. TOC values are summarized in Table 10. MIBK analyses for the extracted sample are also included; these were used to correct TOC measurements for the presence of solvent in scrubbing solutes. The TOC associated with MIBK, toluene, and xylenes captured by the charcoal are also reported in Table 10. A TOC value is not reported for the extracted sample base scrub because of an apparent erroneous result.

Stripping removed a significant amount of organics from the raw SRC-I wastewater, but extraction drastically reduced the organics volatilized during stripping. About 1,750 mg of TOC originally present in the 1 L of raw SRC-I wastewater was stripped, along with ammonia and hydrogen sulfide. For the extracted wastewater, excluding the TOC attributable to the solvent (MIBK), only about 40 mg of TOC was lost. The loss would be 160 mg if the TOC of the solvent were included. Thus, the amount of organics volatilized during stripping of the extracted wastewater is about one order of magnitude less than that of the non-extracted wastewater. Effective separation of the solvent before stripping will reduce the organic volatilization even more, i.e., to about 1/20th that of unextracted water. GC/MS analyses show that neither toluene nor xylene was volatilized during stripping of solvent-extracted water.

In summary, extraction did reduce the quantity of the organics stripped and the residual solvent in the extracted wastewater should be removed in order to keep the organics in the stripper overhead to a

Figure 3

Apparatus for Study of Organics Volatilized during Stripping



SOURCE: Reference 6

Table 10

Volatilization of Organics during Stripping

	Raw SRC water	
Sample	TOC (mg/L) in sample	mg of TOC stripped
First acid trap, 450 mL	2,100	945
Second acid trap, 450 mL	400	180
Base trap, 450 mL	1,380	621
Charcoal traps	Negligible	Negligible[a]
Bottoms, after stripping	11,500	-
Total	-	1,746

	Extracted-stripped water			
Sample	TOC (mg/L) in sample	MIBK (mg/L) in sample	Corrected TOC (mg/L) in sample	mg of TOC stripped
First acid trap, 450 mL	150	145	45	20 (68)
Second acid trap, 450 mL	134	135	40	18 (60)
Base trap, 450 mL	-	50	-	- (16)
Charcoal traps	-	21 (mg)[b]	-	- (15)
Bottoms, after stripping	4,530	-	4,400	- -
Total	-	-	-	38 (159)[c]

[a] Calculated TOC based on the measured MIBK, toluene, and xylenes.
[b] Amount absorbed by the charcoal.
[c] The numbers in parentheses include TOC.

SOURCE: Reference 6

minimum. Stripping of raw water resulted in about 26 times as much volatile organic material being carried overhead, in comparison with stripping of extracted water.

D. TAR ACID PRECIPITATION

For some coal refinery process wastewaters, acidification precipitates an undefined organic material termed "tar acid." As observed in an ICRC study,[5] tar acid apparently impedes biological wastewater treatment. This material, which most likely consists of high molecular weight, nonvolatile, acidic organic compounds, represents a significant but highly variable class of compounds in the process wastewater.

Because these compounds will impact the design and operation of the wastewater treatment system, the effect of phenol recovery on tar acid removal was studied in the laboratory. The most applicable work was performed by Luthy and Campbell,[6] the results of which are summarized below. Also, Catalytic, Inc., as part of its evaluation on the impact of phenol recovery on biological treatment, presented some information on tar acid precipitation in both raw and phenolics-extracted wastewaters. These observations are summarized below.

1. Luthy and Campbell Study[6]

As part of this study, precipitation of tar acids from both raw and pretreated Ft. Lewis SRC-I process condensate was examined. Pretreatment consisted of combinations of solvent extraction and ammonia/sulfide stripping.

Samples of raw, stripped, and extracted-stripped SRC waters were acidified with sulfuric acid. One sample was adjusted to pH 5.0 and the second to pH 2.5. A third sample of each type of wastewater was used to evaluate the effect of ferric iron as a coagulant. In this latter test, pH was reduced to pH 6.5 with sulfuric acid to start precipitation, 800 mg/L of ferric sulfate was added, and the pH was again adjusted to 5.0. After being allowed to settle for 24 hr, the samples were analyzed.

Phenol extraction did reduce the acid required for tar acid precipitation. About 10% reduction was observed. The amounts of acid needed to adjust the pH to 5.0 were 140 and 125 mequiv/L for the stripped and extracted/stripped wastewaters, respectively. The amount of acid actually needed will depend on the residual concentration of ammonia and sulfide remaining after stripping. A higher residual concentration will require more acid. These acid requirements were based on 100-125 mg/L of ammonia and 660-840 mg/L of sulfide.

Tar acid precipitation significantly removed COD but not TOC. COD and TOC values of the samples, both before and after precipitation, are given in Table 11, along with the quantity of tar acid material precipitated. For raw water, tar acid precipitation resulted in about a 28% reduction in COD, but curiously caused little change in TOC. Stripped water showed reductions in both TOC and COD, on the order of one-fourth to one-third. Extracted-stripped samples were reduced in TOC by only 9% and in COD from 28 to 33%. In general, the variation of pH or the addition of ferric sulfate had little effect on the TOC and COD values.

Phenol recovery appeared to reduce the quantity of tar acid, but it did not eliminate tar acid, as had been hoped. Table 11 reports the weight of tar acid material collected from the various samples. This weight was estimated by correcting the total dry weight of solids for calcium and the TDS of entrained water. Because some of the corrections were substantial, the results should be considered as a qualitiative estimate of the solid organic material collected. However, the trend is clear. Extracted-stripped water produces a much smaller quantity of tar acid material than either raw or stripped wastewater at both pH values, with or without ferric sulfate. The results show that at pH 2.5 about 13 g of material per liter is removed from raw water, approximately 9 g/L from stripped water, and approximately 5 g/L from extracted-stripped water.

The tar acid material removed by acidification has a waxy or clayey consistency, while that removed with acidification and $Fe_2(SO_4)_3$ addition was grainy and particulate.

Table 11

Removal of COD and TOC by Tar Acid Precipitation for Raw and Pretreated Ft. Lewis SRC-I Process Condensate

Sample	TOC (mg/L)	COD (mg/L)	Tar acid (g/L) (precipitated)
Raw water	12,000	56,700[a]	
pH = 5.0	11,800	42,660	9.37
pH = 2.5	12,050	40,750	12.8
Iron, pH = 5	12,300	41,030	13.2
Stripped water	7,170	34,500[a]	
pH = 5.0	5,650	25,530	9.5
pH = 2.5	5,340	21,750	8.93
Iron, pH = 5	5,220	21,460	8.43
Extracted-stripped water	2,740[b]	19,770[a]	
pH = 5.0	2,380	14,110	6.03
pH = 2.5	2,320	13,155	4.67
Iron, pH = 5	2,300	13,590	7.03

[a] Corrected for sulfides and MIBK (solvent) for extracted samples.
[b] Corrected for MIBK (solvent) dissolved in water.

SOURCE: Reference 6

2. Catalytic Study[4]

Catalytic, in their biological treatment studies, pretreated Ft. Lewis SRC-I process condensate using two methods. In the first, wastewater was pretreated by solvent extraction using the proprietary Chem-Pro solvent, followed by ammonia/hydrogen sulfide stripping and tar acid precipitation. In the second method, which is a simulation of the Baseline Design, the raw wastewater received only stripping before precipitation.

Extracted-stripped water came from two sources. Some of the water was batch-extracted and stripped at Catalytic; the remainder was the product of Chem-Pro's work. Catalytic extracted the wastewater batchwise, and Chem-Pro employed a continuous-flow column. Also, Catalytic used lime for ammonia-stripping, whereas Chem-Pro, because of limitations at its facility, used caustic.

Catalytic's data indicate that acid requirements for extracted-stripped wastewater are less than those for stripped wastewater. For example, to lower the pH to 4.5 for 1 L of Catalytic-prepared extracted-stripped water, 2.16 ± 0.39 mL of 98 wt % acid was required; for the stripped water, the amount of acid was 3.16 ± 0.45 mL. Statistical hypothesis tests show that this difference is significant at a 95% confidence level.

Catalytic also observed a difference in acid requirement between Catalytic-prepared and Chem-Pro treated samples. Only 1.2 mL of acid/L of Chem-Pro samples was required to drop the pH from 9 to 4.0, compared to 2.16 mL/L for the Catalytic sample to reduce the pH from 11 to 4.5.

Sludge production was significantly different for the two extracted and stripped waters. The Catalytic water produced a large volume of rapidly settling floc, whereas the Chem-Pro water produced a lower volume of precipitate and light floc. Probably much of the difference is due to the fact that Catalytic used lime and Chem-Pro used caustic.

Tar acid sludge characteristics are given below for the two extracted-stripped wastewaters:

Parameters	Sources Catalytic	 Chem-Pro
Total solids (mg/L)	64,000	9,000
Calcium (mg/L)	6,900	59
Sodium (mg/L)	39	650
Sulfate	15,000	1,700

Catalytic's results were similar to those reported by Luthy and Campbell--the sludge contained a significant amount of inorganics.

In summary, the tar acid precipitation experiments show that phenol extraction appears to have reduced the quantity of acid needed, and the amount of sludge produced. As will be discussed again later, phenol extraction apparently eliminates the need for tar acid precipitation. The experiments also suggest that the chemicals used for ammonia stripping (lime or caustic) will affect the acid required as well as sludge produced.

E. BIOLOGICAL TREATMENT STUDY

The effect of phenol extraction on biooxidation of SRC wastewater was studied extensively by Catalytic.[4] The purpose of this study was to evaluate the impact of phenol recovery (or dephenolization) on the biological treatment system. To facilitate comparison, five parallel laboratory-scale biological treatment systems were operated, some treating wastewater that had not been dephenolated and others treating dephenolated wastewaters. The comparison was made in terms of:

- Treatment efficiency and effluent quality
- System stability
- Bioreactor volume requirements
- Need for tar acid removal
- Need for continuous, high-dose PAC augmentation to the bioreactor

Three of the five systems treated dephenolated wastewaters and the other two, nondephenolated wastewaters. Figure 9 illustrates the five systems. A more detailed description of the systems will be forthcoming, but first the feeds to these systems are described.

1. The Feeds

The feed to the first three systems had been subjected to phenol extraction and ammonia/sulfide stripping. Initially, the feed was also treated with a tar acid removal (TAR) step, but that was terminated to determine whether TAR could be eliminated. The feed to the last two systems was not phenol-extracted, but it was treated with TAR. All the feeds were subjected to final concentration adjustments to account for the dilution effect expected in the Demonstration Plant, and to maintain a relatively constant concentration of contaminants.

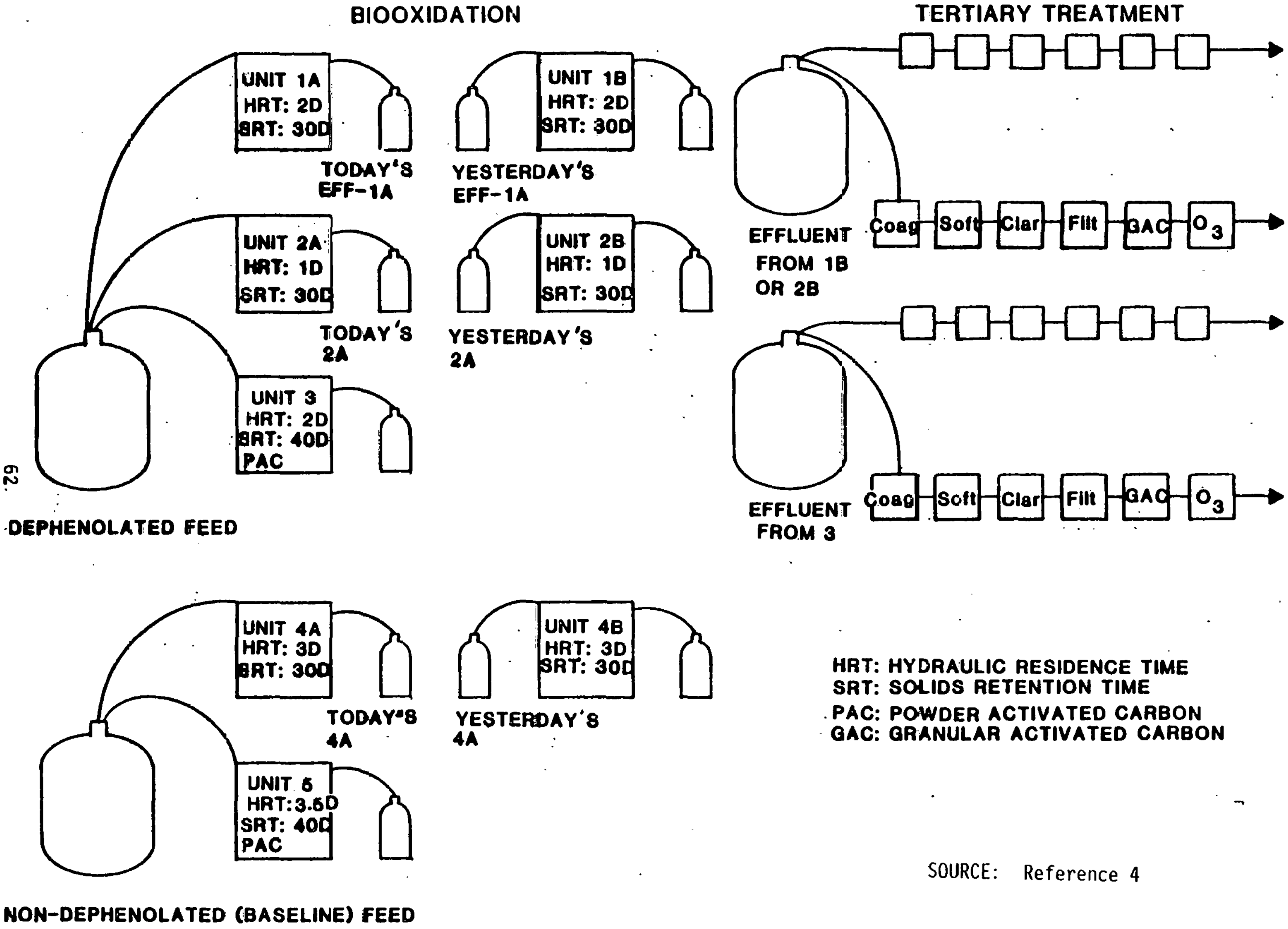
The extraction and stripping were initially performed by Catalytic and later by Chem-Pro. Catalytic prepared dephenolated water by batch extraction (two extractions) using the Chem-Pro solvent. This step was followed by two-pass steam-stripping in packed columns. Raw water was also stripped in the same manner. The first pass was carried out at pH 9.5 for H_2S removal; this was followed by stripping at pH 11.5 (adjusted with lime) to lower the ammonia level.

The tar acid precipitation step was accomplished by lowering wastewater pH to about 4.5 with sulfuric acid. Following a settling period of several hours, the liquid was separated from the tar acid layer. The decanted layer was then neutralized to a pH of about 7. For Chem-Pro stripped water, lime was used to adjust the pH. The Catalytic water, which had been treated with lime in the ammonia stripper step, was neutralized using caustic. Because the Chem-Pro stripping process used caustic, this procedure resulted in both wastewaters having similar calcium concentrations. Tar acid removal for the nondephenolated wastewater was conducted in the same manner, except that lime was used exclusively for neutralization.

Other adjustments were made to the wastewater before it was fed to the bioreactors. Because Ft. Lewis process water is one of the strongest major SRC wastewater streams in terms of phenolics, TOC, and

Figure 9

Five Systems in Biological Treatment Study



SOURCE: Reference 4

COD, it was diluted with tap water to meet given global parameters calculated from the demonstration plant material balance and individual waste stream analyses. Additionally, the bioreactor feed was amended with specified chemicals to meet bioreactor operating requirements. The compositions of the feed waters are presented below:

Average Feed Characteristics

Parameters (mg/L)	Dephenolated feed	Nondephenolated feed
COD	2,100	6,720
TOC	555	1,700
Ammonia-N	888*	183*
Cyanide	4.05*	6.75*
Thiocyanate	192*	194*
Phenolics	11	1,170
Calcium	627	900
Iron	7	6.2
Magnesium	17	16
Phosphorus	65	128
Sodium	730	402
TDS	4,300	7,500

*Supplemented concentration.

2. Biological Treatment Systems

As mentioned previously, the biological study employed five parallel trains. Three were run using dephenolated feed (Catalytic at first, then Chem-Pro), while the other two treated the nondephenolated feed.

System 1 consisted of two stages (1A and 1B) operating in series with dephenolated feed. Each of the stages had a hydraulic residence time (HRT) of 2 days. About 500 mg/L of PAC was maintained in the second stage as a settling aid.

System 2 consisted of two stages (2A and 2B) operating on dephenolated feed that differed from system 1 only in hydraulic retention time. This system had an HRT of 1 day in each bioreactor. These HRTs had been chosen based on initial trials, and they were the shortest HRTs tested. Data from System 2 could be compared with System 1 to see the effects of HRT on removal efficiency.

System 3 consisted of a single-stage reactor (unit 3) using PAC treatment and operating with dephenolated feed. About 500 mg of PAC was added to each liter of feed (about 7,500 mg/L in the mixed liquor). Comparing the performance of System 3 and Systems 1 and 2 would show the effect of PAC augmentation.

System 4 consisted of two stages (4A and 4B) using nonextracted water. The purpose of this system was to simulate the Baseline configuration, without PAC augmentation. The original HRT was maintained at 2.5 days in each stage, but it had to be lengthened to maintain stability. The second stage had a PAC concentration of 500 mg/L.

System 5 consisted of a single PAC technology reactor operating with nonextracted feed. About 1,700 mg of PAC was added per liter of feed, amounting to about 13,000 mg/L in the reactor.

The most important characteristics distinguishing one system from another are the feed type--dephenolated (DP) vs. nondephenolated (NDP)--and whether or not high-dose (i.e., well above 500 mg/L) PAC was added to the mixed liquor. For brevity, the following notations will be used to identify the different systems in the subsequent discussion:

System no.	Notation	PAC	Unit	HRT (days)	SRT (days)
1	DP/NPAC	No	1A	2	30
		*	1B	2	30
2	DP/NPAC	No	2A	1	30
		*	2B	1	30
3	DP/PAC	Yes	3	2	40
4	NDP/NPAC	No	4A	3	30
		*	4B	3	30
5	NDP/PAC	Yes	5	3.5	40

*500 mg/L was added as a settling aid.

3. Effects of Phenol Recovery on Biological Treatment

The effects of phenol recovery can be readily seen by comparing the biological treatment systems with respect to organic removal, ammonia reduction and nitrification, color removal, residual phenolic concentration, need for tar acid precipitation, operational stability, minimum hydraulic residence time, and solids separation.

a. Organic Removal. Table 12 presents COD data for each reactor in the five biological treatment systems at steady-state conditions. Some limited TOC data are also shown for comparison. Time-series plots for COD concentration data are presented in Figures 10-14. The figures show feed COD (FCOD) to the first reactor in each system, as well as effluent COD (ECOD) from each reactor. These graphs indicate that all systems can generally remove a substantial quantity of COD despite fluctuations in feed strength. Even so, a close examination of the COD data reveals significant differences between systems.

The dephenolated systems provided more complete organic removal than the nondephenolated. This is evident from a comparison of the effluent concentrations of COD from all five biological systems (Table 12). During steady-state operation, the effluent COD from the DP

Table 12

Organic Removal

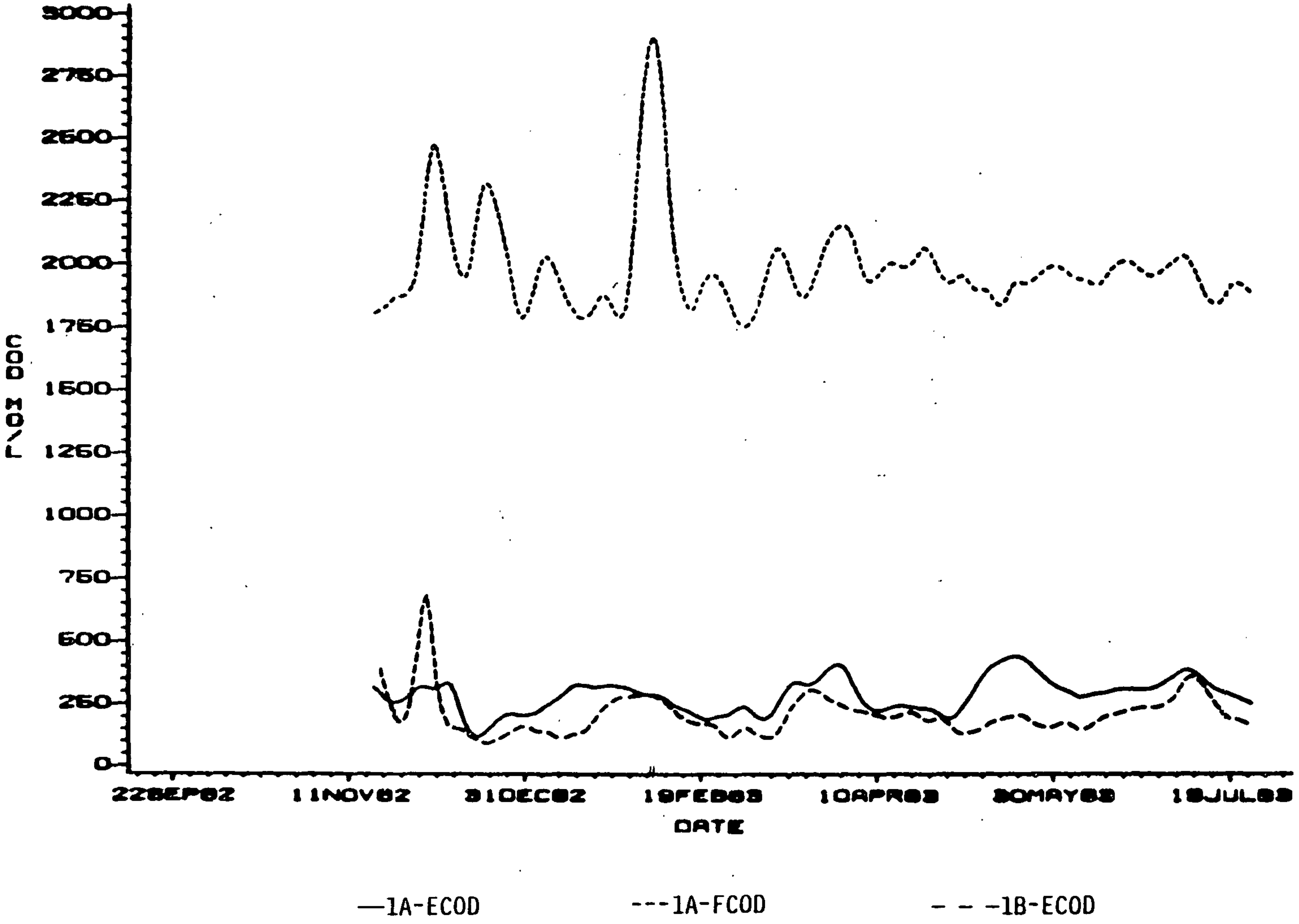
System	Description	Unit	HRT (days)[a]	SRT (days)[a]	Feed COD[b]	Effluent COD[b]	Feed TOC[b]	Effluent TOC[b]
1	DP/NPAC	1A	2	30	1,957 ± 56	319 ± 40	523 ± 74	63
		1B	2	30		221 ± 63		55
2	DP/NPAC	2A	1	30	1,995 ± 123	244 ± 42	521 ± 54	78
		2B	1	30		170 ± 34		49
3	DP/PAC	3	2	40	1,968 ± 115	204 ± 52	526 ± 56	43
4	NDP/NPAC	4A	3	32	6,209 ± 492	1,339 ± 351	1,560	345
		4B	3	30		648 ± 163		230
5	NDP/PAC	5	3.5	45	5,469 ± 613	262 ± 181	1,314 ± 253	103

[a] Nominal value
[b] mg/L.

SOURCE: Reference 4

Figure 10

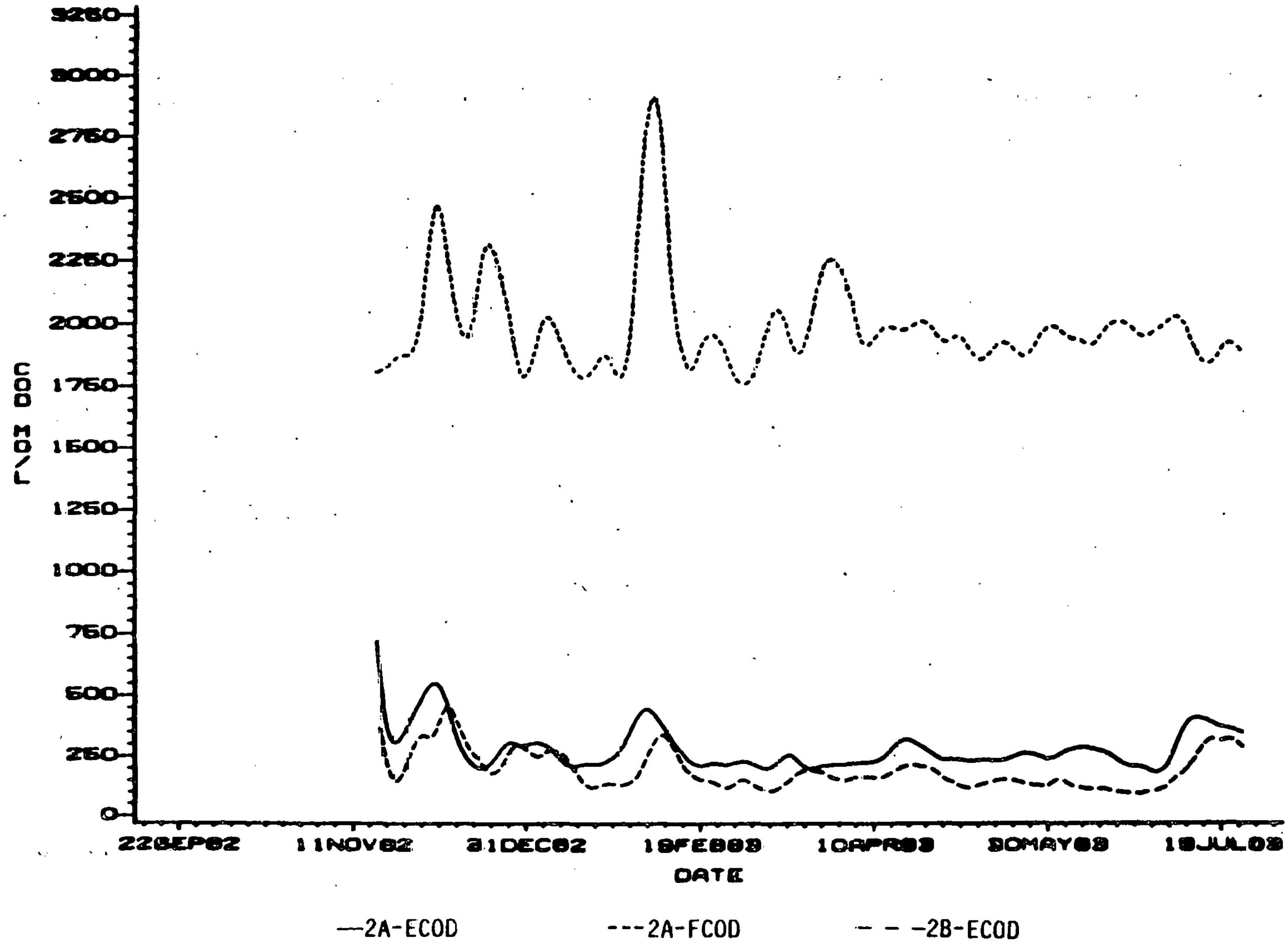
SRC-I Biotreatment Data for System 1:
COD vs. Time



SOURCE: Reference 4

Figure 11

SRC-I Biotreatment Data for System 2:
COD vs. Time

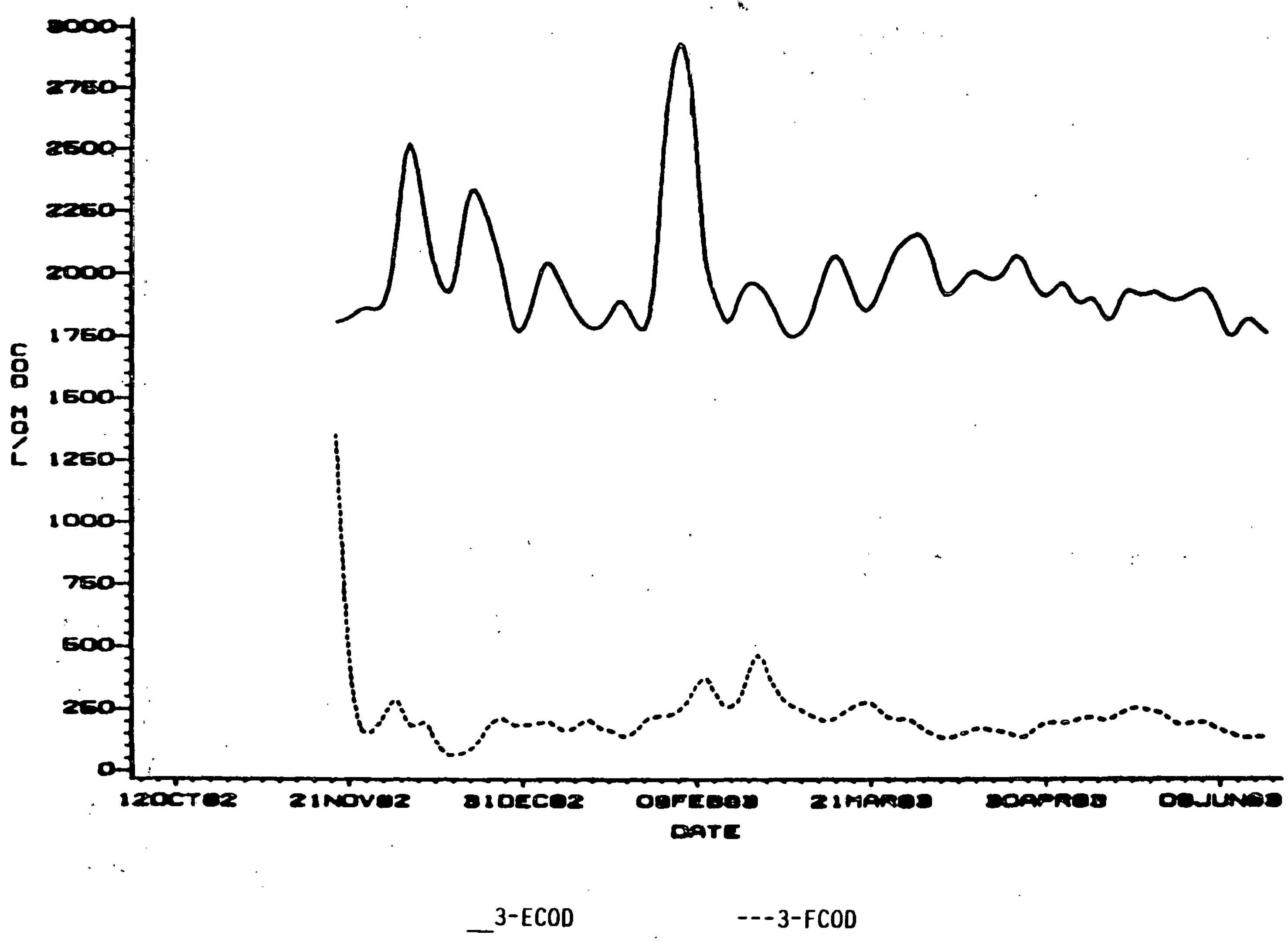


SOURCE: Reference 4

Figure 12

SRC-I Biotreatment Data for System 3:

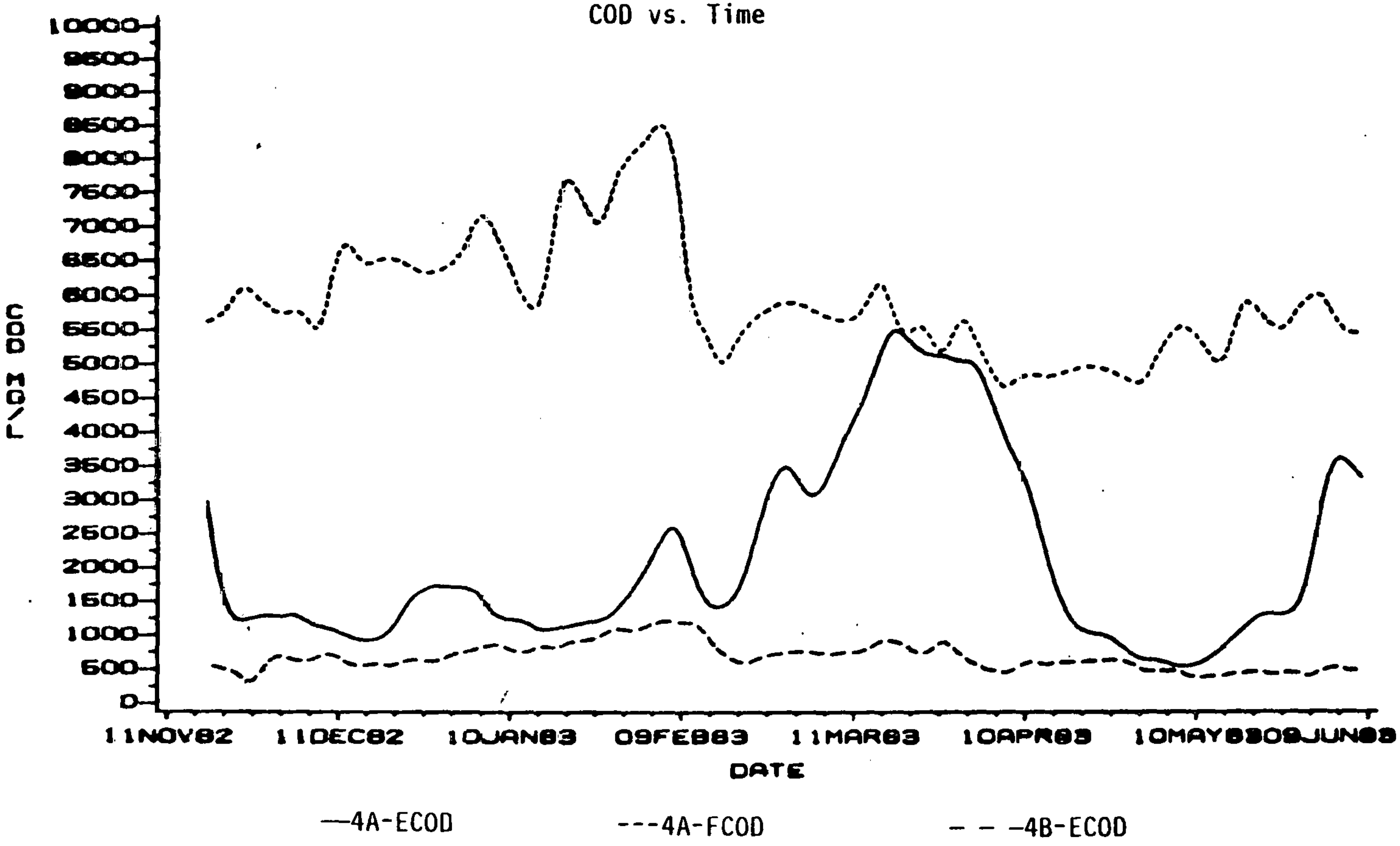
COD vs. Time



SOURCE: Reference 4

Figure 13

SRC-I Biotreatment Data for System 4:
COD vs. Time

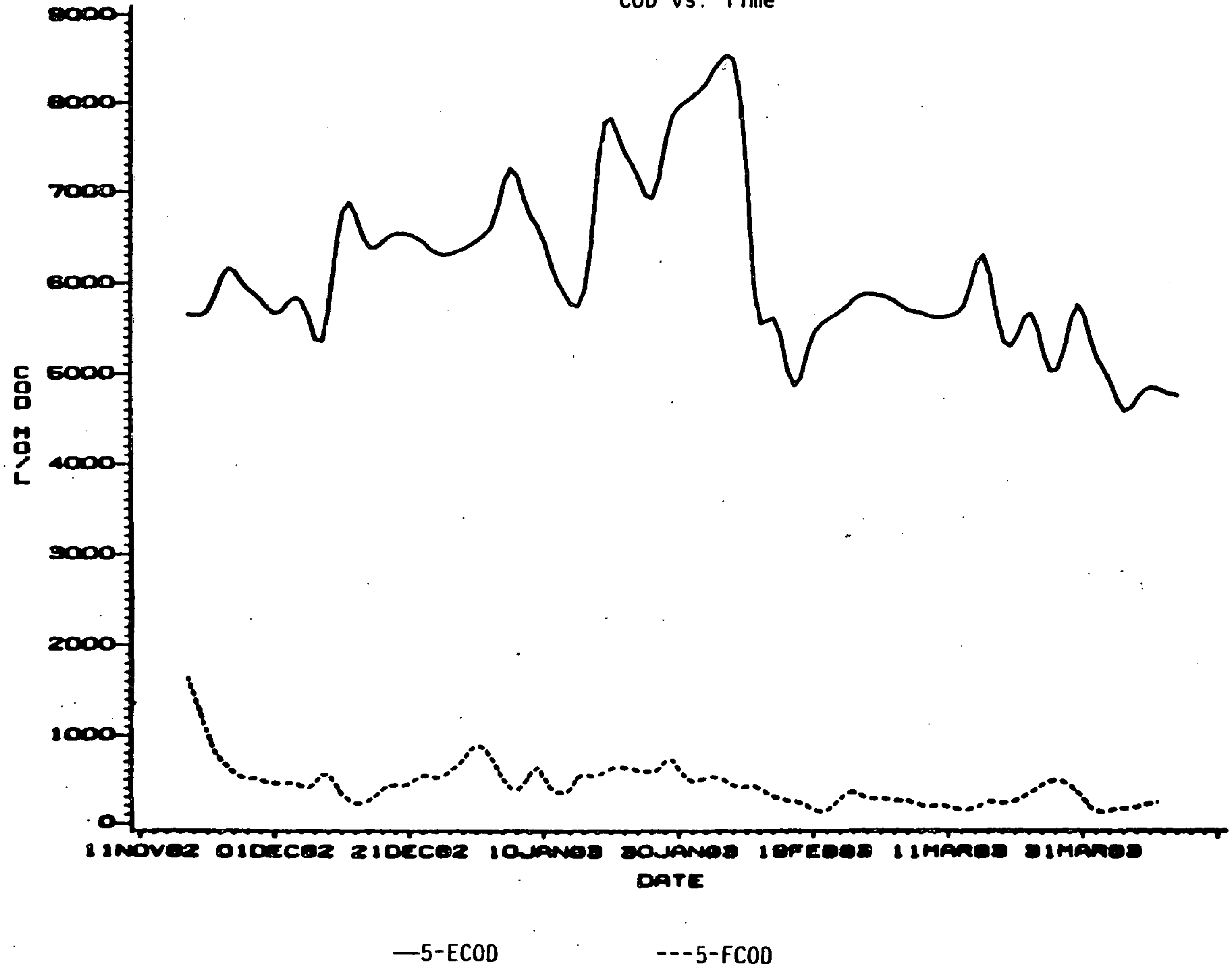


SOURCE: Reference 4

Figure 14

SRC-I Biotreatment Data for System 5:

COD vs. Time



SOURCE: Reference 4

systems ranged from 170 to 221 mg/L, vs. 262 and 648 mg/L for the NDP systems. Even with PAC, the NDP system could not match any of the effluents of the NPAC systems treating a dephenolated feed, on an average basis. Moreover, the NDP/PAC system performance fluctuated more widely (std dev = 181 mg/L for COD) than the DP systems. The DP systems were much more stable, and the effluent COD data showed standard deviations of 34 to 63 mg/L.

The residual TOC concentrations in the effluents of the DP systems were definitely lower than those of the NDP systems. Effluent TOC concentrations of the DP systems ranged from 43 to 55 mg/L throughout all periods of operation, whereas those for the NPAC and PAC NDP units were 230 and 103 mg/L, respectively.

For a dephenolated, non-PAC system, a two-stage configuration performed better than a single-stage configuration with the same HRT. This can be seen by comparing the effluents from Units 1A and 2B. Unit 1A has a 2-day HRT, as does the combination of Units 2A and 2B. The effluent COD from Unit 1A was 319 ± 40 mg/L, and that from Unit 2B was 170 ± 34 mg/L. Operation of the two-stage configuration was closer to plug-flow than that of the single-stage; theoretically, a plug-flow reactor should yield a better effluent than a completely mixed reactor.

The need for a second-stage bioreactor in a non-PAC system was also evidenced by comparing the effluent COD from that reactor and that from the first stage within the same system. For System 1, the effluent COD concentration from the first stage (1A) was 319 ± 40 mg/L, while the second-stage effluent was 221 ± 63 mg/L. The reduction of the mean COD concentration in the second-stage reactor was 98 mg/L, or about 31%. Similarly, for System 2 the effluent COD values were 244 ± 42 and 170 ± 34 mg/L for Units 2A and 2B, respectively. This is a reduction of 74 mg/L, or 30%.

Comparing the DP systems shows that the single-stage PAC system produced an effluent of comparable quality to that of the two-stage NPAC systems. The mean effluent COD concentrations for NPAC Systems 1 and 2 were 221 ± 63 and 170 ± 34 mg/L, respectively. The effluent from System 3 (PAC) contained 204 ± 52 mg/L. All three effluents are, therefore, in the same general range.

For the NDP systems, the difference between PAC (System 5) and NPAC (System 4) was more pronounced. The mean effluent COD from the second-stage reactor in System 4 was 648 ± 163 mg/L, while the System 5 effluent was only 262 ± 181 mg/L. This is a considerable difference, and clearly indicates PAC to be a superior treatment method for NDP systems.

All systems, except for the nondephenolated, non-PAC, seemed to have handled COD shock load well. For example, the COD shock for the DP systems occurred at the end of January 1983; the concentration increased from 2,000 to 3,000 mg/L (see Figures 10, 11, and 12). System 1 (DP/NPAC) did not show any adverse effect whatsoever. System 2 (DP/NPAC) exhibited a slight COD increase in the effluent, but quickly restabilized in one to two weeks. Similarly, the feed COD concentration to System 5 (NDP/PAC) fluctuated widely, but the effluent concentration was remarkably stable (Figure 14).

b. Ammonia Removal and Nitrification. In order to determine the feasibility of biological ammonia removal and nitrification, the feeds to the biological treatment systems were adjusted to 200 mg/L. This concentration is considerably higher than 45 mg/L, the expected concentration for the SRC-I Demonstration Plant.

When the feed was treated with 200 mg/L of ammonia, only three systems (No. 1, 2, and 5) were able to achieve fairly complete ammonia removal (see Table 13). Among the three systems, the NDP system (No. 5) performed better than the two DP systems (No. 1 and 2). Only the NDP system (No. 5) achieved excellent ammonia removal and nitrification. Although DP system 1 also had fairly complete ammonia removal, it did not have complete nitrification; considerable nitrite was not oxidized to nitrate. The other DP system, No. 2, did not have much nitrite, but ammonia removal was almost as complete as that for Systems 1 and 5. Also, the time period required to achieve ammonia removal and nitrification was much longer for the two DP systems than the NDP system. The DP systems were not as stable as the NDP system.

Why the NDP system (No. 5) performed better than the DP systems (No. 1 and 2) is not clear. The addition of PAC was not the cause, because the DP/PAC system (No. 3) actually did not perform as well as

Table 13

Ammonia Removal/Nitrification Steady-State Data

System	Description	Unit	HRT (days)[a]	SRT (days)[a]	Feed NH_3[b]	Eff. NH_3[b]	Eff. NO_2[b]	Eff. NO_3[b]
1	DP/NPAC	1A	2	30	188 ± 6	24 ± 12	115 ± 26	67 ± 35
		1B	2	30	-	5.5 ± 5.2	73 ± 70	147 ± 38
2	DP/NPAC	2A	1	30	205 ± 11	175 ± 3	21 ± 10	14 ± 8
		2B	1	30	-	28 ± 13	5.8 ± 6.0	171 ± 39
3	DP/PAC	3	2	40	189 ± 29	119 ± 48	69 ± 19	40 ± 32
4	NDP/NPAC	4A	3	30	163 ± 17	98 ± 23	8.6 ± 0.5	16 ± 38
		4B	3	30	-	65 ± 22	1.3 ± 1.1	73 ± 31
5	NDP/PAC	5	3.5	45	144 ± 30	6.5 ± 5.1	3.7 ± 7.2	71 ± 53

[a] Nominal value.
[b] Expressed in mg/L as N.

SOURCE: Reference 4

two of the NDP/NPAC systems (No. 1 and 2). It could be because of the seed for the bioreactors. All systems received feed from a previous study[5] which had been operated under conditions almost identical to those for System 5.

The fact that the NDP/PAC system (No. 5) performed better than the DP/NPAC systems (No. 1 and 2) is not very significant. The expected ammonia concentration for the SRC-I Demonstration Plant is much lower than that tested in the laboratories. But it does demonstrate that if phenol recovery is to be adopted, effective ammonia removal will be strongly dependent on successful steam stripping.

If steam-stripping is successful, the ammonia concentration in the 440-gpm stripper bottoms would be 50 mg/L, which is a major source of ammonia to the biological treatment system. Another major source is the 180-gpm GKT washwater purge, which would have 150 mg/L of ammonia, 35 mg/L of cyanides, and 25 mg/L of thiocyanates. Cyanides and thiocyanates are precursors of ammonia; they can be biologically converted to ammonia. With the conversion, the equivalent ammonia concentration in GKT washwater purge is 175 mg/L. After mixing of these two streams with other streams that do not contain ammonia or ammonia precursors, the equivalent concentration of ammonia in the feed to the biological treatment system is about 45 mg/L.

Essentially all of the ammonia will be assimilated by the microbes for growth. For the DP systems, the apparent yield coefficient is 0.184 g of cells produced per g of COD removed. The measured organic nitrogen content of the cells was 12.2 wt %. With the expected COD concentration of 2,000 mg/L, the ammonia concentration required for cell growth is also about 45 mg/L. Therefore, during normal operation, the ammonia concentration in the plant effluent should be close to zero. The design goal of 20 mg/L as described in the Final Environment Impact Statement should be achievable.

However, it must be emphasized that successful ammonia stripping is the key to meeting the goal. Also, the cell nitrogen in the wasted biomass must be contained so that no excess ammonia is returned to the biological treatment system. Cell degradation could release some of the ammonia; the released ammonia should be contained and returned to steam stripping.

c. Color Removal. Both SRC-I wastewater and Ft. Lewis PRW have high color intensities. Typical color values for the DP feeds (after pretreatment and dilution) were in the range of 7,200 ± 3,500 APHA units for the Catalytic-prepared feeds, and 1,175 ± 121 for the Chem-Pro-prepared feeds. The NDP feeds averaged 6,000 APHA units.

The DP systems without PAC (No. 1 and 2) yielded an average residual color concentration of 1,600 and 920 units for Catalytic- and Chem-Pro-pretreated wastewater, respectively. Without PAC, the NDP system (No. 4) did not appreciably reduce color. Even with PAC, the NDP system (No. 5) residual color was in the range of 2,000 to 3,000 units. Clearly, the DP systems were superior to the NDP systems.

Comparing the three DP systems, the DP system with PAC (No. 3) on Chem-Pro feed produced an effluent with residual color of about 400 units, about half that of the DP/NPAC systems (No. 1 and 2). This same ratio is noted for the darker Catalytic feed. This difference will diminish after tertiary treatment which has also color-removal capability.

d. Residual Phenolic Concentration. Phenolics are contaminants of concern because the ambient concentrations in the Green River sometimes exceed water quality standards. The bioreactors removed the phenolics to a low level (see Table 14).

The data indicate that biological treatment systems receiving dephenolated wastewater produced effluent phenolic concentrations of less than 100 μg/L, over all time periods. For steady-state conditions, phenolics were reduced to less than 25 μg/L. There was little difference between the PAC and NPAC systems. For the NDP feeds, only the PAC systems could match this performance. As will be discussed in the Tertiary Treatment Section (III.F), the low residual phenolics will be reduced even further by granular activated carbon.

e. Cyanides and Thiocyanates. Because the Ft. Lewis PRW had significantly lower CN and SCN concentrations than the conservatively estimated values for the feed to the biological systems in the demonstration plant (10 and 200 mg/L, respectively), the feeds were spiked with NaCN and NaSCN. Chemical analyses showed that the SCN concentrations were generally on target after spiking, but the CN concentrations

Table 14

Residual Phenolic Concentrations[a-c]

Systems/bioreactors		SRT (days)	Nominal HRT (days)	Feed phenolics (mg/L)	Effluent phenolics (μg/L)
			Data from Reference 4		
DP/NPAC	1A	30	2	12.7	<112
	1B	30	2	<0.185	<78
DP/NPAC	2A	30	1	17.8	<144
	2B	30	1	<0.274	<66
DP/PAC	3	40	2	15.8	<44
NDP/NPAC	4A	30	3	1,034	4,400
	4B	30	3	--	--
NDP/PAC	5	45	3.5	1,233	84
			Data from Reference 5		
NDP/NPAC	1st stage	23	4.55	896 ± 116	103 ± 35
		18	3.05	1,137 ± 38	64 ± 63
	2nd stage	30	6.26	114 ± 133	110 ± 30
		18.1	5.5	149 ± 18	68 ± 10
		20	4.6	108	42
		27.5	4.22	151 ± 10	17
NDP/PAC	one stage	32	4.75	850 ± 99	25 ± 26
		40	4.5	798 ± 50	72 ± 1.4
		52	4.45	944 ± 113	39 ± 33

[a] Reference 4.
[b] Reference 5.
[c] Including nonsteady (based on COD) time periods.

were not, even when two or three times the calculated concentrations were added. Typical concentrations of CN observed in the feeds were less than 3 mg/L for the DP systems and fluctuated between 0.6 and 12.2 mg/L for the NDP systems. It has been hypothesized that CN reacted with components in the feed, rendering it undetectable.

Table 15 presents the CN and SCN data. Based on the data, no significant differences existed between the influent and effluent CN concentrations, and thus no definitive conclusions can be drawn. However, measurable effluent CN^- concentrations were generally less than 2 mg/L for all systems. There are no significant differences between DP and NDP systems, or between PAC and non-PAC systems.

In contrast, SCN concentrations were significantly reduced. The SCN concentration in the feeds to the DP systems was 176 to 197 mg/L, while the typical concentration in the effluents was below 5 mg/L. For the NDP systems, the effluent SCN concentrations were slightly higher than those for the DP systems but still typically below 10 mg/L. Therefore, the DP systems were slightly more effective than the NDP systems but the differences were not significant. Among the DP systems, PAC addition did not affect SCN removal appreciably for any system.

f. Need for Prebiological Tar Acid Precipitation. As discussed earlier, tar acid precipitation was considered a necessity in a treatment scheme without phenol extraction.[5] However, tar acid precipitation consumes a large quantity of acids and bases, creates additional sludges, and adds a large amount of dissolved solids to the wastewater. Therefore, there was an incentive to eliminate this process, and the need to retain it was investigated.

To test the assumption that phenol extraction might eliminate the need for tar acid precipitation, the tar acid precipitation step was eliminated from the pretreatment sequence in the later stages of this study. Table 16 compares the removal of organics, color, and SCN before and after the elimination of tar acid removal.

The data show that elimination of tar acid precipitation did not affect COD removal, color reduction, or SCN oxidation significantly. Therefore, there is no need for tar acid removal for a dephenolated wastewater.

Table 15

Cyanides/Thiocyanate Removal[a]

System	Description	Bioreactor	HRT	SRT	Cyanide (mg/L)		Thiocyanate (mg/L)	
					Feed	Effluent	Feed	Effluent
1	DP/NPAC	1A	2	30	0.33 ± 0.16	2.20 ± 0.49	176 ± 3	5.7 ± 0.9
		1B	2	30	2.20 ± 0.49	1.75 ± 0.45	5.7 ± 0.9	4.2 ± 0.9
2	DP/NPAC	2A	1	30	2.26 ± 3.81	1.12 ± 0.49	197 ± 9	5.5 ± 1.8
		2B	1	30	1.12 ± 0.49	1.03 ± 0.41	5.5 ± 1.8	4.6 ± 1.2
3	DP/PAC	3	2	40	2.42 ± 2.31	0.80 ± 0.40	191 ± ±8	2.2 ± 0.5
4	NDP/NPAC	4A	3	30	0.79 ± 0.44	1.04 ± 0.52	166 ± 11	44 ± 30
		4B	3	30	0.88 ± 0.50	0.75 ± 0.38	44 ± 30	6.3 ± 1.5
5	NDP/PAC	5	3.5	45	12.3 ± 9.67	1.3 ± 0.78	147 ± 29	7.2 ± 7.1

[a] Steady-state data.

SOURCE: Reference 4

Table 16

Comparison of Performance of Biooxidation with and without Tar Acid Precipitation

System/bioreactor		Period	Tar acid precipitation	COD (mg/L)	Color	SCN
1 (DP/NPAC)	1A	3/20 - 5/16	Yes	296 ± 81	607 ± 228	32 ± 47
		5/24 - 7/25	No	319 ± 40	589 ± 221	5.65 ± 0.91
	1B	3/20 - 5/16	Yes	210 ± 51	832 ± 378	3.05 ± 0.824
		5/24 - 7/25	No	221 ± 62	964 ± 414	4.21 ± 0.91
2 (DP/NPAC)	2A	2/27 - 3/19	Yes	230 ± 39	1,000 ± 200	3.84 ± 1.35
		3/20 - 5/16	No	244 ± 42	1,096 ± 206	2.2 ± 1.02
	2B	2/27 - 3/19	Yes	132 ± 29	914 ± 107	2.18 ± 0.158
		3/20 - 5/16	No	170 ± 34	893 ± 228	4.6 ± 1.2

SOURCE: Reference 4

g. Minimum Hydraulic Residence Time (HRT). Phenol recovery reduced the minimum HRT required for the bioreactors.[4] For DP/NPAC systems, the data indicate that 1-day HRTs are adequate for the first- and second-stage bioreactors. Without phenol recovery, the minimum bioreactor HRT is 3.5 days, if PAC is added continuously and at a high dose. Without PAC, the nondephenolated system cannot match the effluent quality of the DP system even at HRTs of 3 and 3 days (i.e., a combined HRT of 6 days).

The minimum HRTs for a DP/NPAC system were determined by statistically comparing effluent COD and NH_3 concentrations from the second-stage bioreactors of Systems 1 and 2. Recall that System 1 has an HRT of 2 days in each stage, and System 2 had HRTs of 1 day/1 day.

Based on the mean difference of paired observations, the average difference in effluent CODs for both reactor systems was not statistically significant. However, at the 5% level of significance, System 2 removes more ammonia than System 1.

The feed to both systems was about the same each day, but the daily effluent COD and NH_3 levels varied considerably. For this reason, the statistic used to compare performance was the average daily difference in effluent concentration, rather than the difference between the daily averages. This approach was taken in order to take into account some of the effluent variation due to the time-varying concentration of the feed.

The statistics for the differences in the daily effluent ammonia concentrations for the two reactor systems are as follows:

Average ammonia level Reactor 1 effluent:	52.0 mg/L
Average ammonia level Reactor 2 effluent:	43.2 mg/L
Average of daily difference:	8.78 mg/L
Standard deviation of difference:	63.6 mg/L
Standard error of the mean:	4.11 mg/L

At the 95% confidence level, where there is no difference between the reactor systems (i.e., the average difference is equal to zero), the acceptance range of the mean difference in ammonia levels is ±8.06 mg/L.

Since the computed mean difference lies outside this region, the average ammonia in System 1 effluent is concluded to be significantly different (and higher) than that in System 2 effluent.

COD statistics are as follows:

Average COD level System 1 effluent:	200 mg/L
Average COD level System 2 effluent:	193 mg/L
Average of daily differences:	7.8 mg/L
Standard deviation of differences:	103 mg/L
Standard error of the mean:	6.6 mg/L

In this case, at the 95% confidence level, the mean would have to lie in the range of -12.9 to 12.9 mg/L to conclude that there is no difference in the COD levels in the reactor effluents. Since the mean is only 7.9 mg/L, there is no difference in the COD concentrations at the 95% confidence level.

Of concern in the use of the differences in daily values is which pairs to select to use in forming the differences. Because the reactor dynamics differ, simultaneous changes in feeds may not be fully reflected in the effluents at the same time.

The possible effects of different reactor dynamics on the mean difference and standard error of the mean calculated for CODs were examined briefly. The equations and calculations are included in reference 4.

As the calculations show, a typical change in COD influent from 2,000 to 1,500 mg/L for System 1 requires about 3 days to be fully reflected in the effluent. To examine the effect of time-shifting on the mean difference and standard error of the mean, difference pairs were formed at from -3 to +3 days with reference to System 1. The mean differences generated ranged between 5.9 and 9.7 mg/L, while the standard errors were in the range of 6.3 to 7.2 mg/L. Thus, the conclusion remains that COD performance of the two reactors does not differ significantly.

h. Operational Stability. During operation of the bioreactors, there were several changes in the feed compositions, some by design and some unplanned. The most significant changes were a COD excursion and a switch from Catalytic-pretreated to Chem-Pro feed, which had a much higher sodium content. These changes triggered responses in the bioreactors and provided insight into their stability and resilience.

The COD excursion in the feeds to the DP systems occurred on 1 February and lasted for about a week. Before the excursion, the typical feed COD was about 1,800-2,000 mg/L, and the shock load increased the concentration to about 2,900 mg/L (see Figures 10 to 12).

None of the three DP systems was drastically affected by the COD excursion. System 1 exhibited no loss of efficiency. System 2 apparently was affected slightly, but recovered quickly. System 3 was also affected and recovered in 4 weeks.

The nondephenolated systems (No. 4 and 5) were subject to a COD surge of longer duration. The pattern is shown in Figures 13 and 14, the time-series plots of COD. Before 9 February, the feed COD concentration to each system initially fluctuated because of variations in the TOC/COD ratio. (The feed was orginally made up using TOC as the target concentration.) During this time, the effluent COD concentration from each system seemed to be relatively stable, although System 4 does show a slight, gradual rise.

Following the excursion, both system effluents decreased slightly, but, again, were very stable. The most noteworthy aspect of their performance was the dampening effect provided by Unit 4B. Unit 4A, following the excursion, began to perform very poorly, at one point providing virtually no removal. During this time, Unit 4B achieved effluent concentrations that were actually lower than before the excursion (when Unit 4A was operated well).

i. Solids Separation. Batch-settling tests were run on mixed-liquor samples from all five bioreactors. These tests were conducted throughout the course of the study, and the average results are shown in Table 17. There seemed to be no obvious pattern defining the DP and NDP systems.

j. Aeration Power Requirements. Phenol recovery reduces the aeration power requirement significantly. With phenol recovery, the power requirement is about 500 hp; without it, more than 1,500 hp is

Table 17

Results from Batch Settling Tests

System	Bio-reactor	MLSS[a] (mg/L)	ZSV[b] (ft/min)	Underflow (% solids)	SOR[c] (gpd/ft^2)	Flux (lb/ft^2-day)
DP/NPAC	1A	3,204	0.268	2	948	25.0
DP/NPAC	1B	2,350	0.389	2	1,233	24.2
DP/NPAC	2A	7,050	0.190	2	1,214	71.3
DP/NPAC	2B	4,930	0.200	2	922	41.6
DP/PAC	3	11,920	0.233	3	2,130	211
NDP/NPAC	4A	5,450	0.272	2	1,577	70.9
NDP/NPAC	4B	4,013	0.220	2	1,328	54.2
NDP/PAC	5	17,587	0.090	3	901	134

[a] Mixed-liquor suspended solids.
[b] Zone settling velocity.
[c] Surface overflow rate.

SOURCE: Reference 4

required in the bioreactors. Based on 4¢/kwh and 330 days/year, the power savings due to phenol recovery would be more than $236,000.

k. Sludge Production. The DP systems did reduce the amount of biological sludge requiring disposal. The apparent yield coefficient for the DP systems was 0.184 g of cells/g of COD removed, which is about the same as that for the NDP systems. Therefore, the sludge reduction is proportional to the organic loading decrease. For a 1,160-gpm wastewater flow, the sludge production rate is 4,000 lb/day with phenol recovery and 12,000 lb/day without phenol recovery, both on a dry weight basis. Assuming 15 wt % solids after being dewatered, the volumetric rates would be 430 ft^3/day with phenol recovery and 1,300 ft^3/day without it.

l. Foaming. Dephenolization reduces foaming. A "normal" amount of basin foaming produced by aeration was observed in the DP systems, and no control measures were necessary. In NDP systems, however, significantly greater foam levels were almost always present and, for several extended time periods, foaming presented serious operational difficulties.

The NDP/PAC system (Unit 5) was less a problem than the NDP/NPAC System 4, and was satisfactorily controlled by periodically applying an antifoam spray. However, antifoam was less effective in System 4, particularly the first-stage unit, and applications provided only temporary control. A more effective solution was found to be decreasing the air rate through the diffusers, while maintaining a dissolved oxygen level of at least 2 mg/L.

Reasons for inordinate foaming in the NDP systems were never determined. There is no correlation between any measured parameter and the sporadic occurrence of severe foaming. Because foaming was absent in the DP systems, the only explanation is the intermittent introduction of some constituent in NDP feeds that is removed by phenol extraction in the DP feeds.

4. Summary of Biological Treatment Study

In summary, the study confirmed virtually all of the anticipated technical advantages of phenol recovery. The advantages of phenol recovery for the biological treatment system include the following:

- Lower residual organic concentrations such as COD and phenolics
- More complete color removal
- Elimination of the need for prebiological tar acid removal
- Smaller bioreactors
- Less aeration power requirements
- No need for expensive, continuous high doses of PAC
- Less biological sludge for disposal
- Foaming problems alleviated

F. TERTIARY TREATMENT

Catalytic continued their laboratory work by examining a number of unit operations for post-biological effluent tertiary treatment for their Systems 1, 2, and 3 (i.e., those treating dephenolated water). Because of the limitation on the amount of sample available from Systems 4 and 5, they performed tertiary treatment studies on nondephenolated bioreactor effluent produced as part of the earlier wastewater characterization and treatability studies.[5] The objective of the work was to study the effects of dephenolization on tertiary treatment.

The post-biotreatment unit operations used for tertiary treatment of the bioeffluents were tar acid precipitation, coagulation/sedimentation, filtration, granular-activated carbon (GAC) adsorption, and ozonation. The tar acid removal step for the effluents from the dephenolated systems (No. 1, 2, and 3) was discontinued shortly after tests started. More details are discussed in the following section.

1. Post-Biological Tar Acid Precipitation

Catalytic performed jar tests on their System 1 effluent to determine if tar acid existed in the bioreactor effluent from the dephenolized systems. Results shown below indicate no appreciable change in effluent solids or TOC in the absence of the tar acid removal step from the bioreactor pretreatment train.[4]

pH	TSS (mg/L)	Supernatant TOC (mg/L)
7.9 (feed)	250	53
5.8	260	55
4.5	249	46
3.8	241	52
3.1	251	53
2.5	248	47

Effluents from Systems 2 and 3 were also checked by lowering the pH to 2.5. No precipitate was found.

This observation is in contrast to that for the wastewater without phenol extraction. Similarly, jar tests were performed on PAC reactor effluent from nondephenolated water. In this case, even though reactor influent had received tar acid precipitation, the reactor effluent still indicated the presence of tar acids. Results of Catalytic jar tests on the PAC reactor effluent show an increase in solids, which is indicative of tar acid precipitation, and a decrease in TOC upon changes in pH:

pH	TSS (mg/L)	VSS (mg/L)	TOC (mg/L)
7.3	300	-	220
6.1	396	223	222
5.5	410	242	218
4.0	416	258	-
3.3	508	292	-
2.9	500	326	-
2.4	550	374	122
2.1	556	380	-

Based on this information, it appears that dephenolization would eliminate the need for post-biological tar acid precipitation in the wastewater treatment process.

2. Coagulation/Filtration

The next step in tertiary treatment entailed coagulation and sedimentation with ferric chloride followed by mixed-media filtration. Available data do not indicate that dephenolization will have any significant effect on these operations. Ferric chloride ($FeCl_3 \cdot 6H_2O$) at a dosage of 800 mg per L of effluent was found to be effective for both dephenolated and nondephenolated wastewaters.

In either case, coagulation and filtration reduced residual TOC and color in the bioreactor effluent effectively. The following table shows representative removals of key parameters by coagulation:

	NDP/PAC		DP/NPAC	
	Bioeff	After coag.	Bioeff	After coag.
COD (mg/L)	810	385	398	145
TOC (mg/L)	210	34	80	10
BOD (mg/L)	24	2	17	4
TSS (mg/L)	300	10	18	4
Turbidity (NTU)	120	8.8	100	2.9
Phenolic (mg/L)	0.026	0.013	0.025	0.004
Color (APHA)	3,000	750	1,000	400

After coagulation and filtration, the dephenolated wastewaters contained small quantities of the contaminants, including COD, TOC, phenolics, and color. This means that phenol recovery reduces the loading to granular carbon adsorption, which could translate into a lower carbon consumption rate.

3. Granular Activated Carbon Adsorption

Carbon adsorption isotherms were generated for the five bioreactor effluents. The results are as follows:

	TOC removal		Color removal	
Wastewaters	C_o	X/M (g/g)	C_o (APHA unit)	X/M (unit/g)
DP/NPAC	25	79	300	1,800
DP/NPAC	28	126	250	1,000
DP/PAC	19	45	225	2,100
NDP/NPAC	52	111	750	2,100
NDP/PAC	38	66	500	1,100

C_o's are concentrations before carbon adsorption. X/M's represent the amount of TOC or color per gram of carbon in equilibrium with the respective C_o's. The X/M's were obtained by fitting the data with the Langmuir model.

Comparison of the X/M's for TOC between the DP and NDP systems does not reveal any trend. The same holds true for color. Therefore, one cannot state that phenol recovery affects granular carbon adsorption. The primary effect of dephenolization on carbon adsorption would probably be from the TOC concentration in the influent to carbon column, not the carbon capacity.

4. Ozonation

In addition to disinfection, the original goal of ozonation was to remove residual contaminants such as COD, TOC, phenolics, color, and cyanides. Because biological treatment, coagulation, and activated carbon adsorption were very effective in removing most of the contaminants, the feed to ozonation (i.e., the carbon adsorption effluent) contained nondetectable amounts of most of the contaminants. The only contaminant appreciably affected by ozonation was COD.

Table 18 summarizes the results of ozonation for a batch of samples. The COD was reduced substantially, from 38 to 73%. The reduction is probably more significant to the NDP wastewaters than the DP wastewaters, because with ozonation, the NDP wastewaters cannot meet ICRC's anticipated effluent COD limit of 180 mg/L. With phenol recovery, the COD before ozonation was already below 180 mg/L. Therefore, ozonation would not be required if COD reduction was the only objective. Aside from COD, the data do not suggest that phenol recovery affects ozonation and vice versa.

5. Effluent Quality Comparisons

The qualities of the fully treated (including tertiary treatment) effluents produced from the five biological treatment systems were compared with respect to:

Table 18

Results of Ozonation
(mg/L Unless Stated Otherwise)

	DP/NPAC		DP/PAC		NDP/NPAC[a]		NDP/PAC[a]	
Treatment	Ac	Oz	Ac	Oz	Ac	Oz	Ac	Oz
Sample no	(7500)	(7501)	(7503)	(7504)	(7594)	(9319)	(7490)	(7491)
COD	74	46	115	47	424	114	274	143
TOC	ND[b]	ND	ND	ND	ND	12	ND	ND
Color (APHA units)	ND	10	ND	ND	ND	ND	25	ND
Cyanide	ND	ND	ND	ND	ND	ND	ND	ND
Thiocyanate	ND	ND	ND	ND	ND	-	0.3	ND
Nitrite	14	ND	82	ND	0.59	-	0.43	0.33
Nitrate	121	72	28	81	101	123	67	54
Phenolics (μg/L)	75	5	10	13	ND	ND	4	-
Sulfide (μg/L)	10	4	6	ND	ND	-	6	4

[a] After reference 7.
[b] ND = nondetectable.

SOURCE: Reference 4

- The estimated contaminant concentrations in the plant effluent as stated in the FEIS
- Impact of discharging of the plant effluent on river quality and compliance with river water standards
- Aquatic ecotoxicity
- Microbial mutagenicity

A thorough discussion will be presented in Chapter V: Effluent Quality and Impact Analysis, which deals with the suitability of fully treated wastewater on discharge exclusively; only highlights are presented in this section.

a. Comparison with FEIS Values. Generally speaking, all five fully treated effluents meet the estimated average contaminant concentrations stated in the FEIS with a few exceptions. However, these exceptions are insignificant. The estimated ammonia concentration in the FEIS is 5 mg/L; some of the effluents had a higher concentration. However, as discussed earlier, the actual ammonia concentration to the wastewater treatment system should be close to zero as long as the ammonia stripper performs as well as designed. The arsenic concentration of the dephenolated/PAC effluent was 0.35 mg/L, which is higher than the FEIS value of 0.1 mg/L. However, this might be due to sample contamination, because other samples taken upstream of that system had a concentration below 0.1 mg/L.

In addition to the above exceptions, there are several borderline cases, all of them effluent from nondephenolated (NDP) systems. The FEIS value for barium is 1 mg/L; the observed concentrations in the final effluents from the NDP/NPAC and NDP/PAC systems were 0.8 and 0.7 mg/L, respectively. Also, the observed COD in the NDP/PAC effluent was 143 mg/L, which is close to the FEIS value of 150 mg/L. However, another sample (no. 98318) had a COD of only 86 mg/L. The difference may be due to different degrees of ozonation. This discrepancy confirms the importance of ozonation when the wastewater is not treated by phenol recovery.

Therefore, the data show that all of the treatment systems can meet the FEIS values provided that ammonia stripping and ozonation perform as well as designed. The use of phenol recovery appears to provide a wider safety margin.

b. Compliance with Water Quality Standards. Concentrations of the contaminants in the river water were calculated assuming fairly rapid, complete mixing of the effluent and river water and worst-case conditions. The worst case assumes the following conditions occur simultaneously: a 10-day, 7-consecutive day river dry flow, dry plant effluent, maximum ambient contaminant concentration in the river, and maximum concentrations of the contaminants in the effluent. The maximum plant effluent is assumed to be 2.5 times that of the observed values in the laboratory. The calculated river concentrations were then compared with the river water quality standards established by the U.S. EPA or state of Kentucky. Obviously, the worst-case analysis is very conservative.

The conservative analysis has shown that the plant effluent would not adversely impact the existing river water quality. The differences in impact caused by the five effluents are insignificant. Therefore, with respect to compliance with water-quality standards, phenol recovery did not show any advantages.

c. Aquatic Ecotoxicity. Aquatic ecotoxicity studies were performed for the fully treated effluents. The results show that phenol recovery yields a better quality water.[8]

The studies performed were 48-hr Daphnia mortality, 14-day algae growth inhibition, and 28-day Daphnia reproduction. The LC_{50}s (lethal concentration causing 50% mortality) for the fully treated nondephenolated wastewaters were less than 58% (percent dilution of the original samples that would cause 50% mortality of the test organisms), and the LC_{50}s for the fully treated dephenolated wastewaters were greater than 100% (i.e., the wastewater must be concentrated in order to kill 50% of the test organisms). Clearly, the 48-hr Daphnia mortality studies favor dephenolization.

All straight wastewater without dilution inhibited algal growth, although the effect was more pronounced for the nondephenolated wastewaters than the dephenolated wastewaters. The predominant cause of the inhibition appears to be salt. With dilution, the inhibitory effect disappeared quickly. At 2:1 dilution (1 part wastewater and 2 parts diluting water), little inhibitory effect was observed. In fact, at certain dilutions, all wastewaters stimulated growth. Stimulation was highest for the dephenolated, PAC wastewater (DP/PAC), but was about the same for dephenolated and nondephenolated non-PAC wastewaters (DP/NPAC and NDP/NPAC). At a dilution concentration, the salts appeared to have contributed to some stimulation. The DP wastewaters appear to be less inhibitory than the NDP wastewaters at 100% strength. At lower strength, neither DP nor NDP wastewaters were inhibitory. Instead, both stimulated growth. The degree of stimulation was highest for the DP/PAC wastewater, about the same for DP/NPAC and NDP/NPAC wastewaters, and lowest for the NDP/PAC wastewaters. Therefore, there appears to be no clear difference between the DP and NDP wastewaters.

The 28-day Daphnia reproduction studies, which are abbreviated chronic tests, show that dephenolated wastewaters are better than the nondephenolated wastewaters in terms of survival. But in terms of reproduction, the studies were not conclusive. There was no correlation between the degree of treatment and the effects on production.

d. Microbial Mutagenicity. Mutagenic activity in the standard Ames Salmonella/microsome in vitro assay was tested for the raw wastewater, phenol-extracted raw wastewater, coagulated bioreactor effluents (DP/NPAC and NDP/PAC), as well as the fully treated DP/NPAC and NDP/PAC effluents.

The microbial mutagenicity studies did not find any effects of phenol recovery. Both raw wastewater and dephenolated raw wastewater were mutagenic with metabolic activation. Biological treatment, with and without PAC, eliminated the mutagenicity.

e. Summary. In summary, after full treatment, including tertiary treatment, all of the effluents, with or without phenol recovery, can meet the estimated concentrations in the FEIS. However, dephenolization does provide a wider safety margin. Dephenolization also has reduced acute aquatic ecotoxicity of the effluent to Daphnia. Therefore, based on the effluent quality comparison, a wastewater treatment system with phenol recovery (see Figure 6) is the recommended system.

G. ECONOMIC TRADEOFFS

Up to this point, evaluation of phenol recovery has been based mainly on technical merits. Obviously, the economics of the two alternatives shown in Figure 6 must be compared. The cost penalty incurred by adding the phenol recovery system should be weighed against cost savings realized by the downstream unit processes, such as those due to smaller bioreactors and lower aeration power requirements.

Table 19 shows the economic tradeoffs. Without phenol recovery, the total capital cost of wastewater treatment and solid-waste handling and disposal is estimated to be $52,400,000. Phenol recovery adds $3,705,000 to the capital cost, but it also reduces costs for the downstream processes. As a result, the net savings in capital costs for the integrated system is more than $12,000,000. Similarly, although phenol recovery increases the operating costs by $460,000 annually, this is more than offset by the savings downstream, the net reduction in operating costs being more than $1 million/year. Note that the operating costs do not include capital recovery. Had this been considered, the operating cost savings due to phenol recovery would have been even greater.

This cost estimate did not include any costs associated with zero discharge, which is assumed to have a negligible impact on the phenol recovery tradeoff. The costs for the nondephenolated wastewater treatment and solid-waste handling/disposal systems were based on the schemes presented in Figure 5: Revised Baseline Design. The costs for the dephenolated wastewater treatment and solid-waste handling/disposal systems were based on Figure 15: Recommended Wastewater Treatment and Solid-Waste Disposal System, which is located in Chapter IV. Also, the value of the recovered phenol was assumed to be zero, since the recovered phenol is a heterogeneous mixture of phenolic compounds, and, as such, is not readily marketable. The quantity is too small for the 6,000-tpd demonstration plant to justify adding purification equipment. Consequently, the phenol will be used in the plant as a supplemental fuel, which is assumed to have negligible value.

Table 19

Economic Tradeoffs for Phenol Recovery
($ Thousands)

	Without phenol recovery[40] (Alternative I)	With phenol recovery (Alternative II)
Capital costs		
Phenol recovery	$ -	$ 3,705[37]
ASWS (delta only)[a]	-	(964)[37]
Wastewater treatment & solid waste handling and disposal	52,400	37,322[38]
Total	$52,400[b]	$40,063
Annual operating costs		
Phenol recovery	$ -	$ 460[14]
Wastewater treatment & solid waste handling and disposal	10,100	8,540[15]
Total	$10,100	$ 9,000

[a] Phenol recovery includes a single tank for equalizing the four major sour water streams. This surge tank reduces the capacity of the surge tank needed for the ASWS unit, resulting in the cost savings.

[b] This cost is based on the Revised Baseline Design (Figure 5). If the Rust Baseline Design[2] is used, the cost would be $42,700[38]. Because the Revised Baseline Design is more technically viable than the Rust Baseline Design, it is used here for comparison.

H. CONCLUSIONS AND RECOMMENDATIONS DERIVED FROM THE PHENOL RECOVERY EVALUATION

Based on the results of the phenol recovery evaluation, the following conclusions and recommendations can be made:

- Phenol recovery from SRC-I wastewater is technically feasible.
- Phenol extraction reduces the organic loading to biological treatment. Phenolics can be extracted easily from the range of 8,000 to about 50 mg/L or less. TOC can be reduced to one-third of the critical value in the sour water.
- Phenol extraction will minimize the amount of volatile organic compounds lost during ammonia/sulfide stripping; the reduction is about one order of magnitude. With effective removal of the residual solvent from the extracted wastewater, the reduction would be even greater; as much as 26 times was observed.
- Phenol extraction alone does not eliminate "tar acid" materials completely, but it does reduce the quantity. Without dephenolization, the tar acid concentration amounts to approximately 10 g/L; with dephenolization, the amount reduces to several grams/L.
- Although phenol recovery does not eliminate tar acids completely, it seems to have eliminated the need for tar acid removal before biological treatment. This results in a significant savings of chemicals and a reduction in the amount of total dissolved solids introduced to the wastewater.
- Phenol recovery benefits biological treatment. The residual COD and TOC in the wastewater after biological treatment were lower and more stable with dephenolization than without it. With dephenolization the typical residual COD was about 200 ± 45 mg/L, and without it, the COD was 260 ± 100, even with continuous addition of a high dosage of powdered activated carbon (PAC) to the bioreactors.
- Biological ammonia removal and nitrification are not reliable for the SRC-I wastewater. Effective steam-stripping is the key to controlling the ammonia in the plant effluent.

- Phenol recovery reduces the minimum hydraulic residence time (HRT) for the bioreactors. With phenol recovery, the minimum HRT is 2 days; without dephenolization, the minimum HRT is 3.5 days with PAC and as long as 6 days without PAC.
- With phenol recovery, two bioreactors in series with 1-day HRTs each performed better than a single-stage bioreactor with a 2-day HRT.
- With phenol recovery, there is no need for continuous, high-level PAC addition, which is very expensive. Without phenol recovery, PAC is required to attain a comparable effluent quality.
- Reduction of the organic loading to biological treatment also reduced the aeration horsepower requirement by two-thirds. Based on 4¢/kwh and 330 days/year, the power savings due to phenol recovery is more than $200,000/year.
- The biological sludge reduction due to phenol recovery is also about two-thirds. Phenol recovery lowers the sludge production from 1,300 to 430 ft^3/day, assuming the dewatered sludge contains 15 wt % solids.
- The most significant impact of phenol recovery on tertiary treatment is reduction of the organic loading to the granular activated carbon adsorption column.
- With phenol recovery, ozonation will be needed only for disinfection; without phenol recovery, ozonation is also required for COD reduction.
- After tertiary treatment, both dephenolated and nondephenolated wastewaters can meet the anticipated effluent limits, but phenol recovery provides a greater safety margin.
- The cost penalty of adding phenol recovery is more than offset by the savings for downstream processes. The capital costs for the wastewater treatment and solid-waste handling and disposal system with phenol recovery are about $40 million; the system without it costs about $52 million. Phenol recovery also results in net savings in operating costs of about $1 million/year.
- Phenol recovery is recommended.

IV. RECOMMENDED WASTEWATER TREATMENT SYSTEM

With the adoption of a phenol recovery system for the 440-gpm phenolic-bearing sour-water streams, the wastewater treatment system and, to some extent, the solid-waste handling and disposal system need to be modified. The recommended system (Figure 15) is described below.[15]

A. PROCESS DESCRIPTION

Four phenolic-bearing sour-water streams, one each from the SRC processing area and the expanded-bed hydrocracker (EBH) and two from the coker/calcining area, are combined in a surge tank immediately upstream of the phenol recovery system. Following phenol extraction, the sour water enters the ammonia/sulfide water stripper (ASWS). Other non-phenolic sour waters contaminated with hydrogen sulfide and/or ammonia are also sent directly to the ASWS. The ASWS employs lime to free the fixed ammonia for stripping. Portions of the added lime will not be reacted, and will settle out. The unreacted lime will be flashed to reduce the pressure and then salvaged in other parts of the wastewater treatment system where lime is needed.

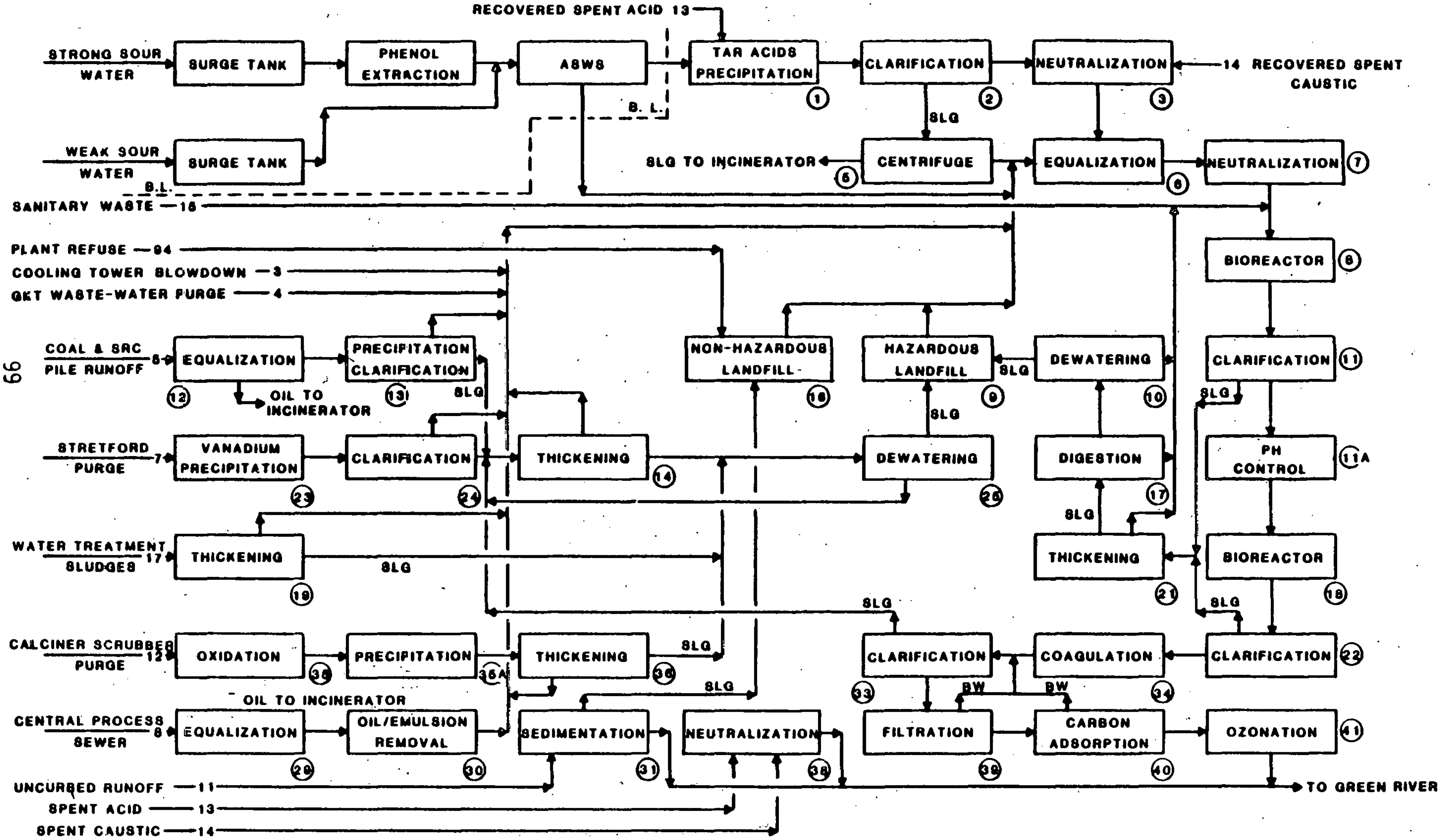
After steam-stripping, the stripper bottoms is sent to tar acid precipitation. The laboratory data have indicated that tar acid precipitation is not required before biological treatment when phenol extraction is implemented. However, phenol extraction did not eliminate tar acid, as had been hoped. The tar acid removal step is therefore retained for the time being. Further research may indicate more conclusively whether there is no need for this step.

After tar acid removal, the sour water is mixed with other weaker streams, such as pretreated coal-/SRC-pile runoffs, cooling tower blowdown, GKT washwater purge, and Stretford purge, in the equalization tank before biological treatment.

The GKT gasifier purge does not contain many organics, but it does contain some ammonia, thiocyanates, and traces of hydrogen sulfide and cyanides that can be removed during biological and tertiary treatment.

Figure 15

Recommended Wastewater Treatment and
Solid Waste Handling/Disposal System



SOURCE: References 15 & 16

The coal-/SRC-pile runoffs are combined and collected in an equalization basin to dampen the flow and composition fluctuation. The heavy metals are removed by the lime precipitation process. The pretreated runoff is then sent to the equalization basin upstream of biological treatment. The Stretford purge is treated with lime and ferrous sulfate to remove vanadium, and the SO_2 scrubber purge is oxidized to convert reduced sulfur compounds to sulfates, which are then precipitated with lime as calcium sulfate.

The central process sewer collects the contaminated runoff from each process area. The runoff is equalized to dampen the surge, and treated to remove oil and emulsions, which entails pH adjustment, chemical precipitation, and dissolved air flotation. After the treatment, the contaminated runoff is further purified biologically and polished with tertiary treatment.

The biological treatment consists of two bioreactors in series, each having its own clarifier. Provisions to add powdered activated carbon to the bioreactor (on an intermittent, low-dose basis) will be included. The biological sludge waste will be aerobically digested, thickened, and then dewatered, and the supernatant returned to the bioreactors.

Following biological treatment, the wastewater will undergo tertiary treatment, which includes coagulation/clarification, filtration, granular activated carbon adsorption, and ozonation. Ozonation is required for disinfection of the sanitary wastes. The reduction in piping costs due to combining all wastes is enough to offset the cost of ozonation. The ozonated effluent can be discharged.

The uncontaminated runoff collected from uncurbed areas throughout the plant will be stored in a retention pond to remove silt and then discharged. Also to be discharged are the neutralized spent regenerants produced from regeneration of the demineralizers for the boiler feedwater treatment. Because the spent regenerants contain unused sulfuric acid and caustic, they will be used for the wastewater treatment to a maximum extent possible. Only the excess will be neutralized and discharged.

Figure 15 also shows how the solid wastes are to be handled and disposed of. The system is identical to what was described in Figure 2B. All sludges will be thickened before dewatering. Hazardous and nonhazardous wastes are treated separately, and disposed of accordingly. As a minimum, the landfills will meet all applicable regulations.

More details about the recommended wastewater treatment system are in the report entitled: Wastewater Treatment System and Solid Wastes Landfill for 6,000 tpd SRC-I Demonstration Plant.[15]

B. DESIGN BASIS

The design basis and criteria have been documented in the Design Basis Memorandum (DBM), Section B, covering Area 17 - Waste Treatment and Disposal Section, Discharge Mode for 6,000-tpd SRC-I Demonstration Plant, Revision C, dated November 10, 1983.[16]

The DBM specifies the characteristics of each wastewater stream that is sent to the off-sites area and the design criteria for individual unit processes. The criteria are consistent with the R&D results for the solid-waste handling and disposal facility, which had not been incorporated into the DBM because the R&D program for solid wastes was not initiated until late 1983. However, the design is consistent with the results, which are published elsewhere.[17]

V. EFFLUENT QUALITY AND IMPACT ANALYSIS

The recommended wastewater treatment system just described will produce an effluent of good quality. This section summarizes all data on effluent composition and assesses the suitability of the effluent for discharge into the Green River, the intended receiving water body. For comparison, similar analyses on the effluent from the alternative treatment system without dephenolization are also provided. Highlights of such a comparison were presented previously in Section III, Phenol Recovery Evaluation, but more details are discussed here.

A. EFFLUENT COMPOSITION

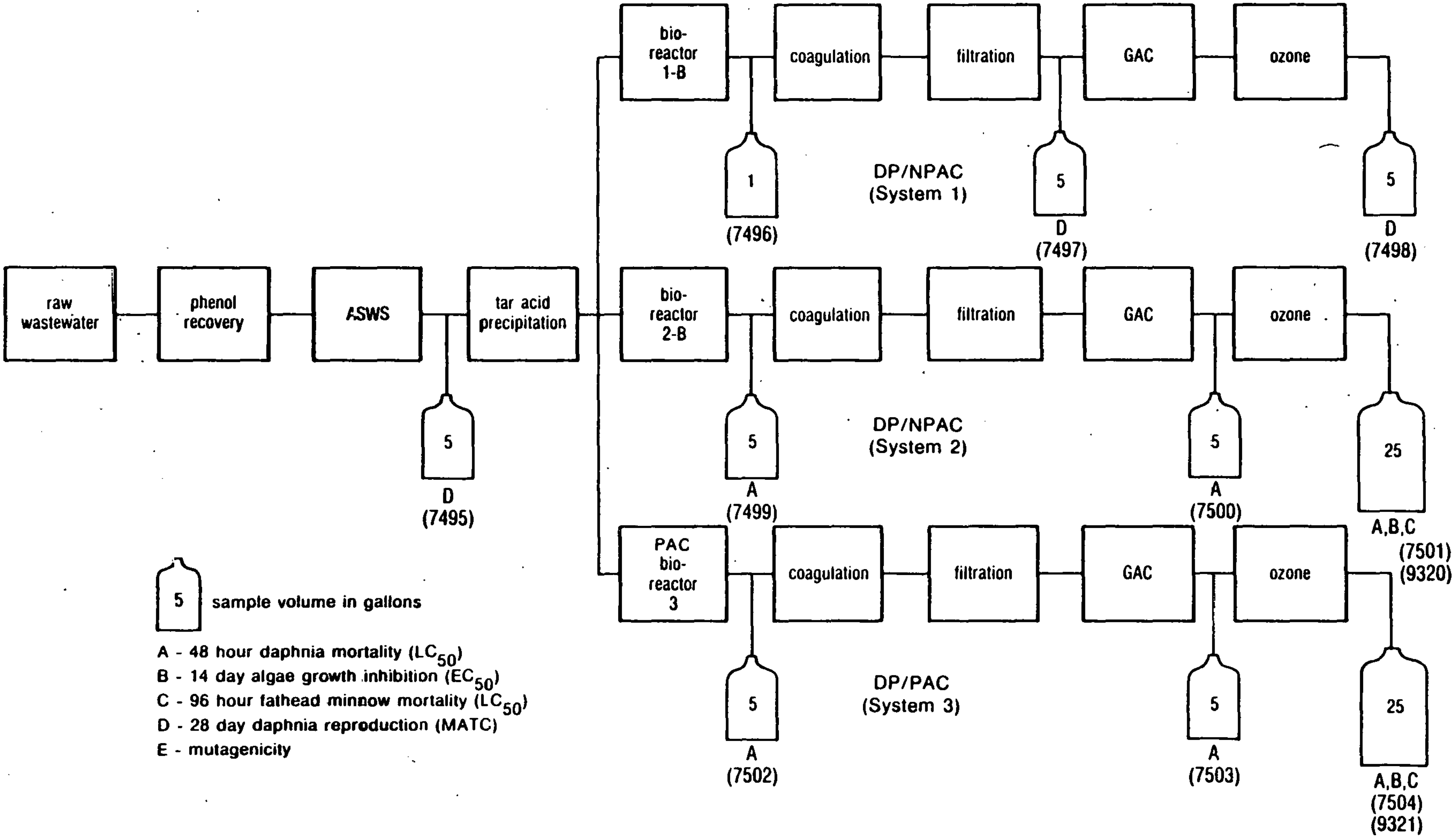
Comprehensive analyses were performed on samples from many sampling points, including influents, intermediate steps in each treatment train, and the final effluents. Figure 16 shows the sample points for three dephenolated (DP) treatment trains. Table 20 presents the analytical results for the samples shown in that figure. Similarly, Figure 17 shows the sample points and Table 21 the corresponding composition for the nondephenolated (NDP) treatment trains. Figures 16 and 17 also illustrate the samples used for the aquatic ecotoxicity and mutagenicity studies, which will be discussed later.

The chemical analyses comprised several categories: (1) conventional parameters such as BOD_5, TOC, and COD; (2) trace inorganic and organic contaminants, including EPA priority pollutants; and (3) common inorganic ions that are environmentally innocuous but have the potential to corrode equipment, e.g., chloride and sulfate. Tables 20 and 21 present all chemical analyses except for trace organic contaminants. These contaminants, which were analyzed by GC/MS, and their respective detection limits are listed in Table 22. Detailed results are documented elsewhere.[4,5,7]

After biological oxidation, all of the priority organic contaminants in the treated wastewaters were below detection limits except for methylene chlorides, chloroform, di-n-butyl phthalate, bis(2-ethyl-

Figure 16

Toxicology Study Sampling Points for
Aquatic Bioassay and Mutagenicity Tests: Systems 1, 2, and 3



SOURCE: Reference 4

Table 20

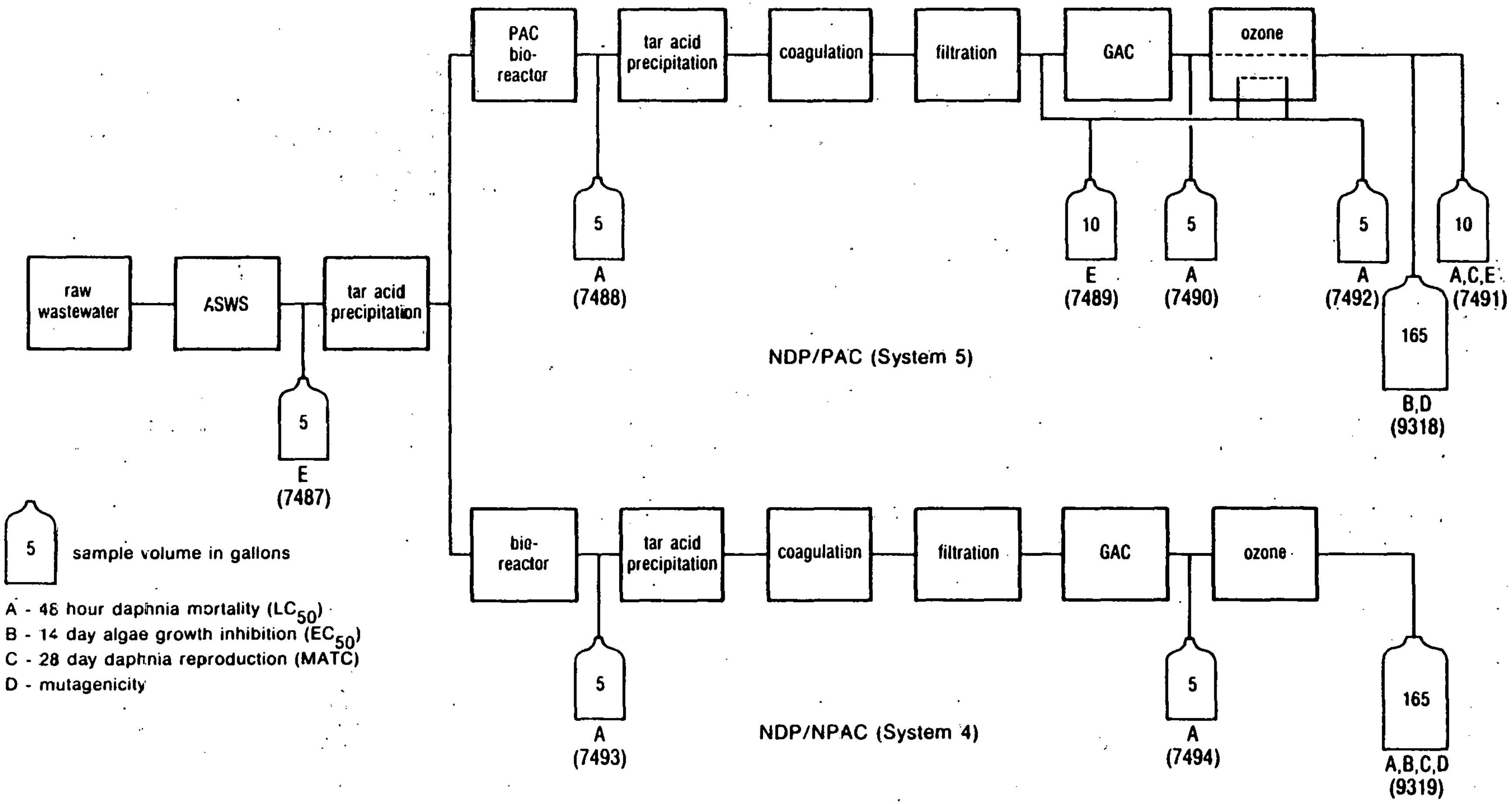
Analytical Results for Dephenolated (DP) Wastewater Treatment Trains

	7495 ASWS EFF	7496 NPAC 1B BIO EFF	7497 NPAC 1B COAG EFF	7498 NPAC 1B OZONE	7499 NPAC 2B BIO EFF	7500 NPAC 2B CARBON	7501 NPAC 2B OZONE	9320 NPAC 2B OZONE	7502 DP/PAC BIO EFF	7503 DP/PAC CARBON	7504 DP/PAC OZONE	9321 DP/PAC OZONE
Alk-pH4.3@CaCO3	3760	67	48	125	87	131	143		304	186	173	
BOD5 mg/l	1520	17	4	ND(1)	46	ND(1)	ND(2)		35	1	ND(2)	
COD mg/l	2880	398	145	61	233	74	46	22	282	115	47	25
TOC mg/l	690	80	10	ND(1)	52	ND(1)	ND(1)	ND(1)	61	ND(1)	ND(1)	ND(1)
TIC mg/l	170	62	15	13	90	13	12		93	27	22	
TDS mg/l	6900	4330	5460	5260	4740	4970	4970	2700	4730	4650	4720	2450
TSS mg/l	14	18	4	12	145	10	2	20	220	8	2	14
pH	12.3	6.9	7.2	8.3	7.1	8.2	7.6		7.7	8.2	7.6	
Conductivity umhos	14700	5560	7430	7170	6340	7330	7290		6220	6717	6750	
Color Pt-Co units	4000	1000	400	10	1500	ND(5)	10	ND(5)	1000	ND(5)	ND(5)	ND(5)
Turbidity-NTU	23	100	2.9	.85	45	.25	1.7		85	.25	.75	
Chloride mg/l	500	290	690	660	360	650	580	318	380	615	650	320
Cyanide mg/l	.041	.149	.194	ND(.004)	.688	ND(.005)	ND(.004)	ND(.004)	.957	ND(.004)	ND(.004)	ND(.004)
Thiocyanate mg/l	31.8	1.8	.6	ND(.2)	2.8	ND(.2)	ND(.2)	ND(.2)	2	ND(.2)	ND(.2)	ND(.2)
Flouride mg/l	1.22	.56	.81	.33	.41	.41	.37		.37	.43	.35	
Ammonia-N mg/l	95	21	2	1	25	ND(.3)	ND(.3)	ND(1)	52	ND(.3)	ND(.3)	ND(1)
Organic-N mg/l	64	10	1	2	9	3	2	ND(1)	21	ND(.3)	ND(.3)	ND(1)
Nitrite-N mg/l	.6	4.25	58.5	19.8	15	14	ND(.25)		103	81.7	ND(.25)	
Nitrate-N mg/l	3.3	86.9	64.5	118	135	121	71.9	62.6	36	28.3	80.5	40.3
Phenolics mg/l	57	.025	.004	.007	.035	.007	.005	ND(.025)	.032	.01	.013	ND(.025)
Sulfide mg/l	.22	ND(.001)	.008	.005	ND(.001)	.01	.004		.25	.006	ND(.001)	
T-Phosphate@P mg/l	.63	8.7	.04	.1	4.3	.08	.095		10.6	.09	.09	
Silica mg/l	179	8.5	5.3	6.6	20.3	6.6	7.5	3.4	21.4	9.2	8.5	3.8
Sulfate mg/l		1600	2100	2100	1900	1800	2000	1100	2000	1800	1800	1000
Aluminum mg/l	3.31	1.6	.15	.28	1.22	.17	.17	ND(.4)	2.01	.1	ND(.09)	ND(.4)
Calcium mg/l	15.2	362	375	395	375	170	170	55	562	280	273	144
Iron mg/l	1.64	1.74	.1	ND(.04)	.94	ND(.04)	ND(.04)	ND(.05)	1.36	ND(.04)	ND(.04)	.08
Magnesium mg/l	15.4	12.8	15	16.9	14.1	18.6	19.8	3	14.2	17.6	18.6	8
Manganese mg/l	.074	.014	.245	.189	.008	.202	.19	.13	.02	.139	.114	.1
Antimony mg/l	ND(.2)	ND(.2)	ND(.2)	ND(.2)	ND(.2)	ND(.2)	ND(.2)		ND(.2)	ND(.2)	ND(.2)	
Arsenic mg/l	1.4	ND(.015)	ND(.015)	ND(.015)	ND(.015)	ND(.015)	ND(.015)		.06	.09	.35	
Barium mg/l	ND(.5)	ND(.5)	ND(.5)	ND(.5)	ND(.5)	ND(.5)	ND(.5)		ND(.5)	ND(.5)	ND(.5)	
Beryllium mg/l	ND(.003)	ND(.003)	ND(.003)	ND(.003)	ND(.003)	ND(.003)	ND(.003)		ND(.003)	ND(.003)	ND(.003)	
Boron mg/l	97	53	56	46	56	44	59	54	70	52	45	60
Cadmium mg/l	ND(.01)	ND(.01)	ND(.01)	ND(.01)	ND(.01)	ND(.01)	ND(.01)		ND(.01)	ND(.01)	ND(.01)	
Chromium mg/l	.078	ND(.03)	ND(.03)	ND(.03)	ND(.03)	ND(.03)	ND(.03)		ND(.03)	ND(.03)	ND(.03)	
Copper mg/l	.06	.08	.03	.03	.07	ND(.02)	.02		.07	ND(.02)	ND(.02)	
Lead mg/l	ND(.11)	ND(.11)	ND(.11)	ND(.11)	ND(.11)	ND(.11)	ND(.11)		ND(.11)	ND(.11)	ND(.11)	
Mercury mg/l	.0436	.0006	.001	.0006	ND(.0004)	ND(.0002)	ND(.0002)		ND(.0004)	ND(.0002)	ND(.0002)	
Nickel mg/l	ND(.06)	ND(.06)	ND(.06)	ND(.06)	ND(.06)	ND(.06)	ND(.06)		ND(.06)	ND(.06)	ND(.06)	
Thallium mg/l	ND(.08)	ND(.08)	ND(.08)	ND(.08)	ND(.08)	ND(.08)	ND(.08)		ND(.08)	ND(.08)	ND(.08)	
Selenium mg/l	.8	.12	ND(.015)	ND(.02)	.085	ND(.015)	ND(.025)		ND(.04)	ND(.026)	ND(.026)	
Silver mg/l	ND(.006)	ND(.006)	ND(.006)	ND(.006)	ND(.006)	ND(.006)	ND(.006)		.022	.014	.014	
Sodium mg/l	1800	720	960	900	810	920	960		730	770	790	
Titanium mg/l	ND(.3)	ND(.3)	ND(.3)	ND(.3)	ND(.3)	ND(.3)	ND(.3)		ND(.3)	ND(.3)	ND(.3)	
Vanadium mg/l	ND(.15)	ND(.15)	ND(.15)	ND(.15)	ND(.15)	ND(.15)	ND(.15)		ND(.15)	ND(.15)	ND(.15)	
Zinc mg/l	.538	.101	.012	.01	.066	.01	.01		.07	.01	.01	

SOURCE: Reference 4

Figure 17

Toxicology Study Sampling Points for Aquatic Bioassay and Mutagenicity Tests: Systems 4 and 5



SOURCE: Reference 4

Table 21

Analytical Results for Nondephenolated (NDP) Wastewater Treatment Trains

	7487	7488	7489	7490	7491	7492	9318	7493	7494	9319
		NDP/PAC	NDP/PAC	NDP/PAC	NDP/PAC	NDP/PAC	NDP/PAC	NDP/NPAC	NDP/NPAC	NDP/NPAC
	ASWS EFF	BIO EFF	COAG EFF	CARBON	OZONE	OZONE	OZONE	BIO EFF	CARBON	OZONE
Alk-pH4.3@CaCO3	6840	536	247	285	268	173		103	122	
BOD5 mg/l	9600	24	2	ND(1)	ND(1)	11		5	4	
COD mg/l	16675	810	385	274	143	314	86	1603	424	114
TOC mg/l	3300	210	34	ND(1)	ND(1)	10	9	400	ND(1)	12
TIC mg/l	900	140	58	53	46	37		20	9	
TDS mg/l	14530	11090	11030	10480	10510	10330	10290	10860	10150	9410
TSS mg/l	12	300	10	6	8	16	28	420	16	18
pH	12.3	7.3	7.0	7.7	7.8	6.7		6.5	8.0	
Conductivity umhos	15700	14400	14700	14400	14400	14700		14600	13900	
Color Pt-Co units	20000	3000	750	25	ND(5)	ND(5)	ND(5)	7000	ND(5)	ND(5)
Turbidity-NTU	4.2	120	8.8	3.6	.45	.62		130	1.8	
Chloride mg/l	544	2300	2410	2500	2470	2525	2580	2240	2400	2580
Cyanide mg/l	ND(.0042)	ND(.004)	ND(.004)	ND(.0069)	ND(.0072)	ND(.004)	ND(.004)	.243	ND(.004)	ND(.004)
Thiocyanate mg/l	97	2.3	1.5	.3	ND(.2)	ND(.2)		12.5	ND(.2)	
Flouride mg/l	.96	1.1	.86	.81	.81	.91	.595	.92	.74	.713
Ammonia-N mg/l	172	4	4	4	2	ND(.3)	ND(1)	30	27	25
Organic-N mg/l	96	36	15	9	10	3		49	9	
Nitrite-N mg/l	ND(.25)	1.1	.43	.43	.33	ND(.25)		ND(.25)	.59	
Nitrate-N mg/l	3.91	67.3	77.6	67	54.4	45.1	74.3	131	101	123
Phenolics mg/l	3165	.026	.013	.004	.063	ND(.001)	.031	.093	.001	ND(.025)
Sulfide mg/l(Total	ND(.001)	ND(.001)	ND(.001)	.006	.004	ND(.001)		ND(.001)	ND(.001)	
T-Phosphate@P mg/l	1.3	15.8	.19	.21	.16	.12	.08	13.1	.04	.03
Silica mg/l	205	403	12	18.3	8.7	17	23.1	34	17	22.5
Sulfate mg/l	86	3500	3500	3400	3400	3300	3600	3500	3500	3000
Aluminum mg/l	3.18	2.26	.3	.16	.24	ND(.09)	ND(.4)	1.41	.13	ND(.4)
Calcium mg/l	53.2	839	604	656	627	593	549	754	558	544
Iron mg/l	2.66	1.22	.94	.72	.18	.35	ND(.05)	.39	.05	ND(.05)
Magnesium mg/l	1.74	12.6	13.3	14	14.4	14.4	14	12.1	14.8	13
Manganese mg/l	ND(.006)	.057	.066	.239	.101	.109	ND(.02)	.012	.224	.05
Antimony mg/l	ND(.2)	ND(.2)	ND(.2)	ND(.2)	ND(.2)	ND(.2)		ND(.2)	ND(.2)	
Arsenic mg/l	.03	.1	.32	.04	.07	ND(.015)		ND(.015)	ND(.015)	
Barium mg/l	ND(.5)	1.5	ND(.5)	ND(.5)	.7	.6		.6	.8	
Beryllium mg/l	.005	ND(.003)	ND(.003)	ND(.003)	ND(.003)	ND(.003)		ND(.003)	ND(.003)	
Boron mg/l	127	76	69	67	65	91	108	84	62	120
Cadmium mg/l	ND(.01)	ND(.01)	.102	.094	.09	.116		ND(.01)	.01	
Chromium mg/l	.06	.03	ND(.03)	ND(.03)	ND(.03)	ND(.03)		ND(.03)	ND(.03)	
Copper mg/l	.06	.06	.06	.04	.04	.06		.05	.04	
Lead mg/l	ND(.11)	ND(.11)	ND(.11)	ND(.11)	ND(.11)	ND(.11)		ND(.11)	ND(.11)	
Mercury mg/l	ND(.0002)	.0004	ND(.0002)	.0018	ND(.0002)	.0004		.0008	.0005	
Nickel mg/l	ND(.06)	ND(.06)	ND(.06)	ND(.06)	ND(.06)	ND(.06)		ND(.06)	ND(.06)	
Thallium mg/l	ND(.08)	ND(.08)	ND(.08)	ND(.08)	ND(.08)	ND(.08)		ND(.08)	ND(.08)	
Selenium mg/l	.8	ND(.015)	ND(.015)	ND(.015)	ND(.03)	ND(.015)		.3	ND(.015)	
Silver mg/l	.018	.073	.044	.055	.044	.039		.058	.033	
Sodium mg/l	2740	2240	2000	2000	1900	1900		1900	1700	
Titanium mg/l	ND(.3)	ND(.3)	ND(.3)	ND(.3)	ND(.3)	ND(.3)		ND(.3)	ND(.3)	
Vanadium mg/l	ND(.15)	ND(.15)	ND(.15)	ND(.15)	ND(.15)	ND(.15)		ND(.15)	ND(.15)	
Zinc mg/l	.406	.394	.349	.083	.059	.365		1.569	ND(.01)	

SOURCE: Reference 4

Table 22

Trace Organic Pollutants Analyzed

		Detection limit (μg/L)
	Volatile organics	
1V.	Acrolein	100
2V.	Acrylonitrile	100
3V.	Benzene	10
4V.	Bis(chloromethyl) ether	10
5V.	Bromoform	10
6V.	Carbon tetrachloride	10
7V.	Chlorobenzene	10
8V.	Chlorodibromomethane	10
9V.	Chloroethane	10
10V.	2-Chloroethylvinyl ether	10
11V.	Chloroform	10
12V.	Dichlorobromomethane	10
13V.	Dichlorodifluoromethane	10
14V.	1,1-Dichloroethane	10
15V.	1,2-Dichloroethane	10
16V.	1,1-Dichloroethylene	10
17V.	1,2-Dichloropropane	10
18V.	1,3-Dichloropropylene	10
19V.	Ethylbenzene	10
20V.	Methyl bromide	10
21V.	Methyl chloride	10
22V.	Methylene chloride	10
23V.	1,1,2,2-Tetrachloroethane	10
24V.	Tetrachloroethane	10
25V.	Toluene	10
26V.	1,2-trans-Dichloroethylene	10
27V.	1,1,1-Trichloroethane	10
28V.	1,1,2-Trichloroethane	10
29V.	Trichloroethylene	10
30V.	Trichlorofluoromethane	10
31V.	Vinyl chloride	10
	Acid-extractable organics	
1A.	2-Chlorophenol	25
2A.	2,4-Dichlorophenol	25
3A.	2,4-Dimethylphenol	25
4A.	4,6-Dinitro-o-cresol	250
5A.	2,4-Dinitrophenol	250
6A.	2-Nitrophenol	25
7A.	4-Nitrophenol	25
8A.	p-Chloro-m-cresol	25
9A.	Pentachlorophenol	25
10A.	Phenol	25
11A.	2,4,6-Trichlorophenol	25

Table 22 (Continued)

		Detection limit (μg/L)
Base-neutral extractable organics		
1B.	Acenaphthene	10
2B.	Acenaphthylene	10
3B.	Anthracene	10
4B.	Benzidine	10
5B.	Benzo(a)anthracene	10
6B.	Benzo(a)pyrene	10
7B.	3,4-Benzofluoranthene	10
8B.	Benzo(ghi)perylene	25
9B.	Benzo(k)fluoranthene	10
10B.	Bis(2-chloroethoxy)methane	10
11B.	Bis(2-chloroethyl) ether	10
12B.	Bis(2-chloroisopropyl) ether	10
13B.	Bis(2-ethylhexyl) phthalate	10
14B.	4-Bromophenyl phenyl ether	10
15B.	Butyl benzyl phthalate	10
16B.	2-Chloronaphthalene	10
17B.	4-Chlorophenyl phenyl ether	10
18B.	Chrysene	10
19B.	Dibenzo(a,H)anthracene	25
20B.	1,2-Dichlorobenzene	10
21B.	1,3-Dichlorobenzene	10
22B.	1,4-Dichlorobenzene	10
23B.	3,3'-Dichlorobenzidine	10
24B.	Diethyl phthalate	10
25B.	Dimethyl phthalate	10
26B.	Di-n-butyl phthalate	10
28B.	2,6-Dinitrotoluene	10
29B.	Di-n-octyl phthalate	10
30B.	1,2-Diphenylhydrazine	10
31B.	Fluoranthene	10
32B.	Fluorene	10
33B.	Hexachlorobenzene	10
34B.	Hexachlorobutadiene	10
35B.	Hexachlorocyclopentadiene	10
36B.	Hexachloroethane	10
37B.	Indeno(1,2,3-cd)pyrene	25
38B.	Isophorone	10
39B.	Naphthalene	10
40B.	Nitrobenzene	10
41B.	N-Nitrosodimethylamine	10
42B.	N-Nitrosodi-n-propylamine	10
43B.	N-Nitrosodiphenylamine	10
44B.	Phenanthrene	10
45B.	Pyrene	10
46B.	1,2,4-Trichlorobenzene	10

SOURCE: Reference 4

hexyl) phthalate, and toluene. The highest methylene chloride concentration measured was about 16 μg/L. The source of the methylene chloride was probably the tap water used to dilute the feed to the bioreactors; the methylene chloride concentration of the tap water was 13 μg/L. Likewise, the chloroform probably originated in the tap water, which had a concentration of 61 μg/L. The highest concentration measured in the treated wastewater was 11 μg/L. Phthalates are plasticizers which are ubiquitous in the laboratory environment.[18] Trace amounts could leach out from plastic containers, tubing, valves, and the like and contaminate the samples. Toluene was detected in only one sample (sample 7503, dephenolated wastewaters after granular activated carbon adsorption), at a concentration of 0.12 μg/L. However, neither the sample upstream (No. 7502) nor the sample downstream (No. 7504) showed any toluene, nor did other samples in other treatment trains. Therefore, it was probably due to contamination of the sample or an artifact.

B. METHODOLOGY FOR ASSESSING THE SUITABILITY FOR DISCHARGE

The suitability of the treated wastewaters for discharge was assessed from several perspectives:

1. Comparison of the measured contaminant concentrations in the treated effluent with estimated concentrations published in the FEIS.[1]
2. Comparison of the measured concentrations with the estimated effluent limits for SRC-I based on the EPA effluent limitations, guidelines, and standards for industries that generate wastewaters containing the same contaminants as various SRC-I wastewaters. The relevant industries are petroleum refining, iron and steel by-product coke making, and metal finishing.
3. Estimation of the concentrations (worst-case analysis) in the Green River after discharge and comparison with the EPA and Kentucky water quality standards or criteria for the river.

4. Determination of aquatic ecotoxicity of the treated wastewaters to various organisms.
5. Determination of microbial mutagenicity (Ames tests).

Each of the above assessments is highlighted in the following sections.

1. Comparison with Estimated Effluent Limits

The FEIS for the demonstration plant included an impact analysis based on estimated concentrations of various contaminants in the plant effluent. Table 23 compares the estimated FEIS values with observed values for the fully treated wastewaters. Table 23 also lists the existing and/or proposed EPA effluent limitations for related industries. The effluent limits for petroleum refining were derived from Petroleum Refining Point Source Category Effluent Limitations, Guidelines, Pretreatment Standards and New Source Performance Standards[19] and the Development Document[20] for those regulations. The effluent limits for the iron and steel industries for coke-making are published elsewhere.[21,22] Those regulations provide final effluent limitation guidelines for the "best available technology economically achievable" (BAT).

Based on such a comparison, the fully treated dephenolized wastewaters (samples 7498, 7501, and 7504) meet, without any exceptions, all the effluent limits by a wide margin. Even the nondephenolated, fully treated wastewaters meet all the anticipated effluent limits except for ammonia, which is a special case, as discussed previously.

2. Impact on Water Quality

A worst-case analysis was made to estimate concentrations of contaminants in the river after discharge. The analysis assumed that the following unfavorable conditions would occur simultaneously:

- Maximum ambient contaminant concentrations in the river before discharge
- 7-day, 10-year river low flow ($_7Q_{10}$)
- Maximum contaminant concentrations in the plant effluent
- Average plant effluent flow in dry weather conditions.

Table 23

Comparison of Fully Treated Wastewaters with Effluent Limitations

	MEASURED CONCENTRATION					EFFLUENT LIMITATIONS		
PARAMETER	DP/NPAC 7498	DP/NPAC 7501	DP/PAC 7504	NDP/NPAC 7491	NDP/PAC 9319	FEIS	Petroleum Refining	Iron and Steel
Alk-pH4.3@CaCO3	125	143	173	268	122			
BOD5 mg/l	ND(1)	ND(2)	ND(2)	ND(1)	4	20	25	
COD mg/l	61	46	47	143	114	150	180	
TOC mg/l	ND(1)	ND(1)	ND(1)	ND(1)	12	150	46	
TIC mg/l	13	12	22	46	9			
TDS mg/l	5260	4970	4720	18510	9410			
TSS mg/l	12	2	2	8	18	20	21	14
pH	8.3	7.6	7.6	7.8	8	6-9	6-9	6-9
Conductivity umhos	7170	7290	6750	14400	13900			
Color Pt-Co units	10	10	ND(5)	ND(5)	ND(5)			
Turbidity-NTU	.85	1.7	.75	.45	1.8			
Chloride mg/l	660	580	650	2470	2580			
Cyanide mg/l	ND(.004)	ND(.004)	ND(.004)	ND(.0072)	ND(.004)	.45		.1
Thiocyanate mg/l	ND(.2)	ND(.2)	ND(.2)	ND(.2)	ND(.2)			
Flouride mg/l	.33	.37	.35	.81	.713			
Ammonia-N mg/l	1	ND(.3)	ND(.3)	2	25	5	17	6
Organic-N mg/l	2	2	ND(.3)	10	9			
Nitrite-N mg/l	19.8	ND(.25)	ND(.25)	.33	.59			
Nitrate-N mg/l	118	71.9	80.5	54.4	123			
Phenolics mg/l	.007	.005	.013	.063	.001	.1	.17	.3
Sulfide mg/l(Total	.005	.004	ND(.001)	.004	ND(.001)	.04	.13	.1
T-Phosphate@P mg/l	.1	.095	.09	.16	.03	5		
Silica mg/l	6.6	7.5	8.5	8.7	22.5			
Sulfate mg/l	2100	2000	1800	3400	3500			
Aluminum mg/l	.20	.17	ND(.09)	.24	.13			
Calcium mg/l	395	170	273	627	558			
Iron mg/l	ND(.04)	ND(.04)	ND(.04)	.18	.05	2		
Magnesium mg/l	16.9	19.8	18.6	14.4	14.8			
Manganese mg/l	.189	.19	.114	.101	.224	2		
Antimony mg/l	ND(.2)	ND(.2)	ND(.2)	ND(.2)	ND(.2)			
Arsenic mg/l	ND(.015)	ND(.015)	.35	.07	ND(.015)	.1		
Barium mg/l	ND(.5)	ND(.5)	ND(.5)	.7	.8	1		
Beryllium mg/l	ND(.003)	ND(.003)	ND(.003)	ND(.003)	ND(.003)	.005		
Boron mg/l	46	59	45	65	120			
Cadmium mg/l	ND(.01)	ND(.01)	ND(.01)	.09	.01	.15		
Chromium mg/l	ND(.03)	ND(.03)	ND(.03)	ND(.03)	ND(.03)	1	.425	
Copper mg/l	.03	.02	ND(.02)	.04	.04	1		
Lead mg/l	ND(.11)	ND(.11)	ND(.11)	ND(.11)	ND(.11)	.25		
Mercury mg/l	.0006	ND(.0002)	ND(.0002)	ND(.0002)	.0005	.001		
Nickel mg/l	ND(.06)	ND(.06)	ND(.06)	ND(.06)	ND(.06)	.5		
Thallium mg/l	ND(.08)	ND(.08)	ND(.08)	ND(.08)	ND(.08)			
Selenium mg/l	ND(.02)	ND(.025)	ND(.026)	ND(.03)	ND(.015)	.35		
Silver mg/l	ND(.006)	ND(.006)	.014	.044	.033	.1		
Sodium mg/l	900	960	790	1900	1700			
Titanium mg/l	ND(.3)	ND(.3)	ND(.3)	ND(.3)	ND(.3)			
Vanadium mg/l	ND(.15)	ND(.15)	ND(.15)	ND(.15)	ND(.15)	1		
Zinc mg/l	.01	.01	.01	.059	ND(.01)	1		

SOURCE: Reference 4

The mixed concentration in the river after discharge was calculated by the following formula:

$$C = [C_e(Q_e) + C_o(Q_o)]/(Q_e + Q_o)$$

where C = the total mixed concentration when combined with the ambient level

C_e = the concentration in the undiluted effluent

C_o = the maximum ambient concentration in the river

Q_e = the volumetric flow rate of the effluent (1,159 gpm)

Q_o = the 7-day, 10-year river low flow (176,827 gpm)

The maximum river concentrations are based on data collected by Dames and Moore[23] from 1977 to 1980 and by the Academy of Natural Sciences from 1980 to 1982.[24] The maximum concentration in the undiluted effluent is assumed to be 2.5 times the value observed in the laboratory. The calculated maximum concentrations in the river, water-quality standards/criteria, and ambient concentrations are presented in Table 24. The concentrations were calculated for four effluents (NDP/NPAC, NDP/PAC, DP/NPAC, and DP/PAC). The DP/NPAC represents the recommended system; the other effluents are presented for comparison.

As Table 24 shows, the recommended DP/NPAC wastewater treatment system produces an effluent that will not significantly impact the ambient river quality. After river water mixes with the fully treated effluent, the concentrations in the river meet most of the standards except for cyanide, ammonia, phenolics, iron, manganese, barium (borderline), copper, mercury, selenium, and silver. However, ambient concentrations of all those parameters for the river are high and already violate the standards. Thus, the SRC-I effluent does not cause any significant increase in the ambient river concentrations. In fact, the quality of the SRC-I effluent from the recommended wastewater treatment system always exceeds the ambient river quality.

Table 24

Compliance with Water Quality Standard--A Worst-Case Analysis[a] (All in mg/L Unless Stated Otherwise)

Parameter	Ambient concentration[1, 23, 24]	River concentration after SRC-I	Water quality standards[1]
Alkalinity ($CaCO_3$)	94	96	500
TDS	590	670	750
Color (APHA units)	0	0	75
Chloride	28	37	250
Cyanide	0.015[b]	0.015[b]	0.005
Fluoride	0.32	0.33	1
Ammonia-N	0.892[b]	0.892[b]	0.05
Nitrate-N	1.38	2.56	10
Phenolics	0.027[b]	0.027[b]	0.005
Sulfide	0	0.000	0.002
Sulfate	144	177	250
Iron	3.28[b]	3.28[b]	1
Manganese	0.75[b]	0.75[b]	0.05
Antimony	0.006	0.006	0.219
Arsenic	0.004	0.004	0.05
Barium	0.925[b]	0.925[b]	1
Beryllium	0	0.000	1.1
Cadmium	0.007	0.007	0.012
Chromium	0.0	0.010	0.1
Copper	0.07[b]	0.07[b]	0.003
Lead	0.007	0.007	0.05
Mercury	0.003[b]	0.003[b]	0.0005
Nickel	0.1	0.100	0.182
Selenium	0.009[b]	0.009[b]	0.01
Silver	0.003[b]	0.003[b]	0.0004
Vanadium	0.02	0.020	0.046
Zinc	0.05	0.050	0.134

---

[a] Worst-case analysis assumes that the following conditions occur simultaneously:

1. The river flow is at its 10-year, 7-consecutive-day low.
2. Effluent concentration is maximum (assumed to be 2.5 times the laboratory values).
3. The ambient concentration is maximum.

[b] Not in compliance with the water-quality standard or on the borderline.

3. Aquatic Ecotoxicity[8]

A number of wastewater samples subjected to different degrees of treatment were studied for their aquatic ecotoxicity. The samples and respective studies are depicted in Figures 16 and 17.

Four types of ecotoxicity studies were conducted:

- 48-hr *Daphnia* acute studies
- 14-day algal growth inhibition assays
- 96-hr fathead minnow acute studies
- 28-day *Daphnia* chronic studies

The 48-hr *Daphnia* acute studies and 96-hr fathead minnow tests determine concentrations that are lethal to 50% of the organisms (LC_{50}). The algal growth inhibition studies yield median effective concentrations (EC_{50}), and the 28-day *Daphnia* chronic studies generate data that can determine the maximum allowable toxic concentration (MATC). With these data, the impact of discharge on aquatic organisms can be determined.

a. *Test Results*. Table 25 shows results of the 48-hr *Daphnia* studies, Table 26 presents the data for the 14-day algal growth and 96-hr fathead minnow studies, and Table 27 shows the data for the 28-day *Daphnia* assays. Results in Tables 25, 26, and 27 are expressed in percent strength of the original wastewater sample. One hundred percent strength means the sample is undiluted; 50% means that the original wastewater is diluted to half of its original strength, and so on. Thus, a sample with a large LC_{50}, EC_{50}, or MATC value is better than a sample with a small value.

The 48-hr *Daphnia* acute studies (Table 25) demonstrated that dephenolization reduces toxicity markedly. With dephenolization, the LC_{50}s of the treated wastewaters, with or without PAC, were greater than 100%. Without dephenolization, the LC_{50} was less than 100%. Among the nondephenolated wastewaters, those treated with granular activated carbon (GAC) were less toxic, while those that were ozonated were actually more toxic. The effect was more intense for the samples generated from the non-PAC (NPAC) waters.

Table 25

Results of 48-hr *Daphnia* Acute Studies

System	Sample no.	Description	LC_{50} (%)
DP/NPAC	7499	Bioeffluent	>100
	7500	GAC effluent	>100
	7501	Final effluent	>100
DP/PAC	7502	Bioeffluent	>100
	7503	GAC effluent	>100
	7504	Final effluent	>100
NDP/NPAC	7493	Bioeffluent	58
	7494	GAC effluent	75
	9319	Final effluent	24
NDP/PAC	7488	Bioeffluent	71
	7490	GAC effluent	75
	7491	Final effluent	57
	7492	Final effluent[a]	61

[a] Bypass GAC.

SOURCE: Reference 8

Table 26

Results of Studies of Algal Growth Inhibition and Fathead Minnow Mortality Studies

14-Day Algal Growth Inhibition

System	Sample no.	Description	EC_{50} (%)
DP/NPAC	7501	Final effluent	>100
DP/PAC	7504	Final effluent	56
NDP/NPAC	9319	Final effluent	56
NDP/PAC	9318	Final effluent	56

96-Hr Fathead Minnow Mortality

System	Sample no.	Description	LC_{50} (%)
DP/NPAC	a	a	a
DP/PAC	a	a	a
NDP/NPAC	9319	Final effluent	61
NDP/PAC	7491	Final effluent	>100

[a] Not tested due to insufficient sample.

SOURCE: Reference 8

Table 27

MATC of 28-day *Daphnia* Chronic Studies

System	Sample no.	Description	Survival[a]	Young/female[b]	Spawn time[c]	Growth rate[d]	Reproductive[e]
DP/NPAC	7501	Final effluent	17.9	1.8	56.6	17.9	1.8
DP/PAC	7504	Final effluent	17.9	17.9	56.6	17.9	17.9
NDP/NPAC	7491	Final effluent	7.4	2.3	7.4	2.3	2.3
NDP/PAC	9319	Final effluent	4.3	13.5	13.5	13.5	13.5

[a] MATC, based on number surviving.
[b] MATC, based on young produced per female.
[c] MATC, based on time to first spawn.
[d] MATC, based on number of young produced per day per daphnid.
[e] The smallest value among the three reproductive MATCs: young/female, spawn time, and growth rate.

SOURCE: Reference 8

The 14-day algal growth inhibition assays (Table 26) showed that the fully treated dephenolated, non-PAC (DP/NPAC) bioreactor effluent (Sample No. 7501), which simulates effluent from the recommended system, did not significantly affect growth; the EC_{50} was greater than 100%. However, the other samples did inhibit growth somewhat, in part due to the high inorganic salt concentrations in the samples.

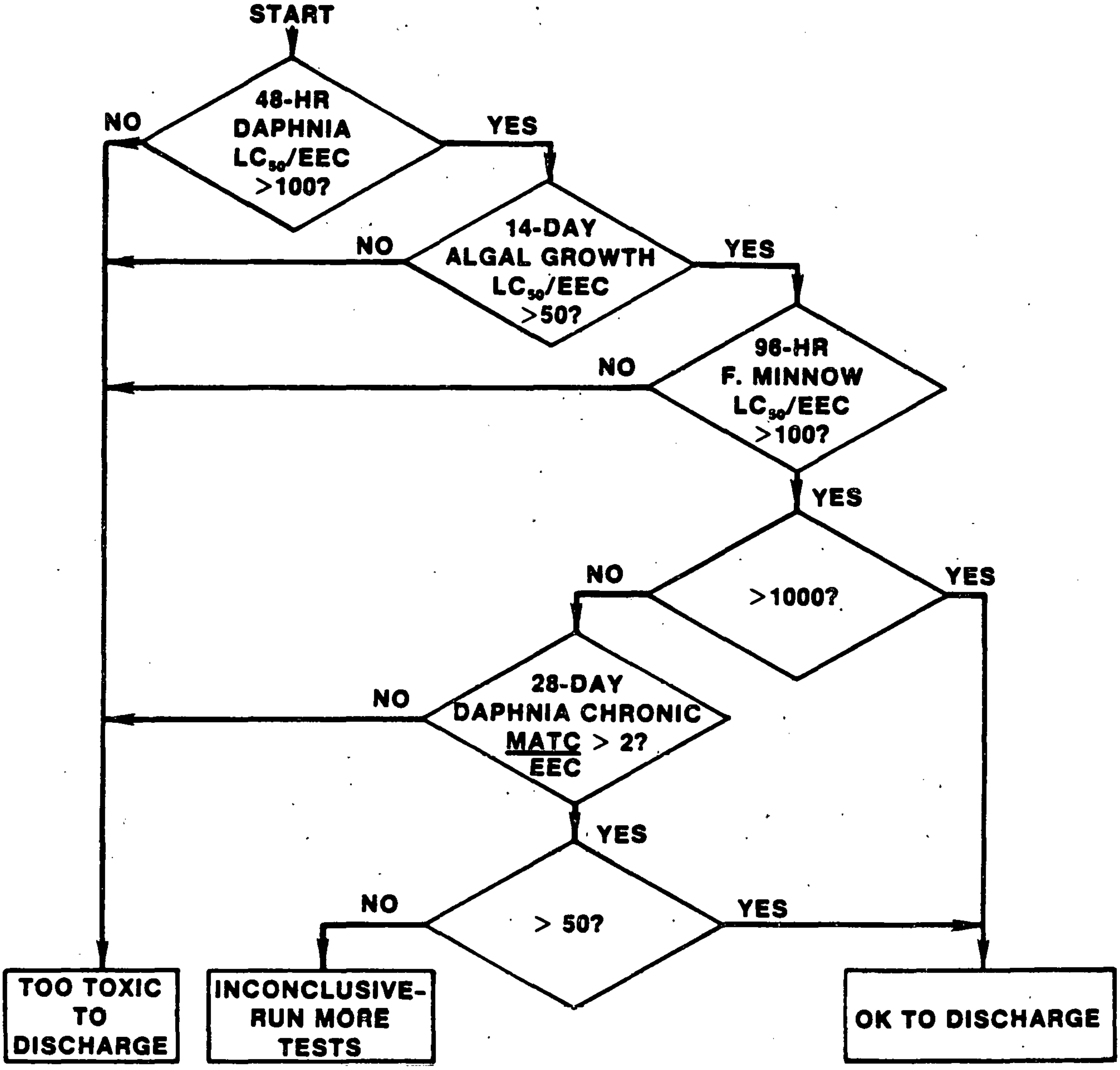
The 96-hr fathead minnow mortality assay measured acute toxicity to fish. Table 26 shows that the LC_{50} for NDP/PAC was greater than 100%, and that the LC_{50} for NDP/NPAC was 61%. Thus, PAC significantly reduced acute toxicity of the NDP wastewaters to fish. Because the assay requires a large quantity of wastewater, and only the nondephenolated wastewaters were available in sufficient amounts, the assays were performed on these waters.

The 28-day Daphnia chronic studies (Table 27) produced somewhat inconclusive results. MATC values for a given sample can be determined from several types of data: survival, young produced per female, spawn time, and number of young produced per day per adult. The survival data yield MATC values that are consistent with the results of the 48-hr Daphnia acute tests, i.e., MATC increased with a higher degree of treatment. In contrast, MATC based on the reproductive data--young produced per female, time to first spawn, and number of young produced per day per adult--varied considerably without any apparent relationship to the degree of treatment. For example, based on the young-produced data, DP/NPAC has the lowest MATC value among all samples tested, whereas the data for young produced per day per daphnid suggest that NDP/NPAC was the most toxic sample tested. The Daphnia chronic studies, therefore, are not as definitive as the other studies and more tests should be conducted. However, for the hazard assessment, the lowest MATC values for each sample were used.

b. Hazard Assessment. The LC_{50}, EC_{50}, and MATC data presented above were used to assess the hazard of the fully treated wastewaters to aquatic life according to the procedure and the criteria shown in Figure 18. The procedure is similar to that proposed by the American Society for Testing Materials,[25] but it has been modified considerably in order to overcome the limitations due to insufficient sample quantity.

Figure 18

Preliminary Hazard Assessment Procedure



The procedure involves comparing the preset criteria in Figure 18 with the ratios of LC_{50}, EC_{50}, and MATC to the estimated environmental concentration (EEC). The conservative EEC used for the assessment was 1/153 (or 0.655% of the effluent strength), which is the ratio of the plant dry-weather flow (1,159 gpm) to ${}_7Q_{10}$ of the river (176,827 gpm).

The calculated ratios for the fully treated effluents are as follows:

		DP/NPAC	DP/PAC	NDP/NPAC	NDP/PAC
Daphnia acute	LC_{50}/EEC	>153	>153	36-114	87-93
Algal growth	EC_{50}/EEC	>153	85	85	85
Fathead minnow	LC_{50}/EEC	-	-	93	>153
Daphnia chronic	MATC/EEC	2.75	27.3	3.5	20.6

Comparing the above ratios with the criteria in Figure 18 shows that all dephenolated wastewaters surpass the criterion for the 48-hr *Daphnia* test, which calls for LC_{50}/EEC to be at least 100. In contrast, the nondephenolated wastewaters did not fare as well. For the NDP/NPAC final effluent (ozonated), the LC_{50}/EEC would be 36, far below the criterion of 100. The nonozonated effluent has an LC_{50}/EEC ratio of 114, barely above 100. Even PAC did not improve the ratio much; the NDP/PAC has a ratio of 93, still below 100. Based on the preliminary procedure, all the nondephenolated wastewaters, with or without PAC, could not be discharged until further treatment.

As for the algal growth inhibition, all samples have an EC_{50}/EEC ratio higher than the criterion of 50. Therefore, none of the samples would have a significantly adverse impact on algal growth.

Of the two nondephenolated wastewaters tested for fathead minnow mortality, the NDP/PAC meets the LC_{50}/EEC criterion of 100, the lower limit. However, there were sufficient data available to determine if the ratio was greater than 1,000, the upper limit indicating suitability for discharge. The NDP/NPAC wastewater failed to meet even the lower limit. There were no tests performed for the dephenolated wastewater due to insufficient sample availability. Therefore, direct comparison of LC_{50}/EEC for those samples with the criterion is not possible. However, the DP wastewaters are expected to meet the criterion as well because fathead minnows generally tend to be less sensitive in acute assays than are daphnids, and the results of the 48-hr Daphnia acute studies have shown that the DP wastewaters were better than the NDP wastewaters.

All of the samples tested for Daphnia chronic effects had an MATC/EEC ratio falling between 2 and 50. Therefore, the assessment has not led to the conclusion that the wastewaters are safe to discharge. Nor does it indicate that the wastewater is too toxic to discharge. More tests need to be conducted to demonstrate that the wastewater would not cause significant chronic adverse effects on aquatic life.

c. Limitations of the Data. The aquatic ecotoxicity studies conducted thus far have many obvious limitations. First, the volume of wastewater samples available precluded a sufficient number of replica. Second, only a few species of aquatic organisms were tested. Third, the representativeness of the samples is debatable; the samples were produced from Ft. Lewis process recycle water, and treated under controlled conditions in the laboratory.

However, despite those limitations, the data do provide some information on aquatic ecotoxicity of the treated coal-liquefaction wastewaters. Little such information existed at the time the study was initiated. The data are useful for hazard assessment; certain conclusions can be made as long as the limitations are understood.

d. Preliminary Conclusions Regarding Hazard Assessment. Based on the analyses conducted thus far, the following preliminary conclusions can be made:

- Phenol extraction reduces the toxicity of SRC-I wastewater to aquatic life.
- With phenol extraction, the fully treated wastewaters meet the criteria for both 48-hr Daphnia acute studies and 14-day algal growth inhibition assays. Without phenol extraction, the treated wastewaters meet the criteria, but only marginally.
- With phenol extraction, the fully treated wastewaters appear to be safe enough for discharge; however, the data are insufficient to conclusively prove that the wastewater is totally suitable for discharge.

- More 28-day *Daphnia* chronic tests should be performed to increase the confidence level of the results.
- More definitive tests, such as 30-day fathead minnow early-life-stage tests and 21-day midget life cycle tests, are needed.

4. Microbial Mutagenicity[26]

ICRC has conducted a comprehensive toxicology testing program for all of its products, intermediates, and waste materials, including wastewaters. The wastewater samples tested are shown in Figures 16 and 17.

Standard Ames *Salmonella*/microsome *in vitro* mutagenicity assays were run using five strains of *Salmonella typhimurium*: TA 1535, TA 1537, TA 2538, TA 98, and TA 100. All assays were performed in the presence and absence of a rat-liver induced metabolic activation (MA) system. The results are as follows:

System	Sample no.	Description	Test results (-MA)	Test results (+MA)
NDP	7487	Raw wastewater	-	+
DP	7495	Extracted raw wastewater	-	+
NDP/PAC	7489	Coagulated bioeffluent	-	-
	7491	Final effluent	-	-
DP/NPAC	7497	Coagulated bioeffluent	-	-
	7498	Final effluent	-	-

Steam-stripped raw wastewaters, both dephenolated and nondephenolated, are mutagenic and show metabolic activation. Phenol recovery did not eliminate the mutagenicity. However, the mutagenicity of all wastewaters disappears after biological treatment, coagulation, and filtration. None of the fully treated effluents were mutagenic.

5. Summary of Impact Analysis

In summary, the information available thus far leads to five conclusions regarding the plant's effluent and its impact upon discharge:

- The recommended wastewater treatment system produced an effluent quality that can meet the effluent concentrations published in the FEIS as well as effluent limits estimated from related industries such as petroleum refining.
- Discharging the treated effluent into the Green River will not have any significant adverse impact on the river water quality in terms of water-quality standards and criteria.
- Priority pollutants, inorganic and organic, can be controlled effectively by the recommended wastewater treatment system.
- Preliminary aquatic ecotoxicity studies, although not conclusive, suggest that the SRC-I wastewater, after full treatment including phenol recovery, is not too toxic to discharge. However, more tests are needed to demonstrate conclusively that the effluent is safe to discharge.
- The treated wastewater is not mutagenic based on the Ames test.

VI. ZERO-DISCHARGE EVALUATION

A. INTRODUCTION

In the Final Environmental Impact Statement (FEIS) published in 1981, DOE endorsed the concept of "zero discharge of wastewater" from the SRC-I Demonstration Plant. The zero-discharge concept was adopted for several reasons. First, wastewater treatability data for coal liquefaction were scanty and little information was available to demonstrate that the treated wastewater was safe to discharge. Second, the regulatory climate at that time favored zero discharge. EPA had proposed zero discharge for petroleum refining operations that generated wastewaters similar to those from SRC-I. Third, DOE had adopted zero discharge for other coal liqeufaction projects contemplated at that time, including the SRC-II Demonstration Plant in West Virginia and all plants in Kentucky, including the H-Coal Project.

However, since completion of the FEIS and Baseline Design, EPA has reversed its position on zero discharge. The current EPA effluent limitations and guidelines for petroleum refining have deleted the zero-discharge requirement.[19] Because of EPA's reversal, one post-Baseline task was to reexamine the regulatory climate with respect to zero discharge.

Parallel to that effort, technical and economic aspects of the Baseline Design zero-discharge concept underwent rigorous reviews. The Baseline Design completed in 1982 incorporated the complete zero-discharge concept published in the FEIS, a description of which was presented in Section I of this report. As mentioned previously, because of the ambitious design and construction schedule at that time, the Baseline Design was prepared without substantial R&D backup. In fact, the design of the zero-discharge section was based primarily on suppositions and published information, and, as a result, had many areas of uncertainty. Addressing these uncertainties was a major post-Baseline goal.

One problem was the lack of a good design basis. The effluent from the wastewater treatment system is the feed to the zero-discharge system. However, material balances for the wastewater treatment system, which adds and removes many constituents affecting the zero discharge units, were not available. Consequently, since characteristics of the feed for the zero-discharge system were never adequately defined, performing material balances for the wastewater treatment system became a post-Baseline task.

Another task was to review alternative conceptual zero-discharge schemes. With a firmer design basis, several alternatives were reexamined to see whether the scheme adopted in the Baseline Design was indeed the best. The reevaluation, which will be discussed later in this report, did confirm that the Baseline Design scheme appeared to be most workable conceptually for SRC-I.

After the Baseline Design selection was confirmed, the next step was to perform an in-depth evaluation of the unit processes involved in the scheme. The unit processes evaluated were reverse osmosis (RO), evaporation, solid waste stabilization, and evaporative cooling.

Reverse osmosis is a membrane process that is prone to fouling and scaling. Hence, successful RO operation requires extensive pretreatment of the feed water to remove potential scalents and foulants. The entire wastewater treatment system can be viewed as RO pretreatment. Experimental work was performed during the post-Baseline period to determine whether or not the wastewater treatment system provided adequate pretreatment. Effects of phenol recovery on the characteristics of the RO feed were also assessed, and several RO membranes were tested to determine whether fouling and scaling occurred.

Evaporator studies were also conducted during the post-Baseline period. The first study was conducted by ICRC to select the type of evaporator, taking into consideration the reliability of the steam supply. The second study involved an evaporator vendor, who conducted an evaluation based on the brine characteristics provided by ICRC.

Also, the Baseline method of disposing of the concentrated slurry generated from the evaporator by stabilization was unproven, and required experimental confirmation. In addition, experimental data were needed to generate a firm design basis. Several stabilization systems were evaluated during the post-Baseline period.

Because the evaporative cooling system is an integral part of the zero-discharge system, the evaluation would have been incomplete without addressing the impact of using RO permeate as the makeup water. Thus, addressing this issue was another post-Baseline task.

Finally, in addition to directly addressing the technical uncertainties of zero discharge, its actual need had to be reassessed in light of more current effluent data. As discussed previously, one reason for adopting zero discharge in the FEIS was the lack of data demonstrating that the treated wastewater was safe to discharge. Because much more information on the treated wastewater was available, the need for zero discharge had to be reassessed.

In summary, the post-Baseline evaluation of zero discharge of wastewater entailed the following tasks:

1. Reassess regulations affecting zero discharge.
2. Prepare material balances to provide a better basis for zero-discharge evaluation.
3. Evaluate conceptually different alternative zero-discharge schemes.
4. Generate as much experimental data as possible for unit processes of the best scheme, to minimize technical uncertainties for the scheme chosen.
5. Assess whether treated effluent would be suitable for discharge, negating the need for a zero-discharge system.

B. REGULATORY ENVIRONMENT

When the SRC-I FEIS was prepared, no proposed or final EPA effluent limitation guidelines or standards for coal liquefaction existed. Yet the National Environmental Policy Act (NEPA), which mandates the publication of an FEIS, stipulates that all federal actions having potential environmental impacts must not only meet all existing environmental regulations, but also comply with any anticipated regulatory requirements.

Because petroleum refining produces wastewaters similar to those from SRC-I, proposed effluent limitations, guidelines, and standards[27] for that industry were used to extrapolate requirements for the SRC-I Demonstration Plant. In the proposed regulations for petroleum-refining point sources, EPA maintained that zero discharge was a demonstrated technology for that industry and, based on available data, was economically achievable. Zero discharge was therefore proposed in the New Source Performance Standards (NSPS) for the petroleum refinery point sources category, and formed the basis for the SRC-I wastewater treatment/reuse concept in the FEIS.

The wastewater treatment system by which the EPA proposed to accomplish zero discharge consisted of the treatment processes considered as best practicable control technology currently available (BPT), followed by tertiary treatment and water reuse. BPT was defined as in-plant wastewater treatment of ammonia/sulfide waters by steam stripping, pretreatment before biological treatment, consisting of oil/emulsion breaking and oil removal, followed by some form of secondary biological treatment system and a final polishing step such as filtration. The additional tertiary treatment steps were defined as some form of refractory/toxic organic adsorption treatment such as powdered activated carbon (PAC) enhancement of biological treatment or granular activated carbon (GAC) treatment after BPT, and heavy metals removal by pH adjustment, precipitation, and clarification. All of these unit operations were proposed in the FEIS and incorporated in the Baseline Design.

The final EPA NSPS for the petroleum refinery point-source category[19] were promulgated (October 1982) after the FEIS had been published (July 1981) and the Baseline Design was completed (April 1982). The final NSPS did not require zero discharge, but reverted to their former (1976) values, which were more stringent than BPT.

Upon reevaluation of the existing data base and evaluation of comments received on the proposed regulation, the EPA decided to reject zero discharge for the following reasons:

a. Although it could eliminate impacts on water quality, zero discharge causes significant adverse environmental impacts elsewhere, including the production of large amounts of solid waste and high energy consumption.

b. The annual costs of achieving zero discharge are extremely high, especially in geographical areas of low evapotranspiration, which requires energy-intensive forced evaporation techniques. The EPA estimated the cost (based on 1979 dollars) for compliance with zero discharge at 8-1/2¢ per barrel of crude processed for a 150,000 bbl/stream day new source refinery in the cracking subcategory.

c. Only marginal additional water pollution reduction benefits would be achieved beyond the existing NSPS requirements, and the high costs of implementing such requirements would raise serious barriers to any decision to construct a new source refinery.

In summary, the regulatory constraint that was assumed to apply to the Baseline Design has significantly changed since the FEIS was published. Although the regulations for the petroleum refining industry are not entirely applicable to coal liquefaction, there is a strong resemblance between the two industries. However, coal liquefaction produces products and process intermediates that are more hazardous than those from petroleum refining. The fact that zero discharge is no longer required for petroleum refineries is not enough justification for effluent discharge from the SRC-I Demonstration Plant. A more valid justification would be demonstrating that the treated wastewater is acceptable for discharge.

C. OVERALL PLANT WATER BALANCE

The water balance depends on many factors, two of which have the greatest impact: the mode of operation for the wastewater treatment/reuse facility, i.e., discharge or zero discharge, and weather conditions. Figures 19 through 22 show water balances for different cases.

Figures 19 and 20 present the balances for the discharge mode, under dry and wet weather conditions, respectively. The balances for the wet weather conditions are based on a 25-year, 24-hr storm with a precipitation of 5.4 in.; the runoff is collected and equalized for treatment over a 2-week time period. The main differences between Figures 19 and 20, of course, stem from the runoffs. The equalized runoff during wet weather conditions add 777 (i.e., the sum of 230 and 547) gpm to the SRC-I Demonstration Plant. Also, during dry weather, there is a loss of 150 gpm at the coal and solid SRC storage areas as water is used for dust control. The net effect is that the plant effluent under dry weather conditions is 1,159 gpm, which is only 56% of the wet weather flow.

Figures 21 and 22 show water balances for the zero-discharge case; the former is for dry weather conditions, and the latter, wet weather. The river water withdrawal rate under dry weather conditions is 3,162 gpm; under wet weather conditions it is 2,317 gpm. The difference is made up by the storm water. Both are considerably lower than the withdrawal rate of 4,176 gpm in the discharge case. Thus, zero discharge reduces the withdrawal rate by about 1,000-2,000 gpm, depending on weather conditions.

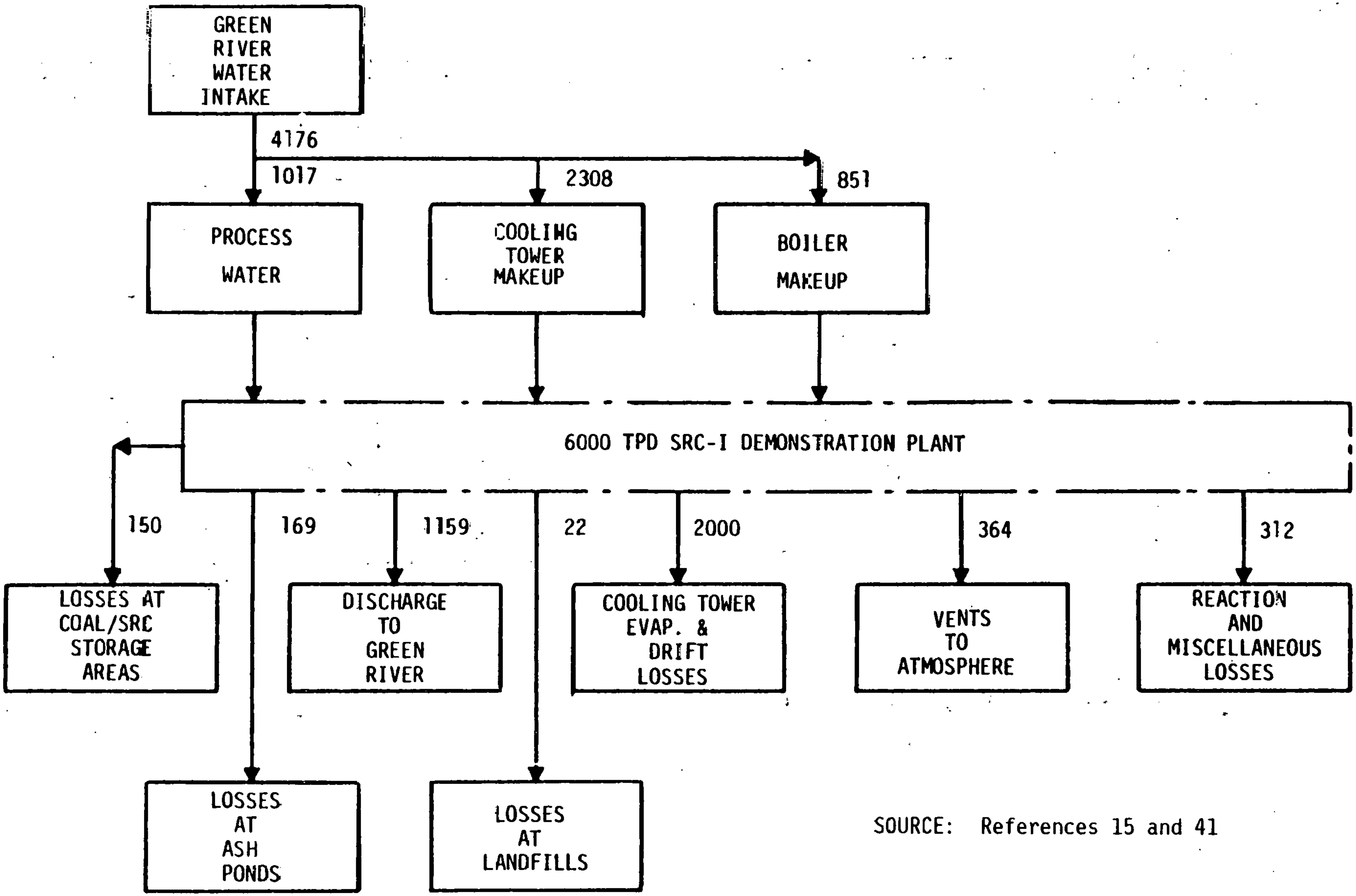
D. MASS FLOW RATES OF MAJOR INORGANICS

Major inorganic constituents that would affect zero discharge are sodium, calcium, chloride, and sulfate. These species also represent the bulk of the total dissolved solids (TDS) in the treated wastewater. In addition to the major species, there are many minor inorganics that are also significant to zero discharge, but their concentrations are much lower. Therefore, their mass flow rates are not presented here.

Some of the major inorganics originate in the raw coal, chloride being the single most significant species. The chloride balance is shown in Figure 23. Kentucky #9 coal has a high chlorine content compared to most coals. About 1,000 lb/hr of chlorine enters the SRC-I Demonstration Plant, 650 lb/hr of which ends up in the wastewater treatment/reuse system via sour water (180 lb/hr), and GKT washwater blowdown

Figure 19

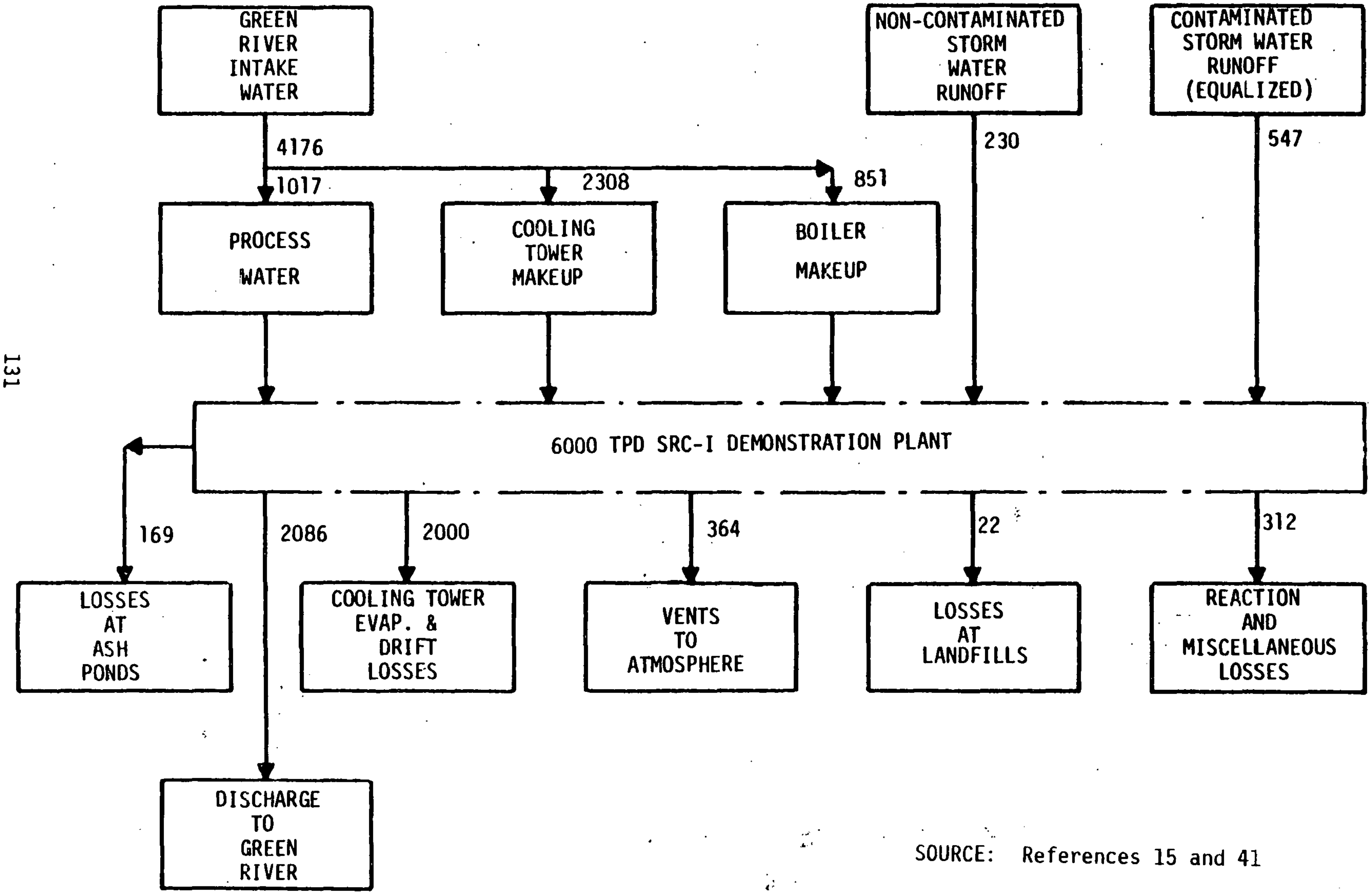
Discharge-Case Dry-Weather Water Balance (gpm)



SOURCE: References 15 and 41

Figure 20

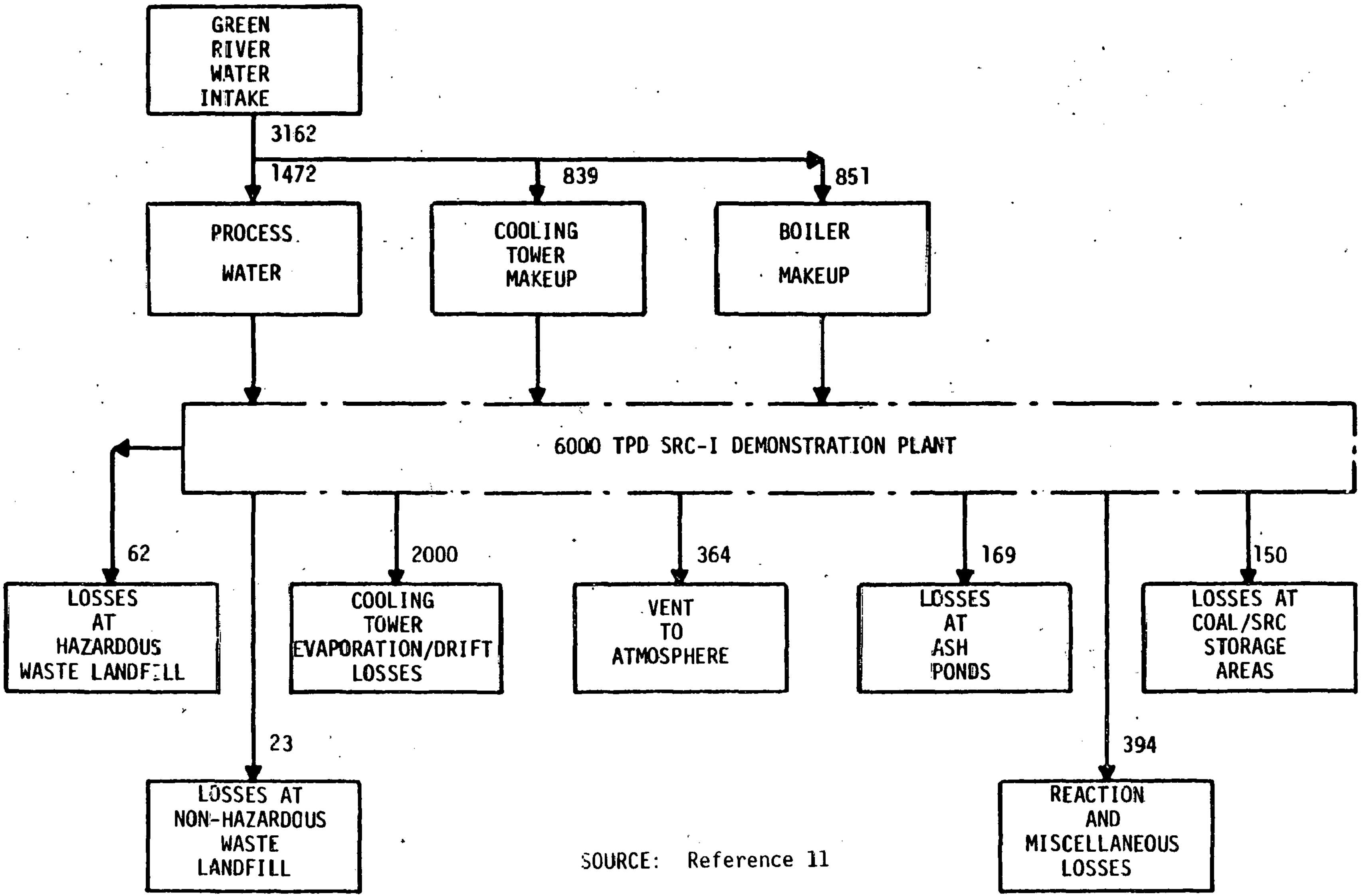
Discharge-Case Wet-Weather Water Balance (gpm)



SOURCE: References 15 and 41

Figure 21

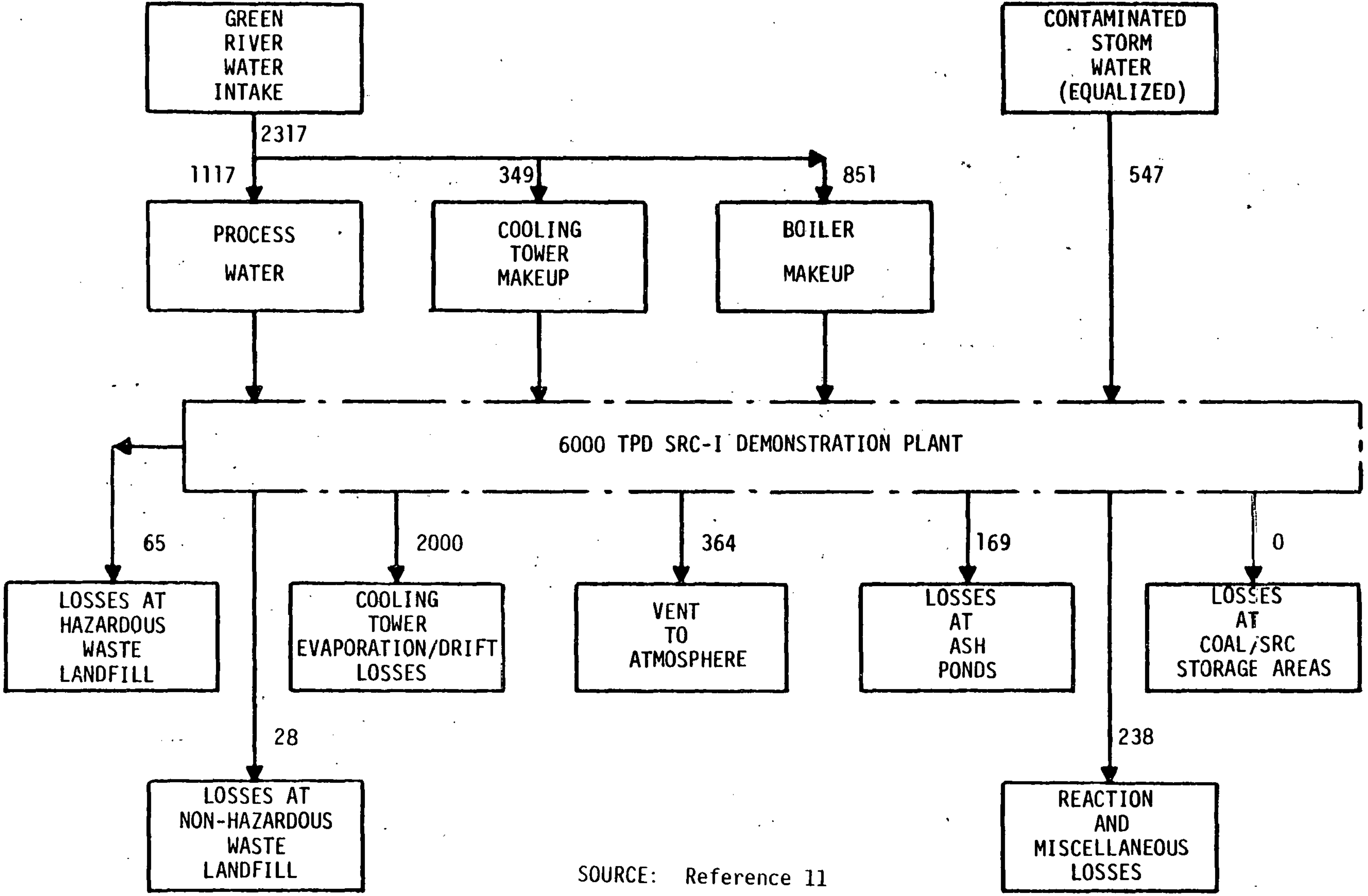
Zero-Discharge Case Dry-Weather Water Balance (gpm)



SOURCE: Reference 11

Figure 22

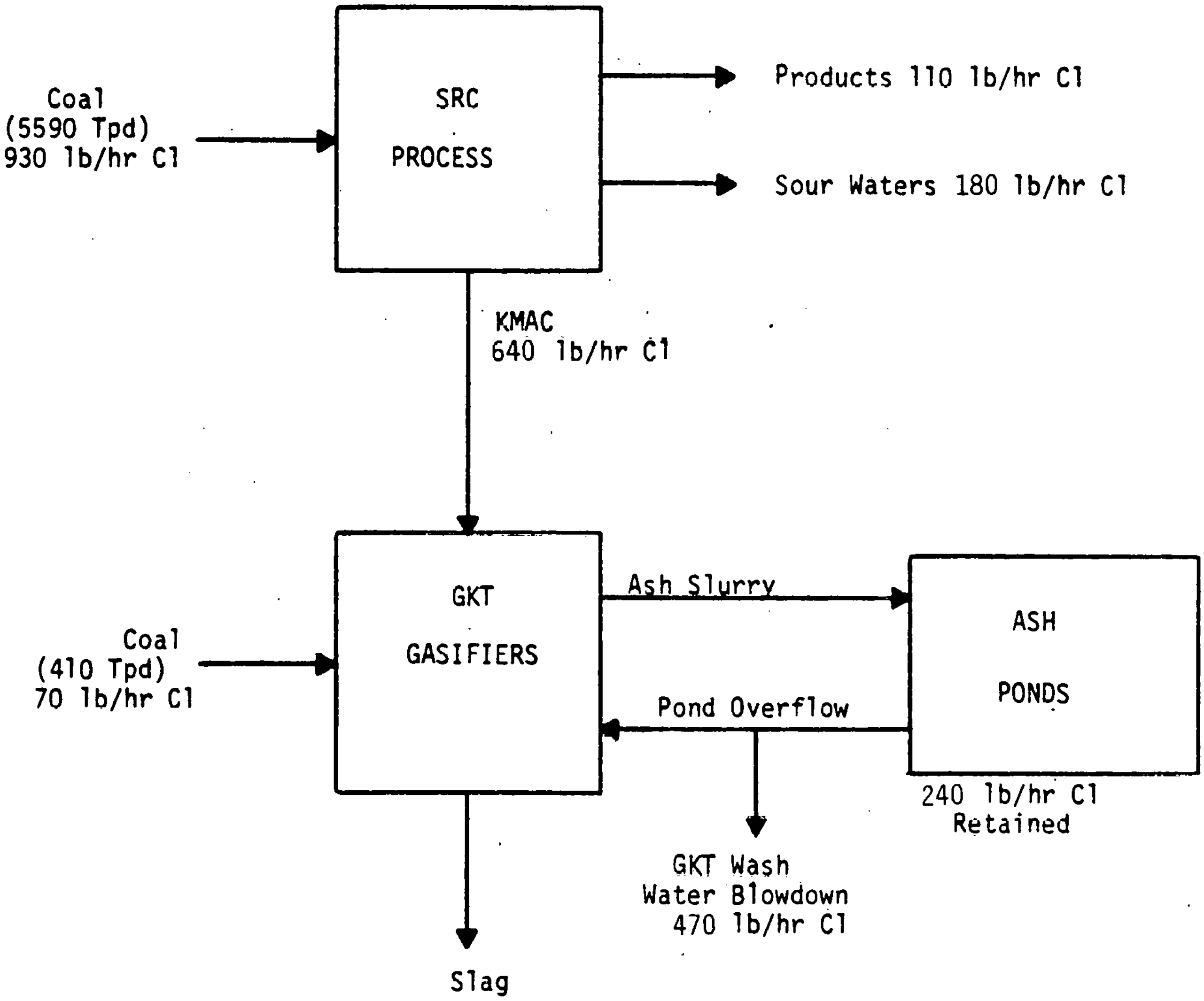
Zero-Discharge Case Wet-Weather Water Balance (gpm)



SOURCE: Reference 11

Figure 23

Chloride Balance for SRC-I Demonstration Plant



(480 lb/hr). Of the remaining chloride, 240 lb/hr is retained with the ash in the ash ponds, and only 110 lb/hr is in the products. More information on the fate of chlorides is available elsewhere.[28-30]

Beside adding TDS to the wastewater, the chlorides also have repercussions on wastewater treatment as well. The 180 lb/hr of chlorine in the sour-water streams is in the form of chloride. The anionic chlorides (Cl^-) associate with cationic ammonium (NH_4^+) to maintain the electroneutrality, which makes the ammonium unstrippable. To strip the ammonium, lime (or caustic) is added at the ASWS. Consequently, more TDS is introduced into the wastewater.

Some inorganics are introduced through corrosion control. For example, in the gasifier, chlorine in the Kerr-McGee ash concentrate (KMAC), a feedstock, is volatilized, and hydrochloric acid is formed. The hydrochloric acid eventually dissolves in the washwater during scrubbing of the syngas. Because hydrochloric acid is corrosive, caustic (NaOH) is added to control corrosion. As a result, the GKT washwater blowdown will contain a large quantity of NaCl. Similarly, caustic is introduced in fuel gas cleanup to scrub the HCl. That, too, increases TDS in the wastewater.

Other organics are added throughout the water and wastewater treatments. Boiler feedwater treatment entails demineralization by ion exchange. The ion exchange resins require regeneration with sulfuric acid and caustic. The spent regenerants are discarded into the wastewater treatment system, and inorganic salts are introduced. Sulfuric acid is used in the cooling system to control pH, and the cooling tower blowdown will contain sulfate salts. Also, sulfuric acid and lime are used throughout the wastewater treatment train for such purposes as pH control, metal removal, and coagulation, and they will affect the species and amount of inorganics in the wastewater.

There are also other miscellaneous inorganic sources. Coal-pile runoff will be contaminated by inorganics such as iron sulfate. Some of the inorganics can be removed by wastewater treatment. Those that are not removed will be present in the feed to the zero-discharge system.

The amounts of inorganics in the zero-discharge feed will be highly variable, depending on such factors as composition variations in the feed coal, coal-pile runoff, and wastewater treatment chemical types and dosage. Therefore, multiple cases of material balances have been made using the ASPEN computer program. However, for simplicity, only the maximum case is presented (see Figure 24 and Table 28 for mass flow rates of individual streams). The material balance is limited to the wastewater treatment section for now to show the TDS in the feed to the zero discharge. The material balance for the zero-discharge section, which will depend on the alternative scheme chosen, will be presented later.

Several clarifications and assumptions for Figure 24 and Table 28 should be noted. First, for brevity, Figure 24 does not show many intermediate blocks that have no effect on material balance. Second, the chloride mass-flow rate in the ASWS bottoms (Stream No. 1) shown in Table 28 is 912 lb/hr, which is higher than the 180 lb/hr discussed previously. The 912 lb/hr is the value used in the Baseline Design material balances for the SRC-processing area. This value is approximately equal to the mass-flow rate of chlorine in the feed coal entering the SRC-I Demonstration Plant. Because reliable data were unavailable, the Baseline Design conservatively assumed that nearly all of the chloride in the coal is present in the sour waters. Hence, for the sake of consistency with the Baseline Design documents, the conservative value is used for most of the material flows in Table 28. However, for comparison, values based on the more realistic chlorine flow rates are also shown (in parentheses) for the ASWS bottoms and the feed to the zero-discharge section. Third, the mass-flow rate of the inorganic species in the cooling tower blowdown is a function of the composition of the makeup water, which in turn depends on the zero-discharge scheme used. The selection of the zero-discharge scheme will be discussed in Section E of this Chapter. Table 28 is based on the scheme adopted in the Baseline Design. On that basis, the cooling tower blowdown, and hence the material balance is controlled by the TDS level in the recirculating cooling water, and the cycles of concentration are limited to 6. Another assumption is that the chemicals needed for pH control before the bioreactors are negligible. Finally, Table 28 is an order-of-magnitude presentation of the inorganic mass flow rate. A more precise analysis cannot be made until detailed engineering.

Figure 24

Mass Flow Rates of Major Inorganics in Wastewater Treatment System

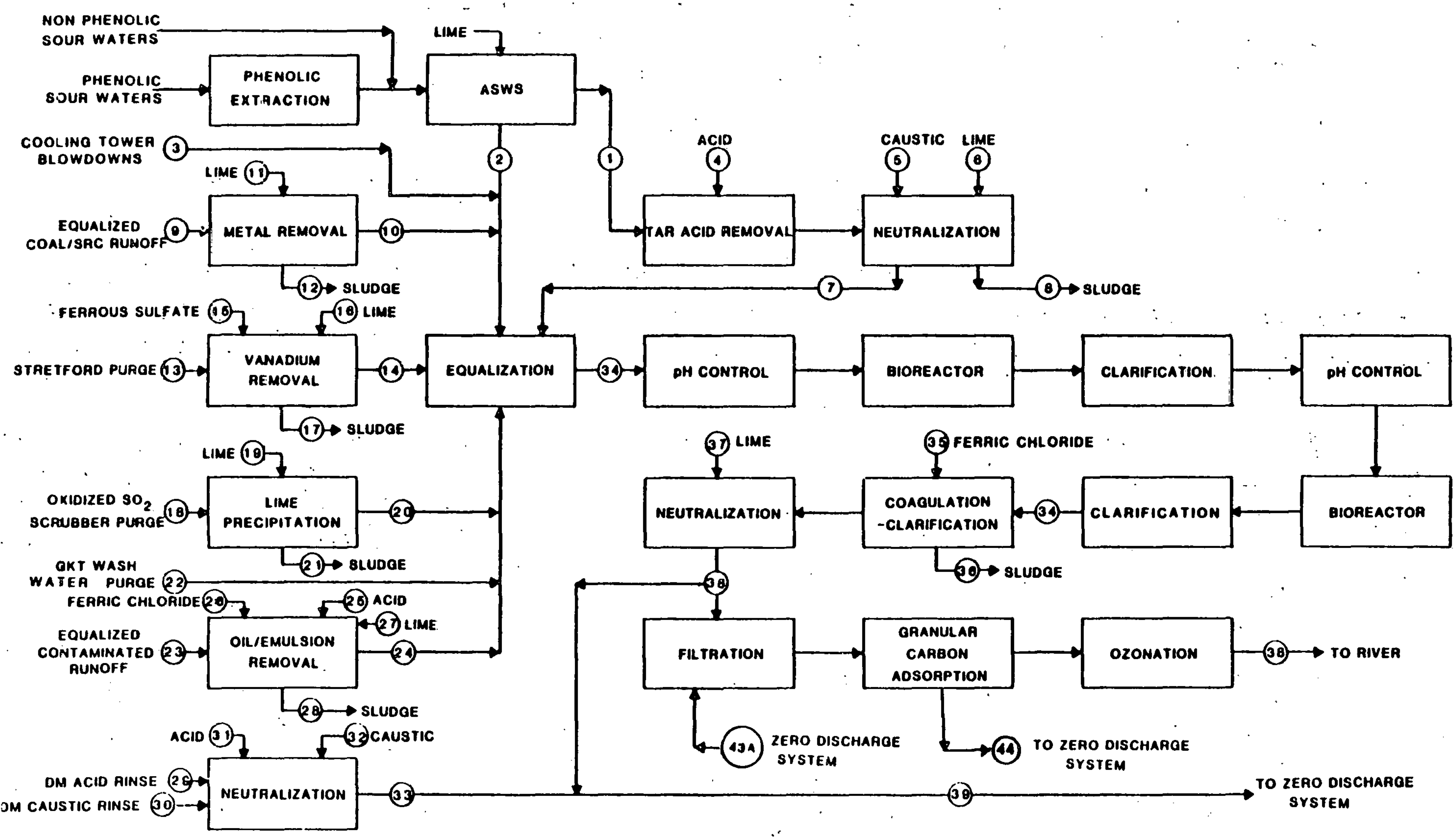


Table 28

Mass Flow Rates of Major Inorganics (lb/hr)

Stream no. and name	Sodium	Calcium	Iron	Chloride	Sulfate
1. ASWS bottoms		686 (101)[a]		912 (180)[a]	
2. ASWS sludge		51		23	
3. Cooling tower blowdowns	10	7		15	83
4. Sulfuric acid					887
5. Caustic	115				
6. Lime		107			
7. Pretreated ASWS bottoms	115	526		912	246
8. Sludge		267			641
9. Coal/SRC pile runoff (equalized)	2	1	544	4	1,386
10. Metal clarifier overflow	2	154		4	210
11. Lime		643			
12. Metal sludge		490	544		1,176
13. Stretford purge	31				63
14. V-Clarifier overflow	31	1			64
15. Ferrous sulfate		4.9			8.4
16. Lime		4.4			
17. V-Sludge		3.4			8.4
18. Oxidized SO_2 scrubber purge	206				534
19. Lime	264				
20. Sulfate clarifier overflow	45				7
21. Sulfate sludge	425				527
22. GKT washwater purge	305			470	
23. Equalized contaminated runoff					
24. Oil removal effluent		49		15	163
25. Sulfuric acid					235
26. Ferric chloride			8	15	
27. Lime		79			
28. Oily sludge		30	8		72
29. DM acid rinse					206
30. DM caustic rinse	144				
31. Sulfuric acid					27
32. Caustic	17				
33. Neutralized DM rinse water	23				55
34. Bioreactor feed	494	872		1,439	774
35. Ferric chloride			165	322	
36. Coagulation sludge		0	165		0
37. Lime		193			
38. Feed to GAC	494	1,065		1,761	774
39. Feed to ZD	517	1,065 (617)[a]		1,761 (1,029)[a]	829 (1,158)[a]

[a] Based on more realistic chloride values.

Based on Table 28, the calculated TDS in the feed to the zero-discharge system, taking into account only sodium, calcium, chloride, and sulfate, is 4,172 lb/hr. For the wet-weather flow of 2,086 gpm (see Figure 20), the TDS concentration is about 4,000 mg/L. Based on the more realistic calcium and chloride numbers, the mass-flow rate of TDS reduces to 3,321 lb/hr, and the TDS concentration becomes about 3,200 mg/L.

E. COMPARISON OF ALTERNATIVE ZERO-DISCHARGE SCHEMES

Evaporative cooling is the vehicle by which the SRC-I Demonstration Plant achieves zero liquid effluent discharge. One main objective of the zero-discharge system is to polish the effluent from the wastewater treatment section by removing inorganics so that it can be used as the makeup to the cooling system.

As the previous water balance shows, the cooling system consumes about 2,000 gpm of water. In the zero-discharge mode, all of the treated wastewater is consumed by the cooling system. Smooth operation of the cooling system is strongly dependent on the quality of the treated wastewater. In terms of organics, the treated wastewater is of high quality, because the treatment system is designed primarily to remove organics. However, the cooling system is also sensitive to inorganic constituents in the makeup water; as the material flows show, the treated wastewater contains high concentrations of inorganics, which are measured as total dissolved solids (TDS). A high TDS concentration in the cooling water can increase galvanic corrosion and/or scaling of the cooling system depending on the constituents. The wastewater treatment system is not designed to remove inorganics, which are normally quite innocuous. However, to use the treated wastewater as cooling water makeup, the inorganics must be reduced.

There are many ways to reduce the inorganics. Numerous alternative schemes were devised, and, after preliminary screening, five were evaluated in some detail, including the Baseline Design scheme. The objective of the comparison was to ensure that the Baseline Design was still the most attractive alternative in light of the information that became available after its completion. Figure 25 illustrates the five schemes.

Before the five schemes are described and compared, several critical assumptions made for the comparison should be noted. The first assumption is that the cooling tower blowdown and the composition are controlled by TDS. The second assumption is that the maximum allowable TDS in the recirculating cooling water is 6,000 mg/L. The limits reported in the literature varied considerably, ranging from 2,000 mg/L[31] to more than 60,000 mg/L,[32] with most reported values being in the lower end of the range. One reason for the disparity may be attributable to different metallurgies and various combinations of constituents making up the TDS. Because the cooling system in the SRC-I Demonstration Plant employs mostly carbon steel, which is not as corrosion-resistant as other alloys, the TDS limit will be on the lower end of the range. The limit chosen for this analysis was 6,000 mg/L. A question exists as to whether a study was made of the cost-effectiveness of using more corrosion-resistant alloys to allow usage of a higher TDS.

1. Scheme 1

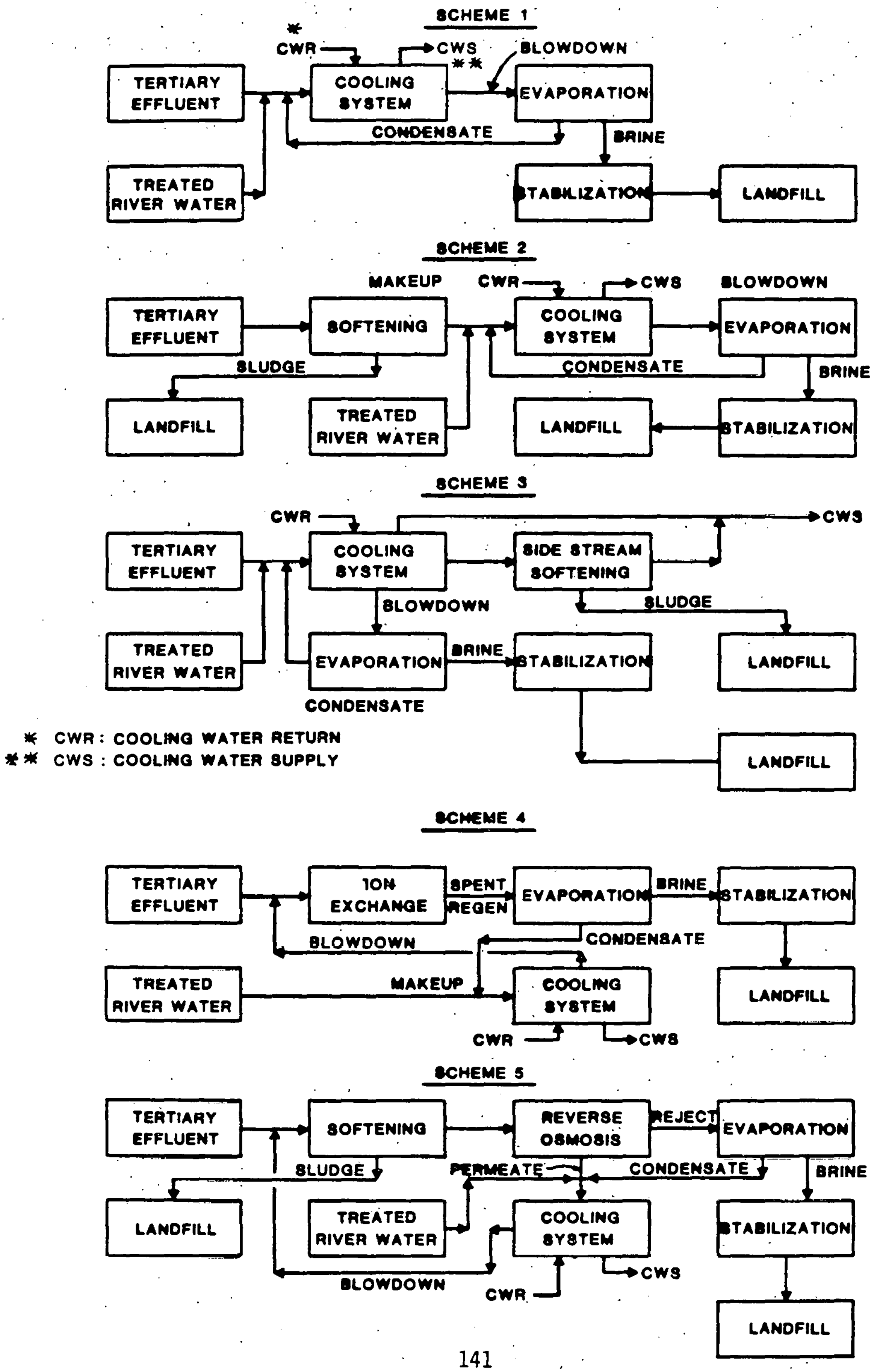
In this system, treated wastewater is used as makeup to the cooling tower without further treatment. The TDS level in the cooling system is controlled entirely by adjusting the blowdown rate. The blowdown is sent to the evaporator, which concentrates it, and the condensate is then recycled to the cooling system as makeup. The brine from the evaporator is stabilized and then landfilled.

To maintain the TDS in the recirculating water at 6,000 mg/L, the blowdown rate must be as high as 1,700 gpm, which represents two cycles of concentration. In fact, the blowdown rate will have to be higher if the potential for calcium sulfate scaling is also considered. The calcium concentration in the treated wastewater is 450 mg/L, and the sulfate concentration is 2,000 mg/L. Both are very high.

A high blowdown rate necessitates a large evaporator and consumes a large amount of energy. To evaporate a blowdown of 1,700 gpm, for example, the capital cost of the evaporator is approximately $8 million, and the operating costs, primarily for electricity, would total $6.6 million per annum. Therefore, this scheme was dismissed.

Figure 25

Alternative Zero Discharge Schemes



2. Scheme 2

To control the calcium sulfate scaling problem in Scheme 1, Scheme 2 includes a step to soften the treated wastewater before it is used as makeup to the cooling system. As in Scheme 1, the blowdown is concentrated in the evaporator, and the condensate is returned to the cooling system. Likewise, the brine from the evaporator is stabilized and then landfilled.

Laboratory data[7] show that softening can reduce calcium to 2 mg/L. Because most of the calcium in the treated wastewater is associated with sulfate and chloride rather than bicarbonate or carbonate, soda ash has to be added to precipitate the calcium. As much as 5,400 mg/L of the soda ash was needed.

Although softening solves the calcium sulfate scaling problem, it creates another problem. Adding soda ash increases TDS; the sodium alone increases the TDS by more than 2,300 mg/L. Furthermore, acid needed to lower the high pH due to softening adds even more. Therefore, the softening exacerbates the high TDS problem.

Even if the TDS limit were set as high as 25,000 mg/L instead of 6,000 mg/L, the blowdown would be almost 800 gpm. Thus, Scheme 2 is no better than Scheme 1, and perhaps worse.

3. Scheme 3

Like Scheme 2, Scheme 3 also has a softening step, but instead of softening the makeup water, Scheme 3 softens a side stream of the recirculating cooling water. Generally, the side-stream approach can be effective because it allows a more concentrated stream to be treated. However, because the SRC-I wastewater has such a high TDS level to begin with, very little further concentration can be tolerated. Therefore, this scheme is very similar to Scheme 2 in regard to flow rates through the softening step, blowdown rates, and TDS concentrations. It was also rejected.

4. Scheme 4

This system employs ion exchange to remove hardness and also TDS. The product water from ion exchange is used as the cooling system makeup, and the spent regenerant is concentrated in the evaporator.

Theoretically, the product of the ion exchange unit should have low TDS, calcium, and other inorganic impurities, and theoretically, the spent regenerants should be much smaller in volume than the cooling blowdown under Scheme 1, 2, or 3. However, the extremely high TDS concentration in the treated SRC-I wastewater alone renders ion exchange uneconomical. The high TDS loading would necessitate more than thirty 12-ft-diameter ion-exchange columns, making the capital cost prohibitive. Furthermore, regeneration of the ion exchange columns requires 300,000 lb/day of acid, and 500,000 lb/day of caustic. The chemical cost alone is $16 million annually. Scheme 4 is, therefore, not an attractive alternative for the SRC-I Demonstration Plant.

5. Scheme 5

Scheme 5 employs reverse osmosis (RO) for TDS control. The treated wastewater is first softened and sent to RO, and the RO reject is evaporated. As with ion exchange, the reverse osmosis unit would provide a high-quality water for cooling tower feed which allows a relatively low rate of blowdown (approximately 250 gpm) while still maintaining TDS in the 6,000-mg/L range. The blowdown from the cooling tower is recycled to the softening step, to prevent calcium scaling of the RO membranes.

Of the five compared, Scheme 5 appeared to be the most attractive, because, if RO works, it would provide an economical way to prevent scaling and corrosion in the cooling system. Scheme 5 would not introduce large quantities of chemicals for regeneration as Scheme 4 would. Scheme 5 also would reduce the blowdown rate and, hence, the size of the evaporator. Also, the energy for evaporation should be reduced.

Scheme 5 is similar to the zero-discharge scheme of the Baseline Design, the main difference being the lack of softening in the Baseline. Because the wastewater contains high concentrations of calcium (500 to 1,000 mg/L), softening has been added to protect the reverse osmosis membranes. This does have the disadvantage of raising the dissolved solids concentration. However, the overall system reliability is greatly increased, which is a more important consideration. Softening alone, however, does not guarantee problem-free operation of the RO process, as will be discussed in a subsequent section.

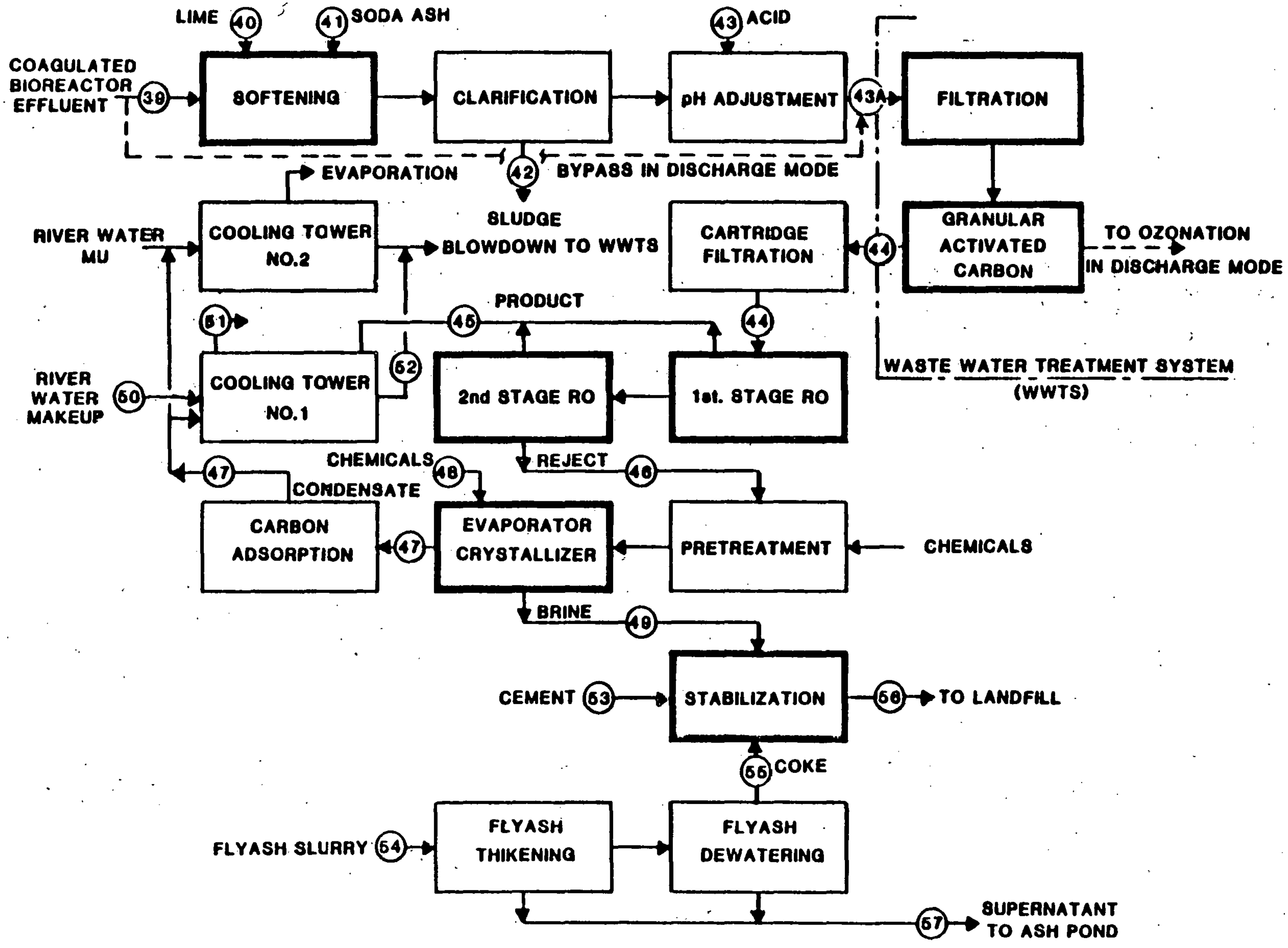
F. PROCESS DESCRIPTION OF THE SELECTED ZERO-DISCHARGE SCHEME

Figure 26 is a more detailed diagram of Scheme 5. The ferric chloride coagulated bioreactor effluent is softened with lime/soda ash to remove calcium. After pH adjustment, the softened effluent returns to filtration and granular activated carbon adsorption, which are in the wastewater treatment section, for further treatment. The carbon adsorption effluent is then subjected to a cartridge filter before entering the RO unit. RO consists of two stages; the product waters from each stage are combined and sent to the cooling tower. The reject from the first stage becomes the feed to the second stage. The reject from the second stage, which is still relatively diluted, is sent to the evaporator/crystallizer for further concentration to reduce the volume for final disposal. But before that, more pretreatment is required. The pretreatment includes hydrogen peroxide oxidation to ensure that all reduced sulfur species, such as sulfite and bisulfite, are virtually eliminated. If not removed, the reduced sulfur compounds will decompose in the evaporator steam to yield SO_2, which is corrosive. Another pretreatment needed would be carbonate removal. The residual bicarbonate and carbonate that can cause scaling in the evaporator are removed by acidification, followed by CO_2 stripping in a decarbonator. Decarbonation also removes oxygen, which causes corrosion. The pretreatment step would also include additional clarification, filtration, and pH adjustment. Most of the water entering the evaporator/crystallizer becomes condensate, which can be used as makeup to the cooling towers. The blowdown from the cooling towers can be sent either to the equalization step upstream of the bioreactor or the softening step. The concentrated brine from the evaporator/crystallizer is stabilized with fly ash, which comes from the GKT gasification area, and a cement. Before it is used as an additive for stabilization, the fly ash has to be thickened and dewatered. After stabilization, the solid waste is disposed of in the landfill.

Because of the limited funds, time, and samples available, the post-Baseline studies were primarily limited to the following areas:

Figure 26

Detailed Block Diagram of the Selected Zero Discharge System



- Softening
- Filtration
- Granular carbon adsorption
- Reverse osmosis (RO)
- Evaporation/crystallization
- Stabilization

Softening, filtration, and granular activated carbon (GAC) adsorption can be considered pretreatment steps for the RO feed water. Filtration and carbon adsorption are also a part of wastewater treatment steps when the plant is operated in the discharge mode. Pretreatment is extremely essential to successful operation of the RO; therefore, considerable R&D effort was devoted to it. These results are discussed next.

G. PRETREATMENT OF FEED WATER TO REVERSE OSMOSIS

As discussed earlier, RO is a key component of the selected zero-discharge scheme. Being a membrane process, RO requires extensive pretreatment to prevent scaling and fouling. Five types of problems are possible: membrane scaling, fouling by metal oxides, device plugging, colloidal fouling, and biological fouling. Membrane scaling can be caused by the precipitation of some of the salts dissolved in the feed water, such as calcium carbonate, calcium sulfate, silica, and barium. Metal oxide fouling usually refers to iron and manganese. Device plugging is caused by particles too large to pass through the feed-brine passage. Aluminum silicate, iron colloids, and aluminum hydroxide are common inorganic foulants. Biological fouling is caused by the growth of microorganisms in the RO device.

The objective of the pretreatment steps was to avoid potential problems. Specifically, the goal of pretreatment was to result in feed water that met the following guidelines:[7]

pH	6-7
Hardness (total)	$\leq$30 mg/L as $CaCO_3$
SiO_2 (dissolved)	$\leq$25 mg/L
Zeta potential	0 ± 6 mV
Fe	<0.1 mg/L
Al	<0.1 mg/L
Sr	<0.1 mg/L
Ba	<0.1 mg/L
SO_3/SO_4 (combined)	*
Langlier saturation index (LSI)	Negative
Silt density index (SDI)	3-5 or less
Suspended solids	<10 mg/L
TOC	50 ± 5 mg/L
Turbidity	$\leq$2 NTU

*Below 80% of solubility products of sparingly soluble sulfate salts.

The above guidelines were either provided by RO vendors or obtained from the literature.[33,34]

The pH limit was set to avoid membrane scaling and degradation. Likewise, the guidelines for hardness, silica, and metals were selected to avoid fouling. The sulfite/sulfate guideline was to safeguard against sulfate scaling. The criterion is based on the solubility of such sulfate salts as calcium, barium, and strontium. The zeta potential is an indicator of colloidal stability. The Langlier saturation index measures the scaling tendency of calcium carbonate, and the silt density index (SDI) measures semiquantitatively the amount of colloids in the feed water. The SDI is derived from the rate of pluggage of a 0.45-μm filter paper run at 30 psig applied pressure. Although SDI is not absolute, it is by far the best method that has been found to determine colloid amount and good correlation can be obtained between SDI and the rate of RO membrane fouling.

Table 29 summarizes the results of the pretreatment for the dephenolated wastewaters. The results of the pretreatment for nondephenolated wastewaters are also shown for comparison (Table 30). The tables show

Table 29

Summary of Results of Pretreatment:[a] DP/NPAC for RO

	Bio eff	Coag eff	Soft eff	Carbon eff	RO feed	Pretreatment criteria
COD	268	113	107	73		--
TOC	76	27	18	2	<1	50
TSS	88	1	1	1	1	10
pH (units)	7.2	6.9	11.3	11.3	6.5	6-7
Chloride	400	690	670	670		--
Alk ($CaCO_3$)	73	69	4,400	4,660		--
Turbidity (NTU)	14.6	4.3	1	0.2	0.2	2
Conductivity (μmhos/cm)	6,376	6,540	14,210	14,210		--
Calculated TDS	4,000	4,500	8,900	8,900	8,900	--
Color (APHA units)	1,750	250	250	5		--
Phenol	0.0082	0.0051	0.005	0.005		--
HCO_3	44	42	927	903		--
CO_3	0	0	1,728	1,908		--
SO_4 and SO_3	2,100	2,000	2,000	2,000	6,000	b
NH_3	75	32	27	26		--
NO_3	165	156	154	154		--
PO_4	7	0.6	0.15	0.19		--
F	0.41	0.4	0.29	0.37		--
SiO_2	37	5	7	15	15	25
Al	2.2	0.15	0.1		<0.08	<0.1
Ba	0.1	0.1	0.1	0.1	<0.1	0.1
Ca	454	454	2.58	1.3		--
Mg	12.2	16.5	3.29	0.32		--
Mn	0.08	0.15	0.02	0.02		--
Fe	1.11	0.56	0.04	0.1	0.06	0.1
Na	810	1,160	3,370	3,330		--
K	4.36	3.59	3.5	3.7		--
Sr	0.23	0.26	0.08		<0.08	<0.1
SDI (units)	--	--	--	--	3	3-5
Zeta potential (mV)	--	--	0	0	0	0 ± 6
T-hardness as $CaCO_3$	--	1,181.5	19.9	4.5	-1.5	30
LSI (units)	--	--	--	--	--	<0

[a] All units in mg/L unless stated otherwise.

[b] Met the criterion.

SOURCE: Reference 4

Table 30

Summary of Results of Pretreatment:[a] NDP/PAC for RO

	Bio eff	Ta eff	Soft eff	RO feed	Pretreatment criteria
COD	616	260	250		--
TOC	228	92	80	8	50
pH (units)	7.3	2.5	11.3	6.5	6-7
Specif. conductance (µmhos/cm)	11,000	14,300	19,000		--
Turbidity (NTU)	130	140	6	<2	2
Color (APHA units)	2,500	1,000	2,000		--
HCO_3	529	0	78		--
CO_3	--	0	1,805		--
SO_4 and SO_3	3,500	4,800	4,200	8,000	[b]
S	0.2	0.2	0.2		--
F	1.1	1.8	0.93		--
SiO_2	38	25	24	26	25
Al	2.3	0.3	0.1	<0.1	<0.1
Ba	0.3	0.8	<0.1		0.1
Ca	850	810	3.6	0.14	--
Mg	11	13.5	0.16		--
Sr	9.5	0.6	<0.08	<0.08	0.1
PO_4	--	--	0.9		--
Mn	--	--	0.2		--
Fe	--	--	0.26	0.12	0.1
Zeta potential (mV)	--	--	0	0	0 ± 6
Total hardness as $CaCO_3$	--	--	9.6	9.6	30
TSS	300	15	2	2	10
SDI (units)	--	--	4	4	3-5
LSI (units)				-2.5	<0
TDS (calculated)					

[a] All units in mg/L unless stated otherwise.
[b] Met the criterion.

SOURCE: Reference 7

the composition not only of the feedwater for RO, but also the wastewater of each pretreatment step.

As Table 29 indicates, the bioreactor effluent contains a very high concentration of calcium (454 mg/L) and magnesium (12 mg/L), with a total hardness of almost 1,200 mg/L as $CaCO_3$. As the tables show, to meet the target total hardness level of 30 mg/L, softening is definitely required. After softening, total hardness was well below 30 mg/L. The laboratory data showed that excess lime and soda ash had to be used in order to meet the total hardness criteria. The soda ash dosage needed was as high as 5,000 to 6,000 mg/L, which will increase total dissolved solids (TDS) in the wastewater. In fact, softening literally doubles the TDS concentration in the wastewaters. Furthermore, the excess alkalinity caused by adding lime and soda ash must be removed and the pH lowered with sulfuric acid or hydrochloric acid to the 6-7 range.

Typically, about 70 mequiv of acid is required for each liter of the RO feed. This further increases the TDS. Increased TDS not only exerts an excessive load on the RO, but also generates more solid wastes.

The sulfate concentration in the RO feed water also met the guidelines. Assuming that the RO achieves 90% product water recovery (i.e., product flow rate/feed flow rate expressed in percent), then the concentration of the sulfate and other ions in the RO reject is 10 times that of the feed. The solubility product of calcium sulfate in the reject stream, after adjusting for ionic strength, would be about 1.53×10^{-5}, about an order of magnitude lower than the guideline of 1.9×10^{-4}, which is 80% of the theoretical value. The solubility limits of barium sulfate and strontium sulfate were met as well.

The feed water also met the other guidelines. For example, TOC was less than 1 mg/L, compared to the guideline of 50. The silica was 15 mg/L, much less than the guideline of 25 mg/L. The target SDI of less than or equal to 3 was also met, as was the target of LSI. Because the pretreatment met its goal, the work proceeded to the RO membrane testings.

The nondephenolated RO feed water, although meeting many of the guidelines, appeared to be inferior to the dephenolated RO feed water.

For example, its sulfate concentration was 8,000 mg/L, which was much higher than that of the dephenolated feed. The higher sulfate content can be attributed to the pre- and post-biological tar acid removal steps required for nondephenolated feed. Again, assuming 90% conversion, the solubility product of the RO brine was calculated to be about 10^{-4}, which is close to the limit of 1.9×10^{-4}. The silica concentration was 26 mg/L, which is on the borderline; the guideline for silica was 25 mg/L. Likewise, iron was also on the borderline; the measured concentration in the RO feed was 0.12 mg/L, compared to the guideline of 0.1 mg/L. The SDI for the feed water was 4, falling in the middle of the recommended range of 3-5.

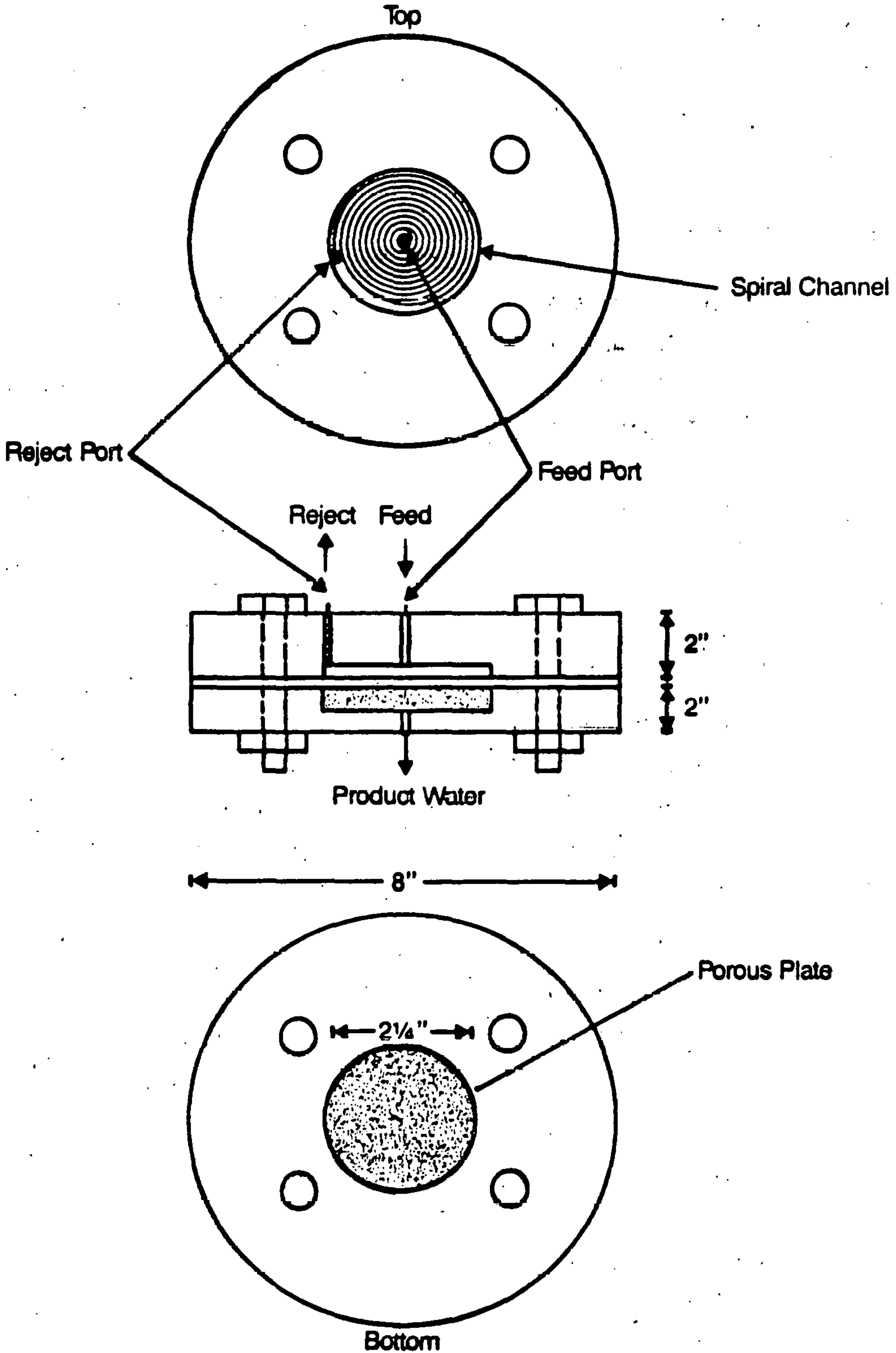
H. RO FLAT-CELL TESTS[7,35]

The objective of the membrane testings was to determine how salt rejection efficiency and flux of water (or product water recovery rate) deteriorated over time. Because of limited quantities of feed water available, flat cells, instead of small full-scale modules, were employed to test different RO membranes.

A RO flat cell consists of two plates and a membrane sandwiched between them (see Figure 27). The feed water enters from the top plate and flows through the spiral channel, and the reject stream exits the end of the channel. As the feed is flowing through the channel, some water permeates across the membrane and becomes product water. The salt rejection data generated from a flat cell are fairly representative of a full-scale module; however, the product water recovery rate data are not. The recovery rate of a flat cell is generally smaller than that of a full-scale module. The reason is that, in order to maintain certain minimum scouring velocity in the channel to avoid plugging, a minimum rejection flow rate must be maintained. The minimum flow rate controls the maximum product water recovery rate attainable in a flat cell. The lower water recovery ratio would mean that, in terms of fouling and scaling, the prevailing conditions in a flat cell are less severe than those in a full-scale module. This limitation must be considered in interpreting the data.

Figure 27

RO Flat Cell



SOURCE: Reference 7

The flat cells are a small part of the RO system shown in Figure 28. Two flat cells were used, one operated at a high pressure (800 psi), denoted as HPFC in the figure, and the other, at a low pressure (400 psi), denoted as LPFC. The tested water was pumped by a metering pump, and fed to each flat cell. To conserve water, the product and reject streams from the flat cells were recombined and recycled.

Four membranes were tested; they differed in formulation and operating pressure:

1. High-pressure membrane - polyetherurea (HPM/PU)
2. Low-pressure membrane - cellulose acetate (LPM/CA1)
3. Low-pressure membrane - cellulose acetate (LPM/CA2)
4. Low-pressure membrane - polyaramide (LPM/PA)

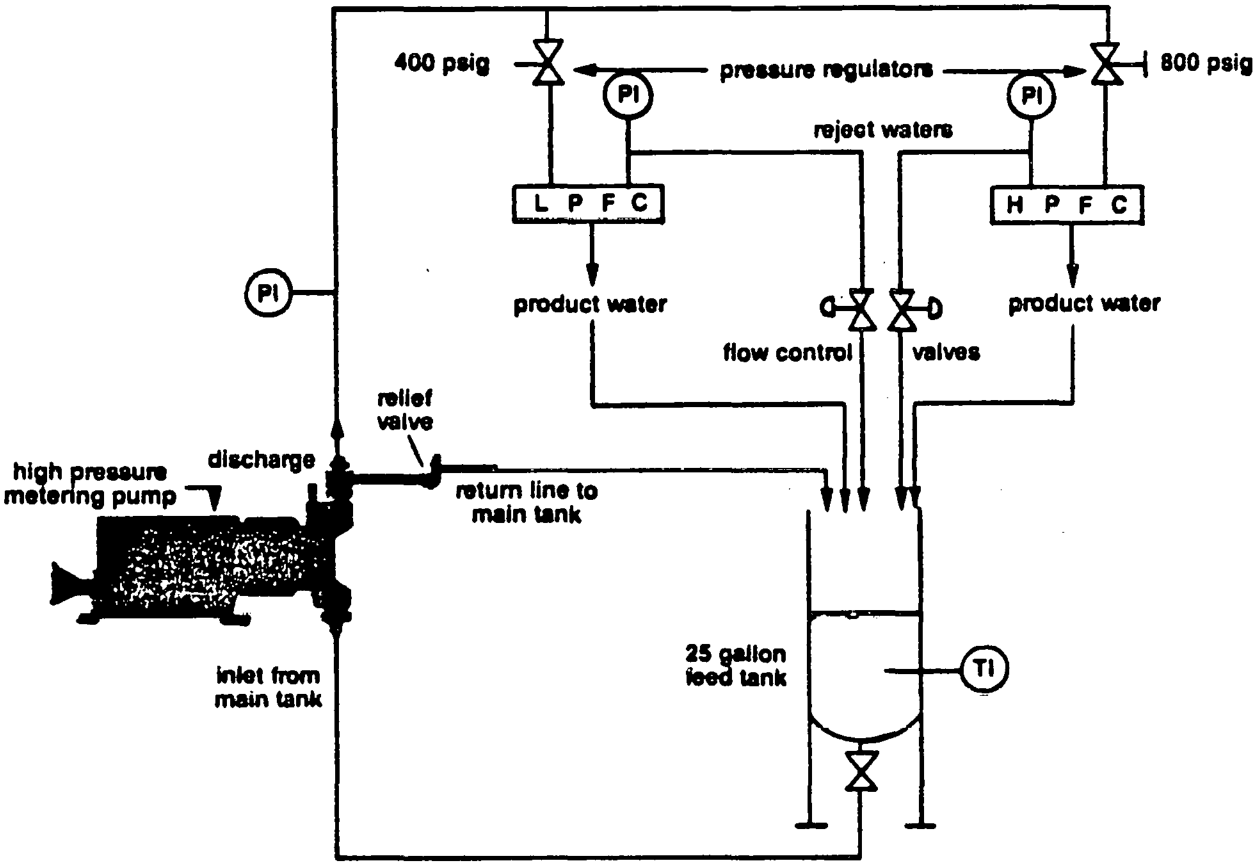
The first membrane, made of polyetherurea, has an operating pressure of 800 psi. The HPM is intended for seawater applications, and can tolerate a high feed TDS, up to 50,000 mg/L. The second and third membranes were both constructed of cellulose acetate, but were supplied by two different vendors. Both were operated at a low pressure of 400 psi and are designed for brackish water applications, with a feed TDS of around 10,000 mg/L. The last membrane, also low pressure, was made of polyaramide, and was not available until the fall of 1983.

The sequence of testing of the membranes involved the following steps:

- Establish the baseline product recovery rate and salt rejection efficiency using 0.1% NaCl solution for a virgin membrane before testing with wastewater.
- Run the tests using actual wastewaters, and observe the decrease in the rejction efficiency and product water recovery. The tests are terminated when a preset duration is completed or a membrane fails.
- Remove the membrane, clean it, and put it back into the flat cell.
- Run tests again using 0.1% NaCl solution, and collect data for comparison with the baseline.

Figure 28

RO Flat Cell System Schematic



LPFC = low-pressure flat cell (brackish water membrane @ 400 psig)
HPFC = high-pressure flat cell (seawater membrane @ 800 psig)

SOURCE: Reference 7

Two wastewaters were tested: NDP/PAC and DP/PAC. The NDP/PAC was used for the first test run, and DP/PAC for the next three test runs. The results are summarized below.

1. Test Run 1: NDP/PAC Wastewater

The first wastewater test run used two flat cells operating in parallel: HPM/PU and LPM/CA1. Plugging of the HPM/PU was evident only after 100 hr of service. The product water recovery rate, which initially was 4%, dropped to 1.4% over the same period. Such a drastic reduction is indicative of membrane fouling. In contrast, the LPM/CA1 did not show signs of fouling. Although the rejection rate of TDS did drop from 88.9% at the beginning to 78.3% after 100 hr, the product water recovery rate remained fairly constant at about 2.2%.

After 100 hr, the flat cells were opened and the membranes inspected. They were coated with a rust-colored sediment. The high-pressure membrane was most heavily fouled. A section of this membrane was put in a small vial containing deionized water, and the vial was then placed in an ultrasonic bath. This dislodged the deposited particles and the water was analyzed to identify the foulants. The results of the analyses are as follows:

Analyses of HPM Sediment

Parameter	mg on membrane
TOC	7.3
Fe	0.23
Ca	<0.001
Mn	<0.001
SO_4	<4.2
SiO_2	11.8

TOC and SiO_2 appeared to be the major foulants. The deposited TOC (7.3 mg) represents approximately 2% of the initial TOC contained in the 10 gal of feedwater. Inspection of the LPM/CA1 showed less solids were deposited than on the HPM/PU, and they were also more loosely attached.

2. Test Run 2: DP/NPAC Wastewater

A new HPM/PU was used in Test Run 2, but the original LPM/CA1 (107 hr of service) continued in operation. Wastewater from the DP/NPAC system was selected for this test.

The TDS rejection rate for the HPM/PU showed little change during the first 120 operating hours. However, the product-water recovery rate reduced from 2% to 1.4%. Over the next 96 hr of operation, the product water recovery rate decreased to 0.5%, which was about 25% of the starting rate. Over a 340-hr operating period, the product water recovery rate deteriorated to 25% of its original value of 2% and the salt rejection rate decreased from 98.8 to 94.6%. The rapid deterioration of the recovery rate again demonstrated that the HPM/PU was unsuitable for SRC-I wastewater, even though the wastewater had been extensively pretreated, including dephenolization.

The LPM/CA1 was also not technically acceptable after about 300 hr of service. The rejection rate dropped from 94.3% to 22.2%, and then further deteriorated to only 6% after 500 hr.

3. Test Run 3: DP/NPAC Wastewater

For the third flat-cell test, a low-pressure, cellulose acetate membrane provided by a different vendor (LPM/CA2) was evaluated. This membrane had not come in contact with the NDP/PAC wastewater. The salt rejection rate remained above 90% for the first 150 hr of operation, and then slowly dropped to 74% over the next 550 hr. After 700 hr, the membrane deteriorated rapidly; in a 31-hr period, the salt rejection rate decreased from 74.2 to 33.3%. The product recovery rate slowly dropped from 1.16% to 1.0% during the first 500 hr of operation, and then fluctuated from 0.5 to 3.0% over the next 200 hr.

4. Test Run 4: DP/NPAC Wastewater

In October 1983, a new type of low-pressure membrane (LPM/PA) became available. It is specifically designed for wastewater treatment and shows significant improvement over the previous membranes tested.

The salt rejection rate was 97% at the beginning of the run and dropped to only 95.9% during the first 700 hr of operation. After continuing for another 300 hr, the rejection rate remained high, at 93%. After 1,030 hr, the run was stopped and the membrane removed for inspection. A small film deposit was observed, but this was easily removed by rinsing with tap water. The membrane was then returned to the flat cell and tested for an additional 500 hr before the run was terminated. This termination was due to schedule constraints, not deterioration of the membrane. In the last 500 hr of operation, the rejection rate never dropped below 92%. Over the entire 1,526 hr of operation, the salt rejection rate dropped only 5%, representing a significant improvement over the other membranes.

Also, samples taken from the feed and product streams at four different times during the run showed no evidence of membrane deterioration.

The sodium chloride rejection tests for this membrane, conducted before and after the run, also indicated that deterioration had not occurred.

5. Conclusions

Several conclusions can be drawn from the flat cell tests:

- Among the four membranes tested, only the low-pressure polyaramide (LPM/PA) membrane was technically feasible. The membrane was tested for more than 1,500 hr at 400 psi without signs of deterioration. The salt rejection rate was more than 95% throughout the test. The polyanamide membrane should be used for future testings.
- All the other membranes (LPM/CA1, LPM/CA2, and HPM/PU) suffered severe deterioration in product water recovery and/or salt rejection rates within a short time period.
- Silica and TOC are the two potential foulants in the SRC-I wastewater that deserve special monitoring. Although they did not plug the membrane in tests of dephenolated wastewater, they did foul the membranes during the tests of nondephenolated wastewater.

- Another factor to be considered in assessing the technical feasibility of RO in the future is the continuous advancement of membrane technology. The newly available membrane, LPM/PA, proved to be much better than the other membranes that had been on the market for some time.

I. EVAPORATOR STUDY

The function of the evaporator is to further concentrate the reject stream from the RO, so that the volume of the zero-discharge residues requiring ultimate disposal can be minimized. The evaporator study entailed selecting the type of evaporator, and devising an evaporator process scheme that can refine the Baseline Design. The objective was to assess the technical feasibility of the evaporator as much as possible, as well as the economic impact of the evaporator on the zero-discharge system.

1. Type of Evaporation System

Two types of evaporation systems were evaluated: a multieffect evaporator, which uses steam as an energy source for evaporation, and a vapor compression evaporator, which employs electricity. The vapor compression evaporator was selected primarily because steam availability was uncertain. ICRC determined that because steam might not always be available at the SRC-I Demonstration Plant to evaporate the RO reject, a vapor recompression evaporator would be more reliable.[41]

2. Basis of the Evaporator Study

One major difficulty during the study was developing a sound design basis. Characteristics of the evaporator feed vary widely with many factors. The characteristics depend not only on such factors as raw wastewater composition and weather conditions (dry or wet), but also the wastewater treatment processes chosen (with or without phenol recovery). Moreover, because RO reject is the feed to the evaporator, the results of the RO evaluation would also affect the design basis for the evaporator study. Ideally, the evaporator study should have been initiated after the phenol recovery evaluation and the RO tests were completed. But the time constraints made this impossible. To overcome the problem, the evaporator study was based on three alternate feeds covering a wide range of conditions. It was envisioned that the revised estimate based on the results of the phenol recovery evaluation and the RO tests could be reasonably extrapolated from the three feeds studied.

Table 31 shows the three alternate feeds studied. The three cases differ in wastewater flow, TDS loading, and composition. Table 31 also presents the revised estimate for comparison. The revised estimate is based on the recommended wastewater treatment scheme shown in Figure 15, and the material balance shown in Figure 24 and Table 28.

The revised estimate is comparable to the alternate cases studied in many respects. The predominant species for all cases are sodium, chloride, and sulfate. The waste flow rate of the revised estimate is near the low end of the range of the alternate cases, and the flow rates of the sodium and chloride are close to the high end of the range. However, there are some significant differences between the current estimate and the three alternate cases. The effects of these difference will be discussed later.

3. Scope

The evaluation of the evaporation system was limited to a paper study because adequate representative samples were unavailable. The scope of the study was limited to devising process schemes with the goal of concentrating the total solid (dissolved and suspended) to 50 wt %. Resources Conservation Company (RCC) of Seattle, Washington was selected to perform the study.

The type of vapor compression evaporator (VCE) recommended by RCC employs a proprietary seed slurry technology to prevent scaling on the heat exchangers. Chemicals are added to form crystals on which, instead of heat exchanger surfaces, scaling preferentially occurs. With this technology, RCC claims that the VCE can concentrate the RO reject many times beyond the theoretical saturation limits of typical scalants, such as calcium sulfate and silica. Based on this technology, RCC devised an evaporation process scheme,[11] which is described in the subsequent section.

Table 31

Alternate Evaporator Section Feed Streams (All Flows in lb/hr)

Component	Alternate 1[11]	Alternate 2[11]	Alternate 3[11]	Revised estimate
TOC	54	48	74	50
TSS	12	9	13	10
Oil and grease	4.5	4.0	6.1	5
Organic nitrogen	60	53	83	50
Tar acids	6.4	5.7	9	5
NH_4	86	74	120	-
CN	2.2	2.0	3.1	2
SCN	4.5	4.0	6.1	5
NO_3	315	280	440	-
Na	1,010	1,180	2,730	3,145
Ca	530	23	26	13
Mg	9	3.6	3.8	4
Mn	0.29	0.27	0.36	0.3
Cu	0.7	0.6	0.9	0.7
Cr	0.11	0.10	0.14	-
K	12	10	17	13
Ba	0.08	0.07	0.11	0.1
Sr	0.23	0.20	0.33	0.2
F	0.4	0.4	0.6	0.4
Cl	860	760	1,200	1,730
CO_3	36	40	42	-
SO_3	400	442	1,700	-
S_2O_3	92	91	93	-
SO_4	1,200	1,287	2,100	4,405
$Fe(OH)_3$	5.5	0.79	1.2	2.5
$Al(OH)_3$	8	2.8	1.8	4.2
SiO_2	42	36	56	40
$B(OH)_3$	51	45	71	50
TDS	4,300	5,000	7,200	9,820
Total wastewater including dissolved solids	127,600	275,500	369,000	160,290

4. The Process Devised

The conceptual scheme is shown in Figure 29. The evaporation system consists of pretreatment, deaeration, vapor compression evaporation (VCE), and crystallization. This scheme is substantially different from that in the Baseline Design.

The Baseline Design does not have any pretreatment. One purpose of pretreatment is to oxidize reduced trace sulfur species such as bisulfite, sulfite, and thiosulfate. In the evaporator steam, these species can decompose to sulfur dioxide, which can corrode the compressor or the VCE. Because the major source of the reduced sulfur species is the SO_2 scrubber in the calciner area, and the scrubber purge has been oxidized (see Figure 15) in the recommended wastewater treatment scheme, the concentration of reduced sulfur species should be less than 100 mg/L. Hydrogen peroxide oxidation can reduce this level to about zero.

Another purpose of pretreatment is to remove bicarbonate and carbonate, because they could cause scaling in the evaporator. Scaling by calcium carbonate cannot be controlled by the seed slurry technology. The removal entails acidification with sulfur or hydrochloric acid, followed by CO_2 removal in a decarbonator. Deaeration also removes dissolved oxygen, which is corrosive. In contrast to the alternate cases, the revised estimate contains a much larger quantity of bicarbonate. This requires a much higher dosage of acid and will change the chemistry of the feed, and increase the TDS loading to the evaporator accordingly.

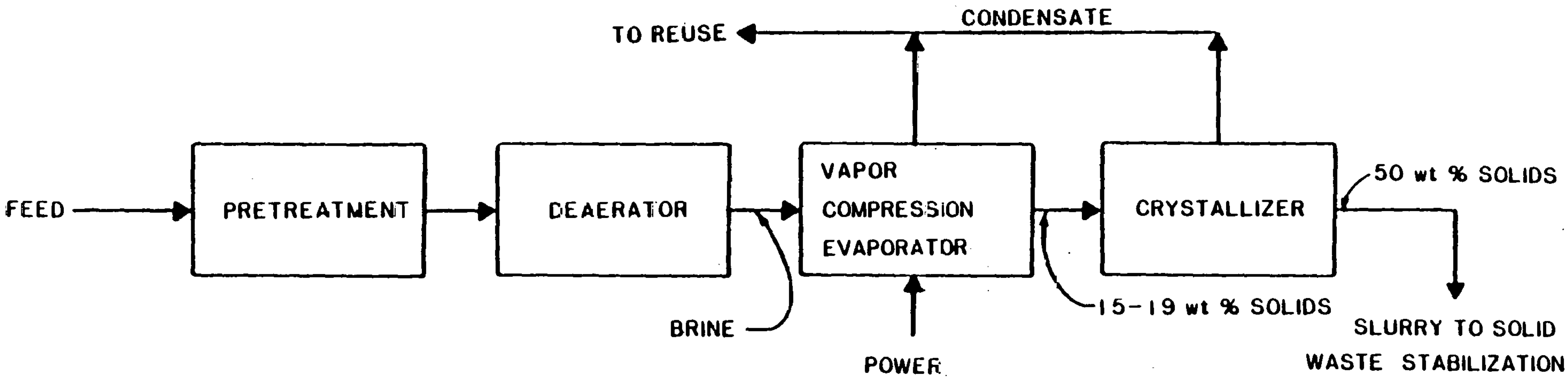
Another required pretreatment step is filtration. The feed to the evaporator may be supersaturated with inorganic salts. Thus, there may be suspended solids present in the feed that should be removed to protect the downstream equipment.

After pretreatment, the feed enters the evaporator. The brine in the evaporator is continuously pumped through vertical, falling-film heat exchanger tubes. As the brine is being heated, some water evaporates into the vapor phase. The vapor is compressed and condensed by a compressor.

The electricity running the vapor compressor provides the energy for evaporation. The evaporator can concentrate the brine to about 15 to 19 wt % of total solids. The concentrated brine is withdrawn from

Figure 29

Evaporation System Process Flow Diagram



SOURCE: Reference 11

the evaporator from the liquid recirculation line and discharged into the crystallizer for further concentration.

The crystallizer is also of the vapor compression type which uses electricity rather than steam. After entering the crystallizer, the hot evaporator waste stream is pumped through a tube-and-shell heat exchanger, where the temperature is raised about 5°F. The heated fluid flashes, and vaporization takes place. The vaporization and subsequent cooling cause local supersaturation of dissolved salts, which in turn forms precipitates. A slurry containing 50 wt % of total solids (TS) is discharged from the crystallizer and sent to stabilization. The vapor is cooled, condensed, and then used as cooling tower makeup.

Although the quantities of crystallizer waste differ for the alternate feeds, the waste properties are similar. The waste contains 50 wt % TS, with about one-half suspended solids and one-half dissolved solids. The dissolved salts are primarily sodium chloride and sodium sulfate. The crystallized solids are primarily sodium sulfate with smaller amounts of calcium sulfate and sodium chloride. Trace amounts of organics, silica, potassium, magnesium, fluoride, ammonium, cyanide, thiocyanate, and metals (Mn, Cu, Cr, Ba, Sr, Fe, Al, B) are also present in the waste; silica is concentrated in the crystals and most of the others are dissolved.

Approximately 80 to 85% of the water in the feed to the evaporation system is recovered as condensate. Some impurities are expected in the condensate because volatiles carry over into the steam and will condense. Species present in the condensate include such volatiles as ammonia and boron. The boron concentration in the condensate should be about 10 mg/L. Other impurities are introduced into the condensate by a mechanical carry-over mechanism. These include inorganic species present in the feed. Inorganic species such as Ca, Mg, Na, and SO_4 are present in amounts totaling 10 mg/L or less. Species such as sulfite or thiosulfate, which may have escaped destruction during pretreatment, could carry over into the condensate.

5. Conclusions

Based on the paper study, the evaporation system appears to be technically feasible if the feed is properly pretreated. However, pilot studies using representative samples are needed to conclusively demonstrate feasibility. Also, this paper study suggests that the Baseline Design scheme for evaporation would need modifications to be functional.

J. IMPACT ON THE COOLING SYSTEM

Evaporation from the cooling system represents the single predominant use of water in the SRC-I Demonstration Plant. Without evaporative cooling, it would be difficult, if not impossible, to achieve zero discharge. Therefore, the evaporative cooling system is a critical component for the wastewater reuse.

The cooling system is intimately and directly related to the unit processes of the zero-discharge system and indirectly related to the wastewater treatment system. The product water from RO and the condensates from the evaporator and the crystallizer constitute the majority, if not all, of the makeup to the cooling system. The performance of those unit processes will have a direct impact on the cooling system. The cooling system will also have a reverse effect on the zero-discharge unit processes as well because the blowdown from the cooling system eventually becomes the feed to those processes.

The interactions between the cooling system, the RO, and the evaporator/crystallizer are complex and factors affecting the interactions are viable. For example, the salt rejection rate and the product water recovery ratio of the RO change with time, which will affect the quantity and composition of the cooling system makeup. The quantity and composition of the RO product water are also affected by weather, which is also time dependent.

The interactions are illustrated by the material balance presented in Figure 26 and Table 32. Because of the variability and complexity of the interactions, it is not possible to show material balances for all cases. Only the "worst case" is shown. The assumptions made for the "worst case" are:

- ° The runoff is of a 25-yr, 24-hr storm, equalized and treated over a two-week period.
- ° The RO recovers 85% of the feed as product water.

Table 32

Material Balance for Zero-Discharge System (Wet Weather)
(All Units in lb/hr)

	Stream no. and name	Total flow	Sodium	Calcium	Chloride	Sulfate	HCO_3^-/CO_3^{2-}	TDS	Sludge[a]
39.	Coagulated bioeffluent	1,062,346	826	1,058	1,922	1,102	325	6,374	-
40.	Lime	6,840	-	345	-	-	-	638	-
41.	Soda ash	30,750	2,669	-	-	-	3,482	6,151	-
42.	Softening sludge	34,930	-	1,397	-	-	2,096	300	3,493
43.	Sulfuric acid	3,990	-	-	-	3,793	-	3,872	-
44.	RO feed	1,067,996	3,495	13	1,922	4,897	-	10,909	-
45.	RO product	907,706	350	0	192	490	-	1,091	-
46.	RO reject	160,290	3,145	13	1,730	4,405	-	9,820	-
47.	Condensate	140,733	-	-	-	-	-	-	-
48.	Chemicals	280	-	36	63	-	-	100	-
49.	Crystallizer waste	19,840	3,145	49	1,793	4,405	-	9,920	-
50.	Makeup from river	0	-	-	-	-	-	-	-
51.	Evaporation (CT No. 1)	852,500	-	-	-	-	-	-	-
52.	Blowdown (CT No. 1)	170,500	350	0	192	490	-	1,091	-
53.	Cement	4,734	-	-	-	-	-	-	-
54.	Fly ash slurry	75,805	-	-	-	-	-	-	15,161
55.	Fly ash cake	18,951	-	-	-	-	-	-	15,161
56.	Stabilized solids	43,525	-	-	-	-	-	-	29,815
57.	Supernatant	56,854	-	-	-	-	-	-	-

[a] Dry basis.

- The salt or TDS rejection rate of RO is 85%.
- The maximum allowable TDS concentration in the recirculating cooling water is 6,000 mg/L.

The material balance for the zero-discharge section shown in Figure 26 and Table 32 is an extension of the material balance for the wastewater treatment section illustrated in Figure 24 and Table 28. Therefore, all the bases and assumptions used for that balance are also applicable to this balance. Also, this balance is consistent with the revised estimate for the feed to the evaporator discussed previously.

Under the worst case, the factor controlling the cycles of concentration and the blowdown from the cooling tower is TDS. The TDS in the combined RO product and the condensate is about 1,000 mg/L, and the TDS in the blowdown is about 6,000 mg/L. To meet the TDS criterion of 6,000 mg/L for the recirculating water, the treated wastewater must be demineralized somewhat before it can be used as makeup water because the TDS in the coagulated bioreactor effluent is already as high as 6,000 mg/L. Hence, the TDS criterion obviously has a significant impact on the feasibility and design of the zero-discharge system. As discussed earlier, the wastewater treatment, or the pretreatment of the feed to the RO unit, increases TDS in the wastewater drastically. For example, the use of lime throughout the wastewater treatment system will cause the treated wastewater to contain a high concentration of calcium. The high calcium concentration necessitates softening, and softening will add more TDS.

The TDS problem associated with the cooling system illustrates one difficulty associated with zero discharge. Another difficulty pertains to the disposal of the TDS; they eventually become solid wastes that require safe disposition.

K. ZERO-DISCHARGE SOLID-WASTE STABILIZATION

Zero discharge generates a large quantity of solid wastes. Successful implementation of zero discharge will rely on acceptable disposition of 60-120 tons per day of zero-discharge residue generated by the plant.

Disposing of the zero-discharge residue is a problem because it is composed primarily of soluble salts. Trace hazardous substances such as organics and heavy metal compounds may also be present, so the slurry cake will be treated as a hazardous waste.

The zero-discharge residue is not suitable for direct disposal in a landfill; it first requires a processing step to increase its physical and chemical stability. Stabilization has been commercially practiced on a variety of solid and liquid wastes (usually inorganic). Generally, however, such wastes are only slightly soluble; very little work has been done on solids composed mainly of soluble salts. Consequently, an R&D program was developed to determine the feasibility of stabilizing these soluble salts. The objectives were as follows:

- To determine the preliminary technical feasibility of zero-discharge residue stabilization.
- To evaluate the technical and economic impact of solid waste stabilization on zero discharge.
- To obtain design data for system engineering.
- To produce conceptual design systems for solid-waste stabilization.

The program was implemented in two phases. The first, or screening, phase of the program determined the feasibility of stabilizing soluble salt slurries using commercially available technologies. However, time constraints on the SRC-I project did not allow a new technology specifically tailored to the SRC-I plant to be developed. In the second phase, a design package was produced based on the information developed from the screening phase. A multivolume report entitled "Evaporator Cake Solid Waste Stabilization Studies" details the information developed in both phases.[36] This report highlights only the significant findings.

1. Screening Tests

The screening phase entailed the following specific tasks:

- Estimate characteristics of the evaporator/crystallizer waste or the feed to the stabilization process. It was determined that a mixture of sodium chloride and sodium sulfate (1:1 mixture by weight) provided a good basis for the screening process because they are the predominant compounds in the waste. The range of concentration in the waste chosen was between 17 and 90 vol % solids in saturated solutions, an expected range of the crystallizer waste in the field.
- Retain technology licensors to conduct screening studies. Two licensors and three technologies were involved. Stablex-Reutter, Inc. (Camden, New Jersey) conducted tests for its proprietary "SEALOSAFE" process, and Conversion Systems, Inc. (Horsham, Pennsylvania) performed tests for two processes (one uses lime/fly ash and the other fly ash/cement as the main additives). Stablex-Reutter produces a "damp sand" textured material that could be compacted in the landfill by land rollers. Conversion Systems, Inc. produces a pourable slurry, similar to concrete. Both eventually form a monolithic mass.
- Conduct screening studies, which encompass: (1) preparation of test cylinders using the synthetic waste and the respective additives; (2) performance of curing time tests and compressive strength tests using the test cylinders; (3) running of leaching tests, including the EPA-EP procedure, and estimates of amounts of salts leached during a 25-yr, 24-hr storm; and (4) determination of volume of the solid waste after stabilization.

Preparation of the test cylinders necessitated a large quantity of SRC-I fly ash, which was not available. Hence, a surrogate fly ash was obtained from a generating facility owned by the Indiana Power and Light Company (IPALCO). This fly ash was chosen because the location of the facility was near the SRC-I plant site and because the fly ash had a good pozzolanic reactivity, which is essential for some stabilization technologies.

To determine the suitability of the SRC-I fly ash as a pozzolan, with the limited sample quantity available, pozzolanic reactivity tests were conducted using an ASTM procedure (C-593) that required only a small quantity of sample. Tests were run on SRC-I fly ash derived from gasification (GKT) of a mixture of Kentucky #9 coal and Kerr-McGee ash concentrate (KMAC), the feedstock for the GKT gasifier during normal operation. The reactivity tests were also conducted for another GKT gasifier fly ash, derived from gasification of Illinois #6 coal. The chemistry of Illinois #6 resembles Kentucky #9 in many respects; both come from the same coal basin. The Illinois #6 gasifier fly ash, which was obtained from another DOE-sponsored synthetic fuel project, is a good simulation of the SRC-I fly ash when the feedstock to the GKT gasifier is 100% Kentucky #9 coal.

Detailed results of the screening phase studies are reported elsewhere;[36] only the highlights are reported here.

a. Sodium Sulfate Crystal Form. The studies showed that the degree of hydration of Na_2SO_4 crystals is critical to stabilization. Sodium sulfate must enter the stabilization process in the decahydrate form ($Na_2SO_4 \cdot 10H_2O$) to minimize landfill surface spalling and leaching. Anhydrous sodium sulfate absorbed 10 water molecules when contacting moisture, which increased the crystal size and ruptured the stabilized matrix.

Sufficient water should be present in the crystallizer waste to satisfy the decahydrate stoichiometry, plus the slurrying requirements, i.e., preventing slurry solidification during cooling. The crystal form of sodium sulfate changes with temperature: below 18°C, it is present in the decahydrate forms, between 18 and 33°C it is in both the decahydrate and anhydrous forms, and above 33°C it is in the anhydrous form. Cooling of the crystallizer waste before stabilization is required.

b. Leaching Tests. The evaluation was primarily concerned with the surface leachability of the cured, stabilized waste. The two licensors used different methods to produce the stabilized landfill, but their final products are similar. Both technologies can produce matrices that have permeabilities of 10^{-7} cm/sec or less.

The cured cylinders were subjected to four 24-hr agitated immersion cycles followed by 24-hr drying (70°F) cycles. Freshly distilled water was used for each cycle, in a quantity equal to a 5-in. depth for each square inch of surface area. Specific conductance measurements were taken at 15-min intervals during the first 2 hr, at 1-hr intervals over hours 2-8, and again at the end of the run. As a minimum, leached sodium, chloride, and sulfate concentrations were determined at the end of each immersion cycle.

The leachate rates, as measured by specific conductance, were high when the surface was first exposed, but then tapered off. In some instances, leachate rates almost flattened by the end of the 24-hr cycle. The leaching rate and total leachate concentration decreased for each successive cycle. Leaching appeared to be limited to the surface of the cylinder.

c. Compressive Strength. All formulations showed adequate compressive strengths for landfilling.

The damp sand/compaction landfill placement procedure (SEALOSAFE) calls for a cured compressive strength (wet) of $\geq$25 psi; the two slurry systems of Conversion Systems call for $\geq$250 psi. Actual compressive strengths ranged from 224 to 1,000 psi. The mixes containing portland cement, fly ash, and anhydrous sodium sulfate showed values of 2,700 to 2,800 psi. Most of the strength is provided by the cement.

d. Water Penetration. Water penetration affects how much salt leaches out. The smaller the penetration, the less leaching. Water penetration below the cylinder surface after immersion testing was measured. For the SEALOSAFE formulations, during a 24-hr immersion cycle, the 17 vol % salt formulation developed surface cracks. During the next cycle, the formulation began to slough and peel. Water penetrated the test cylinders nonuniformly to a depth of 1/2 to 1 in.

No noticeable change in surface hardness or smoothness was detected for the 90 vol % mixes.

Evaluations of water penetration of the Portland cement and lime/fly ash stabilization processes were based on cylinder weight change. There was little change in cylinder weights for any of the formulations after immersion testing. The result, coupled with compressive strength test results, led to the conclusion that there was little surface penetration.

e. Landfill Volume Increase. Volume increase resulting from stabilization was a significant design parameter. Addition of the materials needed for stabilization will increase the volume of the landfill. In comparison with the unstabilized crystallizer waste, the percent volume increases due to stabilization were 60 and 80% for the SEALOSAFE and cement/fly ash technologies, respectively, and about 100% for the lime/dry fly ash process.

It should be noted, however, that the volume increase of the stabilized solids may be offset by a corresponding reduction in the amount of fly ash disposed of in the ash ponds, if the fly ash generated on-site can be used as an additive. On the other hand, if the SRC-I fly ash cannot be used as an additive, and the fly ash has to be imported for the stabilization, then no such offset is possible.

f. Pozzolanic Activity Tests. The ASTM pozzolanic reactivity tests have shown that the GKT gasifier fly ash derived from the mixture of Kentucky #9 coal and KMAC (ash #1) had a low pozzolanic reactivity (228 psi). The other GKT fly ash generated from Illinois #6 coal (ash #2) had a high pozzolanic reactivity (1,014 psi) similar to power plant fly ashes, such as the IPALCO fly ash, which typically have a reactivity of 700-1,000 psi.

Both GKT fly ashes had a much higher loss on ignition (LOI) than typical power plant fly ashes derived from eastern bituminous coals such as the IPALCO fly ash. The LOI for ash #1 was 48%, and that for ash #2 was 35%. A typical LOI value for power plant fly ash is less than 10%. Total carbon contents for ashes 1 and 2 were 42.7 and 27.8%, respectively. The high carbon content might have caused a low pozzolanic reactivity in ash #1.

The low pozzolanic reactivity of ash #1 would preclude the lime/fly ash technology, because its success depends significantly on the pozzolanic reactivity of the fly ash used. Either the SEALOSAFE or cement/fly ash technology would have to be employed because both can tolerate a fly ash with a low pozzolanic reactivity; other additives provide the reactivity.

g. Conclusions. The following preliminary conclusions are drawn from the screening tests:

- Stabilization appears to be technically feasible. After stabilization, leaching of the salts was limited to the surface of the stabilized materials. The stabilized materials exhibited desirable handling properties.
- The limited ASTM pozzolanic reactivity test showed that the GKT fly ash derived from the mixture of Kentucky #9 coal and KMAC is not an effective pozzolan. Unless a fly ash with a high reactivity is imported, the low reactivity of the SRC-I fly ash would preclude the lime/fly ash technology, which is more dependent on the reactivity than the others.
- The volume change due to stabilization is significant. It ranged from 60 to 100%, depending on the technology. The change should be considered in the design. Part of the increase, however, is offset by reduction of the fly ash requiring disposal, if the fly ash generated on-site can be used as an additive for stabilization.

2. Process Design Packages[36]

The objective of this phase of the program was to produce design packages for solid-waste systems based on lime/fly ash and cement/fly ash stabilization chemistry. The packages included the following:

- Process flow diagrams
- Site plans covering the stabilization facilities, landfills, and additional equipment not included in the SRC-I Baseline Design
- Equipment lists and layouts of all new equipment required or equipment that would be deleted from the SRC-I Demonstration Plant as a result of this study
- A conceptual landfill design (conforming to Baseline requirements) that accounts for the increases in solid waste volumes caused by stabilizing reagents and flow conditions

- A standard operating procedure for the facilities contained in the equipment lists
- The estimated capital costs for the constructed systems within ±10% accuracy
- The estimated operating costs (e.g., labor, chemical consumption rates, utilities, placement, and licensing)
- Evaluation of the surface runoff associated with the stabilized formulations provided

Design packages were prepared by Catalytic, Inc.[15] for three alternative systems: (a) lime/dry fly ash, (b) cement/dry fly ash, and (c) cement/wet fly ash.

a. Lime/Dry Fly Ash System. The lime/dry fly ash system is designed to operate on a continual basis, two shifts a day, 7 days a week. There are two complete fly ash feed trains, one operating and one spare. In this system, the processed waste takes on the consistency of wet sand, thus allowing it to be stored in piles for short-term collection and trucked directly to the landfill cell. At the landfill site, the waste is dumped, spread by rubber-tired equipment (to protect the liner of the landfill), and compacted by a vibratory roller operating within the landfill.

Wet fly ash is not recommended for use in this system because of the large amount of lime required. Dry fly ash must be obtained from a coal-fired power plant for this system.

b. Cement/Dry Fly Ash System. This system operates on a batch basis, one shift per day, 7 days a week. Because the waste material produced sets rather quickly, it must be placed in the landfill shortly after being processed. Landfilling is generally restricted to the day shift and operation of the cement/dry fly ash system is likewise limited to this period.

The stabilized waste material is transported in a standard concrete transport truck and dumped into a hopper at the landfill site. Waste is distributed in the landfill cell by pumping it from the hopper via a flexible hose. The general landfill configuration duplicates that of the lime/dry fly ash system.

Like the previous system, this system would have to import fly ash from elsewhere. This is not because the SRC-I fly ash does not have sufficient pozzolanic reactivity, but because dry fly ash is needed. Only wet fly ash is readily available at the SRC-I Demonstration Plant because wet fly ash collection and sluicing systems have been used. Both this system and the previous system must import fly ash.

c. Cement/Wet Fly Ash System. This system uses fly ash sluiced from the GKT gasifier to surface impoundments. A small portion of the fly ash slurry from the sluicing system is diverted into the stabilization system. Before use, the fly ash slurry has to be thickened, and the fly ash dewatered in a vacuum filter. Processing plant and landfill configurations are identical to those for the cement/dry fly ash system. The thickener and vacuum filter replace the fly ash handling and storage facilities.

3. Leachate Management

All three systems return landfill leachate to the evaporator. When it rains, the estimated initial leachate solids concentrations are:

Lime/dry fly ash	2,000 mg/L
Cement/dry fly ash	17,000-20,000 mg/L
Cement/wet fly ash	25,000 mg/L

The concentrations will decrease rapidly with the duration of rainfall. Landfill surface water runoff from rainfall is the main source of leachate. Landfill management will minimize the exposed surface of the stabilized mass, the amount of water that contacts the surface, and the contact time. A good design and careful management may limit leaching to up to 6% of the total dissolved solids (TDS) in the stabilized solids before a landfill is permanently covered with impermeable materials as required by law.

4. Costs

The capital and operating costs for the three systems, extrapolated by ICRC from information in the subcontractor's reports, are summarized below for two currently updated TDS loadings:

	60 tpd ($ M)	120 tpd ($ M)
Lime/dry fly ash		
Total capital	6,455	10,840
Annual operating*	2,810	4,930
Cement/dry fly ash		
Total capital	4,100	6,910
Annual operating*	1,980	3,710
Cement/wet fly ash*		
Total capital	6,670	10,250
Annual operating	1,940	4,425

*These costs do not include penalties for increasing, or credits for lowering fly ash impoundment capital and operating costs.

SOURCE: Reference 36

Although the cement/wet fly ash system is the most expensive in terms of capital costs, it is recommended for the SRC-I application for several reasons. First, the gasifier fly ash produced from the combination of Kerr-McGee ash concentrate and Kentucky #9 coal has a low pozzolanic reactivity, and the low reactivity is not critical to this system. For a cement/fly ash system, the ash serves as a filler. Although it may impart some strength to the final stabilized product, the primary stabilization reaction is with the cement. Therefore, the uncertain pozzolanic quality of the SRC ash does not have a major impact on the applicability of the cement/fly ash system.

The second reason is that this system can use wet fly ash. Dry fly ash is not readily available at the SRC-I Demonstration Plant. To use dry fly ash, the gasifier fly ash collection and transport systems would have to be drastically changed or, alternatively, dry fly ash would have to be imported from an external source. Importing fly ash will increase the volume of the stabilized waste considerably.

5. Volume of Stabilized Zero-Discharge Residue

With the cement/wet fly ash system, the estimated volume for the stabilized solid waste is about 400 yd^3/day (43,500 lb/hr), when the TDS loading is at its maximum of about 10,000 lb/hr or 120 tpd. Together with the softening sludge, the zero discharge will increase the sludge by about a maximum of 55,000 lb/hr, on a wet basis.

L. COST OF IMPLEMENTING ZERO DISCHARGE

The costs associated with the zero-discharge system are considerable. The following are capital and operating cost estimates (in thousands of dollars) for each component of the system:[39, 40]

	Capital*	Operating*
Softening	2,590	1,820
RO	8,750	1,000
Evaporation/crystallization	7,970	1,440
Solid waste stabilization**	10,250	4,425
Totals	$29,560	$8,685

*Based on first-quarter 1981 dollars.
**Including landfills.

Thus, the capital cost for the zero-discharge system is approximately 75% of that for the wastewater treatment system (see Table 19), both systems including solid-waste handling and disposal facilities. The operating costs for both systems are approximately the same. The total capital cost of the wastewater treatment, reuse, and solid-waste disposal facility is about $70 million and the total operating cost, excluding capital recovery, is $18 million per year.

M. ALTERNATIVES TO ZERO DISCHARGE

1. Partial Discharge

Because of the high costs and technical uncertainty associated with zero discharge, the possibility of partial discharge was briefly evaluated. One partial discharge scheme is to segregate the heavily contaminated streams from such lightly contaminated streams as runoffs, treat the two types separately, recycle the heavily contaminated, and discharge the lightly contaminated streams after minimal treatment.

While this scheme may be conceptually attractive, it probably would not reduce the cost significantly, and would not eliminate the technical uncertainty of zero discharge. It would not result in substantial cost savings because most wastewaters (in terms of volume) are heavily contaminated. The combination of the ASWS bottoms, GKT gasifier, and cooling tower blowdown represents 85% of the total dry-weather wastewater flow, and 53% of the total wet-weather flow. Using the six-tenths rule for scaling down costs, the partial discharge scheme would only save about 30% of the capital cost. Equally important, the technical uncertainty associated with zero discharge would still exist.

2. Total Discharge

Another alternative to zero discharge is total discharge. The analyses on the acceptability of discharging the fully treated wastewater have been presented in detail in Chapter V.

The detailed analyses demonstrated that the fully treated wastewater meets, without any exceptions, all anticipated effluent limits by a wide margin. The wastewater treatment system produces an effluent that will not significantly impact the ambient water quality under the most severe conditions.

Furthermore, although the aquatic ecotoxicity data are preliminary, they suggest that the wastewater, after full treatment including phenol extraction, is not too toxic to discharge. The microbial mutagenicity tests have shown that the wastewater treatment as recommended renders the SRC-I wastewater nonmutagenic. Because of the limitation of the data, as described in Chapter V, strong conclusions cannot be drawn without additional tests. Notwithstanding, the data seem to indicate that total discharge might be a viable alternative worth further evaluation.

N. SUMMARY AND CONCLUSIONS OF ZERO-DISCHARGE EVALUATION

The following bulleted items summarize significant findings and major conclusions from the zero-discharge evaluation:

- In accordance with the regulatory climate, the SRC-I FEIS in 1981 proposed zero discharge, and the Baseline Design has reflected this concept. Another reason that zero discharge was proposed was lack of environmental data to allow a definitive water quality impact assessment when the FEIS was prepared. A considerable amount of data has been generated since then.
- The zero-discharge scheme in the Baseline Design consists of reverse osmosis (RO), evaporation, and solid-waste stabilization. Several alternative schemes were assessed during the post-Baseline period to see if the Baseline scheme was, indeed, the most attractive, particularly when considering the more complete material balance that became available following the Baseline.
- The assessment confirmed that the scheme in the Baseline Design is still the best. However, some modifications must be made to improve its technical feasibility. The modifications include addition of softening before RO, more pretreatment before evaporation, inclusion of crystallization after the evaporator, and a different solid-waste stabilization process.
- Softening must be provided before RO because of the high calcium concentration (45-800 mg/L as Ca) due to upstream wastewater treatment.
- Softening with lime and soda ash was able to reduce total hardness to less than 30 mg/L, the preset target. However, softening required between 5,000 and 6,000 mg/L of soda ash. The softening and subsequent acidification doubled total dissolved solids (TDS) in the RO feed water. TDS loadings as high as 10,000 lb/hr (worst case) may be present in the RO feed.

- The RO feed water also had a high sulfate content; however, because the concentration of calcium was so low, calcium sulfate scaling was not experienced in the RO test.
- Because limited amounts of wastewater were available, flat cells were used to evaluate different RO membranes in lieu of a small full-scale module. Also, wastewater was recycled by recombining the permeate and reject streams. While the flat cells generated representative data on salt rejection rates, they could not produce good data on product water recovery. The product water recovery rate of a flat cell is much smaller than that of a full-scale module, and the condition (in terms of scaling and fouling) less severe. Therefore, the flat cell tests served primarily as a screening tool to eliminate membranes.
- Four membranes were tested: one made of polyetherurea, two of cellulose acetate, and one of polyaramide. The polyetherurea is a seawater membrane designed for high pressures (800 psi), and the other three are brackish water or low-pressure (400 psi) membranes.
- When nondephenolated wastewater was used as the feed, the high-pressure membrane fouled quickly (after 100 hr of service), as did one of the cellulose acetate membranes. Chemical analysis of the deposit on the membrane revealed that silica and TOC were the major constituents. That TOC was a major constituent was surprising because TOC in the feed was extremely low (8 mg/L).
- In subsequent tests with dephenolated wastewater as the feed, the high-pressure membranes and the two cellulose acetate low-pressure membranes fared slightly better, but the results were not satisfactory, due to the decline of product recovery and salt rejection.
- The only successful membrane was the polyaramide membrane. With pretreated dephenolated wastewater as the feed, the membrane recovery rate and rejection rate deteriorated only slightly after 1,500 hr of service. The rejection rate for

TDS never dropped below 92%. However, because of the limitations of the flat-cell tests, pilot studies using a full-scale module with spiral-wound or hollow-fiber configuration are still needed to confirm the rejection rate data and to determine the product water recovery rate.

- The polyaramide membrane became available only recently. The fact that this new membrane performed significantly better than the others indicates that membrane technology is advancing. This indicates that the technical feasibility of RO, in particular, and zero discharge, in general, will change with time.
- Because of the unavailability of representative wastewater samples, only paper studies were performed for evaporation of the RO brine.
- An ICRC study concluded that a vapor compression evaporator (VCE), which uses electricity as its energy source, should be used in lieu of multi-effect evaporators, which use steam, because steam availability in a demonstration-scale plant is uncertain.
- Based on another study of a VCE technology that uses a proprietary seed slurry to control scaling, evaporation of the RO brine appears to be feasible. However, a crystallizer (also of vapor compression) will be needed to concentrate the brine to 50 wt % solids, the design target. The evaporator alone cannot achieve such a high degree of concentration. The study also indicates that pretreatment to remove oxygen and bicarbonate/carbonates and to reduce sulfur compounds from the evaporator feed is critical. Neither the crystallizer nor pretreatment was included in the Baseline Design. A pilot study is recommended for confirmation.
- The combined stream of the permeate from the RO and the condensate from the evaporator/crystallizer can be used as the makeup water for the evaporative cooling towers. The makeup should be able to allow the cooling system to operate at six cycles of concentration, assuming that the maximum TDS level

in the recirculating water is 6,000 mg/L, and TDS is the limiting factor.

- The TDS limit of 6,000 mg/L is based on published information. However, the values reported vary widely. Because the TDS criterion will have a significant impact on cooling tower operation and zero-discharge system design, more work is needed to pinpoint the optimal limit.
- Stabilization studies of the zero-discharge residues (the crystallizer waste) were conducted using synthetic samples consisting of sodium chloride and sodium sulfate. The objective of stabilization is to reduce leachability. Without stabilization, the zero-discharge residues are highly water-soluble and leachable.
- Three stabilization technologies were evaluated: (1) SEALOSAFE, a proprietary process marketed by Stablex-Reutter, Inc.; (2) a fly ash/lime system; and (3) a fly ash/portland cement system. Conversion Systems, Inc. conducted laboratory tests on the latter two technologies. The laboratory data produced by Stablex-Reutter and Conversion Systems were used by Catalytic to prepare a process design package.
- The subcontracted laboratory tests showed that all three technologies effectively controlled TDS leaching and produced stabilized solids with desirable handling properties. However, slight but still significant leaching of TDS from the surface of the stabilized solids still occurs. Thus, landfill design and operating practices will be important in limiting dissolved solids in the leachate and storm water runoff. Once the stabilized solids are placed, the landfill must be covered with impermeable materials to avoid exposure to rainfall and runoff as quickly as possible.
- Two fly ashes derived from GKT gasification were tested for pozzolanic reactivity: one was derived from Kentucky #9 coal and Kerr-McGee ash concentrate and the other was from Illinois #6 coal (similar to Kentucky #9 coal) alone. The first fly ash, which is most representative of that from the SRC-I Demonstration Plant, had a low reactivity (228 psi), possibly

due to a high carbon content. The second fly ash exhibited a reactivity (1,014 psi) comparable to that of power plant fly ashes derived from combustion of eastern bituminous coals (700 to 1,000 psi). The low reactivity of the SRC-I fly ash would preclude the use of the lime/fly ash system, which depends heavily on fly ash reactivity to work, unless a good substitute is imported.

- The process design evaluation prepared by Catalytic includes three systems: lime/dry fly ash, cement/dry fly ash, and cement/wet fly ash. Although the cement/wet fly ash system is 63% more expensive in capital cost than the cement/dry fly ash system (the least expensive alternative), it is recommended for two reasons. First, the low pozzolanic reactivity of the gasified KMAC/Kentucky #9 fly ash is not as critical for this system because the cement provides most of the pozzolanic reactivity; the fly ash serves mainly as the filler. Second, the system uses wet rather than dry fly ash. Dry fly ash will not be readily available at the SRC-I Demonstration Plant unless drastic changes are made to incorporate a fly ash collection/transport system, or to import dry fly ash from an external source. Neither option is desirable.
- In summary, based on the results of post-Baseline work, the zero-discharge system in the Baseline Design, with the additions and modifications discussed, seems to be technically feasible. However, the post-Baseline work could not address all uncertainties (primarily because of limited sample availability); more work is needed to definitively demonstrate the technical feasibility.
- Zero discharge imposes a substantial cost penalty; the capital cost is about $30 million (on a first-quarter 1981 basis), and the annual operating cost is close to $9 million, excluding capital recovery. The capital and operating costs for wastewater treatment (and associated solid waste handling and disposal) are $40 million and $9 million/year, respectively. With zero discharge, the total capital cost for wastewater

treatment, reuse, and solid waste handling/disposal is $70 million, and the total annual operating cost is $18 million/year. Thus, zero discharge constitutes 43% of the total capital cost, and 50% of the total operating cost.

- Partial discharge, i.e., recycling heavily contaminated wastewaters and discharging the rest, was considered briefly as an option to zero discharge. It was dismissed because the heavily contaminated wastewaters represent 85% of the plant's normal flow, and they still require the same elaborate treatment before reuse as the zero-discharge option. Consequently, the cost savings in comparison to that of zero discharge is insignifcant. Also, most of the technical uncertainties associated with zero discharge would still be unresolved.
- Total discharge is another alternative to zero discharge. This might be considered a viable option if more data could be generated to demonstrate that the fully treated wastewater is safe and acceptable to discharge. Considerable data generated by the post-Baseline environmental programs, although by no means conclusive, do suggest that the treated wastewater is of high quality. Considering the high cost penalty of zero discharge, this option deserves further examination.

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