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MHD Seed Recovery and Regeneration

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Phase II

Final Report

Contract No. DE-AC22-87-PC79672

**Space and Technology Division
TRW Space and Electronics Group
One Space Park
Redondo Beach, CA 90278**

October 1994

**U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, PA 15236**

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1. INTRODUCTION AND SUMMARY

This final report summarizes the work performed by the Space and Technology Division of the TRW Space and Electronics Group for the U.S. Department of Energy, Pittsburgh Energy Technology Center for the Econoseed process. This process involves the economical recovery and regeneration of potassium seed used in the MHD channel. This work was performed under Contract No. DE-AC22-87-PC79672. The contract period of performance extended from 1987 through 1994 and was divided into two phases. The Phase II test results are the subject of this Final Report. However, the Phase I test results are presented in summary form in Section 2.3 of this Final Report.

The Econoseed process involves the treatment of the potassium sulfate in spent MHD seed with an aqueous calcium formate solution in a continuously stirred reactor system to solubilize, as potassium formate, the potassium content of the seed and to precipitate and recover the sulfate as calcium sulfate. The slurry product from this reaction is centrifuged to separate the calcium sulfate and insoluble seed constituents from the potassium formate solution. The dilute solids-free potassium formate solution is then concentrated in an evaporator. The concentrated potassium formate product is a liquid which can be recycled as a spray into the MHD channel.

Calcium formate is the seed regenerant used in the Econoseed process. Since calcium formate is produced in the United States in relatively small quantities, a new route to the continuous production of large quantities of calcium formate needed to support an MHD power industry was investigated. This route involves the reaction of carbon monoxide gas with lime solids in an aqueous medium.

Phase I

Under Phase I (1987-1988), the DOE sponsored a bench scale project to evaluate the Econoseed process as applied to a high sulfur seed (as derived from Eastern coal). The objectives of the Phase I project were to test the Econoseed process at bench scale and to

prepare a conceptual design of a 300 MW_t commercial plant. The calcium formate production process was acquired from its developer (The Electro Metallurgical Company, a subsidiary of Union Carbide). The potassium formate production operation was successfully demonstrated at bench scale, and the resulting data was incorporated into a 300 MW_t commercial seed regeneration plant design and cost estimate. Economic studies showed that the total cost for seed regeneration by the Econoseed process is in the range of \$0.22 to \$0.25/lb (on a potassium basis) for high sulfur Eastern coal-derived seed, a cost which is less than half the potassium cost of \$0.63/lb for purchasing fresh potassium carbonate. A detailed description of the Phase I test results is presented in the "MHD Seed Recovery and Regeneration Final Report" dated October 14, 1988.

Phase II

A follow-on to the original program was awarded in order to test the Econoseed process as applied to a high sulfur seed (as derived from Eastern coal) at proof-of-concept (POC) scale using a plant design based on the bench scale data generated in Phase I. The objectives of the Phase II program were to: 1) design, construct and operate a POC test plant to demonstrate the process technology using actual high sulfur seed (Illinois No. 6) from UTSI, 2) produce tonnage quantities of recycled seed for testing at the CDIF facility, 3) design, construct and operate a separate, smaller scale POC unit to demonstrate the production of feed material calcium formate from lime and CO gas, 4) perform laboratory studies on the application of a modified Econoseed process as it would be applied to a low sulfur seed (as derived from Western coal), and 5) perform engineering assessment studies on the impact of the laboratory and POC scale operating and equipment data generated in Phase II on the 300 MW_t seed regeneration conceptual design developed in Phase I.

In 1991-1992, TRW designed, constructed and successfully operated a 250 pound per hour potassium formate proof-of-concept (POC) production unit. In addition to generating equipment scaleup/design data, about 11 tons (dry basis) of concentrated liquid potassium formate suitable for recycle to the MSE topping cycle plant were produced from high sulfur Eastern seed supplied by UTSI. TRW also designed, constructed and successfully operated a

50 lb/hr calcium formate POC production unit to generate equipment scaleup/design data. The POC test stand and the evaporation unit are shown in Figure 1-1. The Phase II test results are the subject of this Final Report.

1.1 BACKGROUND

All of the components of MHD power generation (slagging combustor, channel/magnet and heat recovery-seed recovery) have been demonstrated over several hundred to several thousand hours of operation in either workhorse or prototypical equipment - this is with the notable exception of the process for seed regeneration which until this present Phase II program had been tested only in the laboratory (Phase I). Studies by the Faraday Society, the International Energy Agency and the U.S. Electric Power Research Institute have all indicated that seed regeneration, at its present state of development, may well be the weakest link in demonstrating the technical and economic feasibility of MHD power.

It has sometimes been suggested that rather than engage in a seed regeneration Proof-of-Concept (POC) project, it would be better to simply purchase potassium carbonate and in some way dispose of the spent seed, which is potassium sulfate (and sometimes also potassium carbonate) mixed with coal ash. However this approach was rejected because: 1) depending on the coal sulfur content and potassium loading required, a single 1000 MW_e MHD utility would require 300 to 800 million pounds per year of potassium carbonate out of the U.S. annual production of 200 million pounds - an impossible demand on the U.S. industry, 2) the electric power needed to produce potassium carbonate by its commercial electrolytic process is 1.0 kW-hr/lb, which would correspond to as much as 10% of the power generated by the utility for this step alone - thus a 50% efficient MHD power plant would drop by nearly 5 percentage points, and additional thermal energy would still be needed for carbonation and evaporation to dry seed, and 3) there is no environmentally acceptable way to dispose of potassium sulfate as it is water soluble and would leach into the groundwater.

Figure 1-1. Test Stand (Left) and Potassium Formate Evaporation Unit (Right)

It has also been suggested that spent seed (potassium sulfate) be simply recycled and a tail-end FGD be installed at the MHD utility. But this was rejected as: 1) this would result in high sulfate concentration in the channel, which has been shown to shorten channel life, 2) the spent seed would still need to be refined at added cost in a chemical plant to stop buildup of entrapped coal ash, 3) FGD systems are more expensive than present complete seed regeneration cost forecasts, and 4) coal-derived impurities such as chloride would still need to be rejected in a regeneration plant.

Therefore, the Department of Energy decided to engage in a complete Proof-of-Concept scale demonstration of the technical and economic feasibility of regeneration of high sulfur spent MHD seed and conversion of all coal-derived components to environmentally sound disposal products. This Phase II POC test plant endeavor is crucial to the economics of MHD power and could well determine the ultimate commercial success of this method of generating electricity.

In addition, TRW has devised a modified configuration for the Econoseed process for spent seed from lower sulfur coals, such as those found in the West, which has the potential to reduce regeneration costs. The Western coal cost savings are based on separation of the unreacted potassium carbonate in spent seed from the potassium sulfate generated by sulfur capture, thus avoiding complete reprocessing of the spent seed to potassium formate. Economic studies have shown that the total cost for seed regeneration for low sulfur Western coal-derived seed with pre-separation of carbonate and sulfate can be potentially reduced to about \$0.13/lb (on a potassium basis) from about \$0.25/lb (on a potassium basis) without pre-separation of carbonate and sulfate. The DOE added a laboratory scale study of this cost saving low sulfur seed unit operation to the Phase II program in order to provide data aimed at substantiating this potential break-through in the economics of MHD. Western seed laboratory scale seed impurity (chloride) separation studies were also performed.

1.2 TEST RESULTS AND CONCLUSIONS

The Phase II seed regeneration program was divided into four tasks: 1) potassium formate POC unit studies, 2) calcium formate POC unit studies, 3) Western seed laboratory studies, and 4) engineering assessment studies. The results of these studies are summarized in the following sections.

1.2.1 Potassium Formate POC Unit

In the potassium formate POC unit, calcium formate solution is reacted with high sulfur spent seed (which consists of 90% potassium sulfate containing about 10% flyash, as obtained from Eastern high sulfur coal) to produce potassium formate and calcium sulfate (gypsum) by the following reaction:

The reactor effluent is dewatered to separate the precipitated gypsum and insoluble seed constituents from the regenerated seed solution. The dilute potassium formate solution produced by the above reaction is next concentrated in a two-stage evaporation unit. The concentrated potassium formate product can be used as the MHD seed material allowing for liquid injection of the molten salt into the channel at temperatures up to 160°C.

The 250 lbs/hr (5 MW_e) potassium formate POC production unit for Eastern coal has been operated to produce ~11 tons of potassium formate (dry basis) as 67 to 77 wt% solution from high sulfur Eastern coal-derived spent seed while generating equipment scaleup/design data. Eastern coal-derived spent seed from UTSI's CFFF (delivered to TRW in tote bins) comprised the spent seed fed to the POC unit. Calcium formate powder was purchased for the POC test operations.

The main objectives of the test operations of the potassium formate POC unit were to produce tonnage quantities of recycled seed for testing at the CDIF facility using actual high

sulfur seed (Illinois No. 6) from UTSI while simultaneously obtaining the engineering scaleup data required for the design of a commercial size plant.

During production operations (September 1991 through April 1992), approximately 35,000 pounds of Eastern spent seed from the UTSI CFFF were fed to the POC unit along with ~21,000 gallons of 12 weight percent calcium formate solution. A total of ~56,000 gallons of dilute potassium formate solution was produced and stored. The maximum spent seed feed rate achieved during production was 250 pounds per hour. The major achievements were:

- Total stream hours (spent seed feed into unit) were 174 hours.
- Maximum potassium formate (pure basis) production was ~200 pounds per hour.
- Maximum potassium formate solution concentration achieved was ~7.5 wt%.
- High seed sulfate conversions to gypsum (95 to 97%) were achieved with high (>99%) potassium recovery.

At the reaction temperatures utilized (60 to 70°C, 140 to 158°F), there was no evidence of the formation of insoluble syngenite $[K_2Ca(SO_4) \cdot H_2O]$. Reactor residence time during POC operations was 50 to 100 minutes with high sulfate conversion obtained over this entire time range. A relatively dry (0.2 to 0.3 lbs moisture/lb dry solids) gypsum and flyash waste product was produced that passed the EP Toxicity test. The potassium loss to the waste solids was very low at less than 1% of the potassium in the spent seed.

Two runs were performed in the POC unit in which sodium (as sodium sulfate) was added to the spent seed to simulate sodium levels expected in a "recycled" seed. Chloride was present at fairly high levels in all the runs performed in the POC unit. The chloride introduced with the calcium formate feed to the POC unit was present by virtue of a small residue of unconverted calcium chloride, the chemical used in the production of the purchased calcium formate. No significant partitioning of either the sodium or the chloride was seen in the POC reactor.

During evaporation operations between December 1991 and April 1992, approximately 56,000 gallons of dilute (5 to 7 wt%) potassium formate solution were fed to the two-stage evaporation unit which reduced it to ~2,200 gallons of concentrated solution. Maximum feed rate to the unit was ~6 GPM. The major achievements were:

- Total stream hours logged were 200 hours.
- Approximately 21,000 pounds (on a pure KCOOH basis) of concentrated (67 to 77 wt%) potassium formate solution were produced.
- Other constituents in the concentrated seed (calcium, sulfate, carbonate) totaled less than 0.4 wt%.
- Sulfate was less than 0.03 wt% in the concentrated product. That is, the regenerated seed contained ~0.1% of the sulfate that was present in the spent seed fed to the POC.
- Forty-one 55-gallon drums of concentrated product were shipped to the CDIF in Butte, Montana for use as regenerated seed in their MHD channel.

The concentrated product has a freezing point of less than -70°C (although solids will start to crystallize from solution as the temperature is reduced below ambient temperature, 10-20°C) and meets the CDIF requirements for storage and pumping of a liquid regenerated seed. The final product was filtered for removal of any suspended solids prior to shipment to the CDIF.

1.2.2 Calcium Formate POC Unit

TRW is proposing that the large quantities of calcium formate required for MHD seed regeneration be produced by the reaction of carbon monoxide gas with lime solids in an aqueous medium. This route to the continuous production of calcium formate was piloted in 1954 by the Electro Metallurgical Company (of Niagara Falls, New York), a subsidiary of Union Carbide. TRW acquired the pilot plant database. Using this database, which was limited primarily to proof of principle experiments, TRW designed, constructed and successfully operated a 50 lb/hr (~1 to 2 MW_l) calcium formate Proof-of-Concept (POC) production unit to generate equipment scaleup/design data. Since over two-thirds of the

projected cost of seed regeneration is associated with this unit operation and the production of CO gas for reactor feed, verification of the process parameters is crucial to the MHD program.

Aqueous calcium formate solution (at up to 12 wt% concentration) is produced by reacting CO gas with aqueous lime slurry at reaction temperatures of 300°F to 400°F and reaction pressures of 950 psig to 1350 psig.

Hydrated lime slurry feed and a feed gas mixture (CO, N₂, and CO₂) were raised to reaction pressure and preheated before being contacted with each other in the two-stage cocurrent flow pipe reactor. Calcium formate is produced in the reactor by the following reaction:

The reactor effluent is cooled and then reduced to atmospheric pressure across a control valve. The cooled calcium formate effluent solution is separated from unreacted/non-condensable gases and unreacted lime solids.

The main objective in test operations of the calcium formate POC unit was to ascertain which operating parameters influence reactor performance (CO conversion) so as to obtain the engineering scaleup data required for the design of a commercial size plant. The test matrix employed covered the range of reaction temperatures between 300 and 400°F (149 and 204°C), reaction pressures between 950 and 1350 psig and reaction residence times between 5 and 30 minutes. In addition, reactor feed gases containing as little as 40% to as much as 100% carbon monoxide were tested to reflect the range of possible commercial sources of carbon monoxide. Carbon dioxide in the reactor feed gas was varied from 0 to 3% to determine the effect of this potential feed gas impurity. The effect of reactor mixing was investigated by operating the reactors with and without internals.

The unit was operated between October 1992 and May 1993. Chemical analyses were performed on reactor feed and effluent stream test run samples taken during this period. Material balances were then performed using these test run sample analyses and the measured test run stream flows. CO conversions were found to vary in a regular and predictable manner with reaction temperature, pressure, feed gas composition, and residence time. At constant reaction temperature, CO conversion is greater at higher pressure. At constant reaction temperature, CO conversion increases with increased CO concentration in the feed gas. CO conversion increases approximately linearly with temperature, all other factors being equal. At constant reaction pressure, CO conversion increases with reactor residence time.

The major achievements were:

- Approximately 100 hours of testing were performed.
- CO conversions of up to 100% were attained under favorable operating conditions.

1.2.3 Western Seed Laboratory Studies

TRW has devised a modified configuration for the Econoseed process for spent seed from lower sulfur coals, such as those found in the West, which has the potential to reduce regeneration costs. The Western coal cost savings are based on separation of the unreacted potassium carbonate in spent seed from the potassium sulfate generated by sulfur capture. Since potassium carbonate is already a viable fresh seed material, only the separated potassium sulfate needs to be regenerated to potassium formate, thus avoiding complete reprocessing of the spent seed to potassium formate. Laboratory scale K_2CO_3/K_2SO_4 separation studies of this potentially cost saving low sulfur seed unit operation were conducted to provide data aimed at substantiating this break-through in the economics of MHD.

Due to the lower sulfur content of Western coals, the spent seed recovered contains an excess of potassium carbonate over that necessary for 100% sulfur capture. As an example,

for a Montana Rosebud coal-fired MHD system with seed loading at 1.5% potassium, the spent seed contains about 2.5 weights of potassium carbonate to 1 weight potassium sulfate. If this spent seed is fed to the seed regeneration process as originally configured, all of the sulfate and carbonate is converted to formate via the reaction with calcium formate since the process is not selective to the sulfate form. This requires the production of enough calcium formate for reaction with both salts even though two-thirds of the seed material is essentially in the final form for recycle.

In order to take advantage of the lower sulfur content of Western coal by processing only the potassium sulfate to potassium formate, a method for separating the potassium sulfate from the potassium carbonate is necessary. Literature solubility data indicated the possibility of an aqueous separation of potassium carbonate from potassium sulfate. That is, differences in the solubilities of the two salts allows for a suitable separation of the sulfate from the carbonate. Potassium carbonate is more soluble than the sulfate. This means that the spent seed can be contacted with a limited amount of water to dissolve the potassium carbonate leaving essentially all of the K_2SO_4 and mineral matter undissolved. After separation of the solids from the saturated carbonate solution, the solids would then be fed to the Econoseed process for conversion of the potassium sulfate to potassium formate using calcium formate. The regenerated potassium formate seed would then be mixed with the recovered potassium carbonate for seed recycle or the two seed forms could be recycled separately.

The Western seed laboratory studies used "simulated" seed that was representative of Western spent seed containing potassium carbonate and potassium sulfate (as well as impurities such as potassium chloride) at levels as would be derived from typical coals. One objective of these laboratory studies was to determine the amount of water necessary to solubilize only the potassium carbonate component of the seed. The experimentation is applicable to both Western or Eastern coal MHD channel operations that require an amount of potassium in excess of that required for sulfur capture (spent seed will contain unreacted potassium carbonate).

An experiment using K_2CO_3 : K_2SO_4 in ratios expected in spent seed that would be produced in a Western seed MHD facility and using the minimum amount of water necessary to dissolve the carbonate (based on available literature data for the K_2CO_3 - K_2SO_4 - H_2O system), proved to be quite satisfactory with all (99.3%) of the carbonate recovered in solution and 81.2% of the sulfate retained in the solid phase (dry basis). This confirmed the separation expected based on the available literature data for the K_2CO_3 - K_2SO_4 - H_2O system. The literature data on the K_2CO_3 - K_2SO_4 - H_2O system also indicated (and we were able to confirm by experiment) that when using the minimum amount of water necessary for complete dissolution of K_2CO_3 , the higher the K_2CO_3 : K_2SO_4 ratio in the spent seed, the smaller the fraction of K_2SO_4 that would also go into solution. Thus a relatively poor separation of seed into its K_2CO_3 and K_2SO_4 fractions could be expected in seeds having a low K_2CO_3 to K_2SO_4 ratio.

Additional experiments to separate K_2CO_3 from K_2SO_4 in spent seed mixtures were conducted to verify a process scheme proposed by TRW which is designed to result in a sharp separation of K_2CO_3 and K_2SO_4 regardless of the K_2CO_3 : K_2SO_4 ratio in the spent seed. These experiments were conducted with simulated spent seed containing K_2CO_3 : K_2SO_4 at ratios of 0.382:1, 0.587:1 and 1.30:1. The first ratio is typical of spent seed produced from an Eastern coal and the latter two are possible ratios for spent seed produced in a Western coal MHD facility (the largest ratio is at an elevated K_2 :S ratio). The experimental results indicate almost complete separation of carbonate from sulfate for all three of the seed mixtures, with 99% to 100% of the initial carbonate recovered in the solution phase and virtually 100% of the sulfate retained in the solid phase (dry basis).

A number of laboratory studies were directed towards the rejection of chloride from spent seed. Chloride is found in either Eastern or Western coal and any appreciable buildup in the seed upon recycle would corrode the channel and decrease plasma conductivity. Therefore, chloride must be rejected from the seed without simultaneously incurring excessive seed (potassium) losses. The laboratory studies on K_2CO_3 / K_2SO_4 separation indicated that KCl selectively partitions with the K_2CO_3 . K_2CO_3 /KCl solution concentration experiments were performed to test the feasibility of separately removing pure K_2CO_3 and

pure KCl from starting K_2CO_3 solutions containing various amounts of KCl as an impurity. The results indicate the possibility of separately crystallizing virtually pure K_2CO_3 and pure KCl from solution. A number of processing schemes to accomplish this have been proposed.

The major achievements of the Western seed Laboratory studies were:

- A sharp separation of K_2CO_3 and K_2SO_4 can be achieved regardless of the $K_2CO_3:K_2SO_4$ ratio in the spent seed.
- KCl selectively partitions to K_2CO_3 phase during K_2CO_3/K_2SO_4 separation.
- At proper processing conditions KCl, in relatively pure form, can be rejected from seed.

1.2.4 Engineering Assessment Studies

The purpose of the engineering assessment studies was to utilize the Western seed laboratory study data and the Eastern seed POC scale operating and equipment data from Phase II to determine their potential process impact on the Econoseed process as developed in Phase I of the program (conceptual design of a 300 MW_t Econoseed plant for high sulfur seed from Eastern coal). The seed regeneration process represents a significant portion of the overall capital and operating costs for an integrated MHD system producing electric power, and the data from the Phase II seed regeneration program was used to refine the process design parameters and to indicate changes to the Phase I Econoseed design that have the potential to reduce the cost of seed regeneration.

The effect of the following was investigated: 1) removal of carbonate/chloride from the spent seed prior to reaction with calcium formate, 2) impurities rejection in the potassium formate evaporator, 3) chloride rejection from the plant, 4) sources of carbon monoxide feed for the calcium formate production unit, and 5) long term storage of regenerated seed.

1.3 REPORT OUTLINE

The following two sections of this report contain a detailed description of the potassium formate and calcium formate POC units along with discussions of the test results and equipment evaluations. This is followed by a detailed description of the Western seed laboratory experiments and test results. Finally the results of engineering assessment studies are presented in which the potential impact of the data from the operation of the POC units and Western seed laboratory experiments on the 300 MW_t Econoseed seed regeneration plant design was investigated. A list of acronyms and abbreviations is presented in the appendix.

2. POTASSIUM FORMATE POC UNIT

2.1 INTRODUCTION AND SUMMARY

Potassium formate is the regenerated seed form that is recycled to the MHD channel. The Econoseed process involves the treatment of the potassium sulfate in spent MHD seed with an aqueous calcium formate solution in a continuously stirred reactor system to solubilize, as potassium formate, the potassium content of the seed and to precipitate the sulfate as calcium sulfate. The slurry product from this reaction is centrifuged to separate the calcium sulfate and insoluble seed constituents from the potassium formate solution. The dilute solids-free potassium formate solution is then concentrated in an evaporator. The concentrated product is a liquid which can be recycled as a spray into the MHD channel.

In 1991-1992, TRW designed, constructed and successfully operated a 250 pound per hour Potassium Formate Proof-of-Concept (POC) production unit. Approximately 11 tons (dry basis) of concentrated liquid potassium formate suitable for recycle to the MSE topping cycle plant were produced.

The following sections of this Introduction and Summary contain a description of the POC unit and a summary of test results and conclusions.

2.1.1 Process Description

Calcium formate solution is reacted with spent seed (which consists of 90% potassium sulfate and about 10% flyash, as obtained from Eastern high sulfur coal) to produce potassium formate and calcium sulfate (gypsum) by the following reaction:

The reactor effluent is dewatered to separate the precipitated gypsum and insoluble seed constituents from the regenerated seed solution. These solids are washed and recentrifuged to remove traces of potassium formate and to render the solids suitable for disposal. The

dilute potassium formate solution from the initial separation step is next concentrated in a two-stage evaporation unit.

The POC unit is comprised of three subsystems:

- Potassium formate reaction system
- Potassium formate separation/washing system
- Potassium formate evaporation system

A block diagram of the POC unit is shown in Figure 2-1. The Econoseed byproducts are a mixture of gypsum and flyash, and a small amount of calcium carbonate. The concentrated potassium formate product can be used as the MHD seed material allowing for liquid injection of the molten salt into the channel at temperatures up to 160°C.

The potassium formate production unit for Eastern coal has been operated to produce about 11 tons of potassium formate (dry basis) as 67 to 77 wt% solution from high sulfur Eastern coal-derived spent seed while generating equipment scaleup/design data. Eastern coal-derived spent seed from UTSI's CFFF (delivered to TRW in tote bins) comprised the spent seed fed to the POC unit. Calcium formate powder was purchased by TRW (and blended off-site) for the POC test operations.

2.1.2 Test Conditions

The main objectives of the test operations of the potassium formate POC unit were to produce tonnage quantities of recycled seed for testing at the CDIF facility using actual high sulfur seed (Illinois No. 6) from UTSI while simultaneously obtaining the engineering scaleup data required for the design of a commercial size plant.

For the purposes of the following discussion, the potassium formate POC unit will be divided into two areas: 1) dilute potassium formate production (potassium sulfate reaction and solids separation/washing units) which is shown in the left side of Figure 2-1 and which

produces dilute (~ 7 wt%) potassium formate solution, and 2) the two-stage evaporation unit which is shown in the right side of Figure 2-1 and which produces concentrated (> 70 wt%) potassium formate.

Dilute potassium formate production operations and evaporation unit operations were alternated. That is, the dilute formate production equipment was operated for several days (one 8-hour shift per day) to produce dilute (~ 7 wt%) potassium formate solution which was stored in a 16,000 gallon tank. When this storage tank became full, dilute formate production plant operations were stopped and the evaporation unit was operated for several days (one 8-hour shift per day) to deplete the supply of dilute solution and produce concentrated (67-77 wt%) potassium formate solution which was collected in 55-gallon drums for shipment to the CDIF. This method of operation was dictated by the size of the available operating crew at the test site and the fact that a number of items of equipment (centrifuges, etc.) served double duty (i.e. were used in both the dilute formate production operations and evaporation operations).

2.1.3 Test Results and Conclusions

During production operations, the dilute formate production equipment was operated for a total of 174 hours between September 1991 and April 1992. Approximately 35,000 pounds of Eastern spent seed from the UTSI CFFF were fed to the POC unit along with $\sim 21,000$ gallons of 12 weight percent calcium formate solution. A total of $\sim 56,000$ gallons of dilute potassium formate solution was produced and stored. The maximum spent seed feed rate achieved during production was 250 pounds per hour. This is sufficient spent seed to produce ~ 200 pounds per hour of regenerated potassium formate seed (pure basis). The maximum potassium formate solution concentration achieved during operation of the dilute formate production unit was ~ 7.5 wt%.

High seed sulfate conversions to gypsum (95 to 97%) were achieved with high ($> 99\%$) potassium recovery. At the reaction temperatures utilized (60 to 70°C), there was no evidence of the formation of insoluble syngenite $[\text{K}_2\text{Ca}(\text{SO}_4)\cdot\text{H}_2\text{O}]$. Reactor residence time

during POC operations was 50 to 100 minutes with high sulfate conversion obtained over this entire time range. A relatively dry (0.2 to 0.3 lbs moisture/lb dry solids) gypsum and flyash waste product was produced that passed the EP Toxicity test. The potassium loss to the waste solids was very low at less than 1% of the potassium in the spent seed.

Runs were performed in the POC unit in which sodium and chloride were added to the spent seed to simulate levels expected in a "recycled" seed. No partitioning of either the sodium or the chloride was seen.

The dilute formate production equipment performed well mechanically after problems associated with spent seed contamination (with rust particles), reactor level control tuning, and centrifuge cake discharge chute plugging were solved. A number of operational problems were observed such as plugging in piping and control valves which was due in part to the mechanical limitations of the equipment at pilot scale. The formation of a ubiquitous scale was observed on the walls of the reactor. This scale was analyzed as consisting predominantly of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and a small fraction of sodium silicate, $\text{Na}_2\text{O} \cdot \text{SiO}_2$. While this scale did not cause serious problems in the operation of the POC unit, it raises questions on the effect it might have on long duration operations.

During evaporation operations between December 1991 and April 1992, a total of 200 stream hours were logged. Approximately 56,000 gallons of dilute (5 to 7 wt%) potassium formate solution were fed to the two-stage evaporation unit which reduced it to ~2,200 gallons of concentrated solution. Maximum feed rate to the unit was ~6 GPM. Approximately 21,000 pounds (on a pure KCOOH basis) of concentrated (67 to 77 wt%) potassium formate solution were produced in the unit. Other constituents in the concentrated seed (calcium, sulfate, carbonate) totaled less than 0.4% wt%. In particular, sulfate was less than 0.03 wt% in the concentrated product. That is, the regenerated seed contained ~0.1% of the sulfate that was present in the spent seed fed to the POC. The concentrated potassium formate solution was drummed (forty-one 55-gallon drums) and shipped to the CDIF in Butte, Montana for use as regenerated seed in their MHD channel. This product has a freezing point of less than -70°C (although solids will start to crystallize from solution as the

temperature is reduced below ambient temperature, 10-20°C) and meets the CDIF requirements for storage and pumping of a liquid regenerated seed. The final product was filtered for removal of any suspended solids prior to shipping to the CDIF.

In conclusion, the engineering data base gathered during the POC operations (seed plant sized to support a 5 MW_t MHD plant) is suitable for scaleup to a 300 MW_t seed plant design based on a high sulfur seed generated from Eastern coal.

2.2 TEST CIRCUIT DESCRIPTION

There are three subsystems which make up the potassium formate POC test unit:

1) potassium formate reaction, 2) potassium formate separation/washing, and 3) potassium formate evaporation. Process flow diagrams for these three subsystems are presented in Figures 2-2, 2-3 and 2-4, respectively. The material balance used to design the potassium formate POC unit is presented in Table 2-1. All of the subsystems in the potassium formate POC unit were nominally designed to operate continuously to support a production rate of 250 pounds per hour of potassium formate.

The complete POC test unit, as built, contains about 50 major pieces of equipment including reactors, tanks, mixers, pumps, centrifuges, a tote bin handling system, heat exchangers, bag filters, and a two-stage evaporation unit. The major equipment items are listed in Table 2-2. The materials of construction include stainless steel, carbon steel and plastics. The POC unit as constructed contains instruments and controls as well as a computer control room with a data acquisition and control system. The three subsystems of the potassium formate POC test unit plus the data acquisition and control system are described in detail in the following sections.

2.2.1 Potassium Formate Reaction

The potassium formate reaction subsystem, which is depicted in Figure 2-2 consists of a tote bin transportation and dumping system (including fork lift), a weigh belt feeder, two

Figure 2-3. Process Flow Diagram of the Potassium Formate Solids Separation/Washing System

Figure 2-4. Process Flow Diagram of the Potassium Formate Evaporation System

TABLE 2-1. MATERIAL BALANCE ECONOSEED POC PLANT
FORMATE REACTOR, SOLIDS SEPARATION/WASHING AND EVAPORATION

Basis

- 250 lbs/hr potassium formate (dry) production
- No sodium sulfate in spent seed
- 100 percent conversion of potassium sulfate in spent seed to formate with stoichiometric consumption of calcium formate.
- Calcium formate added as 13.0 wt% solution
- Moisture in cake separated in centrifuges/filter = 0.3 lbs/lb dry cake
- Wash water utilized = 5 lbs/lb dry cake
- Makeup water added to reactor to give an evaporator feed containing 9.5 wt% total dissolved solids
- Potassium carbonate added to solids-free reactor effluent to convert dissolved calcium sulfate to insoluble calcium carbonate. Add 200% stoichiometric potassium carbonate (based on total calcium sulfate) to convert 75% of the calcium sulfate.
- A two-stage reactor system is shown. Complete conversion of the potassium sulfate, for material balance purposes, is shown as taking place in the first reactor stage.

TABLE 2-1. MATERIAL BALANCE ECONOSEED POC PLANT
FORMATE REACTOR, SOLIDS SEPARATION/WASHING AND EVAPORATION (CONTINUED)

Stream No.		1	2	3	4	5	6	7
Stream Description	<u>MW</u>	Spent Seed	Calcium Formate Feed	Makeup Water	Reactor Effluent	Reactor Effluent	Centrate	Centrifuge Cake
Solids, lbs/Hr								
Ca(COOH) ₂	130.1							
CaCO ₃	100.1							
CaSO ₄	136.1				196	196		196
KCOOH	84.1							
K ₂ CO ₃	138.2							
K ₂ SO ₄	174.2	259						
Inerts		<u>25</u>			<u>25</u>	<u>25</u>		<u>25</u>
Subtotal Solids, lbs/Hr		284			221	221		221
Liquids, lbs/Hr								
Ca(COOH) ₂	130.1		194					
CaCO ₃	100.1							
CaSO ₄	136.1				11	11	11	
KCOOH	84.1				256	256	250	6
K ₂ CO ₃	138.2							
K ₂ SO ₄	174.2							
H ₂ O	18.0		<u>1298</u>	<u>239</u>	<u>2633</u>	<u>2633</u>	<u>2574</u>	<u>59</u>
Subtotal Liquids, lbs/Hr			1492	239	2900	2900	2835	65
Total Stream, lbs/Hr		284	1492	239	3121	3121	2835	286

TABLE 2-1. MATERIAL BALANCE ECONOSEED POC PLANT
FORMATE REACTOR, SOLIDS SEPARATION/WASHING AND EVAPORATION (CONTINUED)

Stream No.		8	9	10	11	12	13	14	15
Stream Description	<u>MW</u>	K ₂ CO ₃ Powder	Dissolve H ₂ O	K ₂ CO ₃ Solution	Filter Feed	Evaporator Feed	Filter Cake	Wash Water	Wash Slurry
Solids, lbs/Hr									
Ca(COOH) ₂	130.1								
CaCO ₃	100.1				6		6		6
CaSO ₄	136.1								
KCOOH	84.1								
K ₂ CO ₃	138.2	22							
K ₂ SO ₄	174.2								
Inerts		—			—		—		—
Subtotal Solids, lbs/Hr		22			6		6		6
Liquids, lbs/Hr									
Ca(COOH) ₂	130.1								
CaCO ₃	100.1								
CaSO ₄	136.1				3	3			
KCOOH	84.1				250	250			
K ₂ CO ₃	138.2			22	14	14			
K ₂ SO ₄	174.2				10	10			
H ₂ O	18.0	—	<u>66</u>	<u>66</u>	<u>2640</u>	<u>2638</u>	<u>2</u>	<u>30</u>	<u>32</u>
Subtotal Liquids, lbs/Hr			66	88	2917	2915	2	30	32
Total Stream, lbs/Hr		22	66	88	2923	2915	8	30	38

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Stream No.		16	17	18	19	20	21	22	23
Stream Description	MW	Wash Water	Wash Slurry	Centrate/Recycle	Solids for Disposal	Filtered Evaporator Feed	Evaporator Overhead Condensate	Formate Product from Evap	Formate Product for CDIF (estimate)
Solids, lbs/Hr									
Ca(COOH) ₂	130.1								
CaCO ₃	100.1				6				
CaSO ₄	136.1		192		192			3	
KCOOH	84.1								
K ₂ CO ₃	138.2							14	
K ₂ SO ₄	174.2							10	
Inerts			<u>25</u>		<u>25</u>			—	
Subtotal Solids, lbs/Hr			217		223			27	
Liquids, lbs/Hr									
Ca(COOH) ₂	130.1								
CaCO ₃	100.1								
CaSO ₄	136.1		4	4		3			
KCOOH	84.1		6	6		250		250	250
K ₂ CO ₃	138.2					14			
K ₂ SO ₄	174.2					10			
H ₂ O	18.0	<u>1105</u>	<u>1164</u>	<u>1096</u>	<u>68</u>	<u>2638</u>	<u>2555</u>	<u>83</u>	<u>83</u>
Subtotal Liquids, lbs/Hr		1105	1174	1106	68	2915	2555	333	333
Total Stream, lbs/Hr		1105	1391	1106	291	2915	2555	360	333

TABLE 2-2. POTASSIUM FORMATE POC UNIT MAJOR EQUIPMENT

<u>ITEM NO.</u>	<u>NAME</u>
DILUTE POTASSIUM FORMATE REACTION SECTION	
A-101	Tote Bin Tilter (Existing)
A-102	Bin Discharge (Existing)
A-103	Weigh Belt Feeder (Existing)
A-104	Rotary Air Lock (Existing)
B-101	Tote Bins (Existing)
---	Tote Bin Elevator (Existing)
---	Tote Bin Crane (Horizontal Extension of Elevator) (Existing)
E-102	Calcium Formate Solution Heater
M-1021	First Reactor Mixer (Existing)
M-1022	First Reactor Mixer (Existing)
M-1023	First Reactor Mixer (Existing)
M-104	Second Reactor Mixer (Existing)
P-102	Reactor Effluent Slurry Pump (Existing)
P-104	Reactor Effluent Slurry Pump (Existing)
P-107	Calcium Formate Solution Pump (Existing)
T-101	Spent Seed Storage Tank (Existing)
T-102	Reactor (First Stage) (Existing)
T-104	Reactor (Second Stage) (Existing)
T-107	Calcium Formate Solution Storage Tank (Existing)
SOLIDS SEPARATION/WASHING SECTION	
C-201	Centrifuge (Existing)
C-202	Centrifuge (Existing)
D-202	Solids Collection Drums
E-201	Wash Water Heat Exchanger
F-203	Vibrating Candle Filter (Existing)
M-2011	Centrate Tank Mixer
M-2012	Solids Wash Tank Mixer
M-203	Solids Wash Tank Mixer
M-204	Carbonate Dissolve Tank Mixer
P-2011	Centrifugal Centrate Pump (Existing)
P-2012	Centrifugal Wash Slurry Pump (Existing)
P-202	Centrifugal Recycle Wash Pump (Existing)
P-203	Centrifugal Wash Slurry Pump (Existing)
P-204	Potassium Carbonate Metering Pump
T-2011	Centrate Tank
T-2012	Solids Wash Tank
T-202	Centrate Tank
T-203	Solids Wash Tank
T-204	Potassium Carbonate Dissolve Tank
W-202	Drum Scale

TABLE 2-2. POTASSIUM FORMATE POC UNIT MAJOR EQUIPMENT (CONTINUED)

<u>ITEM NO.</u>	<u>NAME</u>
POTASSIUM FORMATE EVAPORATION SECTION	
D-301	Evaporated Product Drums
E-301	Potassium Formate Solution Heater
E-302	Evaporation Feed Tank Circulation Heater
EV-701	Package Two-Stage Evaporation Unit
F-302AB	Bag Filters
F-303	Bag Filter
P-3022	Evaporation Unit Feed Pump (Existing)
P-706	Concentrated Liquid Product Pump (Existing)
P-309	Centrifugal Potassium Formate Solution Pump (Existing)
T-302	Evaporator Feed Tank (Existing)
T-309	Calcium Formate Solution Storage Tank (Existing)

potassium formate reactors, a calcium formate solution storage tank and heater, an impurities feed tank, plus various pumps and mixers.

Eastern coal-derived spent MHD seed is a light tan, dry powder that contains about 90% potassium sulfate, K_2SO_4 , plus 10% coal mineral matter (silicon dioxide, aluminum oxide, iron oxide). The seed was supplied by UTSI and was received in 3.5' x 4' x 8'4" tote bins (109 cubic feet), each capable of holding ~1.5 tons of seed (see Figure 2-5). The loaded tote bins (each weighing ~2 tons) are conveyed to the facility structure by a forklift. The tote bins are raised to the top of the structure by an elevator system and then moved by a rail system to a feed connection with a live bottom solids storage tank (T-101), which has a capacity of 180 cubic feet (about 3 tons). A bin tilter (A-101) (Figure 2-6) unloads the contents of the tote bins into the storage tank. Nitrogen is used to blanket the tote bin feed system to prevent moisture from entering the system.

The spent seed is metered at a rate of about 250 pounds per hour from tank T-101 by the weigh belt feeder (A-103) into a 280 gallon, 3-stage agitated tank, T-102, which serves as the first potassium formate reactor. A spent seed feed rate of 250 pounds per hour results in about 200 pounds per hour of potassium formate product from the downstream processing equipment. The live bottom of seed storage tank T-101 is shown in the top of Figure 2-7. The weigh belt feeder is shown in the bottom of Figure 2-7 and in Figure 2-8. The discharge chute between the weigh belt feeder and the potassium formate reactor is shown in Figure 2-9. The horizontal 3-stage first potassium formate reactor is shown in Figure 2-10.

Prior to the start of operations, a 12% aqueous calcium formate solution is prepared off-site at a vendor's facility and transported to TRW. During production operations, the calcium formate solution is continuously pumped from a 16,000-gallon storage tank (T-107), heated to 70 to 90°C (158 to 194°F) in a steam heated exchanger (E-102) and then delivered to the potassium formate reactor (T-102). Deionized water, live steam for additional heating, and recycled wash water are also added to reactor T-102.

Figure 2-5. Tote Bins

Figure 2-6. Bin Tilter

Figure 2-7. Live Bottom of Seed Storage Tank (Top) and Weigh Belt Feeder (Bottom)

Figure 2-8. Spent Seed Weigh Belt Feeder

Figure 2-9. Discharge Chute Between Weigh Belt Feeder and Formate Reactor

Figure 2-10. Horizontal 3-Stage First Potassium Formate Reactor

The first potassium formate reactor (T-102) is operated at a maximum of 90°C (194°F) with a residence time of 15 to 45 minutes. The resulting slurry which consists of a solution of primarily potassium formate plus smaller amounts of calcium formate, potassium sulfate, calcium sulfate and suspended solids (gypsum and spent seed inerts) is continuously withdrawn from T-102 and pumped to the second potassium formate reactor (T-104) using a centrifugal pump (P-102).

The important chemical reaction involved in this step is as follows:

The second potassium formate reactor (T-104) is a 400 gallon single stage agitated tank which provides an additional 45 to 60 minutes of residence time at a maximum temperature of 90°C (194°F). The resulting slurry which consists of a dilute solution of primarily potassium formate plus smaller amounts of calcium formate, potassium sulfate, calcium sulfate and suspended solids (gypsum and spent seed inerts) is continuously withdrawn from tank T-104 and pumped to the first centrifuge in the potassium formate solids separation/washing system by a centrifugal pump (P-104).

An "impurity" (Na_2SO_4) was added to the first potassium formate reactor (T-102) for specified test runs during test operations to gather information on the effect (partition) of sodium on the reaction system. The calcium formate fed to the POC unit contained chloride (it was made from calcium chloride). Chloride was monitored during specified test operations to gather information on the effect (partition) of chloride in the reaction system.

2.2.2 Potassium Formate Solids Separation/Washing

The potassium formate solids separation/washing subsystem, which is depicted in Figure 2-3, consists of 2 centrifuges, bag and candle filters, plus various tanks, pumps, mixers, and exchangers to separate the gypsum (calcium sulfate) and insoluble seed constituents (coal mineral matter) from the potassium formate solution. These solids are washed with

deionized water and recentrifuged to remove traces of potassium formate and to render the solids suitable for disposal. The wash liquid from the second centrifuge is recycled to the first reactor T-102.

As was mentioned above, the potassium formate slurry from reactor T-104 which consists primarily of potassium formate dissolved in water and suspended solids (gypsum and spent seed inerts) is continuously pumped to the first centrifuge (C-201) in the potassium formate separation/washing subsystem. The two potassium formate centrifuges are shown in Figure 2-11.

The dilute potassium formate centrate from centrifuge C-201 is collected in a polypropylene tank (T-2011) to which a small stream of aqueous potassium carbonate (K_2CO_3) is added. Tank T-2011 is shown in Figure 2-12. (Potassium carbonate powder and DI water are added to an agitated polypropylene tank (T-204) to form a potassium carbonate solution which is metered into centrate tank T-2011 with a metering diaphragm pump, P-204.) Potassium carbonate is added to tank T-2011 to reduce the small amount of dissolved calcium, primarily in the form of soluble calcium sulfate (~ 0.4 wt% solubility), in the formate solution. The potassium carbonate reacts with the soluble calcium to form very insoluble calcium carbonate. The precipitated calcium carbonate is removed downstream in the candle/bag filters (F-203). This step was added to avoid potential calcium compound scaling on the heat exchanger surfaces in the downstream formate evaporation unit.

The important chemical reaction involved in this step is as follows:

The potassium formate solution is continuously withdrawn from tank T-2011 and pumped using a centrifugal pump (P-2011) to a vibrating candle pressure filter (F-203) or a bag filter where any residual trace solids (including calcium carbonate) are removed before the solution is sent to the evaporation subsystem for concentration. The vibrating candle

Figure 2-11. Potassium Formate Classification Centrifuges

Figure 2-12. Centrate Tank T-2011

filter is shown in Figure 2-13 and the bag filter during unloading of solids is shown in Figure 2-14. The filter cake is collected in a 55-gallon drum.

The gypsum and spent seed inert solids from C-201 are reslurried in tank T-2012 with hot (194°F maximum) deionized wash water. The wash water is heated with steam in shell and tube exchanger E-201 before entering T-2012. Hot water is used to keep the solution in tank T-2012 at 194°F. This wash water, after separation from the washed solids, is ultimately recycled to the first potassium formate reactor (T-102). Hot recycled water is one means of adding heat to T-102.

The slurry from wash tank T-2012 consists of a very dilute solution of potassium formate plus suspended solids (gypsum and spent seed inerts) and is continuously pumped to the second centrifuge (C-202) for removal of the wash water and to recover the solids for disposal. These solids as discharged from centrifuge C-202 are shown in Figure 2-15. These solids, which pass the EP toxicity test, are collected in 55-gallon drums (D-202). The 55-gallon drums were hauled away by a disposal company for environmentally safe disposal.

The very dilute, hot potassium formate wash centrate from centrifuge C-202 is collected in a polypropylene tank (T-202) and recycled by pump P-202 to the first potassium formate reactor (T-102).

2.2.3 Potassium Formate Evaporation

The potassium formate evaporation system, which is depicted in Figure 2-4, consists of a packaged two-stage evaporation unit plus two evaporator feed/storage tanks, feed heaters, bag filters, pumps, and a packaged steam boiler. Water is evaporated from the potassium formate seed to produce a concentrated ~75% potassium formate solution product for shipment and recycle to the MHD channel in Butte, Montana. The evaporation unit as it was being erected is shown in Figure 2-16 and after it was installed on its test pad is shown in Figure 2-17.

Figure 2-13. Vibrating Candle Filter

Figure 2-14. Unloading Solids from Bag Filter

Figure 2-15. Gypsum Waste Solids

Figure 2-16. Evaporation Unit Being Erected

Figure 2-17. Installed Potassium Formate Evaporation System

The solids-free dilute ($\sim 7\%$) potassium formate solution from the separation/washing system is continuously pumped to a 16,000 gallon evaporator feed storage tank (T-309). Several days of potassium formate production storage is provided by tank T-309. During evaporation operations, the potassium formate solution is pumped (P-309) from the evaporator feed storage tank (T-309) through exchanger E-301 to the evaporator feed tank (T-302). Steam-heated shell and tube exchanger E-301 is used to heat the stored potassium formate solution from ambient temperature (60°F) to 150°F .

The temperature of the potassium formate solution in feed tank T-302 is maintained at 150°F by adding heat in a pump-around loop external to the tank. Since feed tank T-302 is large (940 gallons), the most efficient way to maintain the potassium formate solution at 150°F is by circulating (with pump P-3022) the tank contents through a steam-heated external double pipe exchanger E-302.

The potassium formate solution is pumped from T-302 through bag filters F-302 A&B to remove any remaining small amounts of suspended solids (e.g. calcium carbonate) from the evaporator feed.

Evaporator EV-701 is a self-contained packaged evaporation unit (provided by *Swenson Process Equipment Inc.*) designed to produce a concentrated potassium formate solution product for shipment to the CDIF in Butte, Montana. The concentration of the dilute potassium formate solution is carried out under vacuum in a series of two evaporation stages utilizing steam as the heat input medium. The first evaporation stage concentrates the potassium formate solution from $\sim 7\%$ to $\sim 30\%$ concentration. In the second evaporation stage, the potassium formate concentration is further increased to $\sim 75\%$.

The feed solution (already at 150°F) to the first evaporation stage is given additional preheat in an exchange with hot steam chest condensate. The preheated feed is then fed to the first stage evaporator circulating loop. The first stage evaporator is of the falling film type. This evaporator has a recirculated flow to cascade a film of liquid down the inside wall of each tube (45 total) in a tube bundle enclosed in a steam chest. As the recirculated

liquid, including the raw feed, cascades down the tubes, it is heated (by steam condensing at 230°F, 7 psig) and evaporation occurs in the tubes which are under vacuum. The vapor-liquid mixture (at ~200°F, 7.5 psia) exits at the bottom of the tubes where the evaporated water vapor is disengaged from the liquid. This steam is condensed in a water-cooled plate-type exchanger (maximum temperature of the condensate is 180°F). The bulk of the concentrated liquor (about 30% potassium formate) is recirculated to the top of the first stage evaporator (along with fresh feed).

Part of the 30% concentrated liquor from the falling film evaporator is pumped to the second evaporation stage which consists of a forced circulation evaporator which also operates under vacuum. Before entering the second stage evaporator, the concentrated liquor from the first stage is centrifuged in C-201 to remove any impurity solids (K_2SO_4 , K_2CO_3 , etc.) which may have precipitated from solution in the first stage evaporator. In the second evaporation stage the 30% feed liquor is concentrated to a ~75% solution. The solution in this evaporation stage is circulated through a steam-heated exchanger (steam at 260°F, 20 psig) to pick up the energy (heat) required for the evaporation (at ~200°F, 2.2 psia) of the bulk of the water in the feed to this evaporation stage. This circulation also prevents crystals of feed impurities, such as potassium sulfate, potassium carbonate and calcium sulfate, which have precipitated from solution upon concentration in the second stage from settling out. The evaporated water vapor generated in the second evaporation stage is condensed in a plate-type exchanger (maximum temperature of the condensate is 130°F). About 200 pounds per hour of potassium formate product are produced.

The potassium formate product was concentrated to ~75% (a pumpable, solids-free liquid at ambient (20°C) temperature) in the evaporator. At a ~75% concentration, potassium formate forms a saturated solution at ~0°C. As mentioned above, the small amounts of potassium sulfate, potassium carbonate and calcium sulfate originally present in the feed to the evaporator may precipitate. Some of this precipitate is in fact removed as mentioned above by a centrifuge between the evaporation stages. The ~75% concentrate from the second evaporation stage is pumped by a progressive cavity pump to 55-gallon drums (Figure 2-18). The material is allowed to cool to ambient temperature in the drums.

Figure 2-18. Filling of 55-Gallon Drums with Concentrated Potassium Formate Solution from Evaporator

This drives some additional potassium sulfate, potassium carbonate and calcium sulfate out of solution. The cooled contents of the drums are then pumped through a bag filter. The solids-free filtrate (~75% potassium formate) is collected in 55-gallon shipping drums (Figure 2-19). The product after sampling/analysis was shipped to the CDIF in Butte, Montana.

The steam used in the evaporator is generated in a 100 HP propane-fired packaged boiler. The steam is generated at 200 psig and reduced to the desired pressures across regulators. Steam jacket condensates are combined and cooled in the feed preheat exchanger before being recycled to the boiler. The overhead process condensates are collected and sent to the cooling water system.

2.2.4 Data Acquisition and Control System

The potassium formate production POC plant is highly instrumented to control the flow, pressure, temperature, tank levels, and pump speeds during operation and to provide for operator safety. Throughout the process, instruments are provided for the purpose of automatically collecting and recording data and controlling flow, level, and temperature. These instruments include pressure transmitters, differential pressure transmitters, flow meters, temperature transmitters, level transmitters, and a weight transmitter. All instruments are input to a computer hardware/software system which records analog data, performs PID control algorithms on these inputs, and sends output signals to the control devices for system control. The level in the tanks is controlled by regulating the speed of the output progressive cavity pumps or by adjusting control valve positions on sidearms of pump-around loops (centrifugal pumps). The temperature of the heat exchangers is controlled by regulating the flow of steam to the exchangers. Automatic system alarms are provided for low flow conditions and high and low tank levels, which are indicative of system blockages, leaks, or pump failures.

The data acquisition and control software was installed on a PC-based system that utilized a 386 microprocessor and was interfaced with a 100 channel hardware interface

Figure 2-19. Filling of 55-Gallon Drum with Concentrated Potassium Formate Seed for Shipment to the CDIF

which received and digitized analog process signals from various locations in the POC test unit. The software provided for manual operation (open circuit operation) of feedback control loops in the event the loops became difficult to tune. The system provided an updated real time display of plant operating parameters every 30 seconds and was configured to monitor and alert an operator when parameters exceeded specified operational limits.

Unlike the potassium formate and calcium formate production units which used the data acquisition and control system described above, the evaporator, as supplied by *Swenson*, was a stand-alone unit equipped with local microprocessor-based process controllers. In this instance, the above data acquisition and control system was used to control temperature, feed, and level loops in the evaporator feed section and only as a data acquisition system for the evaporator.

2.3 SUMMARY OF DATA

Prior to the current Phase II program, The Pittsburgh Energy Technology Center of the DOE sponsored a bench scale project (1987-1988) to evaluate the Econoseed process. The results of the Phase I bench scale program are summarized in Section 2.3.1 and the results of the current Phase II POC scale program are summarized in Section 2.3.2.

2.3.1 Phase I Bench Scale Data

The objectives of the Phase I project were to test the Econoseed process at bench scale and to prepare a conceptual design of a 300 MW_t commercial plant. Each of the unit operations was successfully demonstrated. Specific results are as follows:

1. Data was obtained from the Electro Metallurgical Company, a subsidiary of Union Carbide, which piloted the production of calcium formate from CO and lime. The data indicated that calcium formate can be produced at high yields, based on either carbon monoxide or lime utilization, at temperatures of 170 to 200°C and pressures of 1200 to 1300 psig in continuous column reactors with a total retention time of less than 5 minutes.

2. Two spent seed products (flyash and radiant furnace slag material) obtained from the CFFF were analyzed and assessed. It was found that the flyash product was 90% soluble potassium sulfate and 10% high iron oxide insoluble flyash, together with approximately 0.3% sodium and 0.03% chloride as well as an array of trace elements. The slag material, although containing 10% potassium, was insoluble in water and directly met EP toxicity standards for safe solids disposal. The sodium and chloride content of the spent seed flyash and the spent slag corresponded to the sodium and chloride content of purchased potassium carbonate, showing no increase attributable to the sodium and chloride content of coal.
3. Spent seed collected as flyash from the CFFF was quantitatively converted by reaction with calcium formate to potassium formate or mixtures of potassium formate and potassium sulfate (as per the commercial design) without measurable loss of potassium to insolubles at temperatures of 70 to 90°C, retention time under 25 minutes and at ambient pressure. The conversion was complete virtually as fast as soluble potassium sulfate goes into water solution with a maximum residence time (including dissolution) of 25 minutes for 99.9% conversion at 70°C. Recovery of potassium in solution averaged 100% with no measurable loss to insoluble potassium species. The sodium content of the product potassium formate was about one half that of the spent seed flyash, indicating a selective partition of the sodium to the gypsum-flyash precipitate from this reaction. The chloride content was not reduced, and occasionally showed an increase, probably due to the addition of a small amount of chloride from the purchased calcium formate.
4. Similar results were obtained for processing of radiant furnace slag after leaching the slag with dilute sulfuric acid at room temperature and ambient pressure and then neutralization of the extract with lime. Approximately 95% of the potassium was extractable with dilute sulfuric acid. This solution can be limed to neutrality giving a dilute solution of soluble potassium sulfate which can be treated with calcium formate for regeneration. The initial acid extract of the solution was about

50% potassium and 50% dissolved ash components, but treatment with lime reduced the ash components to 5% of the weight of potassium salts in solution.

5. The solids reject mixture of gypsum and undissolved coal ash filtered rapidly at rates of about 100 to 150 lbs/ft²-hr, was easily washed free of the seed solution and met RCRA EP toxicity requirements for safe disposal.
6. Environmental testing of processed solid wastes showed that the following three wastes are disposable solids according to the EP toxicity analysis: a) the reject flyash-calcium sulfate from regeneration of spent seed flyash, b) the untreated slag, and c) the slag remaining after extraction with sulfuric acid solution and drying.
7. Evaporation of the clarified potassium formate solution to a dry product proceeded normally and the resulting molten potassium formate was shown to have flaking properties suitable for solidification to grindable flakes for recycle to an MHD channel. Detailed analysis showed that the potassium formate product was 92 to 94% potassium formate, 3% gypsum, 0.2% sodium sulfate, and 0.3% chlorine with an additional slate of trace elements, none of which is on the EP toxicity list. Gypsum content was shown to be reduced to less than 0.01% by addition of potassium carbonate to the potassium formate solution prior to evaporation. Crystallization removal of the gypsum during evaporation of the potassium formate solution could be an alternative.
8. The solidified potassium formate was converted to potassium carbonate, an alternative regenerated seed form, by air oxidation at temperatures of 400 to 500°C. Air oxidation under simulated static kiln operation was found to result in 100% conversion of potassium formate to a mixture of 89% potassium carbonate and 11% potassium oxalate. This can be accomplished at a temperature of 500°C and residence times of 30 minutes. It is assumed that more complete conversion to potassium carbonate can be obtained in dynamic rotary kiln operation.

9. Equipment specification data was obtained. Filtration and centrifugation data was obtained for separation of the flyash-calcium sulfate reject from product potassium formate solution showing very rapid separation rates and low cake moistures of 100 to 150 lbs/ft²-hr and 35%, respectively. Sufficient evaporation data was obtained during concentration of potassium formate solution to molten dry liquid for the specification of an evaporation unit operation.
10. Experimentation was performed to validate the engineering design base case conversion of spent seed flyash to a 90:10 mixture of potassium formate and soluble potassium sulfate. Results showed that the reaction proceeded exactly as for production of pure potassium formate, separation of solids from liquids was rapid and complete, the product contained approximately half the sodium content of purchased potassium carbonate (as may have been used in the CFFF unit), and analysis of the product showed that it was indeed 87% potassium formate with the remainder of the major constituents consisting of calcium, sulfate, and excess formate. Also, it was found that upon evaporation, the molten potassium formate-potassium sulfate passed a metal adherence test validating specification of a flaker for the evaporator unit.
11. Economic forecast studies showed that seed can be regenerated at a total cost of approximately \$0.23/lb in the dry potassium formate form or \$0.27/lb in the dry potassium carbonate form, which is less than half the cost of \$0.63 if purchasing fresh potassium carbonate (there would be an additional and undefined cost for spent seed flyash disposal if seed is not regenerated).

This information was used to prepare a design of a 300 MW_t commercial plant during the Phase I program, and during current Phase II of the program was used in the design of the potassium formate and calcium formate POC units. A detailed description of the Phase I test results is presented in the "MHD Seed Recovery and Regeneration Final Report" dated October 14, 1988 (Contract No. DE-AC22-87-PC79672).

2.3.2 Phase II POC Scale Data

For the purposes of the following discussion, the potassium formate production facility will be divided into two area: 1) dilute formate production (potassium sulfate reaction and solids separation/washing units) which produces dilute potassium formate solution, and 2) the two-stage evaporation unit which produces concentrated potassium formate.

Dilute formate production operations and evaporation unit operations were alternated. That is, the dilute formate production equipment was operated for several days to produce dilute (~ 7 wt%) potassium formate solution which was stored in a 16,000 gallon tank. When this storage tank became full, dilute production plant operations were stopped and the evaporation unit was operated for several days to deplete the supply of dilute solution and produce concentrated (67-77 wt%) potassium formate solution which was collected in 55-gallon drums for shipment to the CDIF. This method of operation was dictated by the size of the available operating crew at the test site and the fact that a number of items of equipment (centrifuges, etc.) served double duty (i.e. were used in both dilute formate production and evaporation operations).

During dilute formate production operations between September 1991 and April 1992, a total of 174 stream hours were logged. Approximately 35,000 pounds of Eastern spent seed from the UTSI CFFF were fed to the POC unit along with $\sim 21,000$ gallons of 12 weight percent calcium formate solution (and additional solids wash/dilution water). A total of $\sim 56,000$ gallons of dilute potassium formate was produced and stored. The maximum spent seed feed rate achieved during production was ~ 250 pounds per hour. This is sufficient spent seed to produce ~ 200 pounds per hour of regenerated potassium formate seed (pure basis). The maximum potassium formate solution concentration achieved during operation of the dilute formate production equipment was ~ 7.5 wt%.

The average conversion of soluble spent seed sulfate to gypsum was 95 to 97%. Dilute formate production operations were conducted in the temperature range of 60 to 70°C based on the finding of laboratory studies performed in the Phase I program. The operations were

conducted over a reactor residence time range of 50 to 100 minutes. High sulfate conversion was obtained over this entire time range.

During evaporation operations between December 1991 and April 1992, a total of ~200 stream hours were logged. Approximately 56,000 gallons of dilute (5 to 7 wt%) potassium formate solution were fed to the two-stage evaporation unit. Maximum feed rate to the unit was ~6 GPM. Approximately 21,000 pounds of concentrated (67 to 77 wt%) potassium formate solution were produced in the unit. This regenerated seed solution was packaged in forty-one 55-gallon drums and shipped to the CDIF in Butte, Montana for future use in channel tests.

The contents of several of the drums were sampled and analyzed. The potassium formate content of these drums ranged from 67 to 77 wt%. The regenerated seed contains ~0.1% of the sulfate that was present in the spent seed fed to the POC unit.

The following sections contain a compilation of the more critical test data including a text matrix and run condition summary, performance results (sulfate removal, potassium recovery, sodium partition, chloride partition), a discussion of the environmental suitability of the waste products, and a description of the potassium formate product.

2.3.2.1 Test Matrix and Run Condition Summary

The range of conditions investigated in the potassium formate POC unit is presented in Table 2-3. The pertinent production figures for dilute formate production operations are given in Table 2-4. Approximately 35,000 pounds of Eastern spent seed from the UTSI CFFF were fed to the unit using a weigh belt feeder along with ~21,000 gallons of 12 weight percent calcium formate solution (and additional solids wash/dilution water). A total of ~56,000 gallons of dilute potassium formate was produced and stored. This production was accomplished in a total of forty-one (41) single shift (8-hour) test runs. A summary of the operating conditions for each of the 41 test runs is presented in Table 2-5.

TABLE 2-3. POTASSIUM FORMATE POC OPERATIONS TEST MATRIX

PARAMETER	RANGE INVESTIGATED IN POC
Spent Seed Feed Rate	168 to 320 lbs/hr
Reaction Temperature	141 to 158°F
Reaction Residence Time	51 to 106 minutes
Total Dissolved Solids in Reactor Effluent KCOOH Solution	5 to 8.7 wt%
Calcium Formate:Potassium Sulfate Reactant Stoichiometry	0.98 to 1.56
Sodium:Potassium Ratio in Reactor Feed	0 to 0.10
Chloride:Potassium in Reactor Feed	0.02
Concentrated Potassium Formate Produced	67 to 77%

TABLE 2-4. DILUTE POTASSIUM FORMATE POC UNIT PRODUCTION FIGURES

Shakedown/Operations Time Period	9/91 thru 4/92
Total Number of Runs (Single 8-Hour Shifts)	41*
Total Stream Hours (Spent Seed Feed Into Unit)	174*
Maximum Stream Factor Attained	85%
Total Pounds of Spent Seed Fed	35,600 Lbs
Total Gallons of Calcium Formate Solution Fed	21,100 Gal
Total Gallons of Dilute Potassium Formate Produced	56,500 Gal
Maximum Spent Seed Feed Rate Achieved	~250 Lbs/Hr
Maximum Potassium Formate (Pure Basis) Production Achieved	~200 Lbs/Hr
Maximum Potassium Formate Concentration Achieved	~7.5 wt% KCOOH

* Average stream factor = 57%.

TABLE 2-5. SUMMARY OF OPERATING CONDITIONS FOR POTASSIUM FORMATE POC UNIT

SD #	Date	Elapsed Time* (min)	FLOW CONDITIONS					Nominal Temp (deg F)		Nominal Level++ (% full)		Residence Time** (min)	
			SEED FLOW (lb/hr)	Ca(COOH) ₂ FLOW+ (lb/hr)	MAKEUP H ₂ O (lb/hr)	WASH H ₂ O (lb/hr)	K ₂ CO ₃ FLOW*** (lb/hr)	T102	T104	T102	T104	T102	T104
1	09/20/91	135	168	0	0	1101	56	143	145	52	11	43	60
2	09/23/91	80	102	753	250	851	56	144	151	65	12	36	39
3	09/24/91	270	168	795	250	850	56	149	155	65	16	34	40
4	09/27/91	0	0	0									
5	10/02/91	125	168	731	250	850	56	146	153	44	35	22	52
6	10/07/91	0	0	0									
7	10/11/91	275	168	740	250	850	56	152	156	54	52	28	62
8	10/14/91	115	320	1544	250	1551	113	151	154	55	54	16	35
9	10/15/91	75	320	1548	250	1550	113	148	153	55	64	16	38
10	10/18/91	200	168	736	250	850	49	148	156	45	47	23	60
11	10/22/91	340	168	738	250	851	49	148	156	52	48	27	60

Notes: * total run time with spent seed and Ca(COOH)₂ solution feed

+ specific gravity of 1.09 assumed

** specific gravity of 1.05 assumed

SD #4: run aborted early

SD #6: run terminated due to plugged circulation loop in T-102

++ T-102 @ 100% full (max liquid level) contains ~ 200 gallons

T-104 @ 100% full (max liquid level) contains ~ 350 gallons total (including 119 gallon heel at measured level of 0% full)

*** specific gravity of 1.25 assumed for 25 wt.% sol'n

SD #1: P107 burst disc failed

SD #2: Ca(COOH)₂ flow sensor failed

TABLE 2-5. SUMMARY OF OPERATING CONDITIONS FOR POTASSIUM FORMATE POC UNIT (CONTINUED)

OPS #	Date	Elapsed Time* (min)	FLOW CONDITIONS					Nominal Temp (deg F)		Nominal Level++ (% full)		Residence Time** (min)	
			SEED FLOW (lb/hr)	Ca(COOH)2 FLOW+	MAKEUP H2O	WASH H2O	K2CO3 FLOW***	T102	T104	T102	T104	T102	T104
				(lb/hr, sol'n)	(lb/hr)	(lb/hr)	(lb/hr, sol'n)						
1	10/23/91	235	200	931	250	1122	61	150	156	50	44	21	46
2	10/24/91	245	250	1154	250	1443	76	146	156	49	48	16	39
3	10/31/91	275	200	949	250	1100	188	152	159	72	70	31	59
4	11/26/91	215	200	949	250	1121	188	151	159	71	71	31	59
5	01/09/92	20	200	938	255	1121	156	144	157	79	70	35	58
6	01/10/92	50	200	938	250	1151	156	142	156	58	72	24	59
		235	200	949	0	1351	156	155	158	57	71	24	60
7	01/13/92	400	200	938	0	1339	156	151	156	55	68	23	58
8	01/16/92	130	200	944	0	811	156	151	157	63	69	34	74
		130	200	944	0	1099	156	154	157	63	71	30	66
		55	200	944	0	1099	125	155	158	62	71	29	66

Notes: * total run time with spent seed and Ca(COOH)2 solution feed
+ specific gravity of 1.09 assumed
** specific gravity of 1.05 assumed (may be greater for OPS 5 and above)
*** specific gravity of 1.25 assumed for 25 wt.% sol'n
++ T-102 @ 100% full (max liquid level) contains ~ 200 gallons
T-104 @ 100% full (max liquid level) contains ~ 350 gallons total (including 119 gallon heel at measured level of 0% full)

TABLE 2-5. SUMMARY OF OPERATING CONDITIONS FOR POTASSIUM FORMATE POC UNIT (CONTINUED)

OPS #	Date	Elapsed Time* (min)	FLOW CONDITIONS					Nominal Temp (deg F)		Nominal Level++ (% full)		Residence Time** (min)		
			SEED FLOW (lb/hr)	Ca(COOH)2 FLOW+ (lb/hr, sol'n)	MAKEUP H2O (lb/hr)	WASH H2O (lb/hr)	K2CO3 FLOW*** (lb/hr, sol'n)							
								T102	T104	T102	T104	T102	T104	
9	01/17/92	30	200	949	0	1086	125	145	157	61	66	29	64	
		110	200	938	0	1096	109	153	157	62	71	30	67	
		110	200	944	0	1021	69	152	157	63	72	31	69	
		20	200	949	0	1081	69	150	156	73	70	36	66	
		55	200	952	0	1099	156	152	156	62	71	29	66	
10	01/21/92	125	200	949	0	1171	156	152	149	47	72	21	65	
		210	250	1178	0	1406	156	154	157	48	71	17	53	
2-48	11	01/23/92	375	250	1184	0	1391	156	151	157	50	70	18	52
12	02/10/92	255	250	1184	0	1366	156	150	156	58	71	22	53	
13	02/11/92	395	250	1184	0	1391	156	152	156	49	71	18	53	
14	02/12/92	194	250	1145	0	1406	156	148	155	50	71	18	53	
15	02/13/92	310	250	1053	0	1391	156	153	157	49	71	19	55	
16	02/14/92	290	250	1064	0	1391	156	153	157	49	71	19	55	

Notes: * total run time with spent seed and Ca(COOH)2 solution feed
+ specific gravity of 1.09 assumed
** specific gravity of 1.05 assumed (may be greater for OPS 5 and above)
*** specific gravity of 1.25 assumed for 25 wt.% sol'n
++ T-102 @ 100% full (max liquid level) contains ~ 200 gallons
T-104 @ 100% full (max liquid level) contains ~ 350 gallons total (including 119 gallon heel at measured level of 0% full)

TABLE 2-5. SUMMARY OF OPERATING CONDITIONS FOR POTASSIUM POC UNIT (CONTINUED)

OPS #	Date	Elapsed Time* (min)	FLOW CONDITIONS					Nominal Temp (deg F)		Nominal Level++ (% full)		Residence Time** (min)		
			SEED FLOW (lb/hr)	Ca(COOH)2 FLOW+ (lb/hr, sol'n)	Na2SO4 FLOW (lb/hr)	WASH H2O (lb/hr)	K2CO3 FLOW*** (lb/hr, sol'n)	T102	T104	T102	T104	T102	T104	
2-49	17	02/25/92	150	250	1091	0	1401	156	151	157	47	60	18	49
			160	250	1091	0	1406	78	154	157	48	67	18	52
	18	02/26/92	335	250	1085	0	1361	78	150	156	49	72	19	55
	19	02/27/92	301	250	1085	0	1421	78	150	156	48	66	18	52
	20#	02/28/92	310	250	1075	0	1426	78	153	158	47	50	29	45
	21#	03/25/92	185	250	1090	0	1386	78	139	157	50	75	32	56
	22#	03/26/92	410	250	993	0	1406	78	147	158	50	74	31	57
	23#	03/27/92	205	250	1118	0	1031	78	147	157	49	70	40	61
	24#	03/30/92	355	250	1069	28	1351	78	147	158	50	69	32	54
	25#	03/31/92	400	250	1091	28	1386	78	150	156	50	69	31	53
	26#	04/01/92	275	250	1096	28	1401	78	145	158	51	71	32	53
	27#	04/07/92	235	250	1091	0	1426	78	146	158	52	70	32	53

Notes: * total run time with spent seed and Ca(COOH)2 solution feed
+ specific gravity of 1.09 assumed
** specific gravity of 1.05 assumed (may be greater for OPS 5 and above)
*** specific gravity of 1.25 assumed for 25 wt.% sol'n
++ T-102 @ 100% full (max liquid level) contains ~200 gallons
T-104 @ 100% full (max liquid level) contains ~350 gallons total (including 119 gallon heel at measured level of 0% full)

OPS 20 - OPS 27: T-102 used as SEED dissolve tank only;
NO reagent Ca(COOH)2 sol'n is fed to this tank.

TABLE 2-5. SUMMARY OF OPERATING CONDITIONS FOR POTASSIUM FORMATE POC UNIT (CONTINUED)

OPS #	Date	Elapsed Time* (min)	FLOW CONDITIONS					Nominal Temp (deg F)		Nominal Level++ (% full)		Residence Time** (min)	
			SEED FLOW (lb/hr)	Ca(COOH)2	Na2SO4	WASH	K2CO3	T102	T104	T102	T104	T102	T104
				FLOW+ (lb/hr, sol'n)	FLOW (lb/hr)	H2O (lb/hr)	FLOW*** (lb/hr, sol'n)						
28#	04/09/92	305	250	1102	0	1451	78	145	158	50	65	30	50
29#	04/10/92	80	250	1113	0	1386	78	143	157	51	71	32	54
		400	290	1260	0	1626	91	141	158	50	69		
30#	04/13/92	360	290	1265	0	1576	91	146	158	48	70	26	47

Notes: * total run time with spent seed and Ca(COOH)2 solution feed
+ specific gravity of 1.09 assumed
** specific gravity of 1.05 assumed (may be greater for OPS 5 and above)
*** specific gravity of 1.25 assumed for 25 wt.% sol'n
++ T-102 @ 100% full (max liquid level) contains ~200 gallons
T-104 @ 100% full (max liquid level) contains ~350 gallons total (including 119 gallon heel at measured level of 0% full)

OPS 28 - OPS 30: T-102 used as SEED dissolve tank only;
NO reagent Ca(COOH)2 sol'n is fed to this tank.

A total of 174 hours were logged with feeds flowing into the dilute formate production equipment during the test runs. The balance of the test run hours (130 hours), with no feeds into the unit, was utilized for startup and shutdown. Therefore, the "average" stream factor for dilute formate production operations was 57%. By the end of production operations, startup and shutdown procedures had been streamlined to the extent that a stream factor of 85% was achieved.

The maximum spent seed feed rate achieved during production was ~250 pounds per hour. This is sufficient spent seed to produce ~200 pounds per hour of regenerated potassium formate seed (pure basis). The maximum potassium formate solution concentration achieved during dilute formate production was ~7.5 wt%.

The pertinent production figures for the potassium formate concentration (evaporation) unit are given in Table 2-6. Approximately 56,000 gallons of dilute (5 to 7 wt%) potassium formate solution were fed to the two-stage evaporation unit during a total of thirty-eight (38) single shift (8-hour) test runs. Maximum feed rate to the unit was ~6 GPM. Approximately 21,000 pounds (pure KCOOH basis) of concentrated (67 to 77 wt%) potassium formate solution were produced in the unit. This regenerated seed solution was packaged in forty-one 55-gallon drums for shipment to the CDIF in Butte, Montana for future use in channel tests.

2.3.2.2 *Sulfate Removal*

For dilute formate production operations, the average conversion of soluble spent seed sulfate to gypsum was 95 to 97%. The test runs were generally conducted at feed ratios of formate (via calcium formate) to potassium (via spent seed) of slightly in excess of stoichiometric, a temperature range of 60 to 70°C, and a reactor residence time range of 50 to 100 minutes. High sulfate conversion was obtained over this entire range of conditions. It is likely that the system residence time can be reduced below 50 minutes without affecting sulfate conversion. This could not be easily tested in the POC, however, due to the type and

TABLE 2-6. CONCENTRATED POTASSIUM FORMATE POC UNIT
PRODUCTION FIGURES

Shakedown/Operations Time Period	12/91 thru 4/92
Total Number of Runs (Single 8-Hour Shifts)	38
Total Stream Hours	~200
Maximum Stream Factor Attained	Not Applicable
Maximum Feed Rate of Dilute Potassium Formate	~6 GPM
Concentration of Potassium Formate Feed	5 to 7.5 wt% KCOOH
Concentration of Potassium Formate Product	67 to 77 wt% KCOOH
Total Pounds of Potassium Formate (Pure Basis) Produced	~21,000 Lbs

size of reactors being utilized. (Existing vessels from earlier programs were modified for POC operations.)

The sulfate content of the final concentrated regenerated seed from the evaporation unit was extremely low. In fact, the regenerated product seed contained $\sim 0.1\%$ of the sulfate that was present in the spent seed fed to the POC unit. This was due to the removal of sulfates at other stages of the operation besides the reactor. For example, precipitated solids, consisting primarily of sulfates, are removed between the two stages of evaporation by a centrifuge and after the final evaporator stage by a filter.

2.3.2.3 *Potassium Recovery*

Potassium recovery of $>99\%$ was achieved in the dilute potassium formate unit. Potassium loss to the waste solids was very low at less than 1% of the water soluble potassium in the spent seed feed. This was accomplished with a single water wash of the solids centrifuged from the dilute potassium formate solution leaving the reactor. A two-stage countercurrent wash of the solids may be justified by additional potassium recovery.

Dilute formate production operations were conducted in the temperature range of 60 to 70°C . Laboratory studies performed in the Phase I program had indicated that this was the optimum temperature range for a high recovery of potassium without formation of insoluble syngenite $[\text{K}_2\text{Ca}(\text{SO}_4)\cdot\text{H}_2\text{O}]$. Indeed, no syngenite was found when an x-ray diffraction was run on the gypsum waste solids from the POC.

2.3.2.4 *Sodium Partition*

During a number of test runs, dry sodium sulfate was added to the potassium formate reactor along with the spent seed to give a K:Na weight ratio of $\sim 10:1$. No significant partitioning of the sodium relative to potassium was seen in the dilute formate production unit during these test runs. That is, all of the sodium fed reported with the dilute potassium formate solution produced. This indicates that the potassium formate reactor cannot be used

to selectively reject sodium from the seed (thereby controlling sodium buildup in the recycled seed).

2.3.2.5 Chloride Partition

The calcium formate fed to the POC unit contained a small amount of chloride (it was made from calcium chloride). The ratio of potassium (in the spent seed) to chloride (in the calcium formate) was 50:1. The chloride was not seen to partition as it was processed through the dilute formate production unit. That is, all of the chloride fed reported with the dilute potassium formate solution produced. This indicates that the potassium formate reactor cannot be used to selectively reject chloride from the seed (thereby controlling chloride buildup in the recycled seed).

2.3.2.6 Calcium Removal

A small amount of potassium carbonate was added to the dilute formate solution (following the separation of gypsum-flyash precipitate) to reduce the small amount of dissolved calcium, primarily in the form of calcium sulfate (0.4 wt% solubility), in the formate solution. The potassium carbonate reacts with the soluble calcium to form very insoluble calcium carbonate solids which are subsequently removed downstream in a filter. This step was added to avoid potential calcium compound scaling on the heat exchanger surfaces in the downstream formate evaporation unit. Table 2-7 gives the stream analysis from a representative test run for the dilute formate solution after solids separation (by centrifugation) and then after addition of potassium carbonate and calcium carbonate separation (by filtration).

2.3.2.7 Environmental Suitability of Waste Products

The solids waste product produced in the dilute formate production operations was relatively dry. These solids as discharged from a centrifuge contained 0.2 to 0.3 pounds of surface moisture per pound of dry cake. A sample of this material was subjected to and passed an EP toxicity test. Potassium loss to the waste solids was very low at less than 1% of the potassium in the spent seed.

TABLE 2-7. DILUTE POTASSIUM FORMATE SOLUTION STREAM ANALYSIS
BEFORE AND AFTER CARBONATE REMOVAL

ION IN SOLUTION	DILUTE FORMATE AFTER GYPSUM SEPARATION, WT%	DILUTE FORMATE AFTER CALCIUM REDUCTION, WT%
Potassium	3.12	3.56
Calcium	0.40	0.09
Formate	4.04	3.92
Sulfate	0.50 ¹	0.48
Carbonate	--	0.04
Total Dissolved Solids	8.06	8.09

¹ ~0.4 wt% sulfate attributable to gypsum (calcium sulfate) solubility in the dilute formate solution plus gypsum fines carryover with solution from centrifuge.

2.3.2.8 Potassium Formate Product

Forty-one 55-gallon drums of concentrated potassium formate regenerated seed solution were produced in the two-stage evaporation unit. The contents of several of the drums were sampled and analyzed. The potassium formate content of these drums ranged from 67 to 77 wt%. The following range of concentrated seed impurity levels was seen:

	<u>Wt. %</u>
Calcium	0.05-0.18
Sulfate	0.01-0.03
Carbonate	0.01-0.17%

The specific gravity of the regenerated seed solutions ranged from 1.46-1.59. The sulfate content of the final concentrated regenerated seed solution is extremely low. In fact, the regenerated seed contains ~0.1% of the sulfate that was present in the spent seed fed to the POC. Precipitated solids, consisting primarily of sulfates, are removed between the two stages of evaporation by a centrifuge and after the final evaporation stage in a filter. In a large scale unit, this material could be recycled to the potassium formate reactor for potassium recovery and removal of the sulfate as insoluble gypsum.

Although the concentrated regenerated seed that was shipped to the CDIF contained a maximum of 77 wt% potassium formate, the material actually discharged from the second stage of evaporation may, at times, have contained as much as 80 to 90 wt% potassium formate. This material was pumped from the second stage of the evaporator, operating at ~200°F, into 55 gallon drums and was then allowed to stand and cool. Upon cooling a large amount of potassium formate crystals as well as impurity crystals precipitated from solution to grow on the walls of the drum. The ambient temperature decant liquid from the drums was pumped through a filter and into shipping drums for shipment to the CDIF. This regenerated seed solution (67-77 wt% potassium formate) is free of suspended solids at ambient temperature.

A freezing point determination was made for the regenerated seed to be sent to the CDIF. This material has a freezing point (temperature at which it becomes completely solid) of below -70°C . However, since the regenerated seed is a saturated solution of potassium formate at ambient temperature, moderate reductions in temperature below ambient (for the POC site at the time of drum filling ambient temperature was 10 to 20°C) will reduce the solubility of potassium formate and cause a small amount of potassium formate to precipitate from solution. A solubility curve for potassium formate is shown in Figure 2-20. As can be seen, the solubility of potassium formate in water at ambient temperature (20°C) is ~ 77 wt%.

2.4 DISCUSSION OF INDIVIDUAL TEST RESULTS

2.4.1 Spent Seed Analysis

The spent seed feed (supplied by UTSI from the CFFF operations with Eastern coal) to the POC potassium formate reactor was periodically sampled for analysis during the course of the POC operations. Table 2-8 is a summary of the resulting spent seed analyses. The spent seed samples were dissolved in water and then filtered. The insoluble residue (filter cake) was dried and weighed. The average water insolubles content of the ~ 20 samples of spent seed analyzed was $\sim 18.5\%$. The water soluble fraction (filtrate) of the spent seed was analyzed gravimetrically for sulfate. The potassium content of the water soluble fraction of the first few samples was determined by AA (atomic absorption) analysis. It was found that the amount of potassium determined by analysis was in close agreement with that which would be expected to be present by stoichiometry if all the dissolved sulfate had existed as potassium sulfate (K_2SO_4) in the spent seed. Since the spent seed potassium analysis was quite time consuming (many dilutions were required to reduce the potassium to the parts per million (ppm) level required by the AA instrument), this analysis was not conducted for most of the spent seed samples. The bulk of the potassium values shown in Table 2-8 are values calculated from the sulfate analysis by assuming that the sulfate had been present in the spent seed as potassium sulfate. One spent seed sample was also analyzed for water soluble sodium (0.31 wt%), calcium (0.062 wt%) and magnesium (0.017 wt%). Assuming these components were in the sulfate form in the spent seed, they would only account for $\sim 2\%$ of

Figure 2-20. Solubility Curve for Potassium Formate

TABLE 2-8. ANALYSIS OF SPENT SEED FEED

SAMPLE ID	CONCENTRATION, WT PERCENT			
	K ⁺	SO ₄ ⁻²	INSOLUBLE	TOTAL, WT%
067562	36.2 ¹ (35.6 ³)	43.8 ²	15.6/15.4	95.6/95.4
700198	37.1 ¹ (37.1 ³)	45.6 ²	17.5	100.2
700209	30.8 ¹ (31.6 ³)	38.9 ²	27.1	96.8
AR 4571	36.9 ³	45.4 ²	19.8	102.1
	36.8 ³	45.3 ²	19.5	101.6
06700195	38.8 ³	47.7 ²	15.5	102.0
	39.2 ³	48.2 ²	15.5	102.9
	37.2 ³	45.7 ²	20.4	103.3
	37.9 ³	46.6 ²	15.8	100.3
	37.3 ³	45.8 ²	15.1	98.3
SER11845	37.9 ³	46.5 ²	19.9	104.3
	36.5 ³	44.9 ²	19.8	101.3
	36.8 ³	45.1 ²	19.9	101.8
	36.8 ³	45.1 ²	19.9	101.8
	36.7 ³	45.0 ²	20.0	101.7
10/11/91	36.8 ³	45.2 ²	20.1	102.1
10/18/91	36.4 ³	44.7 ²	20.5	101.6
10/24/91	36.1 ³	44.3 ²	21.3	101.7
10/31/91	35.7 ³	44.0 ²	21.8	101.5
AVERAGE	36.72 K ⁺ 44.23 K ₂ O	45.14 SO ₄ ⁻² 37.63 SO ₃	18.52	100.8

¹ K⁺ determined by atomic absorption (AA)

² SO₄⁻² determined gravimetrically

³ K⁺ calculated from SO₄⁻² analysis to give K₂SO₄

the sulfate present. The remaining ~98% of the sulfate present can be assumed to be associated with the potassium.

UTSI provided TRW with analyses of the composite samples of spent seed taken at the CFFF during an Eastern coal test conducted in November 1989. This information is reported in Table 2-9. Analyses were provided for spent seed collected from both the baghouse and the electrostatic precipitator. The K_2O and SO_3 values reported by UTSI in Table 2-9 are in close agreement with those determined by TRW as reported in Table 2-8. As can be seen from the UTSI analyses the carbonate content of the spent seed was practically nil (<0.1 wt%).

2.4.2 Calcium Formate Feed Analysis

The calcium formate used as a reactant in the potassium formate POC unit was purchased from a Japanese specialty chemical firm. (Note: TRW subsequently built and operated a POC unit to demonstrate the feasibility of producing calcium formate by a new reaction route utilizing relatively inexpensive carbon monoxide and lime. This calcium formate POC unit is discussed in Section 3 of this final report.) The calcium formate was delivered in powdered form. Several samples of the calcium formate were taken for analysis. The analytical results are reported in Table 2-10A. The average calcium formate content of the powder was ~94 wt%. The powder also contained in excess of 3 wt% moisture and ~1.1 wt% chloride. The explanation for the high chloride content of the powder is most likely that the Japanese produced the calcium formate by reaction of calcium chloride with formic acid.

The calcium formate is fed to the potassium formate POC reactor as an aqueous solution. At ambient temperature the solubility of calcium formate in water is ~14 wt%. TRW contracted with a local blender to formulate the solution from the calcium formate powder. In order to avoid the presence of undissolved solids which might still be present near the solution saturation point, TRW specified that the calcium formate powder be blended with water to give a ~12 wt% solution. Samples were taken of the calcium formate

TABLE 2-9. SPENT SEED ANALYSIS PROVIDED BY UTSI¹

SPENT SEED ANALYSIS	WT PERCENT	
	BAG HOUSE	ESP
SiO ₂	8.40	7.95
Al ₂ O ₃	2.60	2.75
Fe ₂ O ₃	2.79	2.88
TiO ₂	0.31	0.29
CaO	0.55	0.50
MgO	0.14	0.13
Na ₂ O	0.59	0.58
K ₂ O	45.06	44.76
SO ₃	37.60	36.08
Carbonate	<0.1	<0.1

¹ Composite sample taken from CFFF in November 1989 when operating unit with Eastern Seed.

TABLE 2-10A. ANALYSIS OF CALCIUM FORMATE POWDER
(PURCHASED FROM ASAHI KAGAKU)

	CONCENTRATION, WT PERCENT			
SAMPLE ID	Ca(COOH) ₂	MOISTURE	Cl ⁻	TOTAL
AR4165				
H21009	93.5 ¹	3.3 ²	1.4 ³	98.2
H21009	94.2 ¹	3.0 ¹	1.2 ³	98.4
H21013	94.8 ¹	2.4 ¹	0.3 ³	97.5
H21013	94.8 ¹	3.2 ¹	0.9 ³	98.9
H21017	95.1 ¹	3.2 ¹	1.1 ³	99.4
H21017	93.8 ¹	3.9 ¹	1.3 ³	99.0
AR4571	93.6,93.8 ¹	NA	1.6	NA
AVERAGE	94.2	3.2	1.1	

¹ Calcium determined by EDTA titration. Ca(COOH)₂ is then calculated based on calcium material balance.

² Moisture determined by weight loss at 100°C.

³ Chloride determined by ion chromatography.

TABLE 2-10B. ANALYSIS OF CALCIUM FORMATE SOLUTION

	CONCENTRATION, WT PERCENT		
SAMPLE ID	Ca ⁺²	COOH ⁻	Cl ⁻
Tanker #1	3.77 ¹	8.47 ²	NA
Tanker #2	3.67 ¹	8.27 ²	NA
Tanker #3	3.71 ¹	8.35 ²	NA
Tanker #4	3.66 ¹	8.24 ²	NA
T-107 (10/31/91)	3.74 ¹	8.39 ³	0.14 ⁴
AVERAGE	3.71	8.34	

¹ Calcium determined by EDTA titration.

² COOH⁻ is calculated based on calcium material balance.

³ COOH⁻ determined by ion chromatography.

⁴ Chloride determined by ion chromatography.

solution delivered by tanker to the POC test site. The analytical results are reported in Table 2-10B. The average calcium formate content of the blended solution was 12.05 wt%. The chloride content determined for a single sample was 0.14 wt%. This chloride value is in line with the average chloride value of 1.1 wt% reported for the calcium formate powder and the dilution factor of ~ 8 that was utilized in the blending operation.

2.4.3 Potassium Recovery and Potassium Loss to Gypsum/Ash Waste Solids

The only waste stream from the potassium formate POC unit is the washed gypsum/coal ash solids sent to disposal. (Note: A relatively small amount of calcium carbonate solids is also precipitated from the dilute potassium formate solution by the addition of potassium carbonate, removed in a filter and sent to disposal. This processing step was added to avoid potential scaling in the downstream formate evaporator and may not be necessary in a commercial seed regeneration unit.) Potassium can be lost in the gypsum/coal ash solids by virtue of the presence of insoluble syngenite ($\text{K}_2\text{CaSO}_4 \cdot \text{H}_2\text{O}$) or due to soluble potassium in the solids moisture. X-ray diffraction of the waste solids did not indicate the presence of syngenite. The surface moisture content of a sample of the washed gypsum/ash solids separated in centrifuge C-202 was determined by thermogravimetric analysis (TGA) to be 0.33 pounds moisture per pound of dry solids. The TGA also revealed that each molecule of calcium sulfate was hydrated, as expected, with two molecules of water to give gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Samples were periodically taken of the centrate from centrifuge C-202. This is the wash water that was separated from the gypsum/coal ash solids that were sent to disposal. The analyses for this stream is shown in Table 2-11. This stream, which is recycled to the potassium formate reactor, has the same composition as the moisture retained on the centrifuge cake. The average potassium content of the wash water/cake moisture was 0.15 wt%. Since the cake contained 0.33 pounds moisture per pound of dry cake, this means that $0.33 \times 0.0015 = 0.0005$ pounds of potassium is lost with each pound of dry cake sent to disposal. Approximately 1.0 (0.99) pound of gypsum is formed per pound of spent seed potassium sulfate converted. A pound of spent seed was shown (see Table 2-8) to contain on the average 0.367 pounds of potassium. Therefore, the potassium loss to the

TABLE 2-11. ANALYSIS OF C-202 CENTRATE (GYPSUM/ASH WASH WATER RECYCLED TO REACTOR)

RUN ID NO.	DATE	TIME	ION CONCENTRATION, WT PERCENT				ION CLOSURE CATIONS/ANIONS	WT RATIO K ⁺ /COOH ⁻
			K ⁺	Ca ⁺²	COOH ⁻	SO ₄ ⁻²		
SD10	10/18/91	13:50	0.049	0.062	0.03 ¹	0.19/0.145 ¹	0.94	1.633
OPS3	10/31/91	13:10	0.07	0.076	0.16 ¹	0.17	0.81	0.438
		15:15	0.089	0.077	0.18 ¹	0.16	0.84	0.494
OPS4	11/26/91	12:30	0.072	0.070	0.087	0.17	0.98	0.828
		13:30	0.072	0.070	0.087	0.17	0.98	0.828
OPS6	01/10/92	13:15	0.06	0.08	0.09	0.16	1.06	0.667
		15:00	0.08	0.07	0.11	0.17	0.98	0.727
OPS7	01/13/92	13:30	0.06	0.07	0.17			0.353
OPS8	01/16/92	11:30	0.13	0.08	0.15	0.19	1.00	0.867
OPS9	01/17/92	11:10	0.10	0.07	0.13	0.41	0.53	0.769
OPS10B	01/21/92	14:00	0.09	0.08	0.12			0.750
OPS11	01/23/92	13:40	0.10	0.07	0.13	0.16	0.97	0.769
OPS13	02/11/92	11:45	0.09	0.11	0.11	0.17	1.26	0.82

¹ Denotes analyses performed at Space Park. All other analyses performed at CTS.

TABLE 2-11. ANALYSIS OF C-202 CENTRATE (GYPSUM/ASH WASH WATER RECYCLED TO REACTOR) (CONTINUED)

RUN ID NO.	DATE	TIME	ION CONCENTRATION, WT PERCENT				ION CLOSURE CATIONS/ANIONS	WT RATIO K ⁺ /COOH ⁻
			K ⁺	Ca ⁺²	COOH ⁻	SO ₄ ⁻²		
OPS15	02/13/92	12:00	0.11	0.10	0.12	0.17	1.26	0.92
		14:45	0.12	0.07	0.14	0.16	1.02	0.86
OPS16	02/14/92	11:00	0.07	0.09	0.15	0.17	0.99	0.47
OPS17	02/25/92	12:00	0.34	0.11	0.36	0.28	1.03	0.94
OPS18	02/26/92	14:45	0.32	0.11	0.34	0.27	1.04	0.94
OPS19	02/27/92	14:45	0.36	0.11	0.34	0.29	1.08	1.06
OPS20	02/28/92	13:10	0.33	0.11	0.33	0.28	1.06	1.00
OPS21	03/25/92	?	0.27	0.10	0.24	0.26	1.11	1.13
OPS23	03/27/92	11:15	0.30	0.14	0.38	0.22	1.13	0.80
OPS24	03/30/92	14:30	0.37	0.08				
OPS25	03/31/92	12:00	0.09	0.06				
		14:00	0.07	0.09				

washed gypsum/coal ash solids is $0.0005/0.367 \times 100 = 0.14\%$ of the potassium in the spent seed.

2.4.4 Sulfate Removal

2.4.4.1 *Sulfate Removal in Potassium Formate Reaction Section*

The slurry effluent from the potassium formate reactors is processed in centrifuge C-201. The centrate from this machine was sampled and analyzed for sulfate (as well as for the other ions present). The C-201 centrate sulfate analyses for twenty (20) POC test runs are summarized in Table 2-12. The sulfate that would be expected in the centrate should no sulfate conversion have occurred in the formate reactors was calculated based on the potassium content of the centrate and the assumption that all this potassium comes from dissolving potassium sulfate from the spent seed. These calculated "no conversion" sulfate figures are tabulated in Table 2-12. It was determined in the bench scale phase (Phase I) of the seed regeneration program that the calcium sulfate solubility in the formate solution is approximately 0.4 grams per 100 grams of solution (0.4 wt%). This is a slightly elevated solubility when compared with the 0.26 grams of calcium sulfate per 100 grams of water (0.26 wt%) reported in the literature. The difference between the measured sulfate content of the C-201 centrate and the sulfate in the C-201 centrate due to calcium sulfate solubility (0.4 wt% calcium sulfate = 0.28 wt% sulfate) is the "unconverted" sulfate reported in Table 2-12. The percent sulfate conversion shown in Table 2-12 is calculated by dividing the "unconverted" sulfate by the "no conversion" sulfate and subtracting the result from one and then multiplying this difference by 100. As can be seen sulfate conversion varied from 90.2% to 100.0%. The average sulfate conversion was 95.7%. It is quite likely that the C-201 centrate also contained a small amount of entrained solid fines (primarily gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). If the sulfate content of the centrate fines is considered, the result would be to reduce the calculated "unconverted" sulfate in the C-201 centrate and thus increase the sulfate conversion in the formate reactors. For the purpose of illustration, TRW has assumed a not unreasonable fines level in the centrate of 0.1 wt% solids. The effect is an increase in the average sulfate conversion from 95.7% (without fines in the centrate) to 97.3%.

TABLE 2-12. POTASSIUM FORMATE REACTOR SULFATE CONVERSION

RUN ID NO.	DATE TIME	EXPECTED SO_4^{-2} IN C-201 CENTRATE "NO CONVERSION" $\text{WT}\%^2$	MEASURED $\text{WT}\% \text{SO}_4^{-2}$	ION BALANCE	CALCULATED "UNCONVERTED" SO_4^{-2} , $\text{WT}\%^1$ (0.0% FINES/0.1% FINES)	% SO_4 CONVERSION	COOH^-/K^+ RATIO	PERCENT STOICH ³
SD8	10/14/91 14:40	3.21	0.46	1.00	0.18/0.11	94.4/96.6	1.302	113%
SD10	10/18/91 13:50	2.39	0.37	0.94	0.09/0.02	96.2/99.2	1.335	116%
SD10	10/18/91 14:55	2.63	0.47	1.01	0.19/0.12	92.8/95.4	1.131	98%
SD11	10/22/91 13:30	2.93	0.35	1.04	0.07/0.0	97.6/100.0	1.337	116%
OPS2	10/24/91 13:45	2.13	0.24	0.98	<0/<0	100.0/100.0	1.802	156%
OPS3	10/31/91 13:15	2.47	0.28	1.05	0/<0	100.0/100.0	1.422	123%
OPS3	10/31/91 15:15	3.13	0.36	1.05	0.08/0.01	97.4/99.7	1.319	114%
OPS4	11/26/91 12:30	2.93	0.47	1.06	0.19/0.12	93.5/95.9	1.176	102%
OPS4	11/26/91 13:30	3.30	0.52	0.98	0.24/0.17	92.7/94.8	1.232	107%

¹ Based on 0.4 wt% CaSO_4 solubility in C-201 centrate ($\sim 0.28 \text{ wt}\% \text{SO}_4^{-2}$).

² Based on $(\text{SO}_4^{-2})/(2 \times \text{K}^+) \times \text{wt}\% \text{K}^+$ in C-201 = $1.23 \times \text{wt}\% \text{K}^+$ in C-201 centrate.

³ % stoich = $(\text{COOH}^-/\text{K}^+)_{\text{meas}}/1.148 \times 100$. (Stoichiometric $\text{COOH}^-/\text{K}^+ = 1.148$.)

TABLE 2-12. POTASSIUM FORMATE REACTOR SULFATE CONVERSION (CONTINUED)

RUN ID NO.	DATE TIME	EXPECTED SO_4^{2-} IN C-201 CENTRATE "NO CONVERSION" WT% ²	MEASURED WT% SO_4^{2-}	ION BALANCE	CALCULATED "UNCONVERTED" SO_4^{2-} , WT% ¹ (0.0% FINES/0.1% FINES)	% SO_4 CONVERSION	COOH/ K^+ RATIO	PERCENT STOICH ³
OPS6	01/10/92 13:15	2.57	0.25	0.94	0.0/0.0	100/100	1.761	153%
OPS6	01/10/92 15:00	3.54	0.17	1.04	0.0/0.0	100/100	1.295	112%
OPS7	01/03/92 13:30	3.57	0.48	0.98	0.20/0.13	94.4/96.4	1.269	110%
OPS8	01/16/92 11:30	3.98	0.55	0.94	0.27/0.20	93.2/95.0	1.297	112%
OPS9	01/17/92 11:10	3.84	0.43	0.95	0.15/0.08	96.1/97.9	1.342	116%
OPS10B	01/21/92 14:00	3.75	0.39	0.97	0.11/0.04	97.1/98.9	1.387	120%
OPS11	01/23/92 13:40	3.48	0.42	0.97	0.14/0.07	96.0/98.0	1.414	123%
OPS15	02/13/92 12:00	3.36	0.39	0.96	0.11/0.04	96.7/98.8	1.267	110%
OPS15	02/13/92 14:50	3.54	0.52	0.97	0.24/0.17	93.2/95.2	1.305	113%

¹ Based on 0.4 wt% CaSO_4 solubility in C-201 centrate (~ 0.28 wt% SO_4^{2-}).

² Based on $(\text{SO}_4^{2-})/(2 \times \text{K}^+) \times \text{wt\% K}^+ \text{ in C-201} = 1.23 \times \text{wt\% K}^+ \text{ in C-201 centrate}$.

³ % stoich = $(\text{COOH}/\text{K}^+)_{\text{meas}}/1.148 \times 100$. (Stoichiometric $\text{COOH}/\text{K}^+ = 1.148$.)

TABLE 2-12. POTASSIUM FORMATE REACTOR SULFATE CONVERSION (CONTINUED)

RUN ID NO.	DATE TIME	EXPECTED SO_4^{-2} IN C-201 CENTRATE "NO CONVERSION" WT% ²	MEASURED WT% SO_4^{-2}	ION BALANCE	CALCULATED "UNCONVERTED" SO_4^{-2} , WT% ¹ (0.0% FINES/0.1% FINES)	% SO_4 CONVERSION	COOH/ K^+ RATIO	PERCENT STOICH ³
OPS16	02/14/92 11:00	3.35	0.51	0.99	0.23/0.16	93.1/95.2	1.242	108%
OPS17	02/25/92 12:00	4.15	0.53	0.97	0.25/0.18	94.0/95.7	1.297	112%
OPS18	02/26/92 14:45	3.84	0.50	1.00	0.22/0.15	94.3/96.1	1.263	109%
OPS19	02/27/92 14:45	3.98	0.55	0.99	0.27/0.20	93.2/95.0	1.253	109%
OPS20	02/28/92 13:10	3.99	0.67	1.00	0.39/0.32	90.2/92.0	1.195	104%
OPS21	3/25/92 ?	3.57	0.42	1.05	0.14/0.07	96.1/98.0	1.406	122%
OPS23	03/27/92 11:15	3.10	0.24	1.03	<0/<0	100/100	1.733	150%
Average						95.7/97.3		

¹ Based on 0.4 wt% CaSO_4 solubility in C-201 centrate (~ 0.28 wt% SO_4^{-2}).

² Based on $(\text{SO}_4^{-2})/(2 \times \text{K}^+) \times \text{wt\% K}^+$ in C-201 = $1.23 \times \text{wt\% K}^+$ in C-201 centrate.

³ % stoich = $(\text{COOH}/\text{K}^+)_{\text{meas}}/1.148 \times 100$. (Stoichiometric $\text{COOH}/\text{K}^+ = 1.148$.)

The formate(COOH^-):potassium(K^+) ratio in the formate reactor effluent (C-201 centrate) is tabulated in Table 2-12, along with the percent of the stoichiometric formate:potassium that this represents. It can be seen that almost all of the runs (except SD10) were conducted with an excess of formate (with its equivalent calcium). This was certainly not the intent. The weigh belt feeder that was utilized to feed spent seed into the formate reactor very frequently fed less seed than was expected based on the belt setting (even though the belt was recalibrated a number of times). The formate reactor stoichiometry (formate:potassium) has been plotted versus reactor sulfate conversion in Figure 2-21. As would be expected, the greater the excess formate (calcium feed), the more complete the reactor sulfate conversion. However, it would appear from this plot that even at reactor stoichiometries less than 100% (reactor slightly deficient in formate (calcium) relative to potassium (sulfate)), high (>90%) sulfate conversions are achievable.

2.4.4.2 *Sulfate Removal in Potassium Formate Evaporation Section*

TRW was concerned about the sulfate that is not converted to CaSO_4 in the formate reactor and thus is not removed from the solution as insoluble gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by the centrifuge. This sulfate will be present (as soluble CaSO_4 or K_2SO_4) in the dilute formate solution fed to the formate evaporator. As water is driven from the solution in the evaporator, sulfate salts will precipitate from solution. Table 2-13 tabulates the sulfate contents of samples of concentrated formate produced in the evaporator. It can be seen that the sulfate content of the concentrated product was very low, 0.01 to 0.03 wt% (average = 0.014 wt%). The average sulfate content of the dilute feed to the evaporator was ~0.42 wt%. The concentration factor achieved in the evaporator is ~10 (from ~7% KCOOH to ~70% KCOOH). Therefore, the percent sulfate in the formate evaporator feed removed as precipitate during the concentration of the formate is $(0.42\% \times 10 - 0.014\%)/(0.42\% \times 10) \times 100 = 99.7\%$. In a commercial seed regeneration plant the sulfate solids precipitated in the evaporator can be separated from the concentrated formate product and recycled to the formate reactor where they will be converted to and removed from the system as insoluble gypsum. Therefore, with a 90+ % sulfate conversion per pass in the formate reactor and a 99.7% rejection of sulfate (for recycle) in the formate evaporator, a commercial seed

Note: the three points at a percent stoichiometric ratio greater than 150 were not used to calculate the linear regression line

Figure 2-21. Sulfate Conversion Versus Potassium Formate Reactor Stoichiometry

TABLE 2-13. SULFATE ANALYSIS OF CONCENTRATED POTASSIUM FORMATE SEED

DRUM NO.	KCOOH ⁻	SO ₄ ⁻²
208	66.6	0.01
211	65.1	0.01
577	69.1	0.01
3	66.0	0.01
32	72.7	0.01
34	73.8	0.02
534	78.2	0.01
535	73.8	0.02
536	72.3	0.01
537	74.6	0.01
538	67.3	0.02
539	66.7	0.03
573	75.1	0.01
574	76.4	0.01
575	73.6	0.02
576	69.7	0.01
AVERAGE	71.3	0.014

regeneration plant has the potential (provided the formate (calcium) added to the reactor is stoichiometrically equivalent to the potassium (sulfate) in the spent seed) to remove in excess of 99.9% of the sulfate from the spent seed as insoluble gypsum.

2.4.5 Sodium Partition

In a commercial coal-fired MHD power plant, sodium, a component of the coal ash, will buildup in the regenerated seed. This sodium buildup will continue until a balance is reached between the sodium added to the seed from the coal and the sodium leaving the seed regeneration system either in a waste stream (such as the washed gypsum solids from the dilute formate reaction system) or as a crystalline byproduct (from the formate evaporator) or, if necessary, in a seed purge stream.

2.4.5.1 *Sodium Partition in Potassium Formate Reactor*

A number of seed regeneration POC tests were conducted in which a metered amount of sodium (as dry sodium sulfate solids) was added along with the once-through spent seed (from the CFFF) to the formate reactor. (Note: the amount of sodium added to the once-through spent seed was selected to simulate a possible composition of seed recycled many times through the MHD power plant and seed regeneration unit.) The reactor effluent slurry was centrifuged in C-201 and the centrate was analyzed for both sodium and potassium. The sodium:potassium ratio in the centrate (as well as that in the waste solids wash water) was computed and compared with the sodium:potassium ratio in the feeds to the formate reactor. A decrease in the sodium:potassium ratio in the centrate relative to that in the reactor feeds would indicate that some "partitioning" of sodium and potassium had occurred in the reactor. That is, although it was found that no insoluble compounds containing potassium were produced in the formate reactor, a decrease in the sodium:potassium ratio in transiting the reactor would indicate that insoluble sodium-containing compounds were produced. Thus a means for separating, or "partitioning," sodium from potassium would exist, which would eliminate or reduce the need for a seed purge as a means of controlling sodium buildup in the regenerated seed. This is desirable as

a seed purge will also remove potassium from the system which will require potassium makeup with its associated purchased chemical cost.

Sodium was added to the formate reactor with the spent seed during OPS24 and OPS25. Approximately 28 lbs/hr of dry sodium sulfate (9.1 lbs/hr of Na) was added manually to the formate reactor. The spent seed was metered into the reactor with a weigh belt feeder. At the time of test it was thought that the weigh belt was feeding at the rate of 250 lbs/hr. Subsequent analysis of the potassium in the reactor effluent would seem to indicate that the spent feed rate was actually ~ 195 lbs/hr. Assuming a spent seed insoluble ash content of $\sim 20\%$, this would mean that $195 \times (1-0.2) \times 78.2/174.2 = 70.0$ lbs/hr of potassium were fed to the reactor (MW of $2K = 78.2$ and MW of $K_2SO_4 = 174.2$). TRW has found that $\sim 2\%$ of the soluble sulfate in the spent seed is tied up as alkali metals (Na, Ca, Mg) other than potassium (see Section 2.4.1). Thus, a corrected value for the potassium added to the formate reactor is $0.98 \times 70.0 = 68.6$ lbs/hr. TRW has also found that the sodium in the spent seed is $\sim 1\%$ of the potassium in the seed. Therefore, the amount of sodium added to the formate reactor during OPS24 and OPS25 was $(0.01 \times 68.6) + 9.1 = 9.8$ lbs/hr. The sodium:potassium ratio in the feeds to the formate reactor (excluding for the moment the relatively small amount of sodium and potassium in the waste solids wash water fed to the reactor) during OPS24 and OPS25 was $9.8:68.6 = 0.143:1$. The sodium and potassium analyses for the reactor effluent solution (C-201 centrate) and the waste solids wash water (C-202 centrate) are given in Table 2-14. The average sodium:potassium ratio in the C-201 centrate was 0.165:1 which is slightly higher than the 0.143:1 ratio in the reactor feeds.

Since, as discussed earlier (see Section 2.4.3), virtually no potassium ($< 1\%$) was seen to be lost to the waste solids, it was expected that if no sodium is also being lost to the waste solids, the sodium:potassium ratio in the C-201 centrate would be equal to sodium:potassium ratio in the feed. If sodium was being lost preferentially to the waste solids, it was expected that the sodium:potassium ratio in the C-201 centrate would be less than the ratio in the feed. The fact that the sodium:potassium ratio in the C-201 centrate is slightly greater than that in the feed may be explained by inaccuracies in the solution analyses or by errors in the assumed sodium and potassium content of the spent seed (which are based on average values

TABLE 2-14. SODIUM AND POTASSIUM PARTITION IN POTASSIUM
FORMATE REACTOR

		C-201 CENTRATE			C-202 CENTRATE		
RUN NO.	DATE TIME	WT% Na	WT% K	Na:K	WT% Na	WT% K	Na:K
OPS24	3/20/92 14:30	0.46	2.87	0.160	0.05	0.37	0.135
OPS31	3/31/92 12:00	0.41	2.75	0.149	0.01	0.09	0.111
OPS31	3/31/92 14:30	0.53	2.82	0.188	0.01	0.07	0.143
AVERAGE				0.165			0.130

for spent seed processed during the POC program). In any case, the numbers would seem to indicate that there is no "partitioning" of sodium and potassium in the formate reactor.

Table 2-14 also includes the sodium and potassium analyses for the water (C-202 centrate) resulting from the washing of the gypsum solids separated in centrifuge C-202. The average sodium:potassium ratio in this stream was 0.130:1 which within the accuracy of the analyses is equal to the 0.143:1 ratio of the feed to the reactor. The fact that the sodium:potassium ratio in the wash water recycle to the reactor is approximately equal to the ratio in the other feeds to the reactor means the earlier assumption that this stream could be neglected in computing the reactor feed sodium:potassium ratio was correct.

2.4.5.2 Sodium Partition in Potassium Formate Evaporator

The POC formate evaporator receives its feed from a 16,000 gallon dilute formate storage tank. Several test runs were conducted in the POC formate reactor before sufficient solution was accumulated to switch over to formate evaporator operation. Thus the dilute formate solutions containing added sodium (OPS24 and OPS25) were mixed in the storage tank with the output from several other test operations in which sodium was not added to the formate reactor. Thus the sodium:potassium ratio in the mixed formate evaporator feed was undoubtedly reduced significantly (it was not actually measured) from that of runs OPS24 and OPS25. Records of the daily volumes of solution accumulated in the 16,000 gallon evaporator feed tank would seem to indicate that the sodium:potassium ratio ($\sim 0.16:1$) seen in the dilute formate solutions generated in the OPS24 and OPS25 tests may have been reduced by a factor of ~ 4 upon mixing with the solution generated in other reactor tests. Thus the sodium:potassium ratio of the mixed dilute formate solution being fed to the evaporator, assuming good mixing in the large feed storage tank, may have been $\sim 0.16/4$ or ~ 0.04 .

Several drums of concentrated product generated from this batch of dilute formate solution were analyzed and had sodium:potassium ratios varying from 0.024 to 0.062, with an average value of 0.04 which is the average value estimated for the evaporator feed. This

information is tabulated in Table 2-15. Thus it would appear that sodium was not separated (partitioned) from potassium in the formate evaporator by the preferential crystallization of sodium containing compounds. This is not a surprising result. Sodium is present in the evaporator at much lower concentrations than potassium and in general sodium salts have comparable solubilities to those of potassium salts.

2.4.6 Chloride Partition

In a commercial coal-fired MHD power plant, chloride, a component of the coal ash, will buildup in the regenerated seed. This chloride buildup will continue until a balance is reached between the chloride added to the seed from the coal and the chloride leaving the seed regeneration system either in a waste stream (such as the washed gypsum solids from the dilute formate reaction system) or as a crystalline byproduct (from the formate evaporator) or, if necessary, in a seed purge stream. TRW has in fact proposed, and investigated at laboratory scale, a process scheme for efficiently removing chloride from spent seed. This process is described in detail in Section 5.3.3 of this report. Uncontrolled chloride buildup in the seed could result in reduction in MHD channel life (due to increased corrosion) and degradation of channel performance (due to decreased plasma conductivity).

2.4.6.1 *Chloride Partition in the Potassium Formate Reactor*

The once-through spent seed from the CFFF contained very little chloride (according to a single reported UTSI seed analysis performed in 1988), less than 0.05 wt%. However, as mentioned in Section 2.4.2 of this report, the calcium formate purchased for the POC operations (which was most likely produced from calcium chloride and formic acid) contained an appreciable amount of chloride (~1.1 wt% chloride). When feeding an amount of calcium formate to the formate reactor that is stoichiometrically equivalent to the potassium sulfate in the spent seed, the potassium:chloride weight ratio in the reactor feeds is ~50:1. This is equivalent to feeding a spent seed containing ~0.7 wt% chloride.

The reacted dilute formate solution generated in the POC operations was collected in a 16,000 gallon tank. A sample of the solution accumulated in this tank through the end of

TABLE 2-15. SODIUM AND POTASSIUM PARTITION IN PRODUCT SEED
FROM EVAPORATOR

DRUM NO.	Na ⁺ , WT%	K ⁺ , WT%	Na:K
208	1.14	29.91	0.038
211	0.72	29.75	0.024
577	0.73	31.70	0.023
3	1.29	29.56	0.044
32	1.98	31.72	0.062
34	1.66	32.62	0.051
AVERAGE			0.040

test OPS3 (tank contained the output of tests SD1 through OPS3) was analyzed for chloride (and formate) content. Whatever formate that is fed to the formate reactor will report in this solution (formate is extremely soluble and its loss from the formate reaction system is minimal, <1%). The calcium formate solution fed to the reactor for test runs SD1 through OPS3 contained an average of 8.39 wt% formate ion (~ 12.2 wt% calcium formate solution was fed to the formate reactor) and 0.14 wt% chloride ion. Thus the chloride:formate ratio in the calcium formate feed to the reactor was $0.14/8.39 = 0.0167$. If chloride is removed ("partitioned") from the solution in the reactor, say as insoluble chloride in the gypsum/insoluble ash waste solids stream, the chloride:formate ratio of the solution accumulated in the reactor effluent storage tank would be less than the chloride:formate ratio in the feed to the reactor. The sample taken from the reactor effluent storage tank contained 2.51 wt% formate ion and 0.057 wt% chloride ion. Thus the chloride:formate ratio in the solution in this tank was $0.057/2.51 = 0.0227$. This compares with a value of 0.0167 for the calcium formate feed to the reactor. The chloride in the spent seed was ignored in this calculation.

Using the spent seed chloride content of 0.05 wt% reported by UTSI (Phase I Final Report, October 1988, page 29) would increase the chloride:formate ratio in the reactor feeds from 0.0167 to 0.0179. The chloride of the spent seed that was fed to the formate reactor was not measured. It is possible that this spent seed may have contained in excess of 0.05% chloride. If this spent seed contained ~ 0.2 wt% chloride, the chloride:formate ratio in the formate reactor feeds would have been 0.0215 versus the chloride:formate ratio of 0.0227 measured in the reactor effluent solution storage tank. The fact that the chloride:formate ratio in the reactor effluent solution is slightly greater than that in the reactor feeds would seem to indicate that there is no separation ("partition") of chloride from the solution in the reactor.

2.4.6.2 Chloride Partition in the Potassium Formate Evaporator

Several samples were taken of the concentrated potassium formate after it had been given time to cool to ambient temperature in drums. Some crystalline material was noted to

have precipitated from solution during the evaporation (before cooldown). Additional crystalline material precipitated from solution (on the walls of the drum) during the subsequent cooldown. Samples of the final cool, concentrated, suspended solids-free liquid potassium formate product were analyzed for formate and chloride ion. The analytical results are summarized in Table 2-16. The chloride:formate ratio of the concentrated products varied from 0.0106 to 0.0159 with the average value being ~ 0.0130 . This compares with an expected value of 0.0167:1 to 0.0227:1, as discussed in Section 2.4.6.1 above, if no separation of the chloride from the formate had occurred in the evaporator. Apparently a moderate amount of chloride crystallized from the potassium formate as it was concentrated and/or during the following cooldown step. The crystalline material precipitated was not analyzed for chloride. These solids consisted of a number of crystalline compounds and it would have been very difficult to get a representative sample. It should be noted that in a commercial seed regeneration plant the potassium formate will be concentrated to a greater degree (to 90+ %) than in the POC unit ($\sim 75\%$). On the other hand, the product formate cooldown step, necessitated at the POC scale by the requirement to ship a pumpable, suspended solids-free seed to the CDIF, would be eliminated in a commercial unit where hot molten formate would be injected upstream of the MHD channel. The net effect of a commercial formate evaporator's process conditions on the extent of chloride crystallization from the potassium formate will have to be determined.

2.4.7 Leaching Tests on Gypsum/Ash Waste Solids

Two waste solid streams were generated in the POC operations. By far the largest waste stream was the washed gypsum/insoluble ash solids produced in the dilute formate reaction system. These solids which are in the slurry effluent from the formate reactor are separated from the dilute formate solution in centrifuge C-201. The centrifuge cake is then washed with water to recover potassium in the cake moisture. The washed solids are separated from the wash solution in centrifuge C-202. The wash solution centrate was recycled to the formate reactor. The washed centrifuge cake was collected in drums for disposal. A sample of this cake (C-202 cake) was taken and submitted to an EP Toxicity test to confirm that it was a nonhazardous material. The results of the test (performed by a

TABLE 2-16. CHLORIDE AND FORMATE PARTITION IN PRODUCT SEED
FROM EVAPORATOR

DRUM NO.	Cl ⁻ , WT%	COOH ⁻ , WT%	Cl:COOH
208	0.48	37.12	0.0129
211	0.43	35.72	0.0120
577	0.41	38.70	0.0106
3	0.62	38.89	0.0159
32	0.57	40.91	0.0139
34	0.54	41.29	0.0131
AVERAGE			0.0130

certified laboratory) are given in Table 2-17. It can be seen that the sample passed the test, as it contained less than the limiting values specified for the priority pollutants.

The second waste solid stream generated in the POC unit (in relatively small quantities) is the calcium carbonate precipitated from solution when potassium carbonate is added to the centrate (solids-free formate reactor effluent) from centrifuge, C-201. The calcium carbonate precipitate is separated from the solution in filter, F-203. A small amount of potassium carbonate is added to the centrate stream to reduce its already low calcium content. This was done to avoid potential calcium scaling problems in the downstream formate evaporator. A sample of the filtered solids (F-203 cake) was submitted to, and passed, an EP Toxicity test. The results of this test are given in Table 2-17.

2.4.8 Concentrated Potassium Formate Product

Tonnage quantities of concentrated potassium formate seed were produced in the seed regeneration POC plant for use in channel tests to be conducted at the Component Development and Integration Facility (CDIF) in Butte, Montana. The CDIF required the seed to be a pumpable liquid at ambient temperature and to be free of suspended solids. This requirement limited the concentration of the seed produced for shipment to the CDIF to a maximum concentration of ~75 wt% potassium formate (a saturated aqueous solution of potassium formate at 20°C (68°F) contains ~77 wt% potassium formate).

2.4.8.1 *Quantities Produced*

A total of forty-one (41) 55-gallon drums of concentrated potassium formate seed were shipped to the CDIF in Butte, Montana in June of 1993. The drums contained a total of 29,040 pounds of solution (~21,227 pounds of potassium formate). Table 2-18 gives the net weight and the estimated potassium formate content of each drum. The average potassium formate concentration of the shipped seed was 73 wt%.

TABLE 2-17. ANALYSIS OF WASTE SOLIDS

PARAMETER	C-202 CAKE 01/10/92	F-203 CAKE 01/10/92	LIMITS (ppm)
Arsenic by Graphite Furnace, mg/L (ppm)	<0.02	0.46	5
Barium, mg/L	0.42	1.5	100
Cadmium, mg/L	<0.02	<0.02	1
Chromium, mg/L	0.04	0.45	5
Lead, mg/L	<0.04	<0.04	5
Mercury, mg/L	<0.01	<0.01	0.2
Selenium by Graphite Furnace, mg/L	<0.04	0.73	1.0
Silver, mg/L	<0.004	<0.004	5
TCLP Extract			
Nitric Acid Digestion, Date	02/06/92	02/06/92	
Nitric Acid Digestion with HCl, Date	02/06/92	02/06/92	
TCLP Extract, Date	02/06/92	02/05/92	

Analysis by B.C. Analytical of Anaheim, Calif.

TABLE 2-18. SUMMARY OF PRODUCT SEED

DRUM NO.	SPECIFIC GRAVITY	GROSS WT, LBS	NET WT, LBS	PERCENT KCOOH	KCOOH WT, LBS	WT PER 25 ML	pH	COLOR
1	1.45	711	673	67.0	451	36.16	9.90	Yellow
2	1.50	735	697	69.1	482	37.43	10.70	Yellow
3	1.47	707	669	67.0	448	36.65	10.00	Yellow
4	1.47	690	652	67.0	437	36.84	10.20	Yellow
5	1.56	779	741	75.0	556	39.07	11.60	Yellow
6	1.53	760	722	74.0	534	38.28	11.30	Yellow
7	1.51	739	701	72.0	505	37.63	10.90	Yellow
8	1.50	754	716	71.0	508	37.60	10.90	Yellow
9	1.56	776	738	75.0	554	38.95	11.60	Yellow
10	1.56	777	739	75.0	554	38.98	11.70	Yellow
11	1.52	754	716	75.0	537	37.95	11.20	Yel/Grn
12	1.52	751	713	73.0	520	38.00	11.30	Yel/Grn
13	1.56	767	729	75.0	547	38.88	11.80	Yellow
14	1.54	764	726	75.0	545	38.58	11.70	Yellow
15	1.57	772	734	76.4	561	39.36	13.70	Yellow
16	1.55	752	714	75.0	536	38.66	11.70	Yellow
17	1.54	748	710	75.0	533	38.47	13.70	Yellow
18	1.55	762	724	75.0	543	38.77	13.60	Yellow
19	1.53	738	700	74.0	518	38.18	13.70	Yel/Grn
20	1.59	762	724	74.8	542	39.69	13.90	Yellow
21	1.51	750	712	72.0	513	37.75	13.60	Yel/Grn
22	1.52	734	696	67.8	472	37.92	13.60	Yel/Grn
23	1.54	746	708	75.0	531	38.61	13.50	Yellow
24	1.51	740	702	72.0	505	37.79	13.60	Yel/Grn
25	1.52	760	722	73.0	527	38.07	13.60	Yel/Grn
26	1.53	740	702	74.0	519	38.20	13.70	Yel/Grn
27	1.54	782	744	75.0	558	38.52	11.70	Yellow
28	1.55	762	724	75.0	543	38.68	11.70	Yellow
29	1.55	769	731	76.7	561	38.85	11.90	Yellow
30	1.56	745	707	75.0	530	38.91	11.60	Yellow
31	1.56	717	679	75.0	509	38.93	11.40	Yellow
32	1.50	732	694	70.0	486	37.43	10.80	Yellow
33	1.52	759	721	73.0	526	37.90	11.20	Yellow
34	1.51	747	709	72.0	510	37.84	11.10	Yellow
35	1.53	723	685	74.0	507	38.29	11.30	Yellow
36	1.53	743	705	74.0	522	38.25	11.10	Yellow
37	1.50	727	689	70.0	482	37.60	10.90	Yellow
38	1.49	713	675	70.7	477	37.27	10.70	Yellow
39	1.54	751	713	75.0	535	38.55	11.40	Yellow
40	1.49	727	689	70.0	482	37.15	10.80	Yellow
41	1.54	734	696	75.0	522	38.44	11.50	Yellow
					Total Weight	21,227 lb 10.6 tons		

2.4.8.2 *Product Analysis*

A number of the product drums shipped to the CDIF were sampled for analysis. The analytical results are summarized in Table 2-19. The potassium formate concentrations of the drums sampled ranged from 67 to 77 wt%. The measured concentration ranges for impurities in the product were 0.01 to 0.03 wt% sulfate, 0.01 to 0.17 wt% carbonate, 0.41 to 0.62 wt% chloride and 0.01 to 0.52 wt% calcium. Sodium analysis was not routinely performed. The sodium content of the concentrated seed should be <0.25 wt% based on the amount of sodium in the spent seed. For the production runs in which the spent seed feed to the formate reactor was supplemented by quantities of sodium sulfate (to determine sodium partition in the regeneration system), the sodium content of the concentrated product increased to 0.72-1.98 wt%. The specific gravity of the concentrated product ranged from 1.45 to 1.59. The pH of the concentrated product ranged from 10 to 14 (Table 2-18).

2.4.9 Material Balances

Detailed material balances were not developed for each of the numerous individual daily runs conducted in the seed regeneration POC potassium formate production facility. A total of forty-one (41) test runs were conducted in the potassium formate reaction/solids separation and washing unit (dilute formate production). An additional thirty-eight (38) test runs were conducted in the potassium formate concentration unit. The critical design data regarding potassium recovery, sulfate removal, and sodium and chloride partitioning was ascertained from the measurement of individual stream flows and stream analyses. Periodically however, test run material balances were performed. These balances were useful for checking equipment settings (for instance, problems with the spent seed weigh belt calibration were reflected in a lower than anticipated collection of gypsum/coal ash waste solids), for projecting formate production quantities and for planning the timely acquisition of chemical consumables (calcium formate, etc.).

2.4.9.1 *Dilute Potassium Formate Production*

A detailed material balance was performed for test run OPS4 (11/26/91). During this particular run TRW manually fed weighed quantities of spent seed to the formate reactor. A

TABLE 2-19. ANALYSIS OF CONCENTRATED SEED PRODUCT

KCOOH ¹	SULFATE	CARBONATE	CHLORIDE	CALCIUM	SODIUM
66.6	0.01	NA	0.48	0.36	1.14 ²
65.1	0.01	NA	0.43	0.35	0.72 ²
69.1	0.01	NA	0.41	0.11	0.73 ²
66.0	0.01	NA	0.62	0.50	1.29 ²
72.7	0.01	NA	0.57	0.52	1.98 ²
73.8	0.02	NA	0.54	0.35	1.66 ²
78.2	0.01	0.01	NA	0.05	NA
73.8	0.02	0.17	NA	0.06	NA
72.3	0.01	0.04	NA	0.05	NA
74.6	0.01	0.05	NA	0.09	NA
67.3	0.02	0.14	NA	0.15	NA
66.7	0.03	0.16	NA	0.18	NA
75.1	0.01	NA	NA	TRACE	NA
76.4	0.01	NA	NA	TRACE	NA
73.6	0.02	NA	NA	TRACE	NA
69.7	0.01	NA	NA	TRACE	NA

¹ Based on K⁺ and COOH² (formate) analysis.

² From sodium "partition" formate reactor runs. Spent seed feed supplemented with sodium sulfate.

total of 700 pounds of spent seed was fed into the formate reactor, T-102, over a period of 3.5 hours (200 lbs/hr). Calcium formate solution was metered into the formate reactor at a measured (flow meter) rate of 1.74 GPM (versus 1.63 GPM as determined after the run by the volume change in the 16,000 gallon calcium formate solution storage tank, T-107). This flow was maintained for a period of 3.67 hours (calcium formate flow was initiated 10 minutes prior to the start of the seed feed to the reactor). Makeup deionized water was metered into the formate reactor at a measured (flow meter) rate of 0.5 GPM and into the solids wash tank, T-2012, at the rate of 2.25 GPM. These flows were maintained for a period of 4.1 hours (water flow was initiated 15 minutes prior to the start of the seed feed to the reactor). The flows of reactor makeup water and calcium formate solution were discontinued at the same time as was the manual seed flow to the reactor. At this time the wash water flow to the solids wash tank, T-2012, was reduced to 1.25 GPM and was then maintained at this rate for another 0.9 hour before being discontinued. A small amount (0.3 GPM) of 25 wt% potassium carbonate solution was added (from tank T-204) to the formate reactor effluent after the removal of the gypsum/ash solids from that stream in centrifuge C-201. This was done to precipitate residual calcium from solution and thereby avoid potential scaling problems in the downstream formate evaporator. The potassium carbonate solution flow was maintained for 3.67 hours.

The vessels in the unit were initially filled with deionized water as follows: reactor T-102 @ 75% full (~160 gallons), reactor T-104 @ 50% full (~260 gallons), centrifuge C-201 centrate tank T-2011 @ 50% full (~50 gallons), centrifuge C-201 cake reslurry tank T-2012 @ 50% full (~50 gallons), and centrifuge C-202 centrate (wash water to reactor) tank T-202 @ 50% full (~50 gallons). At the end of the test, reactors T-102 and T-104 had been emptied (except for a residual volume of 120 gallons in T-104's cone bottom), and T-2011, T-2012 and T-202 each still contained ~50 gallons. The level gauge on the 16,000 gallon tank (T-309) used for dilute formate solution storage indicated an increase in volume of 1,410 gallons. A total of ~690 pounds of washed gypsum/insoluble coal ash cake was collected from centrifuge C-202 in 55 gallon drums, D-202. After potassium carbonate addition, a total of ~135 pounds of calcium carbonate plus gypsum/insoluble coal ash fines were removed (from the dilute formate solution leaving T-2011) as a filter cake in filter

F-203 and collected in drum, D-203. The filtrate from F-203 was then pumped to storage tank T-309. All the material balance information for OPS4 is shown schematically in Figure 2-22. The material balance calculations are shown in Table 2-20.

As can be seen in Table 2-20, an excellent material balance closure was obtained. The volumetric closure was $\sim 95\%$ and the mass closure was $\sim 96\%$.

In addition to the overall material balance performed as described above, TRW also performed reactor balances for those ionic species, potassium (K^+) and formate ($COOH^-$), which are not removed from solution in transit through the reactor (losses of these species to the waste solids had been found to be minimal, $< 1\%$). These balances were performed to determine the approach to steady-state that was achieved in the formate reactors. The formate reactors were modeled as two continuously stirred tank reactors (CSTR's) in series. Since the tanks were initially filled with water (with levels maintained constant until the end of the test run), the starting concentrations (before commencement of the spent seed and calcium formate feeds to the reactor) for both K^+ and $COOH^-$ were 0.0 wt%. The volumetric throughput to each reactor was approximately 265 gallons per hour. Residence times for reactors T-102 and T-104 were specified as 45 minutes and 70 minutes respectively. These residence times are approximately 15% greater than what would be calculated based on the volume of solution in the reactor vessels. The residence times were increased to reflect the volumetric holdup in the circulation loops associated with each vessel. Based on this input, the mathematical model utilized predicts the approach to equilibrium (steady-state) in the reactor effluent (centrifuge C-201 centrate) for the K^+ and $COOH^-$ ionic species as a function of run time. Samples of the C-201 centrate were taken at two times during the run and were analyzed for K^+ and $COOH^-$. The first sampling time corresponded to 2.25 hours after the start of spent seed feed to the reactor (2.42 hours after the start of the calcium formate feed to the reactor since calcium formate feed began 10 minutes before the start of spent seed). The second sample was taken one hour later, 3.25 hours after the start of the spent seed feed (3.42 hours after the start of the calcium formate feed).

Figure 2-22. Material Balance (Test Run OPS4) for Potassium Formate Reaction and Solids Separation/Washing Sections of POC Plant

TABLE 2-20. MATERIAL BALANCE FOR TEST RUN OPS4
REACTION AND SOLIDS SEPARATION/WASHING UNIT

- Start of Run (SOR)/End of Run (EOR) Tank Inventories - Excluding Consumables/Product Storage Tanks

Tank No.	Volumes, Gallons <u>SOR/EOR</u>	Volume Change, Gallons <u>SOR-- > EOR</u>	Estimated Wt. of Liquid, lbs <u>SOR/EOR</u>	Estimated Liquid Wt Change, lbs <u>SOR-- > EOR</u>
T-102	160/0	-160	1335/0	-1335
T-104	260/120	-140	2170/1030 ¹	-1140
T-2011	50/50	0	417/430 ¹	+13
T-2012	50/50	0	417/417	0
T-202	50/50	<u>0</u>	417/430 ¹	<u>+13</u>
Total Tank Inventories		-300 Gallons		-2449 lbs

- Σ FLOWS IN

<u>Description</u>	<u>Volume, Gallons</u>	<u>Estimated Weight, lbs</u>
Spent Seed	Not Applicable	700
Calcium Formate Solution, T-107	383	3,482 ²
Deionized Water	731	6,097
Potassium Carbonate Solution	<u>66</u>	<u>688</u>
Total In	1180 Gallons	10,967 lbs

- Σ FLOWS OUT

Dilute Formate Solution, T-309	1,410	12,112 ³
Gypsum/Ash Waste Solids, D-202	Not Applicable	690
CaCO ₃ /Gypsum Waste Solids, D-203	<u>Not Applicable</u>	<u>135</u>
Total Out	1,410 Gallons	12,937 lbs

- Material Balance: Flow In + In-Plant Inventory Change = Flow Out
- Volumetric Balance: 1,180 Gallons + 300 Gallons = 1,480 Gallons In
1,480 Gallons In Versus 1,410 Gallons Out
- % Closure = Out/In x 100: 1,410/1,480 x 100 = 95.3%
- Mass Balance: 10,967 lbs + 2,449 lbs = 13,416 lbs In
13,416 lbs In Versus 12,937 Lbs Out
- % Closure = Out/In x 100 12,937/13,416 x 100 = 96.4%

NOTES

¹ Specific gravity of solution estimated to be 1.03.

² Specific gravity of 12% calcium formate solution = 1.09.

³ Specific gravity of ~6.5% total dissolved solids (TDS) solution estimated to be 1.03.

If we assume that: 1) 20% of the spent seed feed to reactor T-102 is insoluble ash, 2) 98% of the soluble seed sulfate is associate with potassium (the other 2% with other alkali metals), and 3) 1% of the seed potassium is lost to the gypsum waste solids, then at steady-state 69.7 lbs/hr of K^+ is expected in centrifuge C-201 centrate. Similarly, for 1.74 GPM of 12.2 wt% calcium formate solution fed to reactor T-102 and a 1% loss of formate to the gypsum waste solids, 79.7 lbs/hr of $COOH^-$ in C-201 centrate was expected at steady-state. The first sample of C-201 centrate taken contained 2.38 wt% K^+ and 2.80 wt% $COOH^-$. Thus at a centrifuge C-201 centrate flow of ~ 265 GPH (~ 2275 lbs/hr @ s.g. = 1.03), the C-201 centrate contains 54.1 lbs/hr of K^+ and 63.7 lbs/hr of $COOH^-$. Thus the approach to steady-state at this run time is $54.1/69.7 \times 100 = 77.6\%$ for K^+ and $63.7/79.7 \times 100 = 79.9\%$ for $COOH^-$ which has been fed for 10 minutes longer than K^+ . The second sample of C-201 centrate contained 2.68 wt% K^+ and 3.30 wt% $COOH^-$. The C-201 centrate of this analysis contains 61.0 lbs/hr K^+ and 75.1 lbs/hr of $COOH^-$. Thus the approach to steady-state is $61.0/69.7 \times 100 = 87.5\%$ for K^+ and $75.1/79.7 \times 100 = 94.2\%$ for $COOH^-$. These approaches to steady-state have been plotted in Figure 2-23 along with the curve showing the model predictions. As can be seen, good agreement was obtained between plant data and the model predictions.

2.4.9.2 Concentrated Potassium Formate Production

In a commercial MHD seed regeneration plant, the formate evaporator would be in continuous around-the-clock operation. At the POC level, however, TRW found it more convenient to operate the two-stage formate evaporation unit for a series of single shift (8-hour) days. This involved initially operating only the first of the two evaporator stages. Dilute (5 to 7%) potassium formate solution was continuously fed to this falling film type evaporator at a rate of ~ 5.5 GPM ($\sim 3,300$ lbs/hr). Using steam as a heat source, water was evaporated from the formate solution at a rate of $\sim 2,500$ lbs/hr. An inventory of ~ 300 gallons of 25 to 30 wt% potassium formate was accumulated in the evaporator. At this point, transfer of this material to the second stage of the evaporation unit, a forced circulation type evaporator, commenced. Any solids that had precipitated from solution in the first stage of the evaporator were centrifuged from solution before the solution was fed to

* Steady-state is defined as when the potassium or formate OUT equals the potassium or formate IN

Figure 2-23. Potassium Formate Reactor K⁺ and COOH⁻ Approach to Steady-State Versus Run Time (Along with Model Prediction Curve)

the second evaporation stage. Additional water was evaporated from the solution in the second stage, again with steam as the heat source.

TRW found that it was possible to shutdown overnight and have the evaporator inventories cool without plugging equipment as long as the inventories were only moderately concentrated (50 to 60% potassium formate). The inventories could be rapidly reheated to normal operating temperatures in the first hour of operation the following day. During the final day of the evaporation run, the concentration of the second stage evaporator inventory (~300 gallons) was raised to >75% potassium formate. At this point the inventory was pumped from the second stage evaporator into 55-gallon drums. The solution was allowed to slowly cool in the drums to ambient temperature. In some instances it was noted that as the solution cooled, solids precipitated from solution, generally on the walls of the drum. The solution was decanted from the drums and pumped through a bag filter into 55-gallon shipping drums. This solids-free concentrated potassium formate seed solution (see Section 2.4.8) was shipped to the CDIF in Butte, Montana for use in channel testing.

The material balances computed for the formate evaporation unit were primarily a bookkeeping tool in that they were used to track the concentrations and inventories of potassium formate in the evaporation stages. Dilute formate solution of known composition was metered into the first stage of the evaporator over a period of several days. It was concentrated in this stage, then transferred at a metered rate to the second stage to undergo further concentration. As mentioned above, it was not until the end of the final day of operation that any potassium formate was actually removed from the evaporation unit. At that time the entire inventory of the second evaporator stage (into which the contents of the first evaporator stage had earlier been transferred) was pumped into drums. In practice then all the potassium formate in the dilute solution that was fed to the first evaporation stage was finally collected in concentrated form from the second evaporation stage. Therefore, by metering the formate input to the first evaporation stage, and also measuring the amount of water evaporated from solution in each evaporation stage (evaporated steam is condensed overhead and its rate of accumulation in a receiver was periodically measured), the concentration and inventory of potassium formate in each stage of the evaporator could be

accurately tracked. Table 2-21 is a typical log of the data that was collected during an evaporation unit run. Table 2-22 is the material balance that was subsequently calculated from this data.

2.5 EQUIPMENT EVALUATION/MODIFICATION

Most of the plant equipment and instrumentation performed as expected in their initial configuration. However, several challenging problems were encountered including plugging in piping and control valves, problems with the discharge of cake from the centrifuges, and the formation of a pervasive gypsum scale in equipment and piping.

2.5.1 Potassium Formate Reactor System

2.5.1.1 *Effect of Spent Seed Contaminants*

The maximum spent seed feed rate achieved during production was ~250 pounds per hour. This is sufficient spent seed to produce ~200 pounds per hour of regenerated potassium formate seed (pure basis). The maximum potassium formate solution concentration achieved during dilute formate production operations was ~7.5 wt%. On several occasions TRW attempted to produce more concentrated solutions (design was 8.5 wt%) by reducing the water fed to the unit. These attempts resulted in the onset of plugging in piping and control valves due to the increased solids loading (gypsum, insoluble seed mineral matter) of the slurry being processed. This may be a mechanical problem due to the relatively small size of the piping and valving in the POC plant. It is possible that in a full scale plant operation higher reactor potassium formate concentrations can be achieved.

In addition, the presence of small quantities of tiny rust flakes in the spent seed feed received from UTSI played havoc with the control valves. The rust particles served as nucleation sites for the growth of gypsum 'pellets' in the first potassium formate reactor, T-102. These pellets grew to such a size that they subsequently plugged the control valve in the effluent line from the reactor. The problem was solved by installing a strainer in the reactor circulation loop to remove the pellets as they formed and before they grew large enough to plug the control valve. The presence of rust particles in the spent seed was

TABLE 2-21. TYPICAL EVAPORATION DATA LOG (EVAP17 - 01/29/92)

FIRST EVAPORATION STAGE

TIME	PROCESS PRESSURE PSIA	PROCESS TEMP deg F	BOILING PT ELEVATION deg F	(UNCALIB) DENSITY	(CALC) CONC. KCOOH WT %	PROCESS FEED GPM	MEASURED PROCESS CONDENSATE GPM	PROCESS OVHD TO THERMAL COMPRESSOR GPM	TOTAL PROCESS CONDENSATE GPM
07:15	8.2	214		1.43	43.00	5.0	0.00	1.50	1.50
08:00	7.9	207	25	1.39	33.48	6.0	2.75	1.50	4.25
08:30	8.1	203	20	1.33	28.49	6.0	2.75	1.50	4.25
09:00	8.8	203	16	1.31	25.61	6.0	2.75	1.50	4.25
09:30	8.9	205	17	1.29	24.01	6.0	2.75	1.50	4.25
10:00	9.3	206	16	1.27	22.15	6	2.50	1.50	4.00
10:45	9.6	204		1.26	22.51	5.5	2.50	1.50	4.00
11:00	9.6	207	16	1.27	23.48	5.5	3.00	1.50	4.50
11:30	9.6	207	16	1.26	25.27	5.5	3.00	1.50	4.50
12:20	9.6	208	17	1.27	25.11	5.5	2.63	1.50	4.13
13:00	9.6	208	17	1.28	25.04	5.5	2.63	1.50	4.13
13:30	9.6	209	18	1.30	25.00	5.5	2.63	1.50	4.13
14:25	9.2	209	20	1.32	24.95	5.5	2.63	1.50	4.13
15:30	9.2	212	23	1.36	24.92	5.5	2.63	1.50	4.13

SECOND EVAPORATION STAGE

TIME	PROCESS PRESSURE PSIA	PROCESS TEMP deg F	BOILING PT ELEVATION deg F	(MEASURED) DENSITY	(CALC) CONC. KCOOH WT %	PROCESS FEED GPM	MEASURED PROCESS CONDEN, GPM
08:00	3.7	201	51	1.44	62.00	1.5	1.75
08:30	3.0	198	56		65.12	1.5	1.75
09:00	2.9	199	58	1.52	67.79	1.7	1.88
09:30	2.5	196	62	1.55	70.47	1.6	1.88
10:00	2.4	196	63	1.55	70.81	1.2	1.00
10:45	2.5	196		1.54	71.60	1.1	1.00
11:00	2.5	196	61		71.72	1.2	1.00
11:30	2.5	197	62	1.55	72.00	1.2	1.00
12:20	2.5	201	66	1.55	75.08	1	1.25
13:00	2.4	203	70	1.54	79.30	0.6	1.25
13:05					79.85	0.6	1.25
13:30	2.2	206	76	1.61	80.92	1.2	1.25
14:25	2.1	209	82		84.54	1.0	1.25
15:30	2.1	214	87	1.67	88.90	1.0	1.25

TABLE 2-22. TYPICAL EVAPORATION MATERIAL BALANCE (EVAP17 - 01/29/92)

FIRST EVAPORATION STAGE
(ASSUMPTION: APPROXIMATELY 6.93 WT% KCOOH IN FEED)

TIME	TIME INTERVAL MIN	KCOOH ACCUMUL. LBS	PROCESS CONDENSATE LBS	WATER ACCUMULATED LBS	MASS BAL. (CALC) KCOOH WT %
06:45		435.0		576.6	43
07:15	30	525.1	375.3	1412.1	27.11
08:00	45	377.8	1595.0	750.7	33.48
08:30	30	334.1	1063.4	838.6	28.49
09:00	30	299.7	1063.3	870.3	25.61
09:30	30	289.1	1063.3	915.1	24.01
10:00	30	314.6	1000.8	1105.4	22.15
10:45	45	359.4	1501.2	1237.1	22.51
11:00	15	370.5	562.9	1207.7	23.48
11:30	30	389.0	1125.9	1150.8	25.27
12:20	50	432.5	1720.1	1290.3	25.11
13:00	40	506.7	1376.1	1517.0	25.04
13:30	30	519.1	1032.1	1557.0	25.00
14:25	55	568.5	1892.1	1709.7	24.95
15:30	65	627.3	2236.2	1890.0	24.92

SECOND EVAPORATION STAGE
(ASSUMPTION: APPROXIMATELY 23.0 WT% KCOOH IN FEED)

TIME	TIME INTERVAL MIN	KCOOH ACCUMUL. LBS	PROCESS CONDENSATE LBS	WATER ACCUMULATED LBS	MASS BAL. (CALC) KCOOH WT %
08:00		2810.8		1722.8	62
08:30	30	2962.7	437.9	1586.7	65.12
09:00	30	3105.3	469.1	1475.5	67.79
09:30	30	3224.1	469.1	1351.3	70.47
10:00	30	3306.8	250.2	1363.1	70.81
10:45	45	3410.7	375.3	1352.9	71.60
11:00	15	3449.2	125.1	1360.2	71.72
11:30	30	3529.9	250.2	1373.0	72.00
12:20	50	3651.7	521.2	1212.0	75.08
13:00	40	3709.7	417.0	968.2	79.30
13:05	5	3717.0	52.1	937.7	79.85
13:30	25	3789.3	260.6	893.6	80.92
14:25	55	3921.7	573.4	717.4	84.54
15:30	65	4077.8	677.6	509.4	88.90

thought to be due to the rusting of carbon steel solids handling equipment at the CFFF and of the carbon steel tote bins provided by TRW to transport the spent seed from the CFFF to the POC test site.

2.5.1.2 Scale Formation

The formation of a pervasive gypsum scale was observed in the equipment and piping of the dilute formate production unit. While this did not cause serious problems during the relatively short duration operation of the POC unit, it raises questions on the effect it might have on long duration operations.

2.5.2 Solids Separation and Washing System

2.5.2.1 Centrifuge Performance

The Bird Machinery 9-inch solid bowl centrifuges performed well. The pool depth in these machines can be adjusted with the machine in operation. When the proper pool depth was obtained, these machines produced a relatively dry cake (0.2 to 0.3 lbs moisture per lb dry cake). In addition, visual inspection and sulfate analyses of the dilute potassium formate solution and wash water centrates issuing from the machines seemed to indicate that fines carryover in the centrate was quite low ($<0.3\%$ suspended solids in the centrate).

2.5.2.2 Centrifuge Solids Discharge

Among the challenging problems encountered during production operations was the discharge of cake from the centrifuges. The dry gypsum/insoluble seed mineral matter tended to hang up in the metal ductwork that was originally installed. As originally configured, solids discharge from the 9-inch solid bowl centrifuges was thrown out into a rectangular cross-section duct. The solids were to move a short distance vertically down through the duct into a metal transition piece. The metal transition piece was to direct the down flowing solids into a ~ 10 -foot long flexible metal duct of circular cross-section hung vertically so as to deliver the solids to either the solids wash tank, T-2012, in the case of centrifuge C-201 or to 55-gallon waste collection drums in the case of centrifuge C-202.

The cross-sectional area for solids flow was reduced in going from the rectangular to the circular duct.

In the first few runs conducted in the POC unit, solids got hung up in the transition piece and caused frequent interruptions of the test operations. The problem was resolved by replacing the transition piece and metal circular duct with a length of plastic sheeting which was allowed to hang like a "shower curtain" into either solids wash tank T-2012 or into the 55-gallon washed waste solids collection drums. The clean "shower curtain" hanging from a centrifuge is shown in Figure 2-24 before it was used for the first time. Any solids that on occasion got hung up on the transparent sheeting could be observed and easily prodded loose by shaking the sheeting. The "shower curtain" containing solids during a run is shown in Figure 2-15. In addition, since the solids from centrifuge C-201 were to be reslurried with water in wash tank T-2012, the hot wash water that was normally fed directly into this tank was directed to flow first into the solids discharge duct of the centrifuge, thereby sluicing the solids into wash tank T-2012. Since dry solids for waste disposal were to be discharged from centrifuge C-202, it was not possible to "sluice" solids from this machine. However, the solids discharge section of this machine was fitted with a flush water connection that could be put to use to break the occasional solids plug that would form.

2.5.3 Potassium Formate Concentration System

2.5.3.1 *Heat Transfer Coefficients for Steam Chests*

A total of 56,000 gallons of dilute potassium formate was processed through the evaporation unit. Heat transfer rates in both stages of evaporation remained high and fairly constant during the period of operations, with no evident buildup of scale on the steam chest tube surfaces. This may have been partially due to the addition of a small amount of potassium carbonate upstream of the evaporator to reduce the calcium in the formate solution fed to the evaporator. The potassium carbonate reacts with the gypsum to form very insoluble calcium carbonate which is removed in a filter upstream of the evaporator. Thus the potential for calcium scaling in the evaporator is reduced.

Figure 2-24. Clean "Shower Curtain" Discharge Chute Hanging From Centrifuge

However, the dilute formate solution fed to the evaporator, even after calcium reduction, still contained on the average ~ 0.1 wt% calcium. The concentrated formate product from the evaporator contained on the average ~ 0.2 wt% calcium. The concentration factor achieved in the evaporator was 10 to 15. Therefore, with no feed calcium precipitated, product calcium concentration should have been 1 to 1.5 wt%. The fact that product calcium was only ~ 0.2 wt% indicates that $\sim 90\%$ of the calcium in the feed precipitated in the evaporator without causing apparent scaling of the heat transfer surfaces. Figures 2-25A and B are plots of the calculated heat transfer coefficients for the steam heated exchanger surfaces in both the first and second evaporation stages as a function of run number (time of operation). The coefficients are high and are typical of coefficients to be expected in the types of evaporators utilized. Given the accuracy of the process temperature measurements, there was no apparent degradation (scaling) of evaporator performance over the ~ 200 hours of evaporator test operations conducted during the POC program.

2.5.3.2 *Solution Boiling Point Elevations*

The knowledge of boiling point elevations is crucial for the accurate design of evaporation units. Boiling point elevations can be calculated from the evaporator operating temperature and pressure. The boiling point of water corresponding to the evaporator operating pressure is extracted from the steam tables. The difference between the evaporator operating temperature and the boiling point of water at the evaporator operating pressure is defined as the boiling point elevation. The operating data for each of the two stages of the POC formate evaporator during a typical test run is given in Table 2-23. Material balances were performed to track the potassium formate solution concentration in each of the two stages as a function of time. The boiling point elevations in each of the evaporation stages were calculated as described above and are reported in Table 2-23. A plot, Figure 2-26, of boiling point elevation versus solution potassium formate concentration was developed from the data in Table 2-23. As a point of reference, it is not possible to calculate a boiling point elevation for anhydrous potassium formate. Chemical handbooks report the melting point of

A

B

Figure 2-25. Calculated Heat Transfer Coefficients for Two-Stage Evaporation System

TABLE 2-23. TYPICAL EVAPORATION OPERATING DATA (EVAP17 - 01/29/92)

FIRST EVAPORATION STAGE

TIME	PROCESS PRESSURE PSIA	PROCESS TEMP deg F	BOILING PT ELEVATION deg F	(CALC) CONC. KCOOH WT %
07:15	8.2	214	30	43.00
08:00	7.9	207	25	33.48
08:30	8.1	203	20	28.49
09:00	8.8	203	16	25.61
09:30	8.9	205	17	24.01
10:00	9.3	206	16	22.15
10:45	9.6	204	13	22.51
11:00	9.6	207	16	23.48
11:30	9.6	207	16	25.27
12:20	9.6	208	17	25.11
13:00	9.6	208	17	25.04
13:30	9.6	209	18	25.00
14:25	9.2	209	20	24.95
15:30	9.2	212	23	24.92

SECOND EVAPORATION STAGE

TIME	PROCESS PRESSURE PSIA	PROCESS TEMP deg F	BOILING PT ELEVATION deg F	(CALC) CONC. KCOOH WT %
08:00	3.7	201	51	62.00
08:30	3.0	198	56	65.12
09:00	2.9	199	58	67.79
09:30	2.5	196	62	70.47
10:00	2.4	196	63	70.81
10:45	2.5	196	61	71.60
11:00	2.5	196	61	71.72
11:30	2.5	197	62	72.00
12:20	2.5	201	66	75.08
13:00	2.4	203	70	79.30
13:05				79.85
13:30	2.2	206	76	80.92
14:25	2.1	209	82	84.54
15:30	2.1	214	87	88.90

Figure 2-26. Boiling Point Elevation Versus Potassium Formate Solution Concentration

anhydrous potassium formate as 167°C (333°F) and report that the compound decomposes at temperatures in excess of the melting point.

2.5.3.3 *Potassium Formate Crystallization During Product Cooldown*

The concentrated potassium formate from the second stage of the evaporator is pumped hot (200°F+) into 55-gallon drums and allowed to cool (over a period of days) to ambient temperature (10 to 20°C). It was observed in many instances that by the time the solution had cooled, a significant amount of solids had crystallized out as a rind adhering to the side walls of the cooldown drums. The solids were analyzed to be potassium formate crystals. This precipitation was to be expected since the second stage evaporator was at times operated at final potassium concentrations approaching 90 wt% (see Table 2-23). A saturated solution of potassium formate at 20°C contains ~77 wt% potassium formate (see Figure 2-20). Therefore, upon cooling potassium formate was expected to crystallize from solution to maintain the solution at its saturation point. It is likely, however, that potassium formate did not crystallize in the second stage evaporator. According to Table 2-23, the operating temperature in the second stage was 214°F (101°C) at a calculated (from material balances) potassium formate concentration of 88.9 wt%. According to the potassium formate solubility curve (Figure 2-12), a saturated solution of potassium formate will contain ~ 89 wt% potassium formate at 214°F (101°C).

3. CALCIUM FORMATE POC UNIT

3.1 INTRODUCTION AND SUMMARY

Calcium formate is the seed regenerant used in the Econoseed process. Calcium formate is produced in the United States primarily as a byproduct of trimethylolethane ("Trimet") production. Calcium formate is produced in relatively small quantities (<5 million lbs/yr) via this byproduct route. Since in excess of 30 million lbs/yr of calcium formate would be required for seed regeneration in a single 250 MW_t MHD power plant, a new route to the continuous production of large quantities of calcium formate is needed to support an MHD power industry.

TRW is proposing that the large quantities of calcium formate required for MHD seed regeneration be produced by the reaction of carbon monoxide gas with lime solids in an aqueous medium. This route to the continuous production of calcium formate was piloted in 1954 by the Electro Metallurgical Company (of Niagara Falls, New York), a subsidiary of Union Carbide. TRW acquired the pilot plant database. Using this database, which was limited primarily to proof of principle experiments, TRW designed, constructed and successfully operated a 50 lb/hr Calcium Formate Proof-of-Concept (POC) production unit to generate equipment scaleup/design data.

The following sections of this Introduction and Summary contain a description of the POC unit and a summary of the test conditions, results and conclusions.

3.1.1 Process Description

Aqueous calcium formate solution (at up to 12 wt% concentration) is produced by reacting CO gas with aqueous lime slurry at reaction temperatures of 300°F to 400°F and reaction pressures of 950 psig to 1350 psig.

The POC unit is comprised of five subsystems:

- Lime slurry feed preparation, pressurization and heating system
- Feed gas blending, compression and heating system
- Two stage pressurized, heated reaction system for gas-slurry contacting
- Product cooling and pressure reduction system
- Vapor/liquid/solid separation and product recovery system

A block diagram of the POC unit is shown in Figure 3-1. Prior to each test run, a batch of hydrated lime slurry feed of known lime concentration is prepared in a storage tank. During the run the slurry is pumped to the suction of a metering (diaphragm) pump where it is raised to reaction pressure. The pressurized slurry is preheated to reaction temperature in an oil heated exchanger.

Feed gas mixture for the unit is prepared by metering CO, N₂, and CO₂ into a manifold for mixing. The gas mixture is compressed to reaction pressure in a two-stage compressor before it is preheated to reaction temperature in a steam heated exchanger.

The feed gas and slurry streams are contacted with each other in the two-stage cocurrent flow pipe reactor.

The reactor effluent is cooled by water in a heat exchanger and then reduced to atmospheric pressure across a control valve. The cooled effluent then enters a vapor-liquid separator. The disengaged gas is sent to a flare to incinerate any unreacted combustible gases. Aqueous calcium formate product solution containing the unreacted lime solids are then pumped from the separator to a holding tank. A centrifuge is used to separate the lime solids from the product solution, which is pumped to a storage tank. The recovered solids are collected in drums for disposal.

3.1.2 Test Conditions

The main objective in test operations of the calcium formate POC unit was to ascertain

Figure 3-1. Block Diagram of the Calcium Formate POC Unit

which operating parameters influence reactor performance (CO conversion) so as to obtain the engineering scaleup data required for the design of a commercial size plant. The test matrix employed covered the range of reaction temperatures between 300 and 400°F, reaction pressures between 950 and 1350 psig and reaction residence times between 5 and 30 minutes. In addition, reactor feed gases containing as little as 40% to as much as 100% carbon monoxide were tested to reflect the range of possible commercial sources of carbon monoxide. Carbon dioxide in the reactor feed gas was varied from 0 to 3% to determine the effect of this potential feed gas impurity. The effect of reactor mixing was investigated by operating the reactors with and without internals.

3.1.3 Test Results and Conclusions

Approximately 100 hours of testing were performed in the POC unit between October 1992 and May 1993. Chemical analyses were performed on process feed and effluent streams. Material balances were then performed using these analyses and measured stream flows. CO conversions of up to 100% were attained under favorable operating conditions. CO conversions were found to vary in a regular and predictable manner with: 1) reaction temperature and pressure (at fixed feed gas composition and CO/lime stoichiometry), 2) reaction temperature and feed gas composition (at fixed pressure and CO/lime stoichiometry), and 3) reaction pressure and residence time (at fixed feed gas composition, reaction temperature, and CO/lime stoichiometry).

A number of operational problems (due in part to mechanical limitations of the equipment at pilot scale) were observed: 1) the process tubes of the lime slurry heater scaled and eventually plugged after approximately 75 hours of operation, and 2) frequent plugging and erosion was observed early in the program in the control valves used for pressure reduction service.

3.1.4 Recommendations

A 50 lb/hr calcium formate production unit will support a ~ 2 MW_t MHD power plant. A reactor sized to produce 500 lbs/hr of calcium formate, sufficient to support a ~ 20 MW_t

MHD power plant, should be built and tested prior to a final scaleup to the $\sim 5,000$ lb/hr unit required to support the first 250 to 300 MW_t demonstration plant.

3.2 TEST CIRCUIT DESCRIPTION

There are five subsystems which makeup the calcium formate POC test unit: 1) lime slurry feed preparation, 2) feed gas preparation, 3) the reactor system, 4) effluent pressure reduction, and 5) effluent phase separation. Lime slurry feed preparation and feed gas preparation are shown in Figure 3-2. The reactor system, effluent pressure reduction, and effluent phase separation are shown in Figure 3-3. The material balance used to design the 50 lb/hr POC unit is presented in Table 3-1 along with the design assumptions. With the exception of the batch lime slurry feed preparation and the batch solids separation subsystems, all of the subsystems in the POC unit were nominally designed to operate continuously to support the production of 50 pounds of calcium formate per hour. The design was based on data collected from test operations on a unit built by the Electro Metallurgical Company in 1954 and incorporated TRW's knowledge and experience acquired from previous programs utilizing similar technologies (slurry processing and high pressure processes), as well as information supplied by equipment vendors.

The complete POC test unit, as built, contains about 20 major pieces of equipment including tanks, pumps, a compressor, reactors, a centrifuge, and a flare. The major equipment items are listed in Table 3-2. The materials of construction included stainless steel, polypropylene, stellite, tungsten carbide, and copper-nickel alloy. The POC unit as constructed contains 50 instruments and controls as well as a computer control room with a data acquisition and control system. The five subsystems of the calcium formate POC test unit plus the data acquisition and control system are described in detail in the following sections.

3.2.1 Lime Slurry Feed Preparation (Figure 3-2)

This subsystem includes a mix/holding tank for the lime slurry feed, a diaphragm pump

Figure 3-2. Process Flow Diagram of the Calcium Formate Reactor Feed System

Figure 3-3. Process Flow Diagram of the Calcium Formate Reactor System, Effluent Pressure Reduction, and Effluent Phase Separation

TABLE 3-1. MATERIAL BALANCE BASIS ECONOSEED POC PLANT
CALCIUM FORMATE PRODUCTION

- 50 lbs/hr Calcium Formate Production from Reactor
- Feed Gas = 75% CO, 22% N₂, 3% CO₂
- CO Conversion = 85%
CO₂ Conversion = 85%
Lime Conversion = 85%
- Stoichiometric Lime in Feed
- Lime Slurry = 7 wt % Ca(OH)₂
- Gas to Incinerator Saturated with H₂O_v @ 150°F, 1 psig
- 100% Centrifuge Efficiency for Suspended Ca(OH)₂, CaCO₃
- Centrifuge Cake Contains 1 lb Moisture/lb Dry Solids
- Calcium Formate Aqueous Product ~ 9.5 wt %

TABLE 3-1. MATERIAL BALANCE FOR ECONOSEED POC PLANT
CALCIUM FORMATE PRODUCTION (CONTINUED)

STREAM NO.	1	2	3	4	5
DESCRIPTION	LIME SLURRY	CO TO REACTOR	CO ₂ TO REACTOR	N ₂ TO REACTOR	FEED GAS TO REACTOR
GAS, LBS/HR					
CO		25.3			25.3
CO ₂			1.6		1.6
N ₂				7.5	7.5
H ₂ O	—	—	—	—	—
SUBTOTAL GAS, LBS/HR		25.3	1.6	7.5	34.4
SCFH		343	14	101	458
LIQUID, LBS/HR					
Ca(OH) ₂	1.0				
Ca(COOH) ₂					
H ₂ O	<u>481.0</u>				
SUBTOTAL LIQUID, LBS/HR	482.0				
SOLIDS, LBS/HR					
Ca(OH) ₂	35.2				
CaCO ₃	—				
SUBTOTAL SOLIDS, LBS/HR	35.2				
TOTAL STREAM, LBS/HR	517.2	25.3	1.6	7.5	34.4
GPM	~ 1.0				

TABLE 3-1. MATERIAL BALANCE FOR ECONOSEED POC PLANT
CALCIUM FORMATE PRODUCTION (CONTINUED)

STREAM NO.	6	7	8	9	10
DESCRIPTION	REACTOR EFFLUENT	GAS TO INCINERATOR	SEPARATOR SLURRY	PRODUCT Ca FORMATE SOLUTION	CENTRIFUGE CAKE
GAS, LBS/HR					
CO	3.8	3.8			
CO ₂	0.2	0.2			
N ₂	7.5	7.5			
H ₂ O	—	<u>2.4</u>	—	—	—
SUBTOTAL GAS, LBS/HR	11.5	13.9			
SCFH	163	214			
LIQUID, LBS/HR					
Ca(OH) ₂	1.0		1.0	1.0	
Ca(COOH) ₂	50.0		50.0	49.3	0.7
H ₂ O	<u>481.6</u>	—	<u>479.2</u>	<u>472.4</u>	<u>6.8</u>
SUBTOTAL LIQUID, LBS/HR	532.6		530.2	522.7	7.5
SOLIDS, LBS/HR					
Ca(OH) ₂	4.4		4.4		4.4
CaCO ₃	<u>3.1</u>		<u>3.1</u>		<u>3.1</u>
SUBTOTAL SOLIDS, LBS/HR	7.5		7.5		7.5
TOTAL STREAM, LBS/HR	551.6	13.9	537.7	522.7	15.0
GPM			~ 1.0	~ 1.0	

TABLE 3-2. CALCIUM FORMATE POC UNIT MAJOR EQUIPMENT

<u>ITEM NO.</u>	<u>NAME</u>
REACTOR FEED SYSTEM	
E-501	Lime Slurry Heater
E-503	Feed Gas Heater
E-504	Syltherm Heater
M-104	Lime Slurry Tank Mixer (Existing)
P-104	Lime Slurry Circulating Pump (Existing)
P-501	Lime Slurry High Pressure Pump
P-503	Feed Gas Compressor
P-504	Syltherm Circulating Pump
T-104	Lime Slurry Mix Tank (Existing)
T-504	Syltherm Inventory Tank
REACTOR/PRESSURE LETDOWN/SOLIDS SEPARATION SYSTEM	
C-201	Centrifuge (Existing)
D-501	Calcium Formate Product Solution Drums
D-502	Centrifuge Cake Drums
E-502	Reactor Effluent Cooler
M-1021	Centrifuge Feed Tank Mixer (Existing)
M-1022	Centrifuge Feed Tank Mixer (Existing)
M-1023	Centrifuge Feed Tank Mixer (Existing)
M-2011	Centrate Tank Mixer
P-102	Product Circulation/Centrifuge Feed Pump (Existing)
P-2011	Centrate/Product Pump (Existing)
P-502	Product Transfer Pump
PCV-502	Pressure Letdown Valves
R-501AB	Jacketed Pipe Reactors
T-102	Centrifuge Feed Tank (Existing)
T-2011	Centrate Tank (Existing)
T-502	Vapor/Liquid Separator (Existing)
---	Flare

to elevate the slurry to reaction pressure, a heat exchanger to preheat the slurry to reaction temperature, and a closed loop, heat transfer oil circulation and heating system.

A 350 gallon, stainless steel, cone-bottom holding tank (see Figure 3-4) is used to store a quantity of lime slurry sufficient to supply several tests. The lime slurry is prepared, batch-wise, by filling the tank with deionized water and adding enough hydrated powdered lime solids to create a slurry of predetermined solids consist (7 wt% max). Solids are maintained in suspension by stirring with a tank mixer and by recirculating the tank contents with a centrifugal pump in a pump-around-loop. The circulation rate is 6 GPM at 25 psig discharge pressure. Prior to the start of operations the slurry in the tank is heated to approximately 150°F by live steam injection through a control valve and is maintained at this temperature throughout the test run.

During operations approximately 1 GPM of lime slurry is diverted from the pump around loop to the suction head of a high pressure diaphragm pump (Figure 3-5). The plunger diameter of the pump head is 1½ inches and the maximum stroke length is 3 inches. Discharge capacity is set by manually adjusting the stroke length with a micrometer. The diaphragm is made of teflon, while the ball valves and ball seats are constructed of ceramic and carbide, respectively, due to the abrasiveness of the slurry. The maximum discharge pressure is 1500 psig. A pulsation dampener (shown in the center of Figure 3-5) is installed in the discharge line from the pump to eliminate the output surges inherent in a diaphragm pump and thereby provide a relatively steady pressure and discharge flow of the lime slurry. The pulsation dampener is a pressurized vessel containing a flexible, viton diaphragm (rated for 3000 psig) which separates pressurized gas in the upper chamber from process liquid in the lower chamber. Pump output surges enter this device and are instantaneously absorbed by the gas due to its inherent compressibility.

The pressurized lime slurry then enters a coiled countercurrent heat exchanger (shown on the far right of Figure 3-6) with $\sim 18 \text{ ft}^2$ of heat transfer surface to preheat the slurry to reaction temperature. A coiled heat exchanger was selected for this service because at the scale of this POC unit no other types of heat exchangers were available with a pressure

Figure 3-4. Top of Lime Slurry Feed Preparation Tank

Figure 3-5. High Pressure Lime Slurry Diaphragm Pump (Right) with Pulsation Dampener on Discharge (Center of Photo)

Figure 3-6. Lime Slurry Coiled Heat Exchanger (at Right)

rating of 1500 psig on the process side. The heating medium used is hot oil (Syltherm 800, *Dow Corning*). Using steam to heat the lime slurry was ruled out as it was thought that a steam heated-lime slurry heat exchanger would tend to scale quickly in this service. With the steam side of an exchanger at a constant temperature (dictated by the final temperature to which the lime slurry is to be heated), a large temperature difference between the fluids would have existed at the lime slurry feed end (cold end) of the exchanger. Hydrated lime has a reverse solubility (decreasing solubility with increasing temperature) in water. Thus, the steam heated exchanger tubes, being much hotter than the bulk slurry temperature, would have offered a likely site for scale deposition and the subsequent loss of the ability to heat lime slurry to reactor temperature. A countercurrent oil-lime slurry heat exchanger was designed to give a relatively small and constant temperature difference between the oil and lime slurry. In this instance the heat exchanger tube wall would be only slightly hotter than the bulk lime slurry temperature at any point along the tube. Any lime precipitating from the solution (as the slurry temperature is increased in transit through the exchanger) would more likely form in the bulk fluid (already seeded with suspended solids) than on the tube walls.

The heat transfer loop (Figure 3-2) which utilizes Syltherm 800 (heat transfer fluid/oil) consists of an expansion/inventory tank, a steam-oil heat exchanger, the oil-lime slurry heat exchanger, and an oil circulation pump. The expansion tank is a 20 gallon stainless steel, vertical tank rated for 25 psig and 425°F. The Syltherm inventory is approximately 8 gallons and the tank is blanketed with N₂ gas at a slightly positive pressure to eliminate oxygen, water vapor and other airborne contaminants from entering the system and altering the properties of Syltherm. Syltherm circulation is effected by a centrifugal pump with a discharge pressure and capacity of 25 psig and 4 GPM, respectively. This pump has a carbon versus silicon carbide/teflon wedge type mechanical seal. The material is compatible with the 260°F operating temperature and the 425°F maximum temperature. The wedge construction of the secondary sealing element serves to eliminate leakage of hot Syltherm. Syltherm is pumped to a shell and tube heat exchanger where it is heated by steam to ~360°F. The hot Syltherm then enters the oil-slurry heat exchanger where it heats the lime slurry feed to approximately reaction temperature. The cooled Syltherm is then returned to the expansion tank.

3.2.2 Feed Gas Preparation (Figure 3-2)

The feed gas mixture is prepared by combining metered (through individual sonic orifice plates) amounts of bottled CO, CO₂, and N₂ gases (Figure 3-7) in a manifold at 100 psig. The relative amounts of each gas were chosen so as to give gas mixtures simulating potential commercial sources of carbon monoxide, for example, the conditioned gas from a partial oxidation unit. The gas mixture is compressed to the desired reaction pressure in a two-stage air driven gas compressor (Figure 3-8). The pressurized feed gas then enters a double-pipe exchanger where it is heated with steam to approximately reaction temperature prior to injection into the reactor.

3.2.3 Calcium Formate Production Reactor (Figure 3-3)

The pressurized, preheated lime slurry and carbon monoxide containing gas are fed into the first in a series of two cocurrent flow, vertically configured pipe reactors. Figures 3-9 and 3-10 show the insulated tops and bottoms, respectively, of the two reactors. The gas stream is fed into the bottom of the first reactor through a gas dispersion nozzle (Figure 3-11). The slurry is also fed into the bottom of the reactor but through an open tube located in such a manner as to cause the slurry to mix well with the dispersing gas. The POC reactors were sized (diameter and length) to duplicate the pilot plant reactors operated by the Electro Metallurgical Company in 1954. That pilot unit attempted to maintain intimate phase contact within the reactor by the frequent redistribution of the flowing reactor contents. This was to have been accomplished by the insertion of redistribution trays spaced at 18-inch intervals over the entire length of the reactors. Each of the trays contained a downward facing nozzle through which the reactants were forced to flow. The elevated flow velocity through the nozzle was thought to be sufficient to create the turbulence necessary to reestablish intimate contact between the gas, liquid and solid phases. TRW decided that these types of internals would be both prohibitively expensive and extremely difficult to install in both POC size and full scale commercial reactors. For this reason other methods of maintaining intimate phase contact within the reactors were investigated.

Figure 3-7. Cylinders of Bottled CO, CO₂ and N₂ Gases

Figure 3-8. Two-Stage Gas Compressor

Figure 3-9. View of the Tops of the Pressurized Calcium Formate Reactors (With Insulation)

Figure 3-10. View of the Bottoms of the Pressurized Calcium Formate Reactors (With Insulation) and Steam Traps

Figure 3-11. Gas Dispersion Nozzle

Prior to the completion of the POC design, a cold flow atmospheric pressure reactor test unit (Figure 3-12) was assembled and used to qualitatively assess the effectiveness of various internals for maintaining good interphase contact in a three-phase cocurrent flow pipe reactor. The cold flow pipe reactors were the same diameter as the POC reactors but shorter in length. The unit consisted of two 2-inch diameter vertical clear PVC pipes, each 5 feet long, connected in series by 3/4-inch tubing. Gas was metered into the bottom of the first pipe through a gas dispersion nozzle. Liquid (first water and then a 10% suspension of hydrated lime in water) was also introduced into the bottom of this pipe through an open tube. The outlet from this tube was located in close proximity to the gas exiting the dispersion nozzle in order to promote good initial contact between the phases. The gas/liquid streams then flowed together in a cocurrent manner through the system and upon exiting the second pipe were separated in a large "tee". The liquid was either collected in a 55-gallon drum or recycled to a feed preparation tank when processing aqueous lime suspension.

Three types of internals were tested in this device: 1) the tray type of mixer piloted by the Electro Metallurgical Company in 1954, 2) a static mixer, and 3) 5/8-inch plastic column packing. The static mixer is shown in the clear PVC pipe reactor on the left in Figure 3-12 and the column packing is shown in the clear PVC pipe reactor on the right. During the flow tests, qualitative observations were made on the ability of the contacting devices to reduce bubble size as the gas/liquid streams passed across them. It was observed that both the static mixer and the column packing were as effective as the internal tray nozzle arrangement in promoting bubble break up. No evidence of plugging due to solids deposition was apparent using either in-line mixers or packing (an open packing was used because of the presence of solids in the system). The positive results from these tests and the mechanical and structural problems that would be inherent in designing a reactor to support a nozzle tray arrangement or a static mixer led to the selection of 5/8-inch open packing rings as the contacting device of choice in the actual POC calcium formate reactor.

The two POC pipe reactors are each 20 feet in length and both have an external steam jacket. Both reactor and steam jacket are 316 stainless steel. The internal reactor pipe is 2½-inch schedule 160 pipe and is rated for 2000 psig and 425°F. The external steam jacket

Figure 3-12. Cold Flow Atmospheric Pressure Reactor Test Unit With In-Line Static Mixer in Clear PCV Pipe on the Left and Column Packing in Clear PVC Pipe on the Right

is 5" schedule 40 pipe rated for 250 psig saturated steam. The bottoms of the two pipe reactors with steam jackets (but before insulation was installed) are shown in Figure 3-13. The man in the figure is holding the gas dispersion nozzle in one hand and the packing support in the other. The reactors are connected in series and provision is made to bypass the second reactor if desired.

3.2.4 Effluent Pressure Reduction (Figure 3-3)

The three-phase fluid leaving the reactor (still under pressure) next enters a water cooled heat exchanger (shown at the top of Figure 3-14) where the effluent temperature is reduced to approximately 100°F. The process side of the cooler consists of copper tubes arranged in a helical coil and is rated at 1500 psig.

The cooled effluent stream is then brought to atmospheric pressure in the pressure reduction system. This system consists of two high pressure control valves in parallel. Only one valve is in service at any given time; the second valve is on "standby" and is brought on-line only when needed. The valves are rated for 2500 psig at 100°F. These valves are 1/2-inch split body, angle valves (Figures 3-14 and 3-15). The valve body is made of 316 stainless steel. Two types of valve trim were tested during operations: stellite and tungsten carbide. Stellite is an alloy of cobalt, chromium and tungsten. Both materials were selected for their high wear/abrasion resistance. Tungsten carbide is a specialty material and is harder and more expensive than stellite. Both of these materials were evaluated with the aim of determining the feasibility of using the more inexpensive stellite material in this service. During the course of the POC tests, the tungsten carbide valve trim demonstrated considerably greater resistance to wear than did the stellite trim.

3.2.5 Effluent Phase Separation (Figure 3-3)

The "flashed" reactor effluent from the pressure reduction system is sent to a vapor/liquid separator where unreacted and non-condensable gases are disengaged from the aqueous product slurry. The separator itself is a 60 gallon, 316 stainless steel, vertical tank

Figure 3-13. Man Holding a Gas Dispersion Nozzle in One Hand and Packing Support in the Other (Bottoms of Pressurized Calcium Formate Reactors With Steam Jackets but Without Insulation are in Background)

Figure 3-14. Helical Coil Water-Cooled Heat Exchanger on Calcium Formate Reactor Effluent (Top Left) and High Pressure Control Letdown Valves (Bottom)

Figure 3-15. High Pressure Control Letdown Valves on Calcium Formate Reactor Effluent

with hemispherical heads (Figure 3-16). The tank is rated to 2000 psig and the nominal liquid volume during operations is 20 gallons.

The gas stream from the separator is routed to a flare for incineration of any unreacted carbon monoxide. Figure 3-17 shows the flare during installation. The flare is over ten feet in length and propane is used as an assist gas to sustain the flame. A flame arrestor at the flare inlet prevents flashback into the reactor system.

Product slurry is pumped from the vapor/liquid separator to a 280 gallon horizontal storage tank (Figure 3-18). In subsequent off-line operations, when the storage tank is full, this slurry is pumped to a centrifuge (Figure 3-19) where the residual solids (unreacted lime solids and calcium carbonate byproduct) are separated from the product calcium formate solution. The waste cake is stored in drums for disposal. The product calcium formate solution is collected and stored in lined drums.

3.2.6 Data Acquisition and Control System

The operation of the Calcium Formate POC Test Unit resulted in the generation of an extensive database. Included in this database were measurements of operational parameters such as liquid flow (GPM), gas flows (SCFM), tank levels (% full), feed gas and process pressures (psig), temperatures (°F), and CO content in the vent gas stream. This voluminous information was easily managed by a data acquisition and control system which collected (once every 30 seconds) and stored (once every 5 minutes) process measurements in real time and utilized a portion of it for feedback control.

The data acquisition and control software was installed on a PC-based system that utilized a 386 microprocessor and was interfaced with a 100 channel hardware interface which received and digitized analog process signals from various locations in the POC test unit. The software provided for manual operation (open circuit operation) of feedback control loops in the event the loops became difficult to tune. The system provided an

Figure 3-16. Vapor/Liquid Separator on Calcium Formate Reactor Effluent

Figure 3-17. Flare During Installation

Figure 3-18. Horizontal Calcium Formate Product Slurry Storage Tank

Figure 3-19. Calcium Formate Product Centrifuge

updated real time display of plant operating parameters every 30 seconds and was configured to monitor and alert an operator when parameters exceeded specified operational limits.

Data reduction was performed off-line after each test. The database, stored in ASCII format, was imported into a *Quattro Pro* spreadsheet file for ease of analysis and data correlation. These analyses were used to assess plant performance and as an aid in the evaluation of the suitability of the selected equipment, control strategies, and operating philosophies for this process.

3.3 SUMMARY OF DATA

Approximately 100 hours of run time was accumulated on the calcium formate POC test unit on a single-shift basis between October 1992 and May 1993. The unit was operated in a shakedown mode for 45 hours between October and December. The operations mode comprised the remainder of the testing. Two or three days of tests were conducted each week. The remaining days of downtime were used for plant maintenance and refurbishment, off-line data analysis, and future test planning. On a test day, a typical shift involved 1½ hours of preparation (preheating, feed preparation, software configuration, etc.), followed by 4 to 5 hours of testing. The test day concluded with approximately 1½ hours to secure the plant (cleanup, etc.). Each day of testing was designated as either a shakedown "run" or an operations "run". There was a total of fourteen shakedown runs and seventeen operations runs. The shakedown phase of the testing was judged as being complete when most of the POC unit's initial equipment and instrument problems (see Section 3.5) were resolved and after the plant operating procedures had been modified to their final form. Each run was subdivided into smaller units of time (A, B, C, D) based upon operational changes called for in the test matrix.

The following sections contain a compilation of the more critical test data including a test matrix summary, a run condition summary, reactor performance results (CO and CO₂ conversion), a description of the calcium formate product solution, and a discussion of the environmental suitability of the waste products.

3.3.1 Test Matrix Summary

Reactor performance as measured by CO conversion was believed to be dependent on six independent variables:

- Reactor temperature
- Reactor pressure
- Feed gas CO content
- Reactor residence time
- Feed CO/lime stoichiometry
- Feed slurry lime content (wt% solids)

The ranges investigated in the POC unit for each of these variables is given in Table 3-3. Knowledge of the effects of these variables is crucial for the optimal design of a large scale calcium formate production unit. Two other factors influencing reactor performance were also investigated: 1) the effect of CO₂ in the reactor feed gas, and 2) the effectiveness of reactor packing (versus no packing) for promoting and maintaining reactant contact.

Table 3-3. Calcium Formate POC Operations Test Matrix

TEST VARIABLE	RANGE INVESTIGATED
Feed Gas Composition: CO/CO ₂ /N ₂	Bracket Potential Commercial Sources of CO Gas (40-100% CO, 1-3% CO ₂)
Reactor Pressure	800 PSI - 1350 PSI
Reactor Temperature	280°F - 400°F
Reactor Residence Time	5 Minutes - 30 Minutes
Reactant (CO/Lime) Stoichiometry	0.75 - 1.08
Lime Slurry Solids Loading	5.6 - 7.1 wt%
Reactor Internals	Packing vs. Empty

3.3.2 Run Condition Summary

A summary of the operating conditions for each of the 31 tests is presented in Table 3-4 with the CO conversion results. A total of 38 subtests (OPS18 thru OPS28) were conducted in an empty reactor, the remaining 61 subtests (SD01 thru SD14, OPS15 thru OPS17, and OPS29 thru OPS31) used 5/8-inch open packing rings for reactor internals. The following tests were conducted in a single reactor (the second reactor was bypassed): SD06, OPS16, OPS17, OPS18, and OPS31C,D,E; the remaining tests were conducted with both reactors in series. The lime slurry heater was bypassed for test OPS30 and OPS31, so a portion of the reactor was used to pre-heat the slurry (this was also the case in test SD14, due to failure of the Syltherm heater).

3.3.3 Carbon Monoxide Conversion

The effect of various operating conditions on carbon monoxide conversion was determined. For the same reactor temperature, CO conversion is greater at higher pressure. For a given temperature, CO conversion increases with increased CO concentration in the feed gas. CO conversion increases approximately linearly with temperature, all other factors being equal. At the same reactor pressure, CO conversion increases with reactor residence time. Carbon monoxide conversions up to 100% were achieved at various combinations of operating conditions. Individual test results are tabulated in Table 3-4 and discussed in Section 3.4.

3.3.4 Carbon Dioxide Conversion

Carbon dioxide may be present in the feed gas stream (at levels ranging from 1% to 3% v/v) when CO is generated by coal gasification or partial oxidation. CO₂ was added to the reactor feed gas (at levels ranging from 0% to 3% v/v) in order to assess its effect on CO conversion. Test results show that there is little or no change in CO conversion when CO₂ is present in the feed gas as long as lime is not the limiting reagent. CO₂ conversion was ~100% at all conditions tested. It was concluded that CO₂ reacts much more readily with lime than does CO. Individual test results are tabulated in Table 3-4 and discussed in Section 3.4.

TABLE 3.4 SUMMARY OF OPERATING CONDITIONS FOR CALCIUM FORMATE POC UNIT
Shakedown Run Summary

<u>RUN #</u>	<u>Res. Time (min)</u>	<u>CO Feed (scfm)</u>	<u>N2 Feed (scfm)</u>	<u>Ca(OH)₂ Feed (lb/hr)</u>	<u>Lime Slurry Feed (gpm)</u>	<u>Pressure (psia)</u>	<u>Temp. (deg F)</u>	<u>CO/Lime Stoich</u>	<u>Wt. % Lime</u>	<u>%CO</u>	<u>CO Conversion (%)</u>	<u>[Ca(COOH)₂] (%w/w)</u>
SD02A	8.8	4.10	0.00	24.0	0.84	818	NA	1.000	5.6	100.0	56*** - 68**	5.47
SD02B	6.2	5.78	0.00	33.7	1.18	1011	NA	1.004	5.6	100.0	84*** - 95**	8.06
SD03	7.4	5.51	0.00	37.7	1.00	1365	257-294	0.856	7.2	100.0	26***	2.95
SD04A	8.2	5.10	1.65	27.8	0.90	1357	342	1.074	6.0	75.6	87* - 99**	9.76
SD04B	8.2	4.76	1.54	27.8	0.90	1265	351	1.003	6.0	75.6	99* - 100**	10.92
		4.76	1.54	27.8	0.90	1160	351	1.003	6.0	75.6	75***	7.89
SD05A	9.2	4.22	1.38	24.7	0.80	965	353	1.001	6.0	75.4	64***	6.70
SD05B	9.2	4.18	1.38	24.7	0.80	1165	363	0.991	6.0	75.2	77*** - 84***	8.50
SD05C	9.2	4.20	1.38	24.7	0.80	1365	369	0.996	6.0	75.3	94*** - 100*	9.43
SD06A	4.6	4.22	1.38	24.7	0.80	968	359	1.001	6.0	75.4	36*** - 46*	3.90
SD06B	4.6	4.27	1.36	24.7	0.80	1191	366	1.012	6.0	75.8	46*** - 59*	4.90
SD06C	4.6	4.27	1.38	24.7	0.80	1315	372	1.012	6.0	75.6	50*** - 69*	5.40
SD07A	13	2.91	4.50	17.6	0.57	1015	359	0.968	6.0	39.3	60***	5.90
SD07B	13	2.96	4.47	17.6	0.57	1315	366	0.985	6.0	39.8	84***	8.35
SD07C	52	0.73	1.13	4.4	0.14	1115	NA	0.972	6.0	39.2	NA	6.50
SD07D	26	1.46	2.24	8.7	0.28	1265	345	0.983	6.0	39.5	83***	8.40
SD08A	30.7	1.24	1.83	7.4	0.24	1295	331	0.981	6.0	40.4	80***	8.06
SD08B	30.7	1.22	1.81	7.4	0.24	1115	311	0.966	6.0	40.3	66***	6.62
SD08C	30.7	1.24	1.81	7.4	0.24	915	298	0.981	6.0	40.7	52***	5.33
SD08D	30.7	1.22	1.78	7.4	0.24	715	311	0.966	6.0	40.7	52***	5.33
SD09A	30.7	1.24	1.83	7.4	0.24	1291	328	0.981	6.0	40.4	65***	6.62
SD09B	30.7	1.24	1.81	7.4	0.24	1103	319	0.981	6.0	40.7	51***	5.33
SD09C	30.7	1.25	1.81	7.4	0.24	908	315	0.989	6.0	40.8	37***	3.89
SD10	13.4	2.86	4.16	17.0	0.55	1308	395	0.985	6.0	40.7	64***	6.62
SD11A	13.4	2.85	4.16	17.0	0.55	1315	303	0.982	6.0	40.7	37*** - 40*	3.89
SD11B	13.4	2.87	4.16	17.0	0.55	1115	301	0.989	6.0	40.8	20* - 24***	2.59
SD11C	13.4	2.87	4.09	17.0	0.55	915	299	0.989	6.0	41.2	16* - 24***	2.59
SD12A	13.4	2.85	1.83	17.0	0.55	1260	404	0.982	6.0	60.9	97*,***	9.87
SD12B	13.4	2.82	1.85	17.0	0.55	1108	404	0.971	6.0	60.4	92*,***	9.37
SD12C	13.4	2.80	1.85	17.0	0.55	915	395	0.965	6.0	60.2	90*,***	8.87
SD13A	13.4	2.87	1.85	17.0	0.55	1315	304	0.989	6.0	60.8	58***	5.98
SD13B	13.4	2.87	1.85	17.0	0.55	1115	303	0.989	6.0	60.8	48***	5.01
SD13C	13.4	2.89	1.85	17.0	0.55	915	300	0.996	6.0	61.0	36***	3.90
SD14A	13.4	2.73	4.11	17.0	0.55	1315	290	0.940	6.0	39.9	29***	2.99
SD14B	13.4	2.85	4.13	17.0	0.55	1315	313	0.982	6.0	40.8	50***	5.20
SD14C	13.4	2.82	4.13	17.0	0.55	1315	337	0.971	6.0	40.6	71***	7.19
SD14D	13.4	2.89	4.22	17.0	0.55	1315	359	0.996	6.0	40.6	76***	7.83

* based on measured orifice flow and measured vent flow

** based on measured cylinder volume change and measured vent flow

*** based on measured orifice flow and product solution analysis

**** based on measured cylinder volume change and product solution analysis

TABLE 3-4. SUMMARY OF OPERATING CONDITIONS FOR CALCIUM FORMATE POC UNIT (CONTINUED)
Operations Run Summary

RUN #	Res. Time (min)	CO Feed (scfm)	N2 Feed (scfm)	CO2 Feed (scfm)	Ca(OH)2 Feed (lb/hr)	Lime Slurry Feed (gpm)	Pressure (psia)	Temp. (deg F)	(CO+CO2)/Lime Stoich	Wt. % Lime	%CO	%CO2	CO Conversion (%)	[Ca(COOH)2] (%w/w)
OPS15AA**	13.4	2.87	4.18	0	20.3	0.55	1315	278	0.828	7.1	40.7	0.0	30*	3.20
OPS15AB**	13.4	2.91	4.25	0	20.3	0.55	1315	310	0.840	7.1	40.6	0.0	42*	4.45
OPS15AC**	13.4	2.91	4.22	0	20.3	0.55	1315	334	0.840	7.1	40.8	0.0	68*	7.09
OPS15BA**	13.4	2.87	4.23	0	20.3	0.55	1315	348	0.828	7.1	40.4	0.0	84*	8.48
OPS15BB**	13.4	2.87	4.20	0	20.3	0.55	1265	375	0.828	7.1	40.6	0.0	99.3*	9.94
OPS16***	6.7	2.78	0	0	17.0	0.55	1315	370	0.958	6.0	100.0	0.0	84.2*	8.27
OPS17A***	6.7	2.69	0	0	17.0	0.55	1315	369	0.927	6.0	100.0	0.0	64.7*	6.29
OPS17B***	6.7	2.71	0	0	17.0	0.55	1165	376	0.934	6.0	100.0	0.0	82.7*	7.94
OPS17C***	6.7	2.85	0	0	17.0	0.55	965	379	0.982	6.0	100.0	0.0	75.4*	7.66
OPS17D***	6.7	2.91	0.77	0	17.0	0.55	1315	372	1.002	6.0	79.1	0.0	74.9*	7.76
OPS18A****	6.7	2.80	0	0	17.0	0.55	1365	352	0.965	6.0	100.0	0.0	17.1*	1.81
OPS18B****	6.7	2.76	0	0	17.0	0.55	1165	367	0.951	6.0	100.0	0.0	70.3*	6.98
OPS18C****	6.7	2.76	0	0	17.0	0.55	965	369	0.951	6.0	100.0	0.0	71.4*	7.07
OPS18D****	6.7	2.85	0.79	0	17.0	0.55	1365	363	0.982	6.0	78.3	0.0	69.8*	7.13
OPS19A+	13.4	2.78	0	0	19.2	0.55	1365	348	0.848	6.7	100.0	0.0	100.0*	9.87
OPS19B+	13.4	2.82	0	0	19.2	0.55	1165	368	0.860	6.7	100.0	0.0	97.5*	9.57
OPS19C+	13.4	2.85	0	0	19.2	0.55	965	362	0.869	6.7	100.0	0.0	94.0*	9.32
OPS19D+	13.4	2.85	0.70	0	19.2	0.55	1365	348	0.869	6.7	80.3	0.0	80.3*	8.06
OPS20A+	13.4	2.62	0.70	0	16	0.55	1365	332	0.959	5.6	78.9	0.0	34.7*	3.36
OPS20B+	13.4	2.85	0.70	0	16	0.55	1165	354	1.043	5.6	80.3	0.0	73.1*	7.37
OPS20C+	13.4	2.85	0.70	0	16	0.55	965	349	1.043	5.6	80.3	0.0	73.1*	7.37
OPS21A+	13.4	2.85	0.67	0.047	18.3	0.55	1365	351	0.942	6.4	79.9	1.32	74.4*	7.51
OPS21B+	13.4	2.80	0.66	0.040	18.3	0.55	1165	355	0.922	6.4	80.0	1.14	100.0*	10.84
OPS21C+	13.4	2.89	0.66	0.040	18.3	0.55	965	355	0.950	6.4	80.5	1.11	74.7*	7.65
OPS22A+	13.4	2.89	0.66	0.066	18.9	0.55	1365	351	0.936	6.6	79.9	1.83	100.0*	12.23
OPS22B+	13.4	2.89	0.66	0.066	18.9	0.55	1165	360	0.936	6.6	79.9	1.83	100.0*	12.09
OPS22C+	13.4	2.89	0.66	0.066	18.9	0.55	965	357	0.936	6.6	79.9	1.83	85.0*	8.62
OPS23A+	9.8	3.84	0.90	0.049	24.6	0.75	1215	347	0.937	6.3	80.2	1.02	73.0*	7.3
OPS24A+	9.8	3.73	0.78	0.139	30.5	0.75	1315	353	0.770	7.8	80.2	2.99	92.8*	8.91
OPS24B+	9.8	3.66	0.76	0.139	30.5	0.75	1165	354	0.756	7.8	80.3	3.05	100.0*	12.52
OPS24C+	9.8	3.61	0.75	0.139	30.5	0.75	965	350	0.747	7.8	80.2	3.09	84.3*	7.94
OPS25A+	7.4	5.29	1.21	0.065	31.7	1.00	1265	347	1.001	6.1	80.6	0.99	88.6*	8.98
OPS25B+	7.4	5.22	1.15	0.065	31.7	1.00	1165	348	0.988	6.1	81.1	1.01	81.5*	8.22
OPS25C+	7.4	5.31	1.19	0.066	31.7	1.00	965	347	1.005	6.1	80.9	1.01	63.5*	6.63
OPS26A+	7.4	4.95	1.02	0.165	28.7	1.00	1250 FE502 CO Analyzer	343	1.077	5.55	80.68	2.689	85.8*	8.19
OPS26B+	7.4	4.83	0.97	0.162	28.7	1.00	1081 FE502 CO Analyzer	349	1.052	5.55	81.01	2.717	80.9*	7.59
													70.5	
													75.8	

* based on measured orifice flow and product solution analysis

** two reactors, packed

*** single reactor, packed

**** single reactor, empty

+ two reactors, empty

TABLE 3-4. SUMMARY OF OPERATING CONDITIONS FOR CALCIUM FORMATE POC UNIT (CONTINUED)

Operations Run Summary

RUN #	Res. Time (min)	CO Feed (scfm)	N ₂ Feed (scfm)	CO ₂ Feed (scfm)	Ca(OH) ₂ Feed (lb/hr)	Lime Slurry Feed (gpm)	Pressure (psia)	Temp. (deg F)	(CO+CO ₂)/Lime Stoich	Wt.% L	%CO	%CO ₂	CO Conversion (%)	[Ca(COOH) ₂] (%w/w)
OPS26C+	7.4	5.02	0.97	0.162	28.7	1	961 FE502 CO Analyzer	347	1.090	5.6	81.6	2.6	69.8* 57.8 64.0	6.86
OPS27A+	13.4	2.91	4.04	0	18.9	0.55	1260 FE502 CO Analyzer	265	0.902	6.6	41.9	0.0	23.9* 0 NA	2.61
OPS27B+	13.4	2.91	4.25	0	18.9	0.55	1269 FE502 CO Analyzer	300	0.902	6.6	40.6	0.0	38.1* 23.0 NA	4.09
OPS27C+	13.4	2.94	4.02	0	18.9	0.55	1248 FE502 CO Analyzer	329	0.911	6.6	42.2	0.0	60.1* 34.6 NA	6.34
OPS27D+	13.4	2.94	4.02	0	18.9	0.55	1280 FE502 CO Analyzer	362	0.911	6.6	42.2	0.0	87.8* 77.4 NA	9.01
OPS27E+	13.4	2.91	4.04	0	18.9	0.55	1260 FE502 CO Analyzer	392	0.902	6.6	41.9	0.0	90.9* 85.0 NA	9.23
OPS28A+	13.4	2.8	0.68	0	17.8	0.55	1251 FE502	263	0.921	6.2	80.5	0.0	36.0* 10.1	3.72
OPS28B+	13.4	2.78	0.68	0	17.8	0.55	1261 FE502	296	0.915	6.2	80.3	0.0	58.9* 31.1	5.9
OPS28C+	13.4	2.82	0.68	0	18	0.55	1267 FE502	331	0.928	6.2	80.6	0.0	98.4* 70.0	9.62
OPS28D+	13.4	2.85	0.70	0	18	0.55	1236 FE502	372	0.938	6.2	80.3	0.0	100* 73.7	10.04
OPS28E+	13.4	2.67	0.66	0	17.8	0.55	1255 FE502	394	0.878	6.2	80.2	0.00	92.7* NA	8.65
OPS29A**	13.4	2.82	0.66	0	17.1	0.55	1259 FE502 CO Analyzer	275	0.966	6.0	81.0	0.00	34.5* 2.8 1.1	3.59
OPS29B**	13.4	2.8	0.66	0	17.1	0.55	1240 FE502 CO Analyzer	313	0.959	6.0	80.9	0.00	84.3* 35.3 64.6	8.29
OPS29C**	13.4	2.8	0.68	0	17.1	0.55	1249 FE502 CO Analyzer	343	0.959	5.97	80.46	0.00	100* 68.4 88.3	10.93
OPS29D**	13.4	2.78	0.66	0	17.1	0.55	1258 FE502 CO Analyzer	380	0.952	6.0	80.8	0.00	100* 60.0 47.8	11.25
OPS29E**	13.4	2.85	0.68	0	17.1	0.55	1260 FE502 CO Analyzer	387	0.976	6.0	80.7	0.00	100* 39.0 27.0	11.37
OPS30A**	13.4	3.23	0.72	0	20.6	0.55	1130 FE502 CO Analyzer	276	0.918	7.1	81.8	0.00	33.7* 14.4 37.5	4.02
OPS30B**	13.4	3.16	0.68	0	20.6	0.55	1111 FE502 CO Analyzer	304	0.898	7.1	82.3	0.00	50.5* 36.4 52.3	5.79
OPS30C**	13.4	3.14	0.66	0	20.6	0.55	1098 FE502 CO Analyzer	331	0.893	7.1	82.6	0.00	76.7* 75.0 81.0	8.48
OPS30D**	13.4	3.19	0.66	0	20.6	0.55	1112 FE502 CO Analyzer	379	0.907	7.1	82.9	0.00	98.7* 88.5 97.8	10.79

* based on measured orifice flow and product solution analysis

** two reactors, packed

*** single reactor, packed

**** single reactor, empty

+ two reactors, empty

TABLE 3-4. SUMMARY OF OPERATING CONDITIONS FOR CALCIUM FORMATE POC UNIT (CONTINUED)
Operations Run Summary

RUN #	Res. Time (min)	CO Feed (scfm)	N2 Feed (scfm)	CO2 Feed (scfm)	Ca(OH)2 Feed (lb/hr)	Lime Slurry Feed (gpm)	(CO+CO2)/						CO Conversion (%)	[Ca(COOH)2] (%w/w)
							Pressure (psia)	Temp. (deg F)	Lime Stoich	Wt.% L	%CO	%CO2		
OPS30E**	13.4	3.23	0.7	0	20.6	0.55	1056	402	0.918	7.1	82.2	0.0	88.3*	9.88
													83.5	
													99.2	
OPS31A**	13.4	2.87	4.07	0	17.3	0.55	1054	271	0.972	6.1	41.4	0.0	22.2*	2.38
													0	
													35.0	
OPS31B**	13.4	2.85	3.95	0	17.3	0.55	1104	295	0.965	6.1	41.9	0.0	31.0*	3.27
													4.4	
													25.1	
OPS31C++	6.7	2.87	3.98	0	17.3	0.55	1101	329	0.972	6.1	41.9	0.0	30.0*	3.19
													7.3	
													30.1	
OPS31D++	6.7	2.87	4.02	0	17.3	0.55	1096	361	0.972	6.1	41.7	0.0	42.0*	4.41
													26.3	
													46.6	
OPS31E++	6.7	2.87	3.98	0	17.3	0.55	1047	383	0.972	6.1	41.9	0.0	52.9*	5.49
													20.9	
													54.3	

* based on measured orifice flow and product solution analysis

** two reactors, packed

+ two reactors, empty

++ single reactor, packed

3.3.5 Calcium Formate Product Solution

The calcium formate product solution produced in the POC unit ranged from a concentration of 2.6 wt% calcium formate (during runs SD11B&C at ~20% CO conversion) to 12.5 wt% calcium formate (during run OPS24B at ~100% CO conversion). The solubility of calcium formate in water at 60°F is ~14 wt%. About 1725 gallons of calcium formate solution were produced. Individual test results are tabulated in Table 3-4 and discussed in Section 3.4.

3.3.6 Environmental Suitability of Waste Products

The waste products from the POC unit are: 1) a gas consisting of unconverted CO and inert N₂, and 2) solids consisting of unconverted lime and byproduct calcium carbonate (limestone) separated from the calcium formate product solution. The gas is flared in the POC (in a commercial unit this gas would undoubtedly be processed in a boiler for recovery of its heat content). The solids stream is disposed of as a nonhazardous waste. In a commercial plant the solids would undoubtedly be washed with water to recover the calcium formate in the solids moisture. The washed solids (lime, limestone) would then be disposed of as a nonhazardous waste.

3.4 DISCUSSION OF INDIVIDUAL TEST RESULTS

3.4.1 Lime Feed Analysis

A typical analysis of the lime feed to the POC unit is shown in Table 3-5. The hydrated lime used contained 96 to 97 wt% Ca(OH)₂.

3.4.2 Carbon Monoxide Conversion

Reactor performance was measured by carbon monoxide conversion (utilization) in the reactor. Carbon monoxide conversion is defined as the amount of CO consumed by reaction with lime divided by the amount of CO fed to the reactor. High CO conversion corresponds to high reactor efficiency. For the shakedown runs, CO conversion was calculated by four methods: 1) using the measured flow of feed CO (by sonic orifice) and the measured vent

TABLE 3-5. TYPICAL LIME FEED ANALYSIS

MISSISSIPPI LIME COMPANY
HYDRATED LIME
CODE MR200

MEETS AWWA AND WATER CHEMICALS CODEX SPECIFICATIONS

COMPOUND	CHEMICAL ANALYSIS WT %
Ca(OH) ₂	96.0 to 97.2
CaO - Equivalent	72.6 to 73.6
CaO Total	73.6 to 74.3
CaCO ₃	0.65 to 1.75
CaSO ₄	0.05 to 0.10
S - Equivalent	0.012 to 0.024
SiO ₂	0.38 to 0.55
Al ₂ O ₃	0.20 to 0.30
Fe ₂ O ₃	0.07 to 0.10
MgO	0.40 to 0.55
Free H ₂ O	0.04 to 1.0
P ₂ O ₅	0.008 to 0.012
MnO	0.0015 to 0.0025

	PHYSICAL ANALYSIS
Minus 100 Mesh	100%
Minus 200 Mesh	98.5%
Minus 325 Mesh	92.0%

DENSITY: 20 TO 32 POUNDS PER CUBIC FOOT
(DEPENDING UPON DEGREE OF COMPACTION)

flow (by an integral orifice flowmeter) of gas exiting the reactor, 2) by the measured CO gas supply cylinder volume change and measured vent flow, 3) by the measured CO orifice feed flow and product solution analysis [$\text{Ca}(\text{COOH})_2$ content], and 4) by the CO supply cylinder volume change and the product solution analysis [$\text{Ca}(\text{COOH})_2$ content]. Methods 1 and 2 assume that there is no nitrogen loss via leaks upstream of the vent flow meter. The four methods were used as independent cross-checks of the CO material balance to ensure that reliable performance assessments were made.

Examination of the data for runs SD02 and SD04 shows that there is a large variation in the discrepancies between CO conversions calculated by methods 2 and 4 and conversions calculated by methods 1 and 3. This is attributed to the imprecise measurement of CO supply cylinder pressures, which are only accurate to ± 50 psig, and to the imprecise records of the start and stop times of each test, thus leading to large errors in the calculated gas volume delivery rates to the reactor. For this reason the conversion calculation methods which used cylinder volume changes as a measure of CO delivery to the system were discontinued (methods 2 and 4).

The variation in the CO conversions calculated by methods 1 and 3, however, is approximately constant. Method 1 was either consistently high (SD06A,B,C) or consistently low (SD11B,C) owing to a systematic calibration error in the vent gas flowmeter. Method 3 was considered the most accurate means of determining CO conversion. Here, CO consumption was calculated based on analysis of the calcium formate content of the product solution and the known feed lime slurry flowrate and composition. This calculation is based on the fact that calcium formate is produced in the reactor by the following reaction:

The specific gravity of the product solution was measured and the calcium formate content was obtained by comparison with a curve correlating specific gravity with calcium formate content in solution.

In order to improve the accuracy of CO conversion calculated by measured feed gas flow and vent gas flow, an on-line, continuous CO Non-Dispersive Infrared Analyzer (NDIR) was installed in the gas vent line from the vapor/liquid separator. This instrument provided for runs OPS26 and OPS27 an accurate real-time measurement of the CO composition of the vent gas. Problems were encountered with this instrument after OPS27 (discussed in Section 3.5.3.1) which may have affected the accuracy of its readings for the remainder of the test runs.

Examination of the conversion data (OPS26 thru OPS31) in the operations run summary tables (Table 3-4) shows that results of three independent measures of carbon monoxide conversion are in most instances in close agreement with each other. This means that reactor performance can be reliably assessed.

Carbon monoxide conversions approaching 100% were achieved at various combinations of operating conditions. Carbon monoxide conversion data was plotted as a function of a number of the operating parameters listed in Table 3-3 in order to assess their effect on reactor performance. These plots are presented in Figures 3-20 through 3-22.

3.4.2.1 *Effect of Reactor Pressure*

Figure 3-20 shows the effect of reactor temperature on CO conversion at 1100 and 1250 psia reactor pressures. The reactor temperature is measured by a thermocouple located in the pipe connecting the two reactors. These tests were conducted with a fixed feed gas composition of 80% CO and 20% N₂, a residence time of ~13 minutes, and the CO/lime stoichiometry fixed at ≈ 1.0 . It is observed that for the same reactor temperature, CO conversion is greater at the high pressure. This observation is also noted when comparing test OPS29 with test OPS30.

3.4.2.2 *Effect of Reactor Feed Gas Composition*

Figure 3-21 shows how CO conversion is affected by reactor temperature at CO feed gas compositions of 40%, 60%, and 80% (the balance being nitrogen). In these tests the

Figure 3-20. Effect of Temperature on CO Conversion at Varying Reactor Pressures

Figure 3-21. Effect of Temperature on CO Conversion at Varying Percent CO in Feed Gas

Figure 3-22. Effect of Pressure on CO Conversion at Varying Reactor Residence Times

reactor pressure was fixed at 1250 psia, the residence time was ~ 13 minutes, and the CO/lime stoichiometry was fixed at ≈ 1.0 . This figure shows that for a given temperature, CO conversion increases with increased CO concentration in the feed gas.

3.4.2.3 *Effect of Reactor Temperature*

The other trend that is evident in Figures 3-20 and 3-21 is that CO conversion increases approximately linearly with temperature, all other factors being equal. For example, for an 80% CO gas at 1250 psig and 13.4 minutes residence time at $265 \pm 5^\circ\text{F}$, CO conversion is approximately 30%, while at $350 \pm 5^\circ\text{F}$ CO conversion is 100%. Thus, reactor performance is very sensitive to temperature.

3.4.2.4 *Effect of Reactor Residence Time*

Figure 3-22 shows the effect of reactor pressure on CO conversion at three different reactor residence times: 4.6, 9.2 and 13.4 minutes. In these tests the feed gas composition was fixed at 75% CO, 25% N_2 , the reactor temperature was 365°F , and the CO/lime stoichiometry was fixed at ≈ 1.0 . The residence time is based upon the lime slurry flow into the reactor and is defined as reactor volume divided by the lime slurry feed volumetric flow rate through the reactor. It is evident from this figure that at the same reactor pressure, increased CO conversion is obtained at the longer residence time.

3.4.2.5 *Effect of Reactor Stoichiometry*

Practically all the tests were conducted with slightly in excess of stoichiometric (for 100% CO conversion) lime. In fact no runs were performed in which lime was the limiting reactant. Within the range studied, TRW was not able to detect any trends that would allow correlation of CO conversion with CO/lime stoichiometry.

3.4.2.6 *Effect of Reactor Lime Slurry Feed Concentration*

Lime slurry feed solids loading ranged from 5.6 to 7.1 wt% lime solids. Within the

range studied, TRW was not able to detect any trends that would allow correlation of CO conversion with lime slurry feed solids concentration.

3.4.2.7 *Effect of Lime Preheating*

In tests SD14, OPS30, and OPS31, the lime slurry feed was not preheated prior to entering the reactor. It was expected that CO conversion would decrease because a portion of the reactor would be used to preheat the lime slurry, thus decreasing the effective reaction residence time available at reaction temperature. Comparison of tests OPS29 and OPS30, and tests SD14 and OPS15A, however, show no change in CO conversion. It is thus surmised that the steam jacketed reaction vessel serves as an efficient heat exchanger.

3.4.2.8 *Effect of Reactor Internals*

Several test runs were made with the objective of determining the effect of reactor internals in promoting reaction efficiency, i.e. improving reactor performance over that in an empty reactor. In Table 3-4, OPS27, an empty reactor test at 13.4 minutes residence time, 40% CO in the feed gas, 1250 ± 50 psia reaction pressure, 0.9 CO/lime stoichiometry, and reaction temperatures ranging between 265°F and 400°F, may be compared with OPS15 and SD14, packed reactor tests at approximately the same test conditions. Two other tests which may be compared are OPS28 and OPS29, which were conducted at the same conditions stated above, except that there was 80% CO in the feed gas. Test OPS28 was conducted in an empty reactor and test OPS29 was conducted in a packed reactor. It is clear from these comparisons that no measurable improvement in reactor performance was obtained by filling the reactor with packing rings. Stated another way, for the same conditions of residence time, reactor pressure, reactor temperature, feed gas content, and CO/lime stoichiometry, CO conversions obtained in an empty reactor are, as accurately as can be determined, the same as those obtained in a packed reactor. This is an indication that adequate mixing of the gas and slurry streams may be attributed primarily to the specially designed gas dispersion nozzle used to introduce the gas into the first reactor. This hypothesis is unconfirmed because a reactor test was not conducted without the nozzle in place.

3.4.3 Carbon Dioxide Conversion

Carbon dioxide may be present in the feed gas stream (at levels ranging from 1% to 3% v/v) when CO is generated by coal gasification or partial oxidation. In OPS21 through OPS26, CO₂ was added to the reactor feed gas in order to assess its effect on CO conversion. Comparison of test OPS21A (1% CO₂), OPS22A (2% CO₂), and OPS24A (3% CO₂), with tests SD05C, OPS19D and OPS29C (without CO₂) show that there is little or no change in CO conversion when CO₂ is present in the feed gas as long as lime is not the limiting reagent. When CO₂ is present in the gas, calcium carbonate is produced by the following reaction:

CO₂ conversion was ~100% at all conditions tested. Thus it was concluded that CO₂ reacts much more readily with lime than does CO.

3.4.4 Calcium Formate Product Solution Produced

The calcium formate product solution produced in the POC unit ranged from a concentration of 2.6 wt% calcium formate (during runs SD11B&C at ~20% CO conversion) to 12.5 wt% calcium formate (during run OPS24B at ~100% CO conversion). The solubility of calcium formate in water at 60°F is ~14 wt%. A calibration curve of weight percent calcium formate versus specific gravity (Figure 3-23) was used to determine the concentration of the calcium formate solution produced for each run. The concentration of calcium formate was also determined analytically on a number of occasions and was found to be in good agreement with the concentration determined by specific gravity. About 1725 gallons of calcium formate were produced.

3.5 EQUIPMENT EVALUATION/MODIFICATION

Most of the plant equipment and instrumentation performed as expected in their initial configuration. Minor equipment and instrument problems included leaky seals and gaskets in pumps and steam heat exchangers (E-504, Syltherm heater), level detector failures (LT502,

Figure 3-23. Calibration Curve of Weight Percent Calcium Formate Versus Specific Gravity

vapor/liquid separator level detector), and premature rupture disc failures due to incorrect location and installation. These minor problems were diagnosed early during shakedown test operations and were immediately corrected. More serious instrumentation problems were encountered in the Non-Dispersive Infrared Analyzer (NDIR), the reactor pressure transducer, and in the vent flowmeter (FE502). The major mechanical problems experienced during test operations were with the pressure letdown valves and the lime slurry heater.

3.5.1 Calcium Formate Reactor Feed System

3.5.1.1 *Lime Slurry Heat Exchanger*

During test operations in March 1993, it was observed that the temperature of the pre-heated lime slurry feed to the reactor had dropped from approximately 290°F in October 1992 (when testing commenced) to 200°F. This temperature drop was initially surmised to be the result of fouling in the process tubes of the lime slurry heater (E-501). Figure 3-24 shows the performance history of this heater during shakedown and test operations through March 1993. Heater performance is measured by the heat transfer coefficient of this unit, calculated using the process-side heat duty. At the start of testing the coefficient was 35 Btu/hr-ft²-°F. After approximately 25 hours of testing at slurry flowrates of 0.80 to 1.00 GPM and 6% solids, the heat transfer coefficient settled to an average value of 27 Btu/hr-ft²-°F. During this time period (about 35 hours) slurry with 6% lime solids was pumped at 0.55 GPM. After about 50 hours of testing, the heat exchanger performance began to drop, and by the end of March (after a total of 71 hours of operation) the heat transfer coefficient fell to 5 Btu/hr-ft²-°F. The last 18 hours of testing in March were at slurry loadings of 6% to 7% lime and flowrates between 0.55 and 1.00 GPM.

Several attempts were made to descale the heat exchanger process tubes. The unit was flushed repeatedly with high pressure water and also with weak acetic acid solution. It was observed that the flow through the unit decreased after each flush. After a few more attempts to flush the unit, the tubes became plugged. The process tube sheet (18 BWG, 1/4" copper) is a spirally coiled bundle of tubes stacked one on top of the other and contained in a circular shell. Based on our inability to chemically clean the tubes, it is very likely that the

Figure 3-24. Performance History of Lime Slurry Heater as Measured by the Heat Transfer Coefficient (10/14/92 - 3/30/93)

performance degradation noted was the result of partial plugging of the process tubes rather than scaling of the tubes. That is, some of the coils became plugged and thus reduced the effective heat transfer area. The attempts to descale the tubes probably dislodged large particles of lime solids held up in the manifolds located at the tube ends and forced them into the free coils where they were trapped and eventually plugged up the entire unit. Because the cost of replacing the coil was significant, it was decided to bypass the heater for the remaining tests.

In a larger scale production unit, plugging may not be a problem due to the larger process tubes required in the heat exchanger. If plugging is a concern and the cost of replacement tubes is prohibitive, it is recommended that an easily serviceable plate heat exchanger be specified for this service instead.

3.5.1.2 Lime Slurry High Pressure Pump

The lime slurry high pressure (1500 psig) diaphragm pump (P-501) performed as expected. This type of pump has a long history of commercially proven operation for pumping lime slurries.

3.5.2 Calcium Formate Reactor and Pressure Letdown System

3.5.2.1 Reactor Temperature Control

In test SD14, OPS30, and OPS31, the lime slurry feed was not preheated prior to entering the reactor. It was expected that CO conversion would decrease because a portion of the reactor would be used to preheat the lime slurry, thus decreasing the effective reaction residence time available at reaction temperature. Comparison of tests OPS29 and OPS30, and tests SD14 and OPS15A, however, show no change in CO conversion. It is thus surmised that the steam jacketed reaction vessel serves as an efficient heat exchanger.

A plot of temperature versus time for run OPS30A,B,C,D,E for both reactors is presented in Figure 3-25. Table 3-4 indicates that the effluent temperature from the first

Figure 3-25. Reactor Temperature Versus Elapsed Time for Run OPS30

reactor was 276°F during OPS30A, 304°F during OPS30B, 331°F during OPS30C, 379°F during OPS30D, and 402°F during OPS30E.

3.5.2.2 *Reactor Pressure Control*

Reactor Pressure Transducer

The reactor pressure transducer malfunctioned on several occasions and was returned to the manufacturer for repair. This instrument is integral to the feedback control loop for pressure control. In the absence of this instrument pressure control was performed manually by an operator. In this mode, reactor pressure is maintained to within ± 50 psi. The instrument failure was the result of a manufacturer's defect.

A plot of pressure versus elapsed time for run OPS27 is shown in Figure 3-26. During this run pressure control was performed manually. As can be seen from this plot, the reactor pressure was maintained to within ± 50 psi. However, a plot of pressure versus elapsed time for run OPS31 (Figure 3-27) during which the reactors were operated with automatic feedback control (pressure transducer was working) shows no apparent improvement in pressure control (the reactor pressure was also maintained to within only ± 50 psi). Automatic pressure control could probably be improved by changes in the control loop tuning constants.

Pressure Letdown Valves

Pressure control in the reactor was achieved by maintaining back pressure on the system with a high pressure control valve. The cooled reactor product slurry/gas mixture is reduced in pressure from approximately 1350 psig (maximum) to atmospheric pressure across this high pressure control valve. Two ½-inch angle valves were used in this POC test unit. The valves were rated for 5000 psig. Two different "trim" (valve stem and seat) materials were chosen: stellite and tungsten carbide, the most wear resistant materials available from the manufacturer (Kämmer Valves, Inc.). These valve trims were recommended because it was expected that the unreacted lime solids in the product slurry would be highly abrasive. Stellite trim costs half as much as tungsten carbide, so it was desirable to verify whether or

Figure 3-26. Reactor Pressure Versus Elapsed Time With Manual Pressure Control
(Run OPS27)

Figure 3-27. Reactor Pressure Versus Elapsed Time With Automatic Pressure Control
(Run OPS31)

not it was suitable for this service. Stellite is a widely used cobalt-based wear alloy which contains approximately 61.5% cobalt, 30-31% chromium, 4.5% tungsten, 1.1 to 1.6% carbon, and 2% each of nickel and iron. On the Brinell scale, its hardness is about 400, which is roughly an order of magnitude less than that of tungsten carbide, which has a Brinell hardness of about 3000.

The initial flow characteristic for the trim kits used in each valve were $C_v = 0.1$ for stellite and $C_v = 0.063$ for tungsten carbide. The C_v is a factor which relates the flow through the valve to pressure drop across the valve. Initial tests with these trims proved to be difficult; it was observed that the tungsten carbide valve trim plugged constantly, while the larger C_v stellite trim worked marginally well at reduced pressure (< 1300 psig) but plugged at high pressure. In both cases slurry flowrates were 1 GPM. For the tungsten carbide trim, unreacted lime particles with diameters on the order of 100 mesh ($150 \mu\text{m}$) were too large to pass through the opening and the valve became plugged.

The marginal performance of the larger C_v stellite trim is also explained by the trim dimensions. In this case the seat ring orifice is 0.12 inch with a maximum clearance of 0.0049 inch ($124 \mu\text{m}$) between the valve plug and seat ring in the full open position. In this case, at lower reactor operating pressures, the valve is almost full open and the clearance between the valve plug and seat ring approaches the diameter of the largest unreacted lime solid particles, most of which pass through the valve. Because a few lime solid particles were larger than $150 \mu\text{m}$, the valve periodically became plugged. In contrast, at higher reactor operating pressures, the valve was positioned in a more closed position and was more likely to plug. Upon plugging, this valve could be "stroked" (fully closing then immediately opening the valve) to "flush" out compacted lime solids, hence restoring flow through the valve. Stroking the tungsten carbide valve to restore flow was ineffective because the clearance between the valve plug and seat ring was too small.

The stellite trim failed due to gross erosion of the valve plug after accumulating approximately ten hours of tests in the POC unit (Figures 3-28 through 3-30). This erosion is attributed to the relatively high velocities of the abrasive slurry encountered in this

Figure 3-28. Eroded Stellite Valve Seat

Figure 3-29. Eroded Stellite Valve Stem ($C_v = 0.1$)

Figure 3-30. Eroded Stellite Valve Stem ($C_v = 0.4$)

application. For the 0.1 C_v trim, the effective orifice areas range from 0.0002 in² (10% open) to 0.0018 in² (fully open). At 1 GPM product slurry flow, then, the velocities range from 200 ft/sec to 1600 ft/sec. Although the nominal valve position required to maintain the reactor at 1350 psig is 50% open (320 ft/sec), the velocities probably approach 1000 ft/sec due to partial plugging of the valve.

Kämmer Valves, Inc., the manufacturer of these control valves, was consulted to assist in rectifying these problems. They suggested that a modified stellite trim with a larger C_v (0.4) would improve pressure control in the reactor by providing larger clearances for solids to pass through. The modification would enable the valve stem to be completely retracted from the valve seat during "stroking" operations, thereby improving flushing capability.

There was a three week delivery time for the modified valve so four tests (SD3 thru SD6) were conducted using fixed orifices in the pressure letdown system. Although the aluminum orifice plates were quickly eroded by the abrasive slurry, TRW was able to gather some preliminary CO conversion data which were verified in subsequent testing with a fully operational pressure control system.

A total of 32 hours of run time was accumulated on the modified stellite valve trim (0.4 C_v) before it failed. The seat ring orifice of this valve was 0.18 inch with a maximum clearance of 0.0232 inch (589 μ m) between valve plug and seat ring in the fully open position. For these runs, SD7 through OPS15, the nominal slurry flowrates were 0.55 GPM. At this flowrate, the valve should be between 0 and 10% open in order to maintain the reactor at 900 to 1350 psig. In reality, the valve was positioned at 30 to 40% open for these tests. This indicates that the valve was partially plugged, that is, at these operating conditions a ring or layer of compacted unreacted lime solids was probably formed around the inside of the seat ring orifice, thereby reducing the effective diameter and the clearance between the valve plug and the seat ring. This "coating" of the stellite trim probably contributed to its extended wear life (32 hours versus 10 hours for the 0.1 C_v trim).

After the 0.4 C_v valve trim eroded through, a 0.25 C_v stellite trim was installed on the advice of the engineers at Kämmer Valve, Inc. This trim was used for tests at 0.75 to 1.0 GPM (OPS23 thru OPS26, OPS30, and OPS31) for a total of 9 hours. At the end of testing, this valve showed no evidence of macroscopic erosion.

While awaiting the arrival of replacement stellite trim, several tests were conducted utilizing the tungsten carbide trim. Recall, that during shakedown operations, this trim constantly plugged at slurry flowrates of 1 GPM. However, during test operations at slurry flowrates of 0.55 GPM this trim operated smoothly. A contributor to this improved operation is a procedural modification, whereby the lime slurry was preheated by circulation from the slurry feed tank through the entire reactor system and back into the slurry feed tank for two hours prior to the start of a test. This circulation probably reduced the lime particle size thereby reducing the tendency of the valve to plug. The tungsten carbide trim showed no macroscopic evidence of erosion after 35 operating hours.

It is apparent that in scaleup of this process, tungsten carbide may be the material of choice for the valve trim. It had the longest wear life in these tests and did not fail due to erosion as the stellite trim did. The majority of the problems encountered at POC scale are attributed to the high pressure drop taken across a single valve. In a full scale plant, the pressure letdown should be staged to allow for smaller pressure drops across several valves in series. This configuration would reduce the velocities through each valve and thus reduce abrasive wear on the valve trim.

3.5.3 Instrumentation

3.5.3.1 *Continuous CO Non-Dispersive Infrared Analyzer (NDIR)*

The continuous CO Non-Dispersive Infrared Analyzer or NDIR (installed in the gas vent from T-502) malfunctioned due to improper purging of the sample cell and also because the reference cell was not used. This instrument was over 12 years old, and only a few remnants of the operating manuals were available for use when installing, troubleshooting and operating this unit. These problems were rectified and the unit operated well for several

tests, until an operator error occurred which allowed the vapor/liquid separator (T-502) to overflow and forced liquid into the gas vent line and then into the instrument itself. The infrared (IR) sample and reference cells must be kept free of water at all times, hence the NDIR was inoperable until it was completely purged of water. Test run results based on NDIR readings were of questionable accuracy until it was completely dried. Prior to its getting wet (after Run 26), the NDIR functioned satisfactorily, reporting CO vent gas compositions that were in agreement with those calculated from a CO material balance using the known feed gas flowrate and the measured vent gas flowrate and product solution formate composition.

3.5.3.2 *Vent Flow Orifice*

An integral flow orifice (vent flowmeter) was installed in the vent line from the vapor/liquid separator to measure the flow of vent gases from the system. These gases include inert nitrogen, a small amount of water vapor, and any unreacted CO and CO₂. With the current configuration there were two flow regimes: 1) low flow (1 to 3.5 SCFM), which occurred when the reactor feed gas contained a high CO content and the operating conditions produced high CO conversion, and 2) high flow (4 to 7 SCFM), which occurred when the reactor feed gas contained a small amount of CO and the operating conditions produced low CO conversion. At the current scale of the test unit, there was no orifice available which spanned the full range of expected flows, 0.5 SCFM through 7.0 SCFM. Hence the flowrate was estimated before a test in order to determine the correct size orifice to be installed in the flowmeter. If CO conversions differed drastically from what was expected, the orifice could be grossly oversized or undersized, and an accurate vent flow determination could not be made until the correct orifice was installed. Some tests were, therefore, repeated several times with different size orifices used in the flowmeter in order to get accurate vent flowrates for use in performing CO material balances. This inefficient, trial-and-error, mode of test operations would not be the norm in a larger or full scale plant, which would employ differently designed gas flowmeters (a vortex flowmeter, for example) with wider flow ranges. The types of flowmeters specified for a large plant are not suitable for the low flowrates encountered in the current POC test unit.

4. WESTERN SEED LABORATORY STUDIES

4.1 INTRODUCTION AND SUMMARY

The seed regeneration POC program (as described in Sections 2 and 3 of this Final Report) was directed towards the processing of high sulfur spent seed (consisting of K_2SO_4 and coal ash) produced from high sulfur Eastern coal. In the case of lower sulfur Western coals, the spent seed will be reduced in sulfur content (potassium seed will likely be required in the channel in excess of that required for sulfur capture) and therefore will consist of a mixture of K_2SO_4 , K_2CO_3 and coal ash. The seed regeneration process scheme tested in the POC program could be utilized on Western seed as is, converting both the K_2SO_4 and K_2CO_3 to the $KCOOH$ seed form by reaction with calcium formate. However, the K_2CO_3 is already a viable fresh seed material and can be reused as is, without the need for regeneration (with its associated processing cost), if it can be separated from the spent seed. A reduction in the amount of seed that requires regeneration (for rejection of sulfur, coal ash and impurities such as chloride) directly affects the cost of seed regeneration and therefore the cost of MHD power production. With this in mind, laboratory studies were funded by the DOE to build a data base for a number of TRW-proposed processing schemes that could potentially be employed to recover/regenerate Western-type seed at costs significantly lower than those projected for Eastern-type seed.

It was also recognized that processing methods would have to be developed to prevent the buildup of impurities in the regenerated seed to levels that could potentially degrade channel performance. Of particular concern was chloride, a coal impurity which if allowed to buildup in the seed could potentially affect channel life (corrosion) and channel performance (conductivity). Processing methods were needed that would result in chloride removal from the seed without simultaneously incurring excessive seed (potassium) loss. The building of a data base for rejection of chloride from spent seed was also included as part of the scope of the Western seed laboratory studies.

The Western seed laboratory studies were conducted in 1992-1993. The following three sections of this Introduction and Summary contain a description of the studies performed, a summary of experimental results and conclusions, and recommendations.

4.1.1 Studies Performed

A series of experiments were performed relating to the separation of the K_2SO_4 and K_2CO_3 fractions of the spent seed by selective dissolution in water. These experiments focused on the effect on the K_2SO_4/K_2CO_3 separation of the following parameters: 1) the K_2SO_4 to K_2CO_3 ratio in the seed, 2) the amount of water used for seed dissolution, 3) the temperature of the dissolution process, 4) the contacting time of the dissolution process, 5) the partitioning of the seed impurities, sodium (Na) and chloride (Cl), in the dissolution process, and 6) the effect of an internal recycle stream.

All of the Western seed laboratory studies were conducted with "simulated" spent seed. That is, Western seed mixtures were prepared by the blending of precise amounts of reagent grade K_2CO_3 and K_2SO_4 solids. Small amounts of sodium and chloride salts were occasionally added to the "simulated" seed for those experiments in which the partitioning of these impurities were being investigated. At the initiation of the laboratory studies, a few experiments were conducted with actual Eastern seed ($\sim 90\%$ K_2SO_4 and $\sim 10\%$ coal ash) provided by UTSI from the CFFF to which reagent grade K_2CO_3 was added to "simulate" a typical Western seed. It was found that this material behaved in a K_2CO_3/K_2SO_4 separation experiment similarly to a "simulated" seed that was prepared completely from reagent grade chemicals. Based on this finding, it was decided to conduct the Western seed laboratory studies with "simulated" seed prepared from reagent grade chemicals. This simplified the analytical task considerably. Whereas, the makeup of reagent grade chemicals is already known with great precision, actual seed would be expected to vary in composition from sample to sample. In order to get accurate ion balances in experiments using actual seed, it would be necessary to perform chemical analysis of the seed sample used in each of the many experiments that were to be performed. This would be costly and would also add another source of error to the experiment.

It was determined in the series of experiments outlined above that the bulk of the seed chloride would partition with the K_2CO_3 in the dissolution process. As a result of this finding, a series of experiments were then performed to verify the feasibility of a number of processing schemes (based on evaporation/crystallization) which were proposed for the separation of the chloride from the K_2CO_3 . These experiments focused on the effect of concentrations (K_2CO_3 :KCl ratio) and temperatures on the crystallization of K_2CO_3 and KCl from solution.

Although it was determined that the K_2CO_3 (and chloride) could be selectively dissolved from the K_2SO_4 in the spent seed, a significant fraction of the K_2CO_3 (and chloride) would still report with the K_2SO_4 fraction by virtue of moisture held up on the wet K_2SO_4 cake. A series of experiments were then performed to verify a processing scheme proposed to remove the K_2CO_3 (and chloride) from the wet K_2SO_4 cake.

It is possible that the seed form of choice for future MHD plants may be a mixture of K_2CO_3 and KCOOH (potassium formate). A few simple experiments were performed to provide qualitative information on the blending and flow characteristics of this seed form.

4.1.2 Experimental Results and Conclusions

TRW was able to separate mixed K_2CO_3 / K_2SO_4 solids by selective dissolution of the solids in water. The K_2CO_3 was found to selectively dissolve from the K_2SO_4 . It was found that as the proportion of K_2CO_3 in the solids increases, the minimum amount of water (lbs water per lb solids) required for complete K_2CO_3 dissolution decreases and the fraction of K_2SO_4 taken into solution with the K_2CO_3 decreases. It was also found that, for a given seed mixture, increasing the temperature (from ambient) of the dissolution step reduces the minimum amount of water required for complete K_2CO_3 dissolution and also decreases the fraction of K_2SO_4 taken into solution with the K_2CO_3 . It was also shown that by control of the K_2CO_3 to K_2SO_4 ratio of the dissolver's total inventory (i.e. using an internal recycle), it is possible to make a very sharp separation of the K_2CO_3 and K_2SO_4 in the seed fed to the dissolver even for spent seed that contains a relatively low proportion of K_2CO_3 .

It was found that the sodium and chloride impurities in the spent seed partition to a great extent with the K_2CO_3 in the seed dissolution step. A processing scheme was conceptualized for rejection of the chloride from the K_2CO_3 effluent solution from seed dissolution. This process involved a number of fractional crystallization steps. The feasibility of each of the crystallization steps was successfully verified in the laboratory.

A processing scheme was conceptualized for removal of the residual K_2CO_3 and chloride (present by virtue of the surface moisture) from the wet sulfate solids effluent from the seed dissolution step. The feasibility of reslurrying this cake with a relatively small amount of water to remove the K_2CO_3 and chloride without also dissolving a significant fraction of the K_2SO_4 was successfully verified in the laboratory.

A few simple experiments were performed to provide qualitative information on the blending and flow characteristics of a mixed seed (potassium carbonate and potassium formate). It was observed that at the expected operating temperature of the blending process, the seed mixture was flowable.

4.1.3 Recommendations

TRW has successfully demonstrated the feasibility, on a laboratory (gram) scale, in glassware, of separating a K_2CO_3/K_2SO_4 spent seed into its component fractions and of a method for rejecting chloride from the spent seed. TRW recommends that the proposed processing schemes should next be tested at much larger scale in a Proof-of-Concept (POC) unit. The POC unit should consist of the smallest available versions of commercial equipment. The POC will serve to generate the engineering and scaleup data necessary for the design of the first full scale commercial MHD seed regeneration unit.

4.2 SEPARATION OF POTASSIUM CARBONATE FROM POTASSIUM SULFATE IN SPENT SEED

Data exists in the literature on the solubility relationships in the K_2CO_3 - K_2SO_4 - H_2O system at 25°C (see Mellor's "Comprehensive Treatise on Inorganic and Theoretical

Chemistry", Volume 2, Page 1914). This information is shown graphically in Figure 4-1. A review of this data led TRW to believe that K_2CO_3 could be selectively dissolved from a mixture of K_2CO_3 and K_2SO_4 solids with water. Table 4-1 (from the same reference cited above) gives equilibrium data for this system for cases in which the minimum amount of water is used for complete dissolution of the K_2CO_3 in the K_2CO_3/K_2SO_4 mixture. The initial experiments, in which analytical and laboratory procedures were refined, concentrated on validation of the solubility data for the K_2CO_3 - K_2SO_4 - H_2O system as reported in Table 4-1.

The data in Table 4-1 was reworked so as to be in a more useful form (Table 4-2). Table 4-2 shows the effect of the K_2CO_3 : K_2SO_4 ratio in the seed mix on the fraction of K_2SO_4 taken into solution at complete K_2CO_3 dissolution (with the minimum amount of water) and the total dissolved solids in solution at this point. As can be seen in Table 4-2, as the K_2CO_3 : K_2SO_4 ratio in the seed increases, the minimum amount of water required for complete K_2CO_3 dissolution decreases. The potential sharpness of the K_2CO_3/K_2SO_4 separation also increases with increasing K_2CO_3 : K_2SO_4 ratio in the spent seed.

4.2.1 Effect of Seed Composition on K_2CO_3/K_2SO_4 Separation

4.2.1.1 *Description of Experiments*

Experiments (WSD1 and 19643-56,57,59) were performed to determine the effect of seed composition (K_2CO_3 : K_2SO_4 ratio) on the separation of the seed fractions when the minimum amount of water for complete K_2CO_3 dissolution is used. The objective of these experiments was to duplicate points on the equilibrium curve for the K_2CO_3 - K_2SO_4 - H_2O system (at 25°C) given in the literature (Tables 4-1 and 4-2). Experiment WSD1 was conducted with a 0.589:1 weight ratio of K_2CO_3 : K_2SO_4 in the solids mix and experiments 19643-56,57,59 were conducted with a 1.489:1 weight ratio of K_2CO_3 : K_2SO_4 . The ratio 0.589:1 is a possible ratio of these compounds in spent seed produced in a Western coal MHD facility. The minimum amount of water required to dissolve all of the carbonate present in the initial solid mixture was added to the carbonate/sulfate mixture. The amount

Figure 4-1. The 25°C Isotherm of the Ternary System K_2CO_3 - K_2SO_4 - H_2O

TABLE 4-1. SOLUBILITY RELATIONSHIPS IN THE SYSTEM K_2CO_3 - K_2SO_4 - H_2O AT $25^\circ C$ ¹

ORIGINAL COMPLEX		SATURATED SOLUTION		DENSITY	SOLID PHASES
WT% K_2SO_4	WT% K_2CO_3	WT% K_2SO_4	WT% K_2CO_3		
--	--	10.7	--	1.083	K_2SO_4
21.8	4.6	6.5	5.5	1.103	K_2SO_4
17.2	8.3	4.9	9.4	1.122	K_2SO_4
17.1	14.1	2.8	16.4	1.170	K_2SO_4
13.7	20.4	1.5	23.2	1.230	K_2SO_4
14.6	30.1	0.3	35.0	1.348	K_2SO_4
8.1	41.5	0.08	45.1	1.465	K_2SO_4
16.6	40.6	0.03	48.6	1.506	K_2SO_4
8.4	51.6	0.03	52.8	1.557	$K_2SO_4 + K_2CO_3 \cdot 1.5H_2O$
--	--	--	52.8	1.557	$K_2CO_3 \cdot 1.5H_2O$

¹ From Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume II, page 1914.

TABLE 4-2. PERCENT OF K_2SO_4 DISSOLVED IN WATER VERSUS K_2CO_3 : K_2SO_4 RATIO IN FEED AT 25°C¹

SPENT SEED K_2CO_3 : K_2SO_4 (wt)	CARBONATE SOLUTION (@100% K_2CO_3 DISSOLVED) ² K_2SO_4 : K_2CO_3 (wt)	PERCENT OF FEED K_2SO_4 DISSOLVED ²	TOTAL DISSOLVED SOLIDS IN EQUILIBRIUM SOLUTION ² WT%
0.21:1	1.18:1	24.94%	12.0
0.48:1	0.52:1	25.15%	14.3
0.82:1	0.17:1	14.08%	19.2
1.49:1	0.065:1	9.62%	24.7
2.06:1	0.009:1	1.77%	35.3
2.45:1	0.0006:1	0.15%	48.63
5.12:1	0.002:1	0.91%	45.18

¹ MINIMUM AMOUNT OF WATER IS USED WHICH WILL DISSOLVE 100% OF THE K_2CO_3 . REMAINING SOLID PHASE IS K_2SO_4 .

² CALCULATED FROM K_2CO_3 - K_2SO_4 - H_2O SYSTEM SOLUBILITY DATA (@25°C) PRESENTED IN MELLOR'S COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY, VOLUME II, PAGE 1914.

of water required to accomplish this was determined by interpolation of the equilibrium data from the literature.

Pre-weighed amounts of K_2CO_3 , K_2SO_4 and water were mixed by stirring in a beaker. After stirring, settling/centrifuging, decanting, filtering, etc., the resulting solids and solutions were analyzed for K^+ content by atomic absorption spectroscopy (AA), for $CO_3^{=}$ content by ion chromatography (IC) and/or titration (TT), and for $SO_4^{=}$ content by IC and/or gravimetric analysis (GM). The results of these experiments are discussed in detail in the following section.

4.2.1.2 *Discussion of Individual Test Results*

Table 4-3 is a detailed summary of the material balance data for WSD1 which was conducted with a 0.589:1 (weight ratio) solid mix of K_2CO_3 : K_2SO_4 . As can be seen excellent analytical results were obtained. Closures for the individual ionic species were $100 \pm 0.5\%$. The wet solids analysis was corrected to a dry solids basis from the determined (by difference) amount of water in the wet cake. The moisture holdup on the cake was ~ 0.33 lbs/lb of dry cake. The experimental results compared very closely with those expected based on the available literature data. Complete (99.9%) K_2CO_3 dissolution was achieved. The saturated solution contained 11.68 wt% K_2CO_3 and 3.70 wt% K_2SO_4 (15.38 wt% total dissolved solids, TDS). This compares to an estimated composition based on the literature data of 11.61 wt% K_2CO_3 and 4.26 wt% K_2SO_4 (15.87 wt% TDS). Approximately 18.8% of the K_2SO_4 in the original solid mix was taken into solution. This compares with 21.6% of the K_2SO_4 estimated from the literature data.

Experiments 19643-56,57,59 were conducted with a 1.489:1 (weight ratio) solid mix of K_2CO_3 : K_2SO_4 . This is one of the data points reported in the literature (see Table 4-2). The saturated solutions produced in the three experiments (which differed only in the time allowed for equilibration) were almost identical in composition. These solutions contained an average of 23.1 wt% K_2CO_3 and 1.68 wt% K_2SO_4 (24.78 wt% TDS). This compares

TABLE 4-3. MATERIAL BALANCE DATA FOR WSD1 - EFFECT OF SEED COMPOSITION

WSD1						
START	5.5039 g K ₂ CO ₃		7.3073 g K+			
	9.3412 g K ₂ SO ₄	---->	2.3895 g CO ₃ =			
	39.965 g H ₂ O		5.1478 g SO ₄ =			
			39.965 g H ₂ O			
44.8324 g CENTRATE		9.9665 g WET CAKE			TOTAL	(TOT/START)
	<u>(% w/w)</u>	<u>(g)</u>	<u>(% w/w)</u>	<u>(g)</u>	<u>(g)</u>	<u>CLOSURE</u>
K+	8.34%	3.7390	35.62%	3.5501	7.2891	0.998
CO ₃ =	5.07%	2.2730	1.28%	0.1276	2.4006	1.005
SO ₄ =	2.04%	<u>0.9146</u>	42.28%	<u>4.2138</u>	5.1284	0.996
		6.9266		7.8915		
H ₂ O		44.8324		9.9665		
	-	<u>6.9266</u>	-	<u>7.8915</u>		
		37.9058		2.0750		
CORRECT WET SOLIDS TO DRY SOLIDS:						
	<u>CENTRATE</u>	<u>EXPECTED (MELLOR)</u>	<u>DRY SOLID</u>	<u>EXPECTED (MELLOR)</u>		
g K+	3.9437	4.0200g	3.3454	3.2882g		
g CO ₃ =	2.3974	2.3893g	0.0031	0g		
g SO ₄ =	0.9646	1.1122g	4.1638	4.0367g		
g H ₂ O	39.9808	39.8732g	0.0014	(hydrate)	39.9822	1.000

closely with the 23.2 wt% K_2CO_3 and 1.5 wt% K_2SO_4 (24.7 wt% TDS) reported in the literature (Table 4-2).

As can be seen from these experimental results, the total dissolved solids in the resulting saturated solutions, when using the minimum amount of water for complete K_2CO_3 dissolution, increased from $\sim 15\%$ to $\sim 25\%$ as the $K_2CO_3:K_2SO_4$ ratio in the seed increased from 0.589:1 to 1.489:1. Also the percentage of solid K_2SO_4 that goes into solution decreases from $\sim 20\%$ to $\sim 2\%$ as the $K_2CO_3:K_2SO_4$ ratio in the seed increases from 0.589:1 to 1.489:1.

4.2.1.3 *Summary of Test Results*

The experiments performed as discussed above gave results that were consistent with solubility data for the K_2CO_3 - K_2SO_4 - H_2O system at $25^\circ C$ as reported in the literature (see Tables 4-1 and 4-2). The experimental results confirmed that as the $K_2CO_3:K_2SO_4$ ratio in the seed increases, the minimum amount of water required for complete K_2CO_3 dissolution decreases (the total dissolved solids in the saturated solution increases). Also, with increasing $K_2CO_3:K_2SO_4$ ratio in the seed, at minimum water usage for complete K_2CO_3 dissolution, the sharpness of the K_2CO_3/K_2SO_4 separation increases. That is, at minimum water usage for complete K_2CO_3 dissolution, a smaller fraction of the K_2SO_4 goes into solution as the seed $K_2CO_3:K_2SO_4$ ratio increases.

4.2.2 Effect of the Amount of Water Used for Seed Dissolution on K_2CO_3/K_2SO_4 Separation

4.2.2.1 *Description of Experiments*

A number of experiments were performed (10/16) in which seed material was mixed with less than the minimum amount of water required for complete K_2CO_3 dissolution. Solid mixes containing $K_2CO_3:K_2SO_4$ respectively in a weight ratio of 0.589:1 were contacted in three separate experiments with 37.5%, 50% and 62.5% of the minimum water required (based on interpolated literature data) for complete K_2CO_3 dissolution. Pre-weighed amounts of K_2CO_3 , K_2SO_4 and water were mixed (using a shaker table), centrifuged and

decanted. The resulting solids and solutions were analyzed for K^+ , $CO_3^{=}$ and $SO_4^{=}$. The results of these experiments are discussed in detail in the following section.

4.2.2.2 *Discussion of Individual Test Results*

The fraction of K_2CO_3 dissolved increased from $\sim 80\%$ to $\sim 94\%$ as the amount of water used was increased from 37.5% to 62.5% of the minimum water required for complete K_2CO_3 dissolution. The $K_2SO_4:K_2CO_3$ weight ratio in the saturated solutions increased from $\sim 0.05:1$ to $\sim 0.14:1$ as the amount of water used was increased from 37.5% to 62.5% of the minimum water required for complete K_2CO_3 dissolution. This compares to an expected value of $\sim 0.37:1$ when the minimum amount of water for complete K_2CO_3 dissolution is used.

4.2.2.3 *Summary of Test Results*

The experimental results indicate that as the amount of water used is decreased, the total solids concentration of the saturated solution produced increased. Also, with decreasing water use, the fraction of K_2CO_3 dissolved from the seed decreases to a lesser extent than does the fraction of K_2SO_4 dissolved. That is, with decreasing water use, the saturated solutions produced contain an increasing total dissolved solids content with an increasing $K_2CO_3:K_2SO_4$ ratio.

4.2.3 Effect of Temperature on K_2CO_3/K_2SO_4 Separation

4.2.3.1 *Description of Experiments*

An experiment (WSD14) was performed to determine the effect of temperature on the minimum amount of water required for complete K_2CO_3 dissolution and on the resulting sharpness of the K_2CO_3/K_2SO_4 separation. The experiment was conducted at $60^\circ C$ using a 0.48:1 $K_2CO_3:K_2SO_4$ seed mixture and the results were compared to the available literature data at $25^\circ C$. The experiment was repeated several times with decreasing amounts of water until the "minimum" water point was found. After stirring, centrifuging, decanting, etc., the resulting solids and solutions were analyzed for carbonate and sulfate content. It was

expected that since carbonate (and sulfate) solubility increases with temperature, the minimum water required for complete carbonate dissolution would be less at 60°C than at 25°C, and that therefore there may be an economic benefit to conducting the separation at an elevated temperature. The results of this experiment are discussed in detail in the following section.

4.2.3.2 *Discussion of Individual Test Results*

The experimental results have been plotted in Figure 4-2A. Complete K_2CO_3 dissolution apparently takes place at 60°C when 0.96 to 1.15 parts by weight of water were mixed with 1.0 part by weight of the test solids. This compares with a requirement of 2.92 parts of water per 1.0 part by weight of the same test solids at 25°C (according to the available literature data). In addition to requiring much less water for K_2CO_3 dissolution (resulting in much more concentrated K_2CO_3 solutions), the elevated temperature appears to also result in a much sharper separation of the seed fractions. At 25°C with a 0.48:1 K_2CO_3 : K_2SO_4 seed, the literature data indicates that ~25% of the K_2SO_4 will go into solution when the minimum amount of water is used for complete K_2CO_3 dissolution (see Table 4-2). At 60°C when the minimum amount of water is used for complete K_2CO_3 dissolution, the percentage of K_2SO_4 that goes into solution drops to ~8%. The effect of temperature on the sharpness of the K_2CO_3 / K_2SO_4 separation can be clearly seen in Figure 4-2B.

4.2.3.3 *Summary of Test Results*

It was found that increasing the temperature of dissolution decreased the minimum amount of water required for complete K_2CO_3 dissolution. Concurrently, the sharpness of the K_2CO_3 / K_2SO_4 separation increased. That is, as the temperature was increased, a smaller fraction of the seed K_2SO_4 was taken into solution with the K_2CO_3 when the minimum amount of water required for complete K_2CO_3 dissolution was used. These results indicate that there would be an economic benefit to conducting the seed separation at an elevated temperature.

Figure 4-2A. Percentage of Initial Anion Which Dissolves as a Function of Initial Water Content of Slurry

Figure 4-2B. Variation of Centrate Composition with Initial Water Content of Slurry

4.2.4 Effect of Contact Time on K_2CO_3/K_2SO_4 Separation

4.2.4.1 *Description of Experiments*

An experiment (19643-56,57,59) was conducted in which seed (at a 1.489:1 weight ratio of $K_2CO_3:K_2SO_4$) and the theoretical minimum amount of water required for complete seed K_2CO_3 dissolution were mixed and stirred for contact times varying from 15 to 60 minutes. After stirring, settling, filtering, etc., the resulting solids and solutions were analyzed for K^+ , $CO_3^{=}$ and $SO_4^{=}$ content. The results of this experiment are discussed in detail in the following section.

4.2.4.2 *Discussion of Individual Test Results*

Solids mixtures at a 1.489:1 (by weight) $K_2CO_3:K_2SO_4$ ratio were combined with the minimum amounts of water (per literature data) required for complete K_2CO_3 dissolution at 25°C and stirred for periods of 15, 30 and 60 minutes. The resulting solution concentrations produced are summarized in Table 4-4 along with the saturated solution concentration expected based on the literature data. As can be seen, increased contact time (beyond 15 minutes) makes very little difference in the solution concentration achieved. Apparently equilibrium is reached rather quickly. The experimental results were in excellent agreement with the literature data.

4.2.4.3 *Summary of Test Results*

The dissolved seed saturated solutions produced were virtually identical in composition at contact times in excess of 15 minutes.

4.2.5 Seed Impurities Partition During K_2CO_3/K_2SO_4 Separation

4.2.5.1 *Description of Experiments*

A number of experiments (10/16 and 19643-77) were performed in which relatively small amounts of sodium (as Na_2CO_3 and Na_2SO_4) and chloride (as KCl) were added to 0.589:1 and 0.926:1 (by weight) $K_2CO_3:K_2SO_4$ solids mixtures which were then contacted with water to effect a K_2CO_3/K_2SO_4 separation. The purpose of the experiments was to

TABLE 4-4. SOLUTION CONCENTRATIONS VERSUS CONTACT TIME¹

FEED MIX: $\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4 = 1.489:1$ (WEIGHT)

CONTACT TIME, MINUTES	MEASURED SOLUTION CONCENTRATIONS, WT%	
	K_2SO_4	K_2CO_3
15	1.78 wt%	23.1 wt%
30	1.69	22.83
60	1.56	23.35
SATURATED SOLUTION PER LITERATURE DATA ²		
--	1.5 wt%	23.2 wt%

¹ Minimum amount of water was used for complete K_2CO_3 dissolution at 25°C.

² From Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Volume II, page 1914.

determine the Na and Cl partition from spent seed at varying amounts of water (bracketing the minimum amount of water required for complete K_2CO_3 dissolution). After stirring, settling/centrifuging, decanting, filtering, etc., the resulting solids and solutions were analyzed for K^+ , Na^+ , Cl^- , $CO_3^{=}$ and $SO_4^{=}$. The results of these experiments are discussed in detail in the following section.

4.2.5.2 *Discussion of Individual Test Results*

Experiments (10/16) were performed in which relatively small amounts of sodium (as Na_2CO_3 and Na_2SO_4) and chloride (as KCl) were added to a 0.589:1 (by weight) K_2CO_3 : K_2SO_4 solids mixture. The resulting Na:K ratio in the solids mix was $\sim 0.005:1$ (by weight) and the Cl:K ratio was $\sim 0.0035:1$ (by weight). These solids mixtures then were contacted with quantities of water that were less than the minimum required for complete K_2CO_3 dissolution at $25^\circ C$. The percent sodium taken into solution was seen to increase from 72 to 77% as the amount of water used increased from 37.5% to 62.5% of the minimum amount required for complete K_2CO_3 dissolution. Similarly, the percent chloride taken into solution was seen to increase from 83 to 89% as the amount of water used increased from 37.5% to 62.5% of the minimum amount required for complete K_2CO_3 dissolution.

An additional experiment (19643-77) was performed with a 0.926:1 (by weight) K_2CO_3 : K_2SO_4 solids mixture. This solids mix was spiked with sodium (as Na_2CO_3 and Na_2SO_4) and chloride (as KCl). The resulting Na:K ratio in the solid mix was 0.092:1 (by weight) and the Cl:K ratio was 0.0083:1 (by weight). When this solids mix was contacted with approximately the minimum amount of water required for complete K_2CO_3 dissolution, $\sim 96\%$ of the sodium and $\sim 95\%$ of the chloride were found to have gone into solution.

4.2.5.3 *Summary of Test Results*

The experimental results indicate that at relatively low levels in the seed, both sodium and chloride will, to a large extent, upon contact with water be dissolved from the K_2SO_4 and go into solution with the K_2CO_3 .

4.2.6 Effect of Recycle on K_2CO_3/K_2SO_4 Separation

TRW postulated a processing scheme whereby a sharp separation of the K_2CO_3 and K_2SO_4 could be achieved regardless of the $K_2CO_3:K_2SO_4$ ratio in the spent seed. This could be accomplished if the total inventory of the dissolution system were to be maintained (by recycle of solids-free centrate in a commercial plant) at an elevated $K_2CO_3:K_2SO_4$ ratio.

4.2.6.1 *Description of Experiments*

A number of experiments (WSD7A,B,C) were conducted to verify the proposed separation scheme for production of virtually sulfate-free potassium carbonate seed (see Section 5.3.2.1 for more details on the proposed separation scheme). Previous experiments showed that at the $K_2CO_3:K_2SO_4$ ratio expected for typical Western seeds, a significant amount of K_2SO_4 goes into solution with K_2CO_3 . Ultimately (in an MHD power plant) this sulfate may be recycled to the channel where it has the potential to accumulate to undesirable levels. The experiments performed combined spent seed with simulated recycle solution (and a small amount of makeup water for seed K_2CO_3 dissolution) in the proportions required to give a total mixture $K_2CO_3:K_2SO_4$ ratio of 5.12:1. The simulated recycle solution contained ~45 wt% K_2CO_3 and ~0.09 wt% K_2SO_4 (expected equilibrium solution at a 5.12:1 $K_2CO_3:K_2SO_4$ ratio in system, see Table 4-2). Separate experiments were conducted with 0.382:1, 0.587:1 and 1.295:1 $K_2CO_3:K_2SO_4$ seed feed mixtures. After stirring, centrifuging, etc., the resulting solids and solutions were analyzed for K^+ , $CO_3^{=}$ and $SO_4^{=}$ content. The results of these experiments are discussed in detail in Section 4.2.6.2.

Additional experiments (WSD13) were also performed to determine the partition of chloride from the spent seed in a system using an internal recycle. The purpose of these experiments was to separate K_2CO_3 from K_2SO_4 in a simulated spent seed mixture containing small quantities of chloride ions as impurities. The results of interest were: 1) the distribution of the impurities among the solid and liquid phases, and 2) the influence of the impurities on the sharpness of the carbonate/sulfate separation. The first item is a concern because if the impurities remain in the solid phase they may ultimately be recycled, with the regenerated seed, back to the MHD channel where they could accumulate to unacceptable

levels. Two simulated seeds were prepared. One represented high chloride content spent seed and the other represented low chloride content spent seed. After stirring, filtering, etc., the resulting solids and solutions were analyzed for $\text{CO}_3^{=}$, $\text{SO}_4^{=}$ and Cl^- content. The results of these experiments are discussed in detail in Section 4.2.6.2.

4.2.6.2 Discussion of Individual Test Results

A number of experiments (WSD7) were conducted to verify the concept that regardless of the $\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4$ ratio in the feed seed, a very sharp separation of the seed fractions can be obtained if the total inventory of the dissolution system can be maintained (by recycle of solids-free centrate solution) at a high $\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4$ ratio. Solid mixtures containing $\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4$ at weight ratios of 0.382:1, 0.587:1 and 1.295:1 were mixed with sufficient recycle simulant solution containing ~45 wt% total dissolved solids at a $\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4$ ratio of ~500:1 to give a total system inventory $\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4$ ratio of ~5.12:1. At this ratio the literature data (see Table 4-2) indicates that if the minimum amount of water for dissolution of the K_2CO_3 in the solids mixture fed to the system is added to the dissolver, almost none (<1%) of the K_2SO_4 in the solids mix will dissolve. The material balance results for WSD7A,B&C are summarized in Tables 4-5 through 4-7. As noted, for all three of the solids mixtures tested, ~100% of the K_2CO_3 and <1% of the K_2SO_4 were seen to go into solution.

Experiments (WSD13) were also performed to determine the partition of chloride impurities in a dissolver system with an internal recycle. Experiment WSD13A was based on a solids mix containing $\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4$ at a weight ratio of 0.382:1. Sufficient KCl was added to this mixture to result in a Cl:K weight ratio of ~0.0144:1 in the solids. This was to be considered a "high chloride" case. Experiment WSD13B was based on a solids mix containing $\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4$ at a weight ratio of 0.589:1. Sufficient KCl was added to this mixture to result in a Cl:K weight ratio of ~0.0037:1 in the solids. This was to be considered a "low chloride" case.

TABLE 4-5. MATERIAL BALANCE DATA FOR WSD7A - EFFECT OF RECYCLE
(K₂CO₃:K₂SO₄ WEIGHT RATIO OF FEED SOLIDS = 0.382:1)

WSD7A						
START	RECYCLE		99.05 g			
3.5657 g K ₂ CO ₃	24.53%		24.30 g K+	30.5075 g K+		
9.3408 g K ₂ SO ₄				0 g Na+		
0 g Na ₂ CO ₃	+	19.59%	19.40 g CO ₃ =	----->	20.9520 g CO ₃ =	
0 g Na ₂ SO ₄		0.05%	0.05 g SO ₄ =		5.1972 g SO ₄ =	
0 g KCl	(by analysis)				0 g Cl-	
4.3384 g H ₂ O			55.30 g H ₂ O		59.638 g H ₂ O	
17.2449					116.29	
99.6931 g CENTRATE	16.5687 g WET CAKE		TOTAL		(TOT/START)	
	(% w/w)	(g)		(% w/w)	(g)	CLOSURE
K+	24.78%	24.7040		35.38%	5.8620	30.5660 1.002
Na+	0%	0		0%	0	0 -
CO ₃ =	19.53%	19.4701		8.63%	1.4299	20.8999 0.998
SO ₄ =	0.05%	0.0498		31.38%	5.1993	5.2491 1.010
Cl-	0%	0		0%	0	0 -
		44.2239			12.4911	
H ₂ O		99.6931			16.5687	
	-	44.2239		-	12.4911	
		55.4692			4.0776	

CORRECT WET SOLIDS TO DRY SOLIDS:

	CENTRATE		DRY SOLID		
K+	26.5199 g		4.0460 g		
Na+	0 g		0 g		
CO ₃ =	20.9013 g		-0.0014 g		
SO ₄ =	0.0535 g		5.1956 g		
Cl-	0 g		0 g		
H ₂ O	59.5468 g	(hydrate)	0.0000 g	59.5468	0.998

100% of feed CO₃= recovered in centrate

100% of feed SO₄= recovered in solids

TABLE 4-6. MATERIAL BALANCE DATA FOR WSD7B - EFFECT OF RECYCLE
(K₂CO₃:K₂SO₄ WEIGHT RATIO OF FEED SOLIDS = 0.587:1)

WSD7B						
START			RECYCLE	94.76 g		
5.496 g K2CO3			24.53%	23.24 g K+	30.5551 g K+	
9.3582 g K2SO4					0 g Na+	
0 g Na2CO3	+	19.59%	18.56 g CO3=	----->	20.9496 g CO3=	
0 g Na2SO4		0.05%	0.05 g SO4=		5.2046 g SO4=	
0 g KCl		(by analysis)			0 g Cl-	
<u>6.7097</u> g H2O			52.90 g H2O		<u>59.614</u> g H2O	
21.5639					116.32	
100.0647 g CENTRATE			15.9601 g WET CAKE			TOTAL (TOT/START)
	<u>(% w/w)</u>	<u>(g)</u>	<u>(% w/w)</u>	<u>(g)</u>	<u>(g)</u>	<u>CLOSURE</u>
K+	24.70%	24.7160	35.47%	5.6610	30.3770	0.994
Na+	0%	0	0%	0	0	-
CO3=	19.54%	19.5526	8.21%	1.3103	20.8630	0.996
SO4=	0.05%	0.0500	32.42%	5.1743	5.2243	1.004
Cl-	0%	0	0%	0	0	-
		<u>44.3187</u>		<u>12.1456</u>		
H2O		100.0647		15.9601		
	-	<u>44.3187</u>		- <u>12.1456</u>		
		55.7460		3.8145		

CORRECT WET SOLIDS TO DRY SOLIDS:

	<u>CENTRATE</u>	<u>DRY SOLID</u>		
K ⁺	26.4072 g	3.9698 g		
Na ⁺	0 g	0 g		
CO ₃ =	20.8905 g	-0.0276 g		
SO ₄ =	0.0535 g	5.1708 g		
Cl ⁻	0 g	0 g		
H ₂ O	59.5605 g	(hydrate) 0.0000 g	59.5605	0.999

100% of feed CO₃= recovered in centrate
99% of feed SO₄= recovered in solids

TABLE 4-7. MATERIAL BALANCE DATA FOR WSD7C - EFFECT OF RECYCLE
(K₂CO₃:K₂SO₄ WEIGHT RATIO OF FEED SOLIDS = 1.295:1)

WSD7C						
START			RECYCLE	80.12 g		
12.0445 g K2CO3			24.53%	19.65 g K+	30.6449 g K+	
9.3040 g K2SO4					0 g Na+	
0 g Na2CO3	+	19.59%	15.70 g CO3=	----->	20.9247 g CO3=	
0 g Na2SO4		0.05%	0.04 g SO4=		5.1674 g SO4=	
0 g KCl		(by analysis)			0 g Cl-	
<u>14.6215</u> g H2O			44.73 g H2O		<u>59.3525</u> g H2O	
35.9700					116.09	
100.0647 g CENTRATE			15.9909 g WET CAKE			TOTAL (TOT/START)
	(% w/w)	(g)	(% w/w)	(g)	(g)	CLOSURE
K+	24.52%	24.5359	35.55%	5.6848	30.2206	0.986
Na+	0%	0	0%	0	0	-
CO3=	19.53%	19.5426	8.32%	1.3304	20.8731	0.998
SO4=	0.05%	0.0500	32.41%	5.1827	5.2327	1.013
Cl-	0%	0	0%	0	0	-
		<u>44.1285</u>		<u>12.1979</u>		
H2O		100.0647		15.9909		
	-	<u>44.1285</u>	-	<u>12.1979</u>		
		55.9362		3.7930		

CORRECT WET SOLIDS TO DRY SOLIDS:

	CENTRATE	DRY SOLID		
K+	26.1996 g	4.0210 g		
Na+	0 g	0 g		
CO ₃ =	20.8678 g	0.0053 g		
SO ₄ =	0.0534 g	5.1793 g		
Cl-	0 g	0 g		
H ₂ O	59.7292 g	(hydrate) 0.0024 g	59.7316	1.006

100% of feed CO₃= recovered in centrate

100% of feed SO₄= recovered in solids

The experimental results for WSD13A&B are summarized in Figures 4-3 and 4-4 and Tables 4-8 and 4-9. As can be seen, in both cases virtually all ($>99.8\%$) of the chloride in the solids mixture goes into solution in the dissolver.

4.2.6.3 *Summary of Test Results*

The experimental results confirmed the hypothesis that, regardless of the composition ($\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4$ ratio) of the spent seed, a sharp $\text{K}_2\text{CO}_3/\text{K}_2\text{SO}_4$ separation can be made if the total $\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4$ ratio in the dissolver is properly controlled. In this instance, it was also observed that chloride in the seed, to a great extent, partitions with the K_2CO_3 fraction of the seed in the dissolution process.

4.3 REJECTION OF CHLORIDE FROM SPENT SEED

4.3.1 Rejection of Chloride from Low Chloride Spent Seed

Based on experiments conducted (as described in Section 4.2 above), TRW concluded that chloride would partition with the K_2CO_3 in the $\text{K}_2\text{CO}_3/\text{K}_2\text{SO}_4$ separation and that a sharp separation of K_2CO_3 and K_2SO_4 can be achieved at an elevated $\text{K}_2\text{CO}_3:\text{K}_2\text{SO}_4$ ratio in the dissolution step (as the result of internal recycle of the centrate). TRW then proposed a process scheme for removing the chloride from the K_2CO_3 solution. For the case of a low chloride spent seed this involved:

- 1) crystallizing pure K_2CO_3 from the K_2CO_3 solution by evaporation of water,
- 2) crystallizing K_2CO_3 and KCl from the residual mother liquor from step (1) by reducing its temperature,
- 3) redissolving the K_2CO_3 in the crystals from step (2) in water leaving a residue of KCl crystals, and
- 4) crystallizing K_2CO_3 from the mother liquor from step (3) by evaporation of water.

These steps were to be integrated in a process (with a number of internal recycle streams) that would result in a sharp separation of the K_2CO_3 and KCl in the feed solution. A series

SO₄= MAT BAL CLOSURE = 0.994
 CO₃= MAT BAL CLOSURE = 1.006
 Cl⁻ MAT BAL CLOSURE = 0.989
 K⁺ (BY DIFF) = 1.004
 OVERALL = 0.998

	RECYCLE	FEED	TOTAL	
K ₂ CO ₃	44.6810	3.5712	48.2522	gm
KCl	2.3950	0.1922	2.5872	gm
K ₂ SO ₄	0.0816	9.3450	9.4266	gm
H ₂ O	54.3049	4.4046	58.7095	gm
TOTAL	101.4625	17.5130	118.9755	gm

32.8903 g K⁺
 20.9489 g CO₃=
 1.2304 g Cl⁻
 5.1949 g SO₄=

Stirred for 2 hr at 20 C

Total
 Solution
 118.9755 gm

→ -0.2255 g H₂O → 118.7500 g H₂O to Start

Filtered at 20 C

Filtrate
 F
 107.45 gm

SO₄= 0.042%
 CO₃= 19.308%
 Cl⁻ 1.111%
 K+(by diff) 26.42%

Cake + Residual
 C+R
 11.30 gm

SO₄= 45.301%
 CO₃= 2.940%
 Cl⁻ 0.191%
 K+(by diff) 40.93%

H₂O
 df = 1.70

FD
 182.47 gm

CO₃= 11.370%
 Cl⁻ 0.655%
 SO₄= 0.025%

H₂O
 df = 13.64

CD
 154.20 gm

CO₃= 0.216%
 Cl⁻ 0.014%
 SO₄= 3.320%

WSD13A

WSD13A

TRW 7/14/93		
WESTERN SEED		
LABORATORY PROCEDURE		
SCALE	REV 0	SHEET 1 OF

Figure 4-3. Experimental Results for WSD13A - Effect of Recycle - "High Chloride"
 Case (K₂CO₃:K₂SO₄ Wt Ratio in Net Feed Solids = 0.382:1, Cl:K Wt
 Ratio in Net Feed Solids = 0.0144:1)

SO₄= MAT BAL CLOSURE = 0.997
 CO₃= MAT BAL CLOSURE = 1.009
 Cl⁻ MAT BAL CLOSURE = 0.992
 K⁺ (BY DIFF) = 1.008
 OVERALL = 0.998

	RECYCLE	FEED	TOTAL	
K ₂ CO ₃	42.7314	5.5017	48.2331	gm
KCl	0.4446	0.0571	0.5017	gm
K ₂ SO ₄	0.0777	9.3477	9.4254	gm
H ₂ O	51.9409	6.7319	58.6728	gm
TOTAL	95.1946	21.6384	116.8330	gm

31.7852 g K⁺
 20.9406 g CO₃=
 0.2386 g Cl⁻
 5.1943 g SO₄=

Stirred for 2 hr at 20 C

Total
 Solution
 116.8330 gm

-0.2130 g H₂O → 116.6200 g H₂O to Start

Filtered at 20 C

WSD13B

WSD13B

TRW 7/14/93		
WESTERN SEED		
LABORATORY PROCEDURE		
SCALE	REV 8	SHEET 1 OF

Figure 4-4. Experimental Results for WSD13B - Effect of Recycle - "Low Chloride"
 Case (K₂CO₃:K₂SO₄ Wt Ratio in Net Feed Solids = 0.589:1, Cl:K Wt
 Ratio in Net Feed Solids = 0.0037:1)

TABLE 4-8. MATERIAL BALANCE RESULTS FOR WSD13A - EFFECT OF RECYCLE -
 "HIGH CHLORIDE" CASE (NET SOLIDS FEED K_2CO_3 : K_2SO_4 WT
 RATIO = 0.382:1, NET SOLIDS FEED Cl:K WT RATIO = 0.0144:1)

WSD13A - MATERIAL BALANCE SUMMARY @ 20 DEG C					
0.2480 g moisture/g dry cake					
	Combined Feed*	Dry Cake	Slurry	Wet Cake	Centrate
K ₂ CO ₃	48.2522	0.000	48.252	1.020	47.232
K ₂ SO ₄	9.4266	9.344	0.082	9.346	0.080
KCl	2.5872	0.004	2.583	0.059	2.529
3/2 H ₂ O	0	0.000		0.000	
H ₂ O	58.7095		58.710	1.242	57.47
TOTAL	119	9	110	12	107
		44.89%	Wt.% K+	41.17%	26.17%
		0.00%	Wt.% CO ₃ =	3.80%	19.11%
		55.09%	Wt.% SO ₄ =	44.15%	0.04%
		0.020%	Wt.% Cl-	0.239%	1.121%

COMPARISON OF MODEL PREDICTIONS @ 20 deg C
 w/ RESULTS OF EXPERIMENT WSD13A

CENTRATE			
EXPECTED COMPOSITION		ACTUAL COMPOSITION	
(Model/Sat'd Solution)*		(F Analysis)	
20 deg C	26.17% K+	26.42%	<=== back-calculated
	19.11% CO ₃ =	19.31%	
	0.04% SO ₄ =	0.04%	
	1.12% Cl-	1.11%	

*K₂SO₄, K₂CO₃ from Mellor; KCl from Exp't. WSD3

WET CAKE			
EXPECTED COMPOSITION		ACTUAL COMPOSITION	
(Model/Wet Cake)**		(C Analysis)	
20 deg C	41.17% K+	40.93%	<=== back-calculated
	3.80% CO ₃ =	2.95%	
	44.15% SO ₄ =	45.30%	
	0.24% Cl-	0.19%	

** Model assumes 0.2480 gram moisture/gram dry cake

DRY CAKE			
EXPECTED COMPOSITION		ACTUAL COMPOSITION	
(Model/Dry Cake)**		(C Analysis, dry basis)	
20 deg C	44.89% K+	43.86%	<=== back-calculated
	0% CO ₃ =	0%	
	55.09% SO ₄ =	56.14%	
	0.02% Cl-	0%	

** Model assumes 0.2480 gram moisture/gram dry cake

TABLE 4-9. MATERIAL BALANCE RESULTS FOR WSD13B - EFFECT OF RECYCLE - "LOW CHLORIDE" CASE (NET SOLIDS FEED $K_2CO_3:K_2SO_4$ WT RATIO = 0.589:1, NET SOLIDS FEED $Cl:K$ WT RATIO = 0.0037:1)

WSD13B - MATERIAL BALANCE SUMMARY @ 20 DEG C					
0.1702 g moisture/g dry cake					
	Combined Feed*	Dry Cake	Slurry	Wet Cake 3	Centrate 4
K ₂ CO ₃	48.2331	0.000	48.233	0.714	47.520
K ₂ SO ₄	9.4254	9.343	0.082	9.344	0.081
KCl	0.5017	0.000	0.502	0.007	0.494
3/2 H ₂ O	0	0.000		0.000	
H ₂ O	58.6728		58.673	0.868	57.80
TOTAL	117	9	107	11	106
		44.89%	Wt.% K+	42.09%	25.67%
		0.00%	Wt.% CO ₃ =	2.83%	19.48%
		55.11%	Wt.% SO ₄ =	47.10%	0.04%
		0.000%	Wt.% Cl-	0.032%	0.222%

COMPARISON OF MODEL PREDICTIONS @ 20 deg C
w/ RESULTS OF EXPERIMENT WSD13B

CENTRATE					
EXPECTED COMPOSITION			ACTUAL COMPOSITION		
(Model/Sat'd Solution)*			(F Analysis)		
20 deg C	25.67%	K+	25.94%	<=== back-calculated	
	19.48%	CO ₃ =	19.69%		
	0.04%	SO ₄ =	0.04%		
	0.22%	Cl-	0.22%		

*K₂SO₄, K₂CO₃ from Mellor; KCl from Experiment WSD3

WET CAKE					
EXPECTED COMPOSITION			ACTUAL COMPOSITION		
(Model/Wet Cake)**			(C Analysis)		
20 deg C	42.09%	K+	42.13%	<=== back-calculated	
	2.83%	CO ₃ =	3.02%		
	47.10%	SO ₄ =	46.87%		
	0.032%	Cl-	0.040%		

** Model assumes 0.1702 gram moisture/gram dry cake

DRY CAKE					
EXPECTED COMPOSITION			ACTUAL COMPOSITION		
(Model/Dry Cake)**			(C Analysis, dry basis)		
20 deg C	44.89%	K+	46.06%	<=== back-calculated	
	0%	CO ₃ =	0.18%		
	55.11%	SO ₄ =	54.89%		
	0%	Cl-	0.008%		

** Model assumes 0.1702 gram moisture/gram dry cake

of experiments were planned and performed to verify the individual processing steps described above. For more details on the proposed process for removing chloride from low chloride spent seed see Section 5.3.3.1.

4.3.1.1 *Description of Experiments*

An experiment was performed (WSD5) to show that pure K_2CO_3 can be crystallized from a K_2CO_3 solution containing KCl at a low initial concentration (step 1 above). This experiment was devised to qualitatively validate the proposed K_2CO_3 /KCl separation scheme by confirming that virtually pure K_2CO_3 can be crystallized without co-precipitating KCl from an aqueous K_2CO_3 solution containing KCl as an impurity.

Water was evaporated from a K_2CO_3 -KCl- H_2O solution in a vacuum apparatus. The starting concentration of the solution was 45 wt% K_2CO_3 and 0.47 wt% KCl (0.22 wt% Cl^-) in water. The evaporated water was condensed, collected and measured. Periodically, samples of the solution above the crystalline solids precipitate were taken and filtered. The solution samples were analyzed for K^+ , CO_3^{2-} and Cl^- content to determine if the chloride concentration in a saturated carbonate solution increased when water and carbonate crystals are removed. The carbonate crystals formed during the experiment were analyzed for chloride. The results of this experiment are discussed in detail in Section 4.3.1.2.

A second experiment (WSD8) was performed to confirm the literature double salt point (solution saturated with both K_2CO_3 and KCl) at 84°C. This experiment was devised to quantitatively verify that virtually pure K_2CO_3 can be crystallized without co-precipitating KCl from an aqueous K_2CO_3 solution containing KCl as an impurity. The ultimate objective of the K_2CO_3 crystallization/KCl concentration experiments was to determine, at a given temperature, the maximum concentration of KCl that may be attained in an aqueous saturated K_2CO_3 solution before KCl begins to co-precipitate with K_2CO_3 . This information was readily obtained from a series of experiments in which mixtures with varying initial concentrations of KCl in the saturated K_2CO_3 solutions were heated to the temperature of

interest and were then filtered at this temperature to separate the solid material from the solution in equilibrium with it. The filter cakes were then analyzed for chloride ion content.

Four sub-experiments were performed. In each experiment K_2CO_3 saturation was assured by preparing a mixture containing carbonate at 19% in excess of its saturation value in $K_2CO_3/KCl/H_2O$ solution at $84^\circ C$. In the first experiment, the initial mixture contained KCl at 18% below its saturation level in aqueous K_2CO_3 solution at $84^\circ C$. In the second experiment, KCl was present at its saturation level, and for the last two experiments, KCl was present at 18% and 37% excess saturation, respectively. When the initial solution is not saturated in KCl, no chloride is expected to be found in the filter cake. When the initial solution is saturated in KCl, any excess KCl in the initial mixture is expected to co-precipitate with the K_2CO_3 . Pre-weighed amounts of K_2CO_3 , KCl and water were refluxed at $84^\circ C$, then filtered at temperature. The filtrates and cakes were analyzed for K^+ , $CO_3^{=}$ and Cl^- and the results were compared with the saturation value (double salt point) given in the literature. The results of this experiment are discussed in detail in Section 4.3.1.2.

An experiment was performed (WSD9) to verify steps (2) and (3) in the process description given above (crystallization of K_2CO_3 and KCl from the residual mother liquor from step (1) and redissolving the K_2CO_3 crystals in water). The simulated slurry prepared for this experiment contained a 10:1 ratio of mother liquor to wet cake ($\sim 10\%$ solids). The slurry was refluxed at $84^\circ C$ and then filtered. The filtrate was allowed to cool to room temperature overnight which caused more solids to precipitate from this solution which was initially solids-free but saturated with carbonate and chloride at $84^\circ C$. This step was intended to simulate the conditions in the K_2CO_3/KCl crystallizer at $20^\circ C$. The slurry was filtered and samples of the filtrate and cake taken for analysis. The cake was then used in an experiment which simulated the conditions in the K_2CO_3 dissolver at $20^\circ C$. That is, the cake composition (as measured) and the K_2CO_3/KCl double salt point at $20^\circ C$ given in the literature were used to calculate the minimum amount of water to be added to the cake in order to dissolve all the K_2CO_3 in the cake. This amount of water was added to the cake, the mixture was stirred and then filtered. The filtrate (which should be saturated in both carbonate and chloride) and cake were analyzed for K^+ , CO_3^{+} and Cl^- and compared with

the double salt point saturation values given in the literature. The results of this experiment are discussed in detail in Section 4.3.1.2.

4.3.1.2 *Discussion of Individual Test Results*

4.3.1.2.1 K_2CO_3 Crystallization from a K_2CO_3 /KCl Solution

An experiment was performed (WSD5) to verify that pure K_2CO_3 could be crystallized from a concentrated K_2CO_3 solution also containing KCl. A solution containing 45 wt% K_2CO_3 and 0.47 wt% KCl was prepared. This solution was evaporated at a constant temperature of 200°F (93°C) until ~65% of the original water in the solution was evaporated. Samples of the mother liquor and crystals in the evaporation flask were taken at this point for analysis. (Note: crystals were observed to have had precipitated from solution before this point of evaporation had been reached.) The mother liquor was 57.81 wt% K_2CO_3 and 1.43 wt% KCl. The crystals were pure K_2CO_3 with no detectable chloride content.

How the mother liquor composition compares with what would be expected at ~65% water evaporation is a trial and error calculation with the percent K_2CO_3 crystallized unknown. At ~55% K_2CO_3 crystallization and ~65% water evaporation (with an additional ~9% water taken up as hydrate in the K_2CO_3 crystals), the calculated composition of the residual mother liquor is 57.92 wt% K_2CO_3 and 1.34 wt% KCl. This is a close match to the measured mother liquor composition. It is not expected that KCl would crystallize from solution until the double salt point, the composition at which the mother liquor is saturated with respect to both K_2CO_3 and KCl, is reached. According to the literature (Seidell's "Solubilities of Inorganic and Metal-Organic Compounds," Fourth Edition, Volume II, page 86 (Berg and Nikolajev, 1937), see Table 4-10) this will occur at 200°F (93°C), at a solution composition of 58.5 wt% K_2CO_3 and 2.4 wt% KCl. With regard to this particular experiment, had the evaporation been continued, the onset of KCl co-precipitation would have been expected once ~74% of the water had been evaporated (causing ~75% of the K_2CO_3 to have crystallized from solution).

TABLE 4-10. DOUBLE POINT SOLUTION SATURATED WITH BOTH K_2CO_3 AND KCl ¹

TEMPERATURE °C	GRAMS PER 100 GRAMS SATURATED SOLUTION		GRAMS PER 100 GRAMS WATER		SOLID PHASE
	K_2CO_3	KCl	K_2CO_3	KCl	
20	51.9	0.8	109.7	1.7	$K_2CO_3 \cdot 1\frac{1}{2}H_2O + KCl$
30	52.22	1.03	111.7	2.2	"
50	53.63	1.40	119.8	3.1	"
70	56.06	2.00	133.7	4.8	"
84	57.16	2.21	140.8	5.45	"
100	59.44	2.48	155.0	6.5	"
124.5	65.33	2.68	180.7	7.7	"
133.5 ²					

¹ FROM SEIDELL'S SOLUBILITIES OF INORGANIC AND METAL-ORGANIC COMPOUNDS, FOURTH EDITION, 1965, VOLUME II, PAGE 86 (BERG AND NIKOLAJEV, 1937).

² CONSTANT BOILING SOLUTION.

Additional experiments (WSD8) were conducted to determine, at a given temperature, the maximum KCl concentration that may be attained in an aqueous saturated K_2CO_3 solution before KCl begins to co-precipitate with the K_2CO_3 . This was achieved by mixing varying amounts of K_2CO_3 , KCl and water into a flask, stirring at constant temperature ($84^\circ C$) for ~ 1 hour and then analyzing the resulting solution and solids. A total of four (4) experiments were conducted. In all of the cases excess K_2CO_3 (above that required for double salt point saturation) was utilized. The amount of KCl added was varied from less than to more than that required for double salt point saturation. The material balance results for this experiment are presented in Tables 4-11 through 4-14. For the case (WSD8A) in which insufficient KCl had been added to reach the solution double salt point at $84^\circ C$ (57.16 wt% K_2CO_3 , 2.21 wt% KCl), the crystals analyzed as virtually ($<0.1\%$) chloride free. For the cases (WSD8B,C&D) in which sufficient KCl had been added to reach and then exceed the KCl concentration at the double salt point, the crystal analyses indicated that the excess KCl had remained in the crystal form. In all three of these cases, the saturated solution and cake compositions (Tables 4-15 and 4-16) were essentially that predicted (by the literature, Table 4-10) for the double salt point at $84^\circ C$.

4.3.1.2.2 K_2CO_3 /KCl Crystallization from a Double Salt Point Solution

An experiment (WSD9-step 2) was performed to verify that K_2CO_3 and KCl crystals could be co-precipitated from a double salt point solution by a reduction in solution temperature. A solution was prepared that was saturated in both K_2CO_3 and KCl at $84^\circ C$. This solution was analyzed as containing 56.85 wt% K_2CO_3 and 2.15 wt% KCl. The literature double salt point concentration at $84^\circ C$ is 57.19 wt% and 2.21 wt% KCl. This solution was then allowed to cool overnight to ambient ($20^\circ C$) temperature. Crystals were observed to have precipitated from solution. The cooled solution and crystals were analyzed. The experimental results are presented in Figure 4-5 and Tables 4-17 and 4-18. The crystals consisted of a mixture of K_2CO_3 and KCl. The solution analyzed as 51.92 wt% K_2CO_3 and 0.86 wt% KCl. This is very close to the expected double salt point concentration (51.89 wt% K_2CO_3 and 0.80 wt% KCl) at $20^\circ C$ from the literature (Table 4-10). Thus, reducing the temperature of the $84^\circ C$ double salt point solution to $20^\circ C$, caused the solution to follow

TABLE 4-11. MATERIAL BALANCE RESULTS FOR WSD8A - CO-PRECIPITATION OF KCl FROM A K_2CO_3/KCl SOLUTION - INSUFFICIENT KCl PRESENT

WSD8A (84 deg C)						
START	167.9370 g K_2CO_3			97.3556 g K^+		
	0 g K_2SO_4	---->		0 g Na^+		
	0 g Na_2CO_3			72.9104 g $CO_3=$		
	0 g Na_2SO_4			0 g $SO_4=$		
	4.4501 g KCl			2.1163 g Cl^-		
	<u>105.4731</u> g H_2O			105.4731 g H_2O		
	277.8602					
226.94 g CENTRATE		50.32 g WET CAKE		TOTAL	(TOT/START)	
	<u>(% w/w)</u>	<u>(g)</u>	<u>(% w/w)</u>	<u>(g)</u>	<u>CLOSURE</u>	
K^+	33.01%	74.9129	44.45%	22.3672	97.2801	0.999
Na^+	0%	0.0000	0%	0.0000	0	NA
$CO_3=$	24.59%	55.8045	33.90%	17.0585	72.8630	0.999
$SO_4=$	0%	0.0000	0%	0.0000	0	NA
Cl^-	0.87%	<u>1.9744</u>	0.24%	<u>0.1208</u>	2.0951	0.990
		132.6918		39.5465		
H_2O		226.9400		50.3200 total		
	-	<u>132.6918</u>		- <u>39.5465</u> ions		
		94.2482		10.7735 water + hydrate		
				- <u>6.5574</u> hydrate		
CORRECT WET SOLIDS TO DRY SOLIDS:				4.2161 water>	10.15 g moisture	
	<u>CENTRATE</u>		<u>DRY SOLID</u>	<u>(%w/w)</u>		
K^+	78.2640 g		19.0161 g	47.34%		
Na^+	0.0000 g		0.0000 g			
$CO_3=$	58.3009 g		14.5621 g	36.25%		
$SO_4=$	0.0000 g		0.0000 g			
Cl^-	2.0627 g		0.0324 g	0.08%		
H_2O	98.4643 g	(hydrate)	<u>6.5574</u> g	105.0217	0.996	
			40.1681 g			

TABLE 4-12. MATERIAL BALANCE RESULTS FOR WSD8B - CO-PRECIPITATION OF KCl FROM A K_2CO_3/KCl SOLUTION - EXCESS KCl PRESENT

WSD8B (84 deg C)						
START	168.5230 g K_2CO_3			98.2117 g K^+		
	0 g K_2SO_4	----->		0 g Na^+		
	0 g Na_2CO_3			73.1648 g $CO_3=$		
	0 g Na_2SO_4			0 g $SO_4=$		
	5.4503 g KCl			2.5919 g Cl^-		
	<u>105.2545</u> g H_2O			105.2545 g H_2O		
	279.2278					
223.82 g CENTRATE		54.24 g WET CAKE		TOTAL	(TOT/START)	
	(% w/w) (g)		(% w/w) (g)	(g)	CLOSURE	
K^+	32.91% 73.6592		45.11% 24.4677	98.1268	0.999	
Na^+	0% 0.0000		0% 0.0000	0	NA	
$CO_3=$	24.42% 54.6568		34.10% 18.4958	73.1527	1.000	
$SO_4=$	0% 0.0000		0% 0.0000	0	NA	
Cl^-	0.98% <u>2.1934</u>		0.60% <u>0.3254</u>	2.5189	0.972	
	130.5094		43.2889			
H_2O	223.8200		54.2400 total			
	- <u>130.5094</u>		- <u>43.2889</u> ions			
	93.3106		10.9511 water + hydrate			
			- <u>7.3893</u> hydrate			
CORRECT WET SOLIDS TO DRY SOLIDS:			3.5618 water>	8.54 g moisture		
	<u>CENTRATE</u>		<u>DRY SOLID</u>	<u>(%w/w)</u>		
K^+	76.4708 g		21.6561 g	47.39%		
Na^+	0.0000 g		0.0000 g			
$CO_3=$	56.7431 g		16.4096 g	35.91%		
$SO_4=$	0.0000 g		0.0000 g			
Cl^-	2.2772 g		0.2417 g	0.53%		
H_2O	96.8723 g	(hydrate)	<u>7.3893</u> g	104.2616	0.991	
			45.6966 g			

TABLE 4-13. MATERIAL BALANCE RESULTS FOR WSD8C - CO-PRECIPITATION OF KCl
FROM A K_2CO_3 /KCl SOLUTION - EXCESS KCl PRESENT

WSD8C (84 deg C)						
START	168.1286 g K_2CO_3			98.5168 g K^+		
	0 g K_2SO_4	---->		0 g Na^+		
	0 g Na_2CO_3			72.9936 g $CO_3=$		
	0 g Na_2SO_4			0 g $SO_4=$		
	6.4576 g KCl			3.0709 g Cl^-		
	<u>105.3466</u> g H_2O			105.3466 g H_2O		
	279.9328					
219.80 g CENTRATE		59.03 g WET CAKE		TOTAL	(TOT/START)	
	<u>(% w/w)</u>	<u>(g)</u>	<u>(% w/w)</u>	<u>(g)</u>	<u>CLOSURE</u>	
K^+	32.86%	72.2263	44.01%	25.9791	98.2054	0.997
Na^+	0%	0.0000	0%	0.0000	0	NA
$CO_3=$	24.36%	53.5433	32.63%	19.2615	72.8048	0.997
$SO_4=$	0%	0.0000	0%	0.0000	0	NA
Cl^-	1.01%	<u>2.2200</u>	1.34%	<u>0.7910</u>	3.0110	0.980
		127.9895		46.0316		
H_2O		219.8000		59.0300 total		
	-	<u>127.9895</u>		- <u>46.0316</u> ions		
		91.8105		12.9984 water + hydrate		
				- <u>7.1333</u> hydrate		
CORRECT WET SOLIDS TO DRY SOLIDS:				5.8651 water>	14.04 g moisture	
	<u>CENTRATE</u>		<u>DRY SOLID</u>	<u>(%w/w)</u>		
K^+	76.8403 g		21.3651 g	47.49%		
Na^+	0.0000 g		0.0000 g			
$CO_3=$	56.9638 g		15.8410 g	35.21%		
$SO_4=$	0.0000 g		0.0000 g			
Cl^-	2.3618 g		0.6492 g	1.44%		
H_2O	97.6756 g	(hydrate)	<u>7.1333</u> g	104.8089	0.995	
			44.9886 g			

TABLE 4-14. MATERIAL BALANCE RESULTS FOR WSD8D - CO-PRECIPITATION OF KCl FROM A K₂CO₃/KCl SOLUTION - EXCESS KCl PRESENT

WSD8D (84 deg C)						
START	168.1258 g	K ₂ CO ₃		99.0413 g	K+	
	0 g	K ₂ SO ₄	----->	0 g	Na+	
	0 g	Na ₂ CO ₃		72.9924 g	CO ₃ =	
	0 g	Na ₂ SO ₄		0 g	SO ₄ =	
	7.4607 g	KCl		3.5480 g	Cl-	
	<u>105.4772</u> g	H ₂ O		105.4772 g	H ₂ O	
	281.0637					
220.29 g	CENTRATE		58.67 g	WET CAKE		TOTAL (TOT/START)
	(% w/w)	(g)		(% w/w)	(g)	CLOSURE
K+	32.90%	72.4754		44.56%	26.1434	98.6188 0.996
Na+	0%	0.0000		0%	0.0000	0 NA
CO ₃ =	24.40%	53.7508		32.46%	19.0443	72.7950 0.997
SO ₄ =	0%	0.0000		0%	0.0000	0 NA
Cl-	1.00%	<u>2.2029</u>		2.04%	<u>1.1969</u>	3.3998 0.958
		128.4291			46.3845	
H ₂ O		220.2900		58.6700	total	
	-	<u>128.4291</u>		-	<u>46.3845</u>	ions
		91.8609			12.2855	water + hydrate
				-	<u>7.2486</u>	hydrate
CORRECT WET SOLIDS TO DRY SOLIDS:				5.0369	water>	12.08 g moisture
	CENTRATE			DRY SOLID		(%w/w)
K+	76.4494 g			22.1694 g		47.58%
Na+	0.0000 g			0.0000 g		
CO ₃ =	56.6980 g			16.0970 g		34.55%
SO ₄ =	0.0000 g			0.0000 g		
Cl-	2.3237 g			1.0761 g		2.31%
H ₂ O	96.8979 g		(hydrate)	<u>7.2486</u> g	104.1464	0.987
				46.5911 g		

TABLE 4-15. COMPARISON OF LITERATURE DOUBLE SALT POINT WITH FILTRATE RESULTS OF EXPERIMENT WSD8 - CO-PRECIPITATION OF KCl FROM A K_2CO_3/KCl SOLUTION

EXPECTED COMPOSITION			ACTUAL COMPOSITION	
<u>(Unsaturated Solution)</u>			<u>(Filtrate Analysis)</u>	
WSD8A	33.43%	K+	33.01%	$\leq$ corrected
84 deg C	24.93%	CO ₃ =	24.59%	
	0.861%	Cl-	0.87%	
<u>(Sat'd Sol'n/Dbl Salt Pt.)*</u>			<u>(Filtrate Analysis)</u>	
WSD8B	33.51%	K+	32.91%	$\leq$ corrected
84 deg C	24.82%	CO ₃ =	24.42%	
	1.05%	Cl-	0.98%	
<u>(Sat'd Sol'n/Dbl Salt Pt.)*</u>			<u>(Filtrate Analysis)</u>	
WSD8C	33.51%	K+	32.86%	$\leq$ corrected
84 deg C	24.82%	CO ₃ =	24.36%	
	1.05%	Cl-	1.01%	
<u>(Sat'd Sol'n/Dbl Salt Pt.)*</u>			<u>(Filtrate Analysis)</u>	
WSD8D	33.51%	K+	32.90%	$\leq$ corrected
84 deg C	24.82%	CO ₃ =	24.40%	
	1.05%	Cl-	1.00%	

*Seidell's "Solubilities of Inorganic and Metal-Organic Compounds," Fourth Edition, Volume II, page 86
(Berg and Nikolajev, 1937)

TABLE 4-16. COMPARISON OF MODEL PREDICTIONS FOR DRY CAKE (BASED ON LITERATURE DOUBLE SALT POINT) WITH RESULTS OF EXPERIMENT WSD8 - CO-PRECIPIATION OF KCl FROM A K_2CO_3 /KCl SOLUTION

DRY CAKES				
EXPECTED COMPOSITION			ACTUAL COMPOSITION	
<u>(Model/Dry Cake)*</u>			<u>(Cake Analysis, Dry Basis)</u>	
WSD8A	47.33%	K+	47.34%	<=== corrected
84 deg C	36.31%	CO3=	36.25%	
	0%	Cl-	0.08%	
<u>(Model/Dry Cake)**</u>			<u>(Cake Analysis, Dry Basis)</u>	
WSD8B	47.33%	K+	47.39%	<=== corrected
84 deg C	36.30%	CO3=	35.91%	
	0.02%	Cl-	0.53%	
<u>(Model/Dry Cake)***</u>			<u>(Cake Analysis, Dry Basis)</u>	
WSD8C	47.48%	K+	47.49%	<=== corrected
84 deg C	35.23%	CO3=	35.21%	
	1.42%	Cl-	1.44%	
<u>(Model/Dry Cake)****</u>			<u>(Cake Analysis, Dry Basis)</u>	
WSD8D	47.63%	K+	47.58%	<=== corrected
84 deg C	34.20%	CO3=	34.55%	
	2.77%	Cl-	2.31%	

Model based on literature double salt point @ 84 deg C

* assumes 0.25 gram moisture/gram dry cake

** assumes 0.19 gram moisture/gram dry cake

*** assumes 0.31 gram moisture/gram dry cake

**** assumes 0.26 gram moisture/gram dry cake

Figure 4-5. Experimental Results for WSD9 (Steps 1 and 2) - K₂CO₃ Crystallization Followed by K₂CO₃/KCl Crystallization from a Double Salt Point Solution

TABLE 4-17. COMPARISON OF MODEL PREDICTIONS FOR K_2CO_3 CRYSTALLIZATION (STEP 1), K_2CO_3/KCl CRYSTALLIZATION (STEP 2) AND K_2CO_3 DISSOLUTION (STEP 3) (BASED ON LITERATURE DOUBLE SALT POINT) WITH RESULTS OF EXPERIMENT WSD9

EXPECTED COMPOSITION			ACTUAL COMPOSITION	
<u>(Model/Sat'd Solution)*</u>			<u>(F1 Analysis)</u>	
Step One	33.51%	K+	33.28%	<=== corrected
84 deg C	24.83%	CO3=	24.68%	
	1.05%	Cl-	1.02%	
<u>(Model/Sat'd Solution)*</u>			<u>(F2 Analysis)</u>	
Step Two	29.78%	K+	29.82%	<=== corrected
20 deg C	22.53%	CO3=	22.54%	
	0.38%	Cl-	0.41%	
<u>(Model/Sat'd Solution)*</u>			<u>(F3 Analysis)</u>	
Step Three	29.78%	K+	29.83%	<=== corrected
20 deg C	22.53%	CO3=	22.53%	
	0.38%	Cl-	0.43%	

*Seidell (Berg & Nikolajev)

WET CAKES				
EXPECTED COMPOSITION			ACTUAL COMPOSITION	
<u>(Model/Wet Cake)**</u>			<u>(C1 Analysis)</u>	
Step One	46.07%	K+	43.62%	<=== corrected
84 deg C	35.27%	CO3=	32.82%	
	0.10%	Cl-	0.77%	
<u>(Model/Wet Cake)**</u>			<u>(C2 Analysis)</u>	
Step Two	46.08%	K+	45.23%	<=== corrected
20 deg C	32.56%	CO3=	32.06%	
	3.31%	Cl-	3.13%	
<u>(Model/Wet Cake)**</u>			<u>(C3 Analysis)</u>	
Step Three	50.38%	K+	50.04%	<=== corrected
20 deg C	2.05%	CO3=	4.54%	
	43.27%	Cl-	40.01%	

** Model assumes 0.1 gram moisture/gram dry cake

TABLE 4-18. COMPARISON OF MODEL PREDICTIONS FOR K_2CO_3 CRYSTALLIZATION (STEP 1), K_2CO_3/KCl CRYSTALLIZATION (STEP 2) AND K_2CO_3 DISSOLUTION (STEP 3) (USING ACTUAL CAKE MOISTURE VALUES) WITH RESULTS OF EXPERIMENT WSD9

WET CAKES				
EXPECTED COMPOSITION			ACTUAL COMPOSITION	
<u>(Model/Wet Cake)*</u>			<u>(C1 Analysis)</u>	
Step One	43.60%	K+	43.62%	<=== corrected
84 deg C	33.21%	CO3=	32.82%	
	0.28%	Cl-	0.77%	
<u>(Model/Wet Cake)**</u>			<u>(C2 Analysis)</u>	
Step Two	45.24%	K+	45.23%	<=== corrected
20 deg C	32.04%	CO3=	32.06%	
	3.16%	Cl-	3.13%	
<u>(Model/Wet Cake)***</u>			<u>(C3 Analysis)</u>	
Step Three	50.38%	K+	50.04%	<=== corrected
20 deg C	2.05%	CO3=	4.54%	
	43.27%	Cl-	40.01%	

* assumes 0.37 gram moisture/gram dry cake

** assumes 0.16 gram moisture/gram dry cake

*** assumes 0.10 gram moisture/gram dry cake

the double salt point curve (Figure 4-6) and resulted in the co-precipitation of K_2CO_3 and KCl.

4.3.1.2.3 Selective Dissolution of K_2CO_3 from K_2CO_3 /KCl Crystals

An experiment (WSD9-step 3) was performed to verify that K_2CO_3 could be selectively dissolved from a mixture of K_2CO_3 /KCl crystals with water. The K_2CO_3 /KCl crystals that co-precipitated in experiment WSD9-step 2, as described above, were mixed with an amount of water that was calculated (based on literature data) to be the minimum amount required for complete dissolution of the K_2CO_3 . The dissolution was carried out at 20°C. The residual undissolved crystals and the solids-free solution were analyzed. The experimental results are presented in Figure 4-7 and Tables 4-17 and 4-18. The wet crystals analyzed as being 84.1 wt% KCl and 10.5 wt% K_2CO_3 . It was determined by water balance that the wet crystals contained ~0.1 lbs moisture/lb dry crystals. Correcting for this moisture content, the dry crystals contained ~95 Wt% KCl and ~5 wt% K_2CO_3 . Based on this analysis, it can be seen that TRW had slightly underestimated the minimum amount of water required for complete K_2CO_3 dissolution (residual dry crystals in this instance would be 100% KCl). The saturated solution in equilibrium with the crystals contained 51.89 wt% K_2CO_3 and 0.90 wt% KCl. This is very close to the expected 20°C double salt point concentration of 51.89 wt% K_2CO_3 and 0.80 wt% KCl as reported in the literature (Table 4-10). Therefore, it appears that K_2CO_3 can be selectively dissolved from a mixture of K_2CO_3 and KCl crystals.

4.3.1.3 *Summary of Test Results*

4.3.1.3.1 K_2CO_3 Crystallization from a K_2CO_3 /KCl Solution

Experiments (WSD5, WSD8 and WSD9) were performed that successfully demonstrated that pure K_2CO_3 could be crystallized from an aqueous K_2CO_3 /KCl solution as long as the K_2CO_3 :KCl ratio in the feed solution is greater than the K_2CO_3 :KCl ratio in the saturated solution at the double salt point at the crystallization temperature. The equilibrium solution concentrations measured at the double salt point were in close agreement with those reported in the literature for the K_2CO_3 -KCl- H_2O system.

Figure 4-6. Double Salt Point Curve for Aqueous Solution Saturated with Both K_2CO_3 and KCl

Figure 4-7. Experimental Results for WSD9 (Step 3) - Selective Dissolution of K₂CO₃ form K₂CO₃/KCl Crystals

4.3.1.3.2 K_2CO_3/KCl Crystallization from a Double-Salt Point Solution

An experiment (WSD9) was performed that successfully demonstrated that K_2CO_3/KCl crystals could be precipitated from a double salt point saturated solution by reducing the solution temperature. The equilibrium solution concentrations measured at the double salt point at the reduced temperature were in close agreement with those reported in the literature for the $K_2CO_3-KCl-H_2O$ system.

4.3.1.3.3 Selective Dissolution of K_2CO_3 from K_2CO_3/KCl Crystals

An experiment (WSD9) was performed that successfully demonstrated that K_2CO_3 (and some KCl) could be dissolved from a mixture of K_2CO_3/KCl crystals with water leaving a residue of relatively pure KCl crystals. The measured dissolver equilibrium solution concentration was in close agreement with that reported in the literature for the $K_2CO_3-KCl-H_2O$ system.

4.3.2 Rejection of Chloride from High Chloride Spent Seed

A process scheme similar to the one described in Section 4.3.1 above for a low chloride seed was proposed for a high chloride seed (see Section 5.3.3.2 for more details of the proposed process for removing chloride from high chloride spent seed). The main difference is that in step (1) KCl (instead of K_2CO_3) is precipitated from solution. Steps (2), (3) and (4) are the same as described above. The four steps are as follows:

- 1) crystallizing pure KCl from the K_2CO_3 solution by evaporation of water,
- 2) crystallizing K_2CO_3 and KCl from the residual mother liquor from step (1) by reducing its temperature,
- 3) redissolving the K_2CO_3 in the crystals from step (2) in water leaving a residue of KCl crystals, and
- 4) crystallizing K_2CO_3 from the mother liquor from step (3) by evaporation of water.

4.3.2.1 *Description of Experiment*

An experiment (WSD10) was designed and performed to show that pure KCl can be crystallized from a K_2CO_3 solution containing KCl at a relatively high initial concentration as long as the KCl: K_2CO_3 ratio is greater than the KCl: K_2CO_3 ratio of the saturated solution at the crystallizer double salt point.

The simulated K_2CO_3 -KCl slurry prepared for this experiment contained a 10:1 ratio of mother liquor-to-wet cake (initially consisting of KCl crystals). The slurry was refluxed at 84°C and then filtered. The filtrate and cake were analyzed for $CO_3^{=}$ and Cl^- . The results of this experiment are discussed in detail in Section 4.3.2.2.

4.3.2.2 *Discussion of Individual Test Results*

As water is evaporated from the K_2CO_3 /KCl solution, KCl should start to precipitate from solution before the K_2CO_3 if the KCl: K_2CO_3 ratio in the evaporator feed solution is greater than the KCl: K_2CO_3 ratio in the double salt point solution at the evaporator/crystallizer operating temperature. This could very well be the case for an MHD plant utilizing a high chloride content coal and operating with a relatively low K_2 :S ratio in the channel. In WSD10, crystallizer operation was simulated for a feed solution having a KCl: K_2CO_3 ratio in excess of the ratio expected at the crystallizer's double salt point, the concentration at which KCl crystals should begin to be contaminated by the co-precipitation of K_2CO_3 . In WSD10, KCl crystals were mixed with a simulated mother liquor solution (double salt point solution at 84°C) in a ~1:10 weight ratio (to give a ~10 wt% slurry). This slurry was agitated and held at temperature for 2 hours. At this time samples were taken of the solution and the crystals.

The experimental results are presented in Figure 4-8 and Tables 4-19 and 4-22. It was expected that the system would undergo no change. That is, the crystalline material would remain pure KCl and the solution would remain at the double salt point. The crystals however analyzed on a dry basis to be ~75 wt% KCl, 21 wt% K_2CO_3 (with ~4 wt% hydrate H_2O). The solution was analyzed to contain 56.89 wt% K_2CO_3 and 2.06 wt% KCl.

Figure 4-8. Experimental Results for WSD10 - KCl Crystallization from a K₂CO₃/KCl Solution

TABLE 4-19. MATERIAL BALANCE RESULTS FOR WSD10 - KCl CRYSTALLIZATION FROM A K_2CO_3 /KCl SOLUTION - @ 84°C - ADJUSTED FEED BASIS¹
¹(adjusted for unfiltered flask residue (3.4 gms) plus system water loss (0.99 + 0.91 = 1.90 gms))

Saturation Values		84 deg C		Wt.% K+	33.51%
K ₂ CO ₃	1.408	g/gH ₂ O	Wt.% CO ₃	24.82%	
KCl	0.0545	g/gH ₂ O	Wt.% Cl-	1.05%	
WSD10 SUMMARY					
0.24 g moisture/g dry cake					
	Feed	Dry Cake	Liquid	Wet Cake	Centrate
				3	4
K ₂ CO ₃	124.8191	3.486	121.333	6.774	118.045
KCl	24.5254	19.829	4.696	19.956	4.569
3/2 H ₂ O	0	0.682		0.682	
H ₂ O	86.8555		86.174	2.335	83.839
TOTAL	236	24	212	30	206
		51.56%	Wt.% K+	48.07%	33.51%
		6.31%	Wt.% CO ₃	9.89%	24.82%
		39.295%	Wt.% Cl-	31.904%	1.052%

COMPARISON OF MODEL PREDICTIONS @ 84 deg C
w/ RESULTS OF EXPERIMENT WSD10

CENTRATE

EXPECTED COMPOSITION

ACTUAL COMPOSITION

(Model/Sat'd Solution)*

(F1 Analysis)

Step One	33.51%	K+	33.27%	<=== back-calculated
84 deg C	24.82%	CO ₃ =	24.70%	
	1.05%	Cl-	0.98%	

* Seidell (Berg & Nikolajev)

WET CAKE

EXPECTED COMPOSITION

ACTUAL COMPOSITION

(Model/Wet Cake)**

(C1 Analysis)

Step One	48.07%	K+	47.68%	<=== back-calculated
84 deg C	9.89%	CO ₃ =	12.29%	
	31.90%	Cl-	28.71%	

** Model assumes 0.24 gram moisture/gram dry cake

DRY CAKE

EXPECTED COMPOSITION

ACTUAL COMPOSITION

(Model/Dry Cake)**

(C1 Analysis, dry basis)

Step One	51.56%	K+	51.13%	<=== back-calculated
84 deg C	6.31%	CO ₃ =	9.32%	
	39.30%	Cl-	35.36%	

** Model assumes 0.24 gram moisture/gram dry cake

TABLE 4-20. MATERIAL BALANCE RESULTS FOR WSD10 - KCl CRYSTALLIZATION FROM A K_2CO_3/KCl SOLUTION - @ $\sim 80^\circ C$ - ADJUSTED FEED BASIS¹
¹(adjusted for unfiltered flask residue (3.4 gms) plus system water loss (0.99 + 0.91 = 1.90 gms))

Saturation					
Values	74 - 80 deg C		Wt.% K+		33.27%
K2CO3	1.386	g/gH2O	Wt.% CO3	24.70%	
KCl	0.0502	g/gH2O	Wt.% Cl-	0.98%	
WSD10 SUMMARY					
0.24 g moisture/g dry cake					
	Feed	Dry Cake	Liquid	Wet Cake	Centrate
				3	4
K2CO3	124.8191	6.087	118.732	9.836	114.983
KCl	24.5254	20.225	4.300	20.361	4.165
3/2 H2O	0	1.190		1.190	
H2O	86.8555		85.665	2.705	82.961
TOTAL	236	28	209	34	202
		51.09%	Wt.% K+	47.65%	33.27%
		9.61%	Wt.% CO3	12.53%	24.70%
		34.972%	Wt.% Cl-	28.402%	0.980%

COMPARISON OF MODEL PREDICTIONS @ ~ 80 deg C
w/ RESULTS OF EXPERIMENT WSD10

CENTRATE

EXPECTED COMPOSITION

ACTUAL COMPOSITION

(Model/Sat'd Solution)*

(F1 Analysis)

Step One	33.27%	K+	33.27%	<=== back-calculated
84 deg C	24.70%	CO ₃ =	24.70%	
	0.98%	Cl-	0.98%	

* Actual

WET CAKE

EXPECTED COMPOSITION

ACTUAL COMPOSITION

(Model/Wet Cake)**

(C1 Analysis)

Step One	47.65%	K+	47.68%	<=== back-calculated
84 deg C	12.53%	CO ₃ =	12.29%	
	28.40%	Cl-	28.71%	

** Model assumes 0.24 gram moisture/gram dry cake

DRY CAKE

EXPECTED COMPOSITION

ACTUAL COMPOSITION

(Model/Dry Cake)**

(C1 Analysis, dry basis)

Step One	51.09	K+	51.13%	<=== back-calculated
84 deg C	9.61%	CO ₃ =	9.32%	
	34.97%	Cl-	35.36%	

** Model assumes 0.24 gram moisture/gram dry cake

TABLE 4-21. MATERIAL BALANCE RESULTS FOR WSD10 - KCl CRYSTALLIZATION FROM A K_2CO_3 /KCl SOLUTION - @ 84°C AND DESIRED FEED COMPOSITION

Saturation		84 deg C		Wt.% K+	
Values					33.51%
K ₂ CO ₃	1.408	g/gH ₂ O		Wt.% CO ₃	24.82%
KCl	0.0545	g/gH ₂ O		Wt.% Cl-	1.05%
WSD10 SUMMARY					
0.24 g moisture/g dry cake					
	Feed	Dry Cake	Liquid	Wet Cake 3	Centrate 4
K ₂ CO ₃	126.657	0.000	126.657	2.740	123.917
KCl	24.902	19.999	4.903	20.106	4.796
3/2 H ₂ O	0	0.000		0.000	
H ₂ O	89.955		89.955	1.946	88.009
TOTAL	242	20	222	25	217
		52.44%	Wt.% K+	48.79%	33.51%
		0.00%	Wt.% CO ₃	4.80%	24.82%
		47.554%	Wt.% Cl-	38.566%	1.052%

TABLE 4-22. MATERIAL BALANCE RESULTS FOR WSD10 - KCl CRYSTALLIZATION FROM A K_2CO_3 /KCl SOLUTION - @ 84°C AND ACTUAL FEED COMPOSITION (includes measured water loss of 1.9 gms)

Saturation		84 deg C		Wt.% K+	
Values					33.51%
K ₂ CO ₃	1.408	g/gH ₂ O		Wt.% CO ₃	24.82%
KCl	0.0545	g/gH ₂ O		Wt.% Cl-	1.05%
WSD10 SUMMARY					
0.24 g moisture/g dry cake					
	Feed	Dry Cake	Liquid	Wet Cake 3	Centrate 4
K ₂ CO ₃	126.6591	3.729	122.930	7.099	119.560
KCl	24.9054	20.147	4.758	20.278	4.628
3/2 H ₂ O	0	0.729		0.729	
H ₂ O	88.0376		87.309	2.394	84.915
TOTAL	240	25	215	30	209
		51.52%	Wt.% K+	48.04%	33.51%
		6.58%	Wt.% CO ₃	10.11%	24.82%
		38.940%	Wt.% Cl-	31.617%	1.052%

This is close to the double salt point composition expected at $\sim 80^{\circ}\text{C}$. As mentioned the temperature during WSD10 was to have been 84°C . It is possible that a tight enough control on the temperature was not exercised during the experiment. A reduction in temperature of $\sim 4^{\circ}\text{C}$ would have caused both K_2CO_3 and KCl to precipitate from solution thus contaminating the existing KCl crystals with K_2CO_3 . In addition, a system water balance indicated that $\sim 2\%$ of the system's water was lost (due to evaporation leakage) during the experiment. This water loss resulted in K_2CO_3 precipitation from solution (in the ratio of ~ 1.4 grams of K_2CO_3 per gram of water lost) and further contaminated the KCl crystals with K_2CO_3 crystals. In fact $\sim 50\%$ of the K_2CO_3 in the KCl crystals can be credited to this water loss. Had the temperature of the experiment been more tightly controlled and if water vapor leakage from the equipment had not existed (problems less likely to occur in commercial-scale equipment), it is likely that the KCl crystals would have remained essentially K_2CO_3 free. This experiment therefore indicates that given the necessary feed solution ($\text{KCl}:\text{K}_2\text{CO}_3$ in the feed greater than $\text{KCl}:\text{K}_2\text{CO}_3$ at the double salt point) and the proper crystallizer control (temperature), relatively pure KCl can be precipitated from a $\text{K}_2\text{CO}_3/\text{KCl}$ solution.

4.3.2.3 *Summary of Test Results*

Experiments (WSD10) were performed that successfully demonstrated that pure KCl could be crystallized from an aqueous $\text{K}_2\text{CO}_3/\text{KCl}$ solution as long as the $\text{KCl}:\text{K}_2\text{CO}_3$ ratio in the feed solution is greater than the $\text{KCl}:\text{K}_2\text{CO}_3$ ratio in the saturated solution at the double salt point at the crystallization temperature. The equilibrium solution concentrations measured at the double salt point were in close agreement with those reported in the literature for the $\text{K}_2\text{CO}_3\text{-KCl-H}_2\text{O}$ system.

4.4 SEPARATION OF RESIDUAL CARBONATE AND CHLORIDE FROM SULFATE CAKE

The data from the experiments discussed in Section 4.2 above have shown that a sharp separation can be made between K_2CO_3 (and KCl) and K_2SO_4 by selective dissolution of the seed in water. Depending on the wetness of the separated K_2SO_4 cake, a significant fraction

of the feed K_2CO_3 and KCl, although in solution, could be carried as moisture on the cake. Without further treatment of this cake, any K_2CO_3 in the cake moisture will be converted to KCOOH (potassium formate) unnecessarily, and at a cost, in the seed regeneration reactor. The KCl in the cake moisture will likely pass through the regeneration reactor to be recycled to the channel, causing a buildup of the chloride content in the channel plasma. A process scheme was proposed that would selectively separate K_2CO_3 and KCl from the wet K_2SO_4 cake (see Section 5.3.2.2 for more details of the proposed process for the separation of residual carbonate and chloride from wet K_2SO_4 cake).

4.4.1 Description of Experiments

An experiment (WSD12) was designed and performed to demonstrate that K_2CO_3 and KCl can be selectively removed from a wet K_2SO_4 cake by reslurrying the cake with a relatively small amount of water and then separating the resulting phases.

Three simulated slurries were prepared for this experiment at 32, 38 and 45 wt% solids (K_2SO_4) to confirm the expectation that sulfate solubility decreases in a multi-phase system when there is less water available. None of these solutions was saturated in carbonate or chloride, so all of the carbonate and chloride present in the feed (at a weight ratio of K_2CO_3 :KCl of 10.2:1) were expected to be found in the filtrate in this ratio. The slurries were stirred and then filtered. The filtrates and cakes were analyzed for $CO_3^{=}$, Cl^- and $SO_4^{=}$ content. The results of this experiment are discussed in detail in Section 4.4.2.

4.4.2 Discussion of Individual Test Results

In WSD12 simulated sulfate cake (wet with surface moisture containing K_2CO_3 and KCl) was reslurried at 20°C with relatively small amounts of water to form 32, 38 and 45 wt% solids slurries. The slurries were agitated for 2 hours. Samples of the solids and the solids-free solution were taken at this point for analysis. The results of the experiment are summarized in Figures 4-9 through 4-11 and Tables 4-23 through 4-25. As can be seen, in all three cases complete chloride removal from the cake (dry basis) was achieved. The chloride removal achieved for all three cases, on a wet cake basis, was ~97%. In all three

Figure 4-9. Experimental Results for WSD12A - Carbonate (and Chloride) Separation from Wet Sulfate Cake (32 wt% Solids Slurry)

Figure 4-10. Experimental Results for WSD12B - Carbonate (and Chloride) Separation from Wet Sulfate Cake (38 wt% Solids Slurry)

Figure 4-11. Experimental Results for WSD12C - Carbonate (and Chloride) Separation from Wet Sulfate Cake (45 wt% Solids Slurry)

TABLE 4-23. MATERIAL BALANCE RESULTS FOR WDS12A - CARBONATE (AND CHLORIDE) SEPARATION FROM WET SULFATE CAKE (32 WT% SOLIDS SLURRY) - @ 20°C

			WSD12A SUMMARY		0.0931 g moisture/g dry cake			
			Feed*	Dry Cake	Liquid	Wet Cake 3	Centrate 4	
$\frac{K_2CO}{KCl}$	10.2	<===	K2CO3	5.7509	0.000	5.751	0.178	5.573
			K2SO4	49.9859	43.672	6.314	43.867	6.119
			KCl	0.5631	0.000	0.563	0.017	0.546
			3/2 H2O	0	0.000		0.000	
			H2O	118.7002		118.700	3.675	115.03
TOTAL			175	44	131	48	127	
				44.89%	Wt.% K+	41.48%	4.86%	
32% slurry				0.00%	Wt.% CO3	0.16%	1.90%	
				55.11%	Wt.% SO4	50.64%	2.65%	
				0.000%	Wt.% Cl-	0.017%	0.204%	

COMPARISON OF MODEL PREDICTIONS @ 20 deg C
w/ RESULTS OF EXPERIMENT WSD12A

		CENTRATE					
		EXPECTED COMPOSITION			ACTUAL COMPOSITION		
		(Model/Unsat'd Solution)*			(F Analysis)		
$\frac{K_2CO_3}{KCl}$	10.2	<===	20 deg C	4.86%	K+	5.83%	<=== back-calculated
				1.90%	CO3=	1.86%	10.2 $\frac{K_2CO_3}{KCl}$
				2.65%	SO4=	3.95%	
				0.204%	Cl-	0.200%	1.5 $\frac{K_2SO_4}{K_2CO_3+KCl}$

*K₂SO₄ = KCl + K₂CO₃; all KCl, K₂CO₃ in solution

		WET CAKE			
		EXPECTED COMPOSITION	ACTUAL COMPOSITION		
		(Model/Wet Cake)**	(C Analysis)		
20 deg C		41.58%	K+	41.41%	==== back-calculated
		0.16%	CO ₃ =	0.15%	
		50.78%	SO ₄ =	50.61%	
		0.017%	Cl-	0.020%	

* Model assumes 0.0931 gram moisture/gram dry cake

		DRY CAKE			
		EXPECTED COMPOSITION	ACTUAL COMPOSITION		
		(Model/Dry Cake)**	(C Analysis, dry basis)		
20 deg C		44.89%	K+	44.86%	==== back-calculated
		0%	CO ₃ =	0%	
		55.11%	SO ₄ =	55.14%	
		0%	Cl-	0.003%	

* Model assumes 0.0931 gram moisture/gram dry cake

TABLE 4-24. MATERIAL BALANCE RESULTS FOR WDS12B - CARBONATE (AND CHLORIDE) SEPARATION FROM WET SULFATE CAKE (38 WT% SOLIDS SLURRY) - @ 20°C

			WSD12B SUMMARY		0.0768 g moisture/g dry cake			
			Feed*	Dry Cake	Liquid	Wet Cake 3	Centrate 4	
$\frac{K_2CO}{KCl}$	10.0	<===	K2CO3	6.3573	0.000	6.357	0.208	6.150
			K2SO4	56.3704	49.376	6.9948	49.604	6.766
			KCl	0.6375	0.000	0.638	0.021	0.617
			3/2 H2O	0	0.000		0.000	
			H2O	102.0547		102.055	3.335	98.72
			TOTAL	165	49	116	53	112
				44.89%	Wt.% K+	42.12%	6.09%	
38% slurry				0.00%	Wt.% CO3	0.17%	2.38%	
				55.11%	Wt.% SO4	51.42%	3.32%	
				0.000%	Wt.% Cl-	0.019%	0.261%	

COMPARISON OF MODEL PREDICTIONS @ 20 deg C
w/ RESULTS OF EXPERIMENT WSD12B

		CENTRATE					
		EXPECTED COMPOSITION	ACTUAL COMPOSITION				
		(Model/Unsat'd Solution)*	(F Analysis)				
$\frac{K_2CO_3}{KCl}$	10.0	<===	20 deg C	6.09%	K+	6.30%	<=== back-calculated
				2.38%	CO3=	2.35%	9.5 $\frac{K_2CO_3}{KCl}$
				3.32%	SO4=	3.62%	
				0.261%	Cl-	0.270%	1.1 $\frac{K_2SO_4}{K_2CO_3+KCl}$

*K₂SO₄ = KCL + K₂CO₃; all KCL, K₂CO₃ in sol'n

		WET CAKE			
		EXPECTED COMPOSITION	ACTUAL COMPOSITION		
		(Model/Wet Cake)**	(C Analysis)		
20 deg C		42.12%	K+	41.99%	<=== back-calculated
		0.17%	CO ₃ =	0.13%	
		51.42%	SO ₄ =	51.39%	
		0.019%	Cl-	0.010%	

* Model assumes 0.0768 gram moisture/gram dry cake

		DRY CAKE			
		EXPECTED COMPOSITION	ACTUAL COMPOSITION		
		(Model/Dry Cake)**	(C Analysis, dry basis)		
20 deg C		44.89%	K+	44.82%	<=== back-calculated
		0%	CO ₃ =	0%	
		55.11%	SO ₄ =	55.18%	
		0%	Cl-	0%	

* Model assumes 0.0768 gram moisture/gram dry cake

TABLE 4-25. MATERIAL BALANCE RESULTS FOR WDS12C - CARBONATE (AND CHLORIDE) SEPARATION FROM WET SULFATE CAKE (45 WT% SOLIDS SLURRY) - @ 20°C

			WSD12C SUMMARY		0.0625 g moisture/g dry cake			
			Feed*	Dry Cake	Liquid	Wet Cake 3	Centrate 4	
$\frac{K_2CO}{KCl}$	10.0	<===	K2CO3	7.4877	0.000	7.488	0.254	7.234
			K2SO4	65.9747	57.737	8.2378	58.016	7.958
			KCl	0.7501	0.000	0.750	0.025	0.725
			3/2 H2O	0	0.000		0.000	
			H2O	89.9076		89.908	3.050	86.86
TOTAL			164	58	106	61	103	
45% slurry				44.89%	Wt.% K+	42.71%	7.83%	
				0.00%	Wt.% CO3	0.18%	3.06%	
				55.11%	Wt.% SO4	52.12%	4.27%	
				0.000%	Wt.% Cl-	0.020%	0.335%	

COMPARISON OF MODEL PREDICTIONS @ 20 deg C
w/ RESULTS OF EXPERIMENT WSD12C

		CENTRATE					
		EXPECTED COMPOSITION	ACTUAL COMPOSITION				
		(Model/Unsat'd Solution)*	(F Analysis)				
$\frac{K_2CO}{KCl}$	10.0	<===	20 deg C	7.83%	K+	6.65%	<=== back-calculated
				3.06%	CO3=	3.10%	10.0 $\frac{K_2CO_3}{KCl}$
				4.27%	SO4=	2.75%	
				0.335%	Cl-	0.340%	0.6 $\frac{K_2SO_4}{K_2CO_3+KCl}$

*K₂SO₄ = KCl + K₂CO₃; all KCl, K₂CO₃ in sol'n

		WET CAKE			
		EXPECTED COMPOSITION	ACTUAL COMPOSITION		
		(Model/Wet Cake)**	(C Analysis)		
20 deg C		42.71%	K+	45.26%	<=== back-calculated
		0.18%	CO ₃ =	0.27%	
		52.12%	SO ₄ =	51.85%	
		0.020%	Cl-	0.010%	

* Model assumes 0.0625 gram moisture/gram dry cake

		DRY CAKE			
		EXPECTED COMPOSITION	ACTUAL COMPOSITION		
		(Model/Dry Cake)**	(C Analysis, dry basis)		
20 deg C		44.89%	K+	44.88%	<=== back-calculated
		0%	CO ₃ =	0.088%	
		55.11%	SO ₄ =	55.03%	
		0%	Cl-	0%	

*Model assumes 0.0625 gram moisture/gram dry cake

cases, essentially complete carbonate removal from the cake (dry basis) was achieved. In WSD12C, in which the least amount of water was used to reslurry the sulfate cake, 99.3% carbonate removal from the cake (dry basis) was achieved. The carbonate removal for all three cases, on a wet cake basis, was $\sim 97\%$. The percentage of K_2SO_4 that dissolves and is removed in the solution increased from $\sim 7.2\%$ to 13.2% to 18.4% as the amount of reslurry water was increased (wt% solids in the slurry decreased).

4.4.3 Summary of Test Results

The results of this experiment verify that the K_2CO_3 and KCl present (by virtue of cake surface moisture) in K_2SO_4 cake can be selectively removed with water without simultaneously dissolving an excessive amount of K_2SO_4 .

4.5 MIXED SEED BLENDING CHARACTERIZATION

It is possible that the seed form in the first commercial MHD plant will be a mixture of K_2CO_3 crystals in a concentrated KCOOH (potassium formate) liquid. A few crude experiments were performed to provide qualitative information on the feasibility of blending a $\sim 1:1$ mixture of K_2CO_3 crystals and concentrated (70%) KCOOH solution.

A number of experiments were performed to obtain qualitative information on the blending and flow characteristics of a mixed (K_2CO_3 and KCOOH) seed form. The experiments described in this section were conducted with seed mixtures having a potassium carbonate to potassium formate (K_2CO_3 :KCOOH) ratio of approximately 0.91 to 1.0.

Experiment One - At room temperature, solid, anhydrous K_2CO_3 , was added to a 70 wt% aqueous solution of KCOOH (concentration was verified by specific gravity measurement) and stirred. The granular K_2CO_3 did not readily dissolve in the formate solution. After several minutes of stirring, the slurry thickened and formed a suspension of granular solids. The viscosity was high enough to stop the stirring action. At this point the white slurry had the consistency of a "milkshake", and was somewhat pourable. The slurry was transferred to a storage jar and covered. After approximately two hours, the "milkshake" consistency was

no longer apparent, the slurry had become an apparently homogeneous, white paste that was "semi-stiff" and unpourable at room temperature. This paste was very deliquescent when uncovered, absorbing atmospheric moisture and dissolving in it. The paste was also readily soluble in water.

Experiment Two - The purpose of this experiment was to determine the temperature at which the paste formed in Experiment One begins to flow. The paste was heated in a covered beaker in an oil bath on a hot plate. At 150°F, the paste began to soften. At 182°F, the paste softened enough to observe "creep" flow along the walls of the beaker. The cover was removed and the temperature raised to 250°F, at which point solids began to "fall out" of solution, and a translucent liquid remained on top. The solution boiled between 250 and 280°F. When all of the water was boiled off, the remaining slurry was pourable, while hot, and froze upon cooling.

Experiment Three - A saturated solution of K_2CO_3 was added to a 70 wt% aqueous solution of KCOOH, such that the ratio of K_2CO_3 to KCOOH was 0.91 to 1. The result was a liquid solution with a slight yellow tinge to it. This solution appeared to be slightly more viscous than water, and was slightly murky. Upon standing overnight in a covered jar, clear hexagonal, rod-like crystals formed at the bottom of the jar.

Experiment Four - The purpose of this experiment was to evaporate the solution prepared in Experiment Three to dryness. After one hour at 250°F, crystals formed under the top surface of the solution and white solids precipitated on the bottom. The solution boiled between 250 and 262°F. As the solution was stirred, the crystals appeared to dissolve into the white mass below. As water was evaporated, the solution became a white, liquid-like mass, with solids falling out of suspension. Upon cooling, the liquid slurry froze. This solid mass was not soluble in ambient temperature water, but it was soluble in boiling water.

Experiment Five - The purpose of this experiment was to oxidize at 600°C the paste prepared in Experiment One. It was expected that the water would be driven off and the KCOOH

would be oxidized to K_2CO_3 and the existing K_2CO_3 would be unchanged. Weight loss measurements confirmed that this was the case. The resulting solid was a white "hard" mass.

4.6 ANALYTICAL TECHNIQUES UTILIZED

Wet chemistry techniques were used for anion analysis. Sulfate was determined by precipitating $BaSO_4$ from $BaCl_2$ solution, carbonate by titration with HCl solution, and chloride by titration with $AgNO_3$ solution. Cations (potassium and sodium) were determined by atomic absorption spectroscopy (AA).

5. ENGINEERING ASSESSMENT STUDIES

5.1 INTRODUCTION AND SUMMARY

A conceptual design for a 300 MW₁ Seed Regeneration Plant for an Eastern coal-fired MHD power plant was prepared in Phase I of the program (see Section 5.2). This design was based primarily on the laboratory data generated during Phase I of the program. Proof-of-Concept (POC) plant operations and Western seed laboratory studies were conducted during Phase II of the seed regeneration program. Upon completion of these tasks, an engineering assessment was undertaken to determine the potential impact of the Phase II data on the design of a seed regeneration plant (see Section 5.3).

5.1.1 Seed Regeneration Design Areas Investigated

The engineering assessment task focused on: 1) potential sources of carbon monoxide for the calcium formate production unit, 2) separation of spent seed into its K_2CO_3 and K_2SO_4 fractions prior to regeneration of the K_2SO_4 , and 3) removal of chloride impurity from the spent seed.

5.1.2 Findings and Conclusions

High carbon monoxide conversions in the calcium formate POC production unit were achieved with gas feeds which were relatively dilute (~40%) in carbon monoxide content. This finding opens the door for the utilization of potentially inexpensive sources of carbon monoxide for the production of calcium formate.

A number of process schemes for the separation of the K_2CO_3 and K_2SO_4 fractions of the spent seed (a K_2CO_3/K_2SO_4 spent seed is expected for most Western coals and for low sulfur Eastern coals) prior to seed regeneration were devised and successfully verified in the laboratory. Since the K_2CO_3 fraction of the spent seed is a viable fresh seed material, it can be recycled to the MHD system once it is separated from the K_2SO_4 and concentrated, eliminating the regeneration step for this fraction of the spent seed. This could significantly reduce the cost of seed regeneration and MHD power generation.

A number of process schemes for the rejection of chloride impurity from the spent seed (without simultaneous high seed loss) were devised and successfully verified in the laboratory. Efficient rejection of chloride during seed regeneration will prevent buildup of this impurity in the recycled seed. Chloride buildup in the recycled seed could potentially shorten channel life (increased corrosion) and/or degrade channel performance (decreased channel plasma conductivity).

5.1.3 Recommendations

The process schemes proposed for the separation of the K_2CO_3 and K_2SO_4 fractions of the spent seed and for the rejection of chloride impurity from the spent seed (see Section 5.3) should next be tested at Proof-of-Concept (POC) scale. These units would utilize the smallest versions of commercially available process equipment. The test information generated by the POC units would provide the engineering data base required for the low risk design of a scaled-up commercial-sized MHD seed regeneration plant.

5.2 300 MW_t SEED REGENERATION PLANT CONCEPTUAL DESIGN FOR EASTERN SEED PREPARED DURING PHASE I OF THE PROGRAM

5.2.1 Introduction

This section presents a conceptual design for the Econoseed Process for the regeneration of spent MHD seed material from a 300 MW_t MHD plant using Illinois No. 6 coal. This design was prepared at the end of the Phase I bench scale program. The conceptual design consists of process flow diagrams, a material balance, energy and utility requirements, an equipment list, an estimate of capital and operating costs, and parametric cost studies. The Econoseed Process regenerates the spent seed material, consisting mostly of potassium sulfate, by the reaction with calcium formate to form potassium formate according to the following reaction:

Sulfur is removed as gypsum by centrifuges. Any potassium carbonate in the spent seed

also reacts with the calcium formate to produce potassium formate and calcium carbonate solids which are also removed with the gypsum. The reaction for the potassium carbonate is as follows:

Insoluble materials such as flyash and metal salts are removed with the gypsum and calcium carbonate.

The potassium formate solution is the regenerated seed material which when injected into the MHD combustor forms K_2CO_3 by the following reaction:

This eliminates the necessity of crystallization and calcining of the formate solution and allows for the injection of a solution rather than solids into the MHD combustor. Alternatively, the potassium formate may be oxidized in air to form K_2CO_3 if solids are the preferred seed material.

The calcium formate required for the seed regeneration is produced by the reaction of slaked lime with carbon monoxide by the following reaction:

The carbon monoxide used for the production of calcium formate may be produced by any of several methods including coal gasification, natural gas reforming, natural gas/ CO_2 reforming, or partial oxidation of natural gas or other hydrocarbon fuels. The choice of CO production methods is dependent on economics and system integration with the MHD power plant. The method used in this economic analysis is partial oxidation of natural gas (with coal as an alternative fuel).

Raw materials required for the process are lime, fuel for CO production, and seed makeup which is K_2SO_4 . The seed makeup material is required to replace potassium which is lost with the solids as insoluble salts or KCOOH solution remaining on the spent solids.

5.2.2 Design Basis and Requirements

5.2.2.1 *General*

The conceptual design for the seed regeneration process is based on a 300 MW_t MHD combustor using Illinois No. 6 coal feed. An analysis of the coal used for this design is presented in Table 5-1. The coal flow rate to the MHD system is based on the higher heating value (HHV).

5.2.2.2 *Seed Requirements*

In order to define a basis of design for the seed regeneration process, the quantity and composition of seed required for the MHD process must be defined. The primary requirements for seed quantities are:

1. The potassium loading in the channel should be 1.5% K by weight with respect to the total flow rate of combustion products and inerts.
2. The carbonate to sulfur ratio should be equal to 1.0 on a molar basis to provide capture of SO_x via the following reaction:

In order to determine the quantity and composition of seed required upon continued recycle of regenerated seed, a material balance for 300 MW_t MHD combustion and seed injection was performed. The combustion material balance is shown in Table 5-2A and the seed injection material balance is given in Table 5-2B.

The design basis for the combustion is as follows:

TABLE 5-1. ILLINOIS NO. 6 COAL ANALYSIS

Ultimate Analysis

96%, Moisture Free

Hydrogen	4.83
Carbon	68.49
Nitrogen	1.32
Oxygen	9.22
Sulfur	3.62
Ash	12.52
	<hr/> 100.00

Ash Analysis, %

SiO ₂	44.7
Al ₂ O ₃	20.9
CaO	5.8
Fe ₂ O ₃	24.1
MgO	1.8
TiO ₂	1.0
K ₂ O	2.3
Na ₂ O	2.3
P ₂ O ₅	0.12
Chloride	0.2
Zinc	0.12
Lead	0.03

Proximate Analysis, Moisture Free

Volatiles	41.7
Fixed Carbon	45.8
Moisture, as received, %	9.0

Heating Value

Dry BTU/lb	12,400
------------	--------

Fusions

Initial Deformation Temp, deg F	1,960
Softening Temp, deg F	2,030
Fluid Temp, deg F	2,260

TABLE 5-2A. COMBUSTION MATERIAL BALANCE

COAL COMPOSITION- ILL #6 *****BASED ON HIGHER HEATING VALUE***

WT. %
MOISTURE FREE

HYDROGE	4.83%	HEATING VALUE,HHV	12400 BTU/LB
CARBON	68.49%	DRY BASIS	
NITROGEN	1.32%		
OXYGEN	9.22%		
SULFUR	3.62%	NET HEAT RELEASE BASED ON MOISTURE CONTENT	
ASH	12.52%	0.02 LB H2O/LB DRY COAL AS MOISTURE	
		0.43 LB H2O/LB DRY COAL AS COMBUSTION	
TOTAL	100.00%	0.45 TOTAL H2O	
MOISTURE	2.00%	1054.3 HEAT OF VAPORIZATION AT 70 F	
		475.36 BTU/LB OF COAL FOR VAPORIZATION	
		11925 NET HEAT RELEASE,BTU/LB COAL	

MATERIAL BALANCE

BASIS: 300 MWt = 1023.6 MM BTU/HR
 95.0% THEORETICAL AIR
 30.0% ASH AS FLY ASH

DRY COAL REQUIRED 82548 LB/HR
 COMBUSTION AIR ENRICHED TO 35% OXYGEN

AVAILABLE OXYGEN CALCS

O2 AVAILA	IN AIR	MOLES
	IN COAL	5273.811
		237.851

TOTAL	5511.662
-------	----------

LESS O2 REQD FOR:

H2O	988.959
SO2	93.196
C + 1/2 O2-->CO	2353.538

NET AVAILABLE FOR CO + 1/2 O2-->CO2	2075.969
--	----------

THEORETICAL O2 REQD:

FOR: HYDROGEN	988.96	MOLE/HR
CARBON	4707.08	
SULFUR	93.20	

CO FORMED	555.138
-----------	---------

CO2 FORMED	4151.938
------------	----------

TOTAL	5789.23	MOLE/HR
-------	---------	---------

EXCESS O2	0.000
-----------	-------

LESS	237.85	O2 IN COAL
------	--------	------------

5551.38

	MOL WT	FEED COAL	COMBUSTION AIR	COMBUSTION PRODUCT	SLAG
COAL:					
HYDROGE	2.02	3987.1			
CARBON	12.01	56537.4			
NITROGEN	28.01	1089.6			
OXYGEN	32.00	7611.0			
SULFUR	32.06	2968.3			
ASH		10335.1		3100.5	7234.54
SUBTOTAL DRY		82548.4		3100.5	7234.5
MOISTURE		1651.0			
GASES:					
N2	28.01		274369.39	275459.03	
O2	32.00		168755.61	0.00	
CO2	44.01			182726.57	
H2O	18.02			37283.56	
CO	28.01			15549.72	
SO2	64.06			5970.43	
SUBTOTAL GAS		0.0	443125.0	516989.3	0.0
TOTAL		84199.35	443125.00	520089.82	7234.54

5-7

SODIUM REJECTION	
***FRACTION REJECT	0.048
FRACTION RECYCLED	0.952

		POWER	
COST @\$/	0.3	150	MWE
	\$301.20	0.20	CENTS/KW
5	0.0177072		

- Illinois No. 6 coal
- Coal flow rate based on HHV
- Overall - 95% theoretic oxygen for combustion
- 70% ash rejection as slag in the combustor; 30% of the coal ash to channel as flyash
- Combustion air enriched to 35% oxygen.

Using the above basis for combustion, 82,548 lbs/hr of coal are required producing a total flowrate of gases and flyash to the MHD channel of about 520,000 lbs/hr.

The calculations for seed required are shown in Table 5-2B which is a reiterative model for calculating the injected seed and spent seed quantities and composition. The basis for this calculation is:

1. 1½ wt% K in the channel
2. Moles CO_3 /moles S = 1.0
3. Recovered flyash seed (water soluble seed) contains 40% alkali (as K and Na)
4. Recovered slag seed (water insoluble seed) contains 10% alkali (as K and Na)
5. Sodium in the recycled seed is allowed to build to a level of 1 mole Na per 6 moles K.

Items 3 and 4 above are based on the analyses of spent seed material obtained from UTSI for use in the Phase I laboratory tasks. Since the samples provided were based on a single pass of fresh K_2CO_3 seed material rather than multiple passes of regenerated seed, there was only small amounts of contaminants such as sodium in the samples. This would not be the case where regenerated seed was recycled.

The Illinois No. 6 coal used for the MHD combustor contains 12.52% ash. The ash contains 2.3% each K_2O and Na_2O which are assumed to ionize like seed upon entering the

channel. For the seed requirements material balance shown in Table 5-2B, it is assumed that 70% of the ash is rejected as slag in the combustor while also rejecting 70% of the Na_2O and K_2O in the ash as slag.

The remaining K and Na from the coal ash is assumed to enter the channel which accounts for an addition of 59.2 lbs/hr potassium plus 52.9 lbs/hr sodium. This sodium and potassium would be recovered along with the recovered seed as K_2SO_4 , K_2CO_3 , Na_2SO_4 , and Na_2CO_3 . After repeated recycle of regenerated seed, the ratio of sodium to potassium in the seed would eventually equal the ratio of sodium to potassium in the coal ash if no seed was rejected or if the seed regeneration process provides no processing steps to separate sodium from potassium salts. At this point in the development of the Econoseed process it is assumed that the process does not reduce the Na/K ratio by rejection of sodium due to differences in solubilities of sodium salts versus potassium salts although this may be the case. The extent of sodium rejection, if any, must be determined on seed samples that contain measurable amounts of sodium similar to levels reached upon multiple recycle of seed.

For this design, rejection of sodium and other water soluble ash contaminants such as chlorine is accomplished by allowing the sodium and other contaminants to build up to acceptable levels in the recycled seed, then purging a portion of the recovered seed material to equal the input of contaminants.

The material balance given in Table 5-2B shows an input of 52.9 lbs/hr sodium from the coal ash which must be rejected at steady-state levels. The slag portion of the recovered seed which is water insoluble contains about 13 lbs/hr of sodium. Since this is an insoluble material suitable for landfill, the slag would not be processed for seed recovery but rather rejected as disposable material. This stream accounts for about 1/3 of the sodium and other contaminant purge required to maintain steady-state. By rejecting about 4.8% of the flyash (water soluble), the remaining sodium is removed at steady-state rates equal to the sodium input with combustion coal. The rejection of these seed streams also rejects potassium that must be made up by the addition of K_2SO_4 or K_2CO_3 to the process. At a steady-state level

of 6 moles K/mole Na, the total losses of potassium incurred for the purpose of sodium rejection are:

	<u>K loss</u>
Slag Seed (insoluble)	126 lb/hr
4.8% of Flyash Seed (soluble)	<u>383</u> lb/hr
Total	509 lb/hr

This represents about 6% of the 8058 lbs/hr potassium required for seed injection. If a higher ratio of K/Na were desired for MHD channel operation, a larger portion of the recovered flyash would have to be rejected to maintain steady-state sodium levels thus requiring more seed makeup. Conversely, a lower potassium makeup would be required if the K/Na ratio in the seed was lower than 6:1. The optimization of the ratio of K to Na in the seed requires trade-off studies of seed processing costs versus MHD channel performance and costs. These trade-off studies must be done on an overall system level beyond the scope of this design effort.

Using the aforementioned criteria in the model shown in Table 5-2B, the flow rates and composition of the feed seed, seed slag and flyash are calculated and shown below:

<u>Lbs/Hr</u>	<u>Recycled Seed</u>	<u>Seed Slag</u>	<u>Flyash Slag</u>
K ₂ CO ₃	11,039		
K ₂ SO ₄	4,040		17,810
Na ₂ CO ₃	1,411		
Na ₂ SO ₄	549		2,563
Na		13	
K		126	
Slag (Inerts)	_____	<u>1,253</u>	<u>1,735</u>
Total	17,039	1,392	22,108

The above flow rates form the basis for the design of the Econoseed process. Other

requirements and assumptions that form the basis of design for the Econoseed process are presented in the Process Description Section (Section 5.2.3).

5.2.3 Process Description

Figure 5-1 shows an overall block flow diagram for the Econoseed process which consists of the following unit operations:

1. CO Gas Generation System
2. Calcium Formate Reactor System
3. Recovered Seed Handling, Storage and Conveying System
4. Potassium Formation Reactor System
5. Potassium Formate Roasting System (optional)

The following paragraphs give a description of each section of the process with material balances and process flow diagrams.

5.2.3.1 *CO Gas Generation System*

The Econoseed process requires a source of carbon monoxide for production of the calcium formate that is used to solubilize the potassium sulfate in the spent seed. A natural gas partial oxidation (POX) unit has been selected to generate the necessary carbon monoxide.

Fluor-Daniel provided the heat and material balances and cost estimate for the natural gas POX unit. Figure 5-2 is a block flow drawing for the POX unit and Table 5-3 is the accompanying material balance.

Natural gas partial oxidation is a well established process which was developed in the 1950's by Shell and Texaco. Natural gas (2.6 million SCFD) and oxygen (80 TPD) from battery limits are compressed to 1200 psig and fed into a high pressure, refractory-lined

Figure 5-1. Overall Block Flow Diagram of Commercial Econoseed Plant

NATURAL GAS PARTIAL OXIDATION

Figure 5-2. Block Flow Diagram for Natural Gas POX CO Generation Unit

TRW - SEED REGENERATION FACILITY		CO PRODUCTION UNIT	
FLUOR DANIEL		NONE	
233DCP 023-PPD 1			
O HIS FOR INFORMATION			

TABLE 5-3. NATURAL GAS POX CO GENERATION MATERIAL BALANCE

		Natural Gas Feed		Oxygen		Feed to Membrane Separator		Fuel Gas		Carbon Monoxide to Ca Formate Reactor	
Component	M.W.	Lbmole/H	Mole%	Lbmole/H	Mole %	Lbmole/H	Mole %	Lbmole/H	Mole %	Lbmole/H	Mole %
H2	2.016					424.83	56.87	418.35	85.16	6.48	2.53
N2	28.013			10.54	5.00	10.54	1.41	1.17	0.24	9.37	3.66
CO	28.011					251.22	33.63	46.62	9.49	204.60	80.01
CO2	44.010					23.13	3.10	19.44	3.96	3.69	1.44
CH4	16.043	275.53	94.90			36.60	4.90	5.02	1.02	31.58	12.35
C2H6	30.070	10.16	3.50								
C3H8	44.097	3.48	1.20								
nC4H10	58.124	0.58	0.20								
nC5H12	72.151	0.58	0.20								
O2	31.999			200.36	95.00						
H2O	18.015					0.66	0.09	0.66	0.13		
Total		290.33	100.00	210.90	100.00	746.99	100.00	491.26	100.00	255.72	100.00
Lbs/Hr		4955		6707		9806		3130		6676	
Temp, (F)		80		84		100		140		140	
Press, (psia)		500		16.7		1070		35		1040	
Million SCFD		2.6		1.9		6.8		4.5		2.3	

partial oxidation reactor. A small amount of recycled process water, carrying recycled soot, is also injected with the feed streams in order to operate at total carbon conversion. The relative feed rates of oxidant and hydrocarbon are carefully controlled to maintain the desired reaction temperature and carbon conversion.

The partial oxidation reactions occur very rapidly at temperatures as high as 2,700°F (1480°C) and reach equilibrium. The major reactions that occur are as follows:

The hot synthesis gas (syngas) exiting the POX reactor will consist mostly of hydrogen and carbon monoxide with small quantities of carbon dioxide, steam, methane and nitrogen compounds. Because of the very short residence time and the elevated temperature in the reactor, no complex hydrocarbons are formed in detectable amounts.

The hot synthesis gas exiting the reactor is cooled in a syngas waste heat boiler through the generation of 15,000 pounds per hour of saturated 600 psig steam. The synthesis gas is then scrubbed free of soot particles by direct contact with water. The soot from the scrubbing operation is recycled back to the reactor. The scrubbed syngas is further cooled by exchanging heat first with boiler feed water makeup, second with membrane separator feed gas, and finally with cooling water. The condensate formed as a result of these cooling

operations is separated from the cooled syngas in a knock-out drum and recycled back to the soot scrubber.

The syngas (@140°F) from the syngas cooling step flows to the membrane separation unit for upgrading of the carbon monoxide purity.

Membrane separation operates on the principle of selective permeation. Each gas introduced into the separator has a characteristic permeation rate that is a function of its ability to dissolve in, and diffuse through, a polymeric membrane of given properties. When a pressurized feed stream of mixed gases flows through the separator, a "fast" or more permeable gas, like hydrogen, will diffuse through the membrane at a higher rate than a "slow," less permeable gas, like carbon monoxide. The permeate and residue streams are then channeled through two gas outlets and piped to their respective use points.

The CO-rich gas (at 80% CO) from the membrane separator at 140°F and 1,040 psia flows to the calcium formate reactor.

The CO-lean gas from the membrane separator at 140°F and 35 psia has a higher heating value of 318 Btu/SCF. It is sent to the MHD unit to be combusted as a fuel gas.

As an alternative case, for remotely sited coal fed MHD plants for which natural gas is not available, Fluor-Daniel considered a coal partial oxidation (POX) unit for carbon monoxide generation. Figure 5-3 is the block flow drawing for this unit and Table 5-4 is the accompanying material balance.

The coal POX unit is fed 60 TPD (dry basis) of pulverized coal and 53 TPD of oxygen from battery limits. The oxygen is compressed and the coal is slurried with water and pumped to high pressure for injection into a refractory lined gasifier operating at 1200 psig and temperatures as high as 2700°F. Texaco has operated a unit of this size at their Montebello Test Site.

[illegible]

TABLE 5-4. COAL POX CO GENERATION MATERIAL BALANCE

		Coal Slurry		Oxygen		Feed to Acid Gas Removal		Sour Gas	
Component	M.W.	Lbmole/H	Wt %	Lbmole/H	Mole %	Lbmole/H	Mole %	Lbmole/H	Mole %
H2	2.016					159.11	35.22		
N2	28.013			6.92	5.00	9.28	2.05		
CO	28.011					215.54	47.71		
CO2	44.010					61.00	13.50	55.5	88.25
CH4	16.043					0.79	0.17	0.02	0.03
H2S	34.080					5.42	1.20	4.56	7.25
COS	60.075					0.25	0.06	0.13	0.21
O2	31.999			131.5	95.00				
H2O	18.015	2361.6	32.00			0.40	0.09	2.68	4.26
Coal (Dry)		5018.4	68.00						
Total		7380.0	100.00	138.42	100.00	451.79	100.00	62.89	100.00
Lbs/Hr		7380.0		4401.7		9522.4		2654.4	
Temp, (F)		80		84		100		100	
Press, (psia)		14.4		16.7		1075		20	
Million SCFD				1.3		4.1		0.6	

TABLE 5-4. COAL POX CO GENERATION MATERIAL BALANCE (CONTINUED)

		Feed to Membrane Separator		Fuel Gas		Carbon Monoxide to Ca Formate Reactor	
Component	M.W.	Lbmole/H	Mole %	Lbmole/H	Mole %	Lbmole/H	Mole %
H ₂	2.016	159.11	40.64	122.01	89.72	37.10	14.52
N ₂	28.013	9.28	2.37	0.71	0.52	8.57	3.35
CO	28.011	215.54	55.05	10.94	8.04	204.60	80.07
CO ₂	44.010	5.50	1.40	1.53	1.13	3.97	1.55
CH ₄	16.043	0.77	0.20	0.10	0.07	0.67	0.26
H ₂ S	34.080	0.86	0.22	0.31	0.23	0.55	0.03
COS	60.075	0.12	0.03	0.04	0.03	0.06	
O ₂	31.999						
H ₂ O	18.015	0.35	0.09	0.35	0.26		
Coal (Dry)							
Total		391.53	100.00	135.99	100.00	255.54	100.00
Lbs/Hr		6915.4		660.5		6254.9	
Temp, (F)		100		140		140	
Press, (psia)		1070		35		1040	
Million SCFD		3.6		1.2		2.3	

The hot synthesis gas exiting the POX reactor will consist mostly of hydrogen and carbon monoxide with small quantities of carbon dioxide, steam, methane, sulfur and nitrogen compounds. Because of the very short residence times and the elevated temperature in the reactor, no complex hydrocarbons are formed in detectable amounts. The ash in the coal melts to form slag. Most of the slag falls into a water quench at the bottom of the gasifier. The resultant ash slurry leaves the gasifier and enters the ash dewatering unit.

The hot synthesis gas exiting the gasifier is quenched with water in a gas cooling and scrubbing unit. Use of a waste heat boiler to recover the high level heat from the hot, particulate-containing gas is not considered economic at the small scale of this unit. The particulate-free gas from the scrubbing unit is then cooled further by generation of 100 psig steam and in air and water cooled exchangers.

The cooled gas containing 13.5% CO₂ and 1.26% H₂S (and COS) is processed through an acid gas removal unit to reduce the CO₂ level in the gas to the downstream calcium formate reactor. The sour gas from the acid gas removal unit is sent to the MHD combustor. The sweetened gas from the acid gas removal unit, containing 1.4% CO₂ and 0.25% H₂S (and COS) is processed through the membrane separator.

The CO-rich gas (at 80% CO) from the membrane separator at 140°F and 1,040 psia flows to the calcium formate reactor.

The CO-lean gas from the membrane separator at 140°F and 35 psia has a higher heating value of 318 Btu/SCF. It is sent to the MHD unit to be combusted as a fuel gas.

Another source of coal-derived carbon monoxide that may merit investigation is the extraction of a slip-stream of hot, CO-containing gas from the first stage of the MHD combustor. If judged practical, this would mean that the first stage of the MHD combustor would have to be slightly enlarged because of the increased throughput. However, a net savings may result as this incremental combustor cost is probably less than the cost of the stand-alone coal gasifier required to generate the necessary carbon monoxide.

5.2.3.2 Calcium Formate Reaction Section

Figure 5-4 shows a process flow diagram for the calcium formate reactor section. The material balance is given in Table 5-5. The design basis for the calcium formate reactor is as follows:

● Lime slurry concentration to reactor, wt% Ca(OH)_2	10%
● CO feed required, % of stoichiometric	98%
● CO conversion to formate, % of feed	92%
● Lime conversion to formate or carbonate, % of feed	93%
● Retained cake moisture content on centrifuge cake, lb/moisture/lb solid	0.25
● Reactor conditions	1200 psig, 330°F

A 10% slaked lime slurry is prepared in agitated mix tank CF-R-1, which is 8 feet 5 inches diameter x 16 feet 10 inches high. The tank provides 0.5 hours residence time for mixing the lime with 54,000 lbs/hr fresh water and 17,000 lbs/hr of recycle water from downstream wash operations. Lime is provided from a 4000 ft³ silo which has the capacity for 24 hours storage. The lime is fed to a screw feeder at the mix tank by a pneumatic conveyor at the rate of 5,800 lbs/hr. The lime slurry is heated in the mix tank to 133°F by the heat of reaction of CaO to Ca(OH)_2 . From the mix tank, the slurry is pumped to two heat exchangers CF-E-1 and CF-E-2 where it is heated to 250°F (stream CF-4) using 35 psia flash steam and 150 psia steam prior to injection into the calcium formate reactor.

At the calcium formate reactor CF-R-2, the lime slurry is contacted with the CO-rich gas (stream CF-5) at 1200 psia and 300°F producing Ca(COOH)_2 and unreacted lime solids. The reactor is a two-stage column reactor, each stage being 2 feet diameter x 20 feet high, providing a total residence time of about 7 minutes. It is assumed that Ca(OH)_2 utilization is 93 percent and CO utilization is 92 percent. Reactor heating is provided by the heats of reaction and the heated feed slurry and gas feed.

CALCIUM FORMATE REACTOR
 DATE: OCT 6, 1989
 REV. 2
 TRW

Figure 5-4. Calcium Formate Reactor Section Block Flow Diagram

The slurry effluent from the reactor feeds a flash drum CF-D-1 where steam and unreacted gases are disengaged from the slurry at 35 psia. The vent gas (stream CF-7) containing mostly hydrogen and steam is used for preheating the reactor feed in heat exchanger CF-E-1. The vent gas from CF-E-1 contains mostly hydrogen which is used as fuel. The flash drum effluent (stream CF-8) at 259°F and 35 psia is a 16 percent solution of $\text{Ca}(\text{COOH})_2$ containing insoluble $\text{Ca}(\text{OH})_2$. The effluent is cooled to 212°F in a second flash drum CF-D-2 at atmospheric pressure. The cooled slurry (stream CF-10) is fed to a solid bowl centrifuge CF-C-1 where the dewatered solids (stream CF-11) are withdrawn and fed to a wash drum CF-D-3. The centrate from the centrifuge (stream CF-12) is the feed $\text{Ca}(\text{COOH})_2$ solution to the potassium formate reactor.

The centrifuge cake from CF-C-1 is contacted with 20 weights of water/weight of solids (stream CF-13) in the wash drum CF-D-3. The wash drum slurry (stream CF-14) is dewatered in a second centrifuge CF-C-2 producing a solids cake (stream CF-15) containing CaCO_3 and unreacted lime that is sent to disposal. The centrate from CF-C-2 (stream CF-16) is a weak calcium formate solution that is recycled back to the lime slaker CF-R-1 as makeup water.

5.2.3.3 Potassium Formate Reaction Section

The process flow diagram for the potassium formate reactor is shown in Figures 5-5A and 5-5B. In this section spent solid seed material is dissolved in the calcium formate solution where the reaction produces potassium formate and insoluble CaSO_4 . The reactor slurry is then dewatered and the solids washed in several countercurrent stages to reduce formate losses. The centrate from the first dewatering stage is about a 10% solution of potassium formate with dissolved, unreacted sodium and potassium sulfate. This centrate is fed to the evaporator section where the potassium formate is concentrated for use as recycled seed.

Tables 5-6A and 5-6B give the material balance for this section. Only the water soluble flyash seed is processed for recycle. The slag seed recovered, which is water insoluble, is

Figure 5-5A. Potassium Formate Reactor Section Block Flow Diagram

Figure 5-5B. Potassium Formate Separation/Washing Section Block Flow Diagram

TABLE 5-6A. POTASSIUM FORMATE REACTOR MATERIAL BALANCE

SEED PROCESSING MATERIAL BALANCE MODEL

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DESIGN BASIS PARAMETERS:

RECOVERED SPENT SEED:	MW	FLYASH SEED	SLAG SEED	REQUIRED RECYCLE
K ₂ CO ₃	138.205	0.0686		11039.1110
K ₂ SO ₄	174.258	17809.5350		4040.0000
NA ₂ CO ₃	105.9889	0.0093		1410.9720
NA ₂ SO ₄	142.0412	2562.7367		548.8490
K	39.098		126.1296	
NA			13.0926	
ASH(INERTS)		1735.4148	1253.0000	
TOTAL		22107.7644	1392.2222	

POTASSIUM FORMATE REACTION SECTION

DESIGN PARAMETERS:

CALCULATED PARAMETERS:

FRACTION OF SEED TO DISPOSAL	0.04784				
FRACTION TO FORMATE REACTOR	0.95216				
SULFATE CONVERSION TO FORMATE	81.32%	PERCENT KCOOH IN RX EFF	7.78%	RECOVERED SEED:	
K2CO3 ADDITION,LB/HR	120	K2CO3 EQUIVALENT IN RX EFF	11039.95	K2CO3 EQUIV.	11039.9525
CA FORMATE COMPOSITION:		K2SO4 EQUIVALENT IN RX EFF	3187.55	K2SO4	3187.5519
Ca(COOH)2	16.026%			NA2CO3 EQUIV	1478.3698
Ca(OH)2	0.002%	TOTAL K OUT	7676.734	NA2SO4	458.6900
H2O	83.972%	TOTAL K IN	7677.4185		
CaSO4	0.000%	RECOVERY	99.99%	TOTAL K	7676.7338
TOTAL	100.000%	LOSS	0.6846758	TOTAL NA	789.8201
WATER ADDITION TO REACTOR,LB/H	22,100			K/NA WEIGHT	9.7196
WASH WATER ADDED,LB H2O/LB SOL	5	PERCENT NACOOH IN RX EFF	1.10%	K/NA MOLAR	5.7152
CENTR. CAKE MOISTURE, LB/LB SOLI	0.3	NA2CO3 EQUIVALENT IN RX EFF	1478.3698	MOLES CO3	93.8291356
		NA2SO4 EQUIVALENT IN RX EFF	458.69		
		TOTAL NA OUT	789.82011		
		TOTAL NA IN	789.89049		
		RECOVERY	99.99%		
		LOSS	0.0703868		
		PERCENT NACOOH & KCOOH IN RX EF	8.88%		
		TOTAL DISSOLVED SOLIDS IN REACTOR EFFLUENT	10.99%		

19455.3866

TABLE 5-6B. POTASSIUM FORMATE REACTOR MATERIAL BALANCE

STREAM	KF-1	KF-2	KF-3	KF-4	KF-5	KF-6	KF-7	KF-8	KF-9	KF-10	KF-11	KF-12	KF-13	KF-14	KF-15	KF-16
DESCRIPTION	RECOVERED FLYASH SEED	FLYASH SEED BYPASS TO DISPOSAL	SEED TO FORMATE REACTOR	WATER TO REACTOR	CALCIUM FORMATE TO REACTOR	K ₂ CO ₃ TO REACTOR	REACTOR EFFLUENT	CENT SOLIDS	KCOOH CENTRATE TO EVAPORATOR	WASH DRUM EFFLUENT	CENT SOLIDS	CENTRATE	WASH WATER	WASH DRUM EFFLUENT	SOILDS TO DISPOSAL	CENTRATE RECYCLE
SOLIDS	MW															
K ₂ SO ₄	174.258	17809.535	852.01	16957.53												
K ₂ CO ₃	138.205	0.07	0.00	0.07		120.00										
NA ₂ CO ₃	105.989	0.01	0.00	0.01												
NA ₂ SO ₄	142.041	2562.74	122.60	2440.14												
INERTS		1735.41	83.02	1652.39			1652.39	1652.39		1652.39	1652.39			1652.39	1652.39	
CaSO ₄	136.142						12656.79	12656.79		12656.79	12656.79			12656.79	12656.79	
CaCO ₃	100.098						86.97	86.97		86.97	86.97			86.97	86.97	
H ₂ O	18.015															
TOTAL SOLIDS	22107.76	1057.64	21050.13	0.00	0.00	120.00	14396.15	14396.15	0.00	14396.15	14396.15	0.00	0.00	14396.15	14396.15	
LIQUIDS																
K ₂ SO ₄	174.258						3267.26	79.71	3187.55	84.21	4.77	79.44		4.77	0.27	4.50
K ₂ CO ₃	138.205															
KCOOH	84.116						13771.45	335.98	13435.47	354.93	20.09	334.84		20.09	1.14	18.95
NA ₂ SO ₄	142.041						470.16	11.47	458.69	12.12	0.69	11.43		0.69	0.04	0.85
NA ₂ CO ₃	105.989								0.00	0.00	0.00	0.00		0.00	0.00	0.00
NACOOH	68.008						1944.20	47.43	1896.77	50.11	2.84	47.27		2.84	0.16	2.68
H ₂ O	18.015			22100.00	63961.16		157568.86	3844.19	153724.66	75798.16	4290.46	71507.69	71980.74	76271.20	4317.24	71953.96
Ca(OH) ₂	74.095				1.52				0.00	0.00	0.00	0.00		0.00	0.00	0.00
Ca(COOH) ₂	130.116				12206.95				0.00	0.00	0.00	0.00		0.00	0.00	0.00
CaSO ₄	136.142				0.00				0.00	0.00	0.00	0.00		0.00	0.00	0.00
KOH	56.105						2.06	0.05	2.01	0.05	0.00	0.05		0.00	0.00	0.00
NAOH	39.997						0.25	0.01	0.25	0.01	0.00	0.01		0.00	0.00	0.00
TOTAL LIQUIDS				22100.00	76169.63		177024.24	4318.84	172705.40	76299.58	4318.84	71980.73	71980.74	76299.58	4318.84	71980.74
TOTAL FLOW	22107.76	1057.64	21050.13	22100.00	76169.63	120.00	191420.39	18714.99	172705.40	90695.72	18714.99	71980.73	71980.74	90695.73	18714.99	71980.74
PERCENT SOLIDS							7.5%			15.9%	76.9%			15.9%	76.9%	
K, LB HR	7991.8532	382.3303	7609.5230	0.0000	0.0000	67.6955	7868.7059	191.9721	7676.7338	202.8017	11.4793	191.3223	0.0000	11.4793	0.6498	10.8298
NA LB/HR	829.5775	39.6870	789.8905	0.0000	0.0000	0.0000	809.5711	19.7510	789.8201	20.8652	1.1811	19.6842	0.0000	1.1811	0.0669	1.1142
M K ₂ SO ₄ /M NA ₂ SO ₄			5.664625413													

disposed of to remove a portion of the sodium buildup in the recycled seed. The recovered water soluble flyash seed (stream KF-1) contains mostly K_2SO_4 and Na_2SO_4 . In order to reject more sodium and maintain the sodium levels at steady-state, 4.8% of the recovered seed is also rejected as disposal material (stream KF-2). The remaining seed (stream KF-3) is stored at the seed regeneration plant in a storage silo that is 8000 ft³ providing 24 hours storage capacity. The spent seed material is fed to the potassium formate reactor KF-R-1 using a weigh belt feeder KF-W-1, conveyor KF-CN-1 and grinder KF-G-1 to delump the material for rapid dissolution. In the reactor the spent seed is dissolved in the calcium formate solution (stream KF-5), recycled centrate water from the solids washing operation (stream KF-12), potassium carbonate (stream KF-6), and additional fresh water (stream KF-4) that are added to adjust the solution concentration in the reactor. The reactor is a 8700 gallon stirred vessel sized to provide 15 minutes residence time for the reaction of sulfates to KCOOH and NaCOOH. The calcium formate is the limiting reactant which is added at 81% of the stoichiometric amount for total conversion of the sulfates to formates. Only 81% conversion is required to provide enough formate or carbonate in the recycled seed for sulfur capture in the MHD channel. The remainder of seed material is recycled as K_2SO_4 to provide enough total potassium to meet the 1½% K criteria for channel operation. The reactor operates at atmospheric pressure and 180°F. The reactor effluent stream (stream KF-7) contains 8.9% KCOOH and NaCOOH and a total of about 11% total dissolved solids. Stream KF-7 also contains about 7.5% solids consisting of inerts from the spent seed, $CaSO_4$ and $CaCO_3$. The $CaCO_3$ in the reactor effluent comes from the addition of K_2CO_3 to the reactor to make up a portion of the potassium seed losses. The K_2CO_3 is also added here to aid in the precipitation of calcium as $CaCO_3$ which is orders of magnitude more insoluble than gypsum ($CaSO_4$). The reactor effluent (stream KF-7) is fed to a centrifuge KF-C-1 where the solids are removed from the formate liquor centrate (stream KF-9). The centrate becomes the weak formate solution that is the feed to the evaporator system. Upon concentration, this stream becomes the recycled seed product from the process.

The solids from the centrifuge (stream KF-8) are fed to a wash drum KF-D-4 where the solids are washed with water in a multi-stage system of wash drums followed by dewatering in centrifuges (KF-C-2 and KF-C-3). The wash system is operated countercurrently to

minimize water usage which in the end must be removed from the formate solution by evaporation.

At the end of the wash train the washed solids (stream KF-15) contain only trace amounts of potassium and sodium salts making the cake suitable for disposal as landfill.

5.2.3.4 *KCOOH Evaporation and Roasting Section*

The centrate from KF-C-1 is the regenerated seed solution containing KCOOH, NaCOOH, K_2SO_4 and Na_2SO_4 with a concentration of total dissolved solids of about 11%. There are two options available at this point for recycling the regenerated seed. Option 1 is to concentrate the formate solution with evaporation to remove essentially all of the water producing an anhydrous mixture of KCOOH and NaCOOH containing K_2SO_4 and Na_2SO_4 . The recycled seed in this case would be a molten slurry at temperatures above 333°F (167°C) (melting point of KCOOH), containing about 25% solids as K_2SO_4 and Na_2SO_4 that would precipitate upon evaporation to dryness. This regenerated seed material upon injection into the MHD channel would oxidize via the following reaction:

This reaction is exothermic providing 184,878 Btu/lb-mole of heat release to the MHD channel. Option 1 has the advantage of liquid injection into the channel using slurry pumps where the flow of seed can be accurately controlled avoiding the solids handling problems of solid seed injection that require solids conveying systems.

Option 2 is to evaporate the potassium formate solution to about 90% solids then roast the formate in air producing solid K_2CO_3 and Na_2CO_3 seed containing some sulfates. This can be done continuously in a rotary kiln at 932°F (500°C) using the heat of reaction to provide most of the heat of roasting.

Both options are evaluated in this design to compare the economics of each. For the

seed regeneration process as a stand-alone facility, Option 1 would be the more economical route since it avoids the capital investment of the rotary kiln system and the associated solids cooling and handling equipment. Molten KCOOH has never been tested as a seed material, however, and may not give the same MHD channel performance as K_2CO_3 seed due to the differences in conductivity and temperature in the channel.

Option 1 - Potassium Formate Seed Product

The process flow diagram for evaporation of formate is shown in Figure 5-6 and the material balance is given in Table 5-7. The formate solution from the potassium formate reactor section (stream EK-1) is fed to a four effect evaporation system where the solution is concentrated to anhydrous KCOOH. A four effect system is used to conserve steam but at the expense of evaporator heat transfer surface area. The multiple effect system conserves steam by using the steam from one effect as heating steam for subsequent effects or stages. In this arrangement, which is common practice in the caustic soda industry, the net steam requirement can be reduced to slightly more than 1/4 the steam required if the same evaporation was done in a single stage or effect. It is assumed that the material of construction for the evaporator is stainless steel. Milder temperatures and concentrations in the first and second effects may allow for the use of carbon steel with some cost savings. This will be evaluated during POC testing.

The evaporator overhead water (stream EK-3) is condensed and used for process water. The anhydrous evaporator bottoms (stream EK-2) is a molten mixture of KCOOH and NaCOOH with precipitated solid K_2SO_4 and Na_2SO_4 that falls out of solution as water is removed. The molten formate slurry is stored in a stirred, heated tank to keep the material liquid and the solids in suspension for transfer to the MHD channel as seed.

Option 2 - Potassium Carbonate Seed Product

In this mode of operation, the evaporation system is essentially the same as in Option 1 except that the formate solution is concentrated to only 90% solids rather than anhydrous in the multiple effect evaporator. More water is left in the formate seed mixture since this

Figure 5-6. Potassium Formate Evaporation System Block Flow Diagram

TABLE 5-7. POTASSIUM FORMATE EVAPORATOR MATERIAL BALANCE

OPTION 1-POTASSIUM FORMATE EVAPORATION TO LIQUID FORMATE SEED MATERIAL

EVAPORATOR FEED: FROM
FORMATE
REACTOR

K ₂ SO ₄	3187.6
KCOOH	13435.5
NAOH	0.3
H ₂ O	153724.7
KOH	2.0
NA ₂ SO ₄	458.7
NACOOH	1896.8

TOTAL	172705.6
-------	----------

DISS. SOLIDS CONC. AFTER MULTIPLE EFFECT, %WT	99.9%
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MAKE UP K ₂ SO ₄ SEED ADDED, LB/HR	852.4
--	-------

PRODUCT SEED:

K ₂ SO ₄	4040.0
NACOOH	1896.8
KCOOH	13435.5
H ₂ O	19.0
NA ₂ SO ₄	458.7
NAOH	0.3
KOH	2.0

TOTAL	19852.3
POTASSIUM EQUIVALEN	8059.27

DESCRIPTION	STREAM	EK-1	EK-2	EK-3	EK-4	EK-5
		COMBINED	EVAP	EVAPOR.	MAKEUP	PRODUCT
		EVAP	EVAP	WATER	SEED	SEED
		FEED	BOTTOMS	VENT		
SOLIDS	MW					
K ₂ SO ₄	174.258				852.40	
K ₂ CO ₃	138.205					
INERTS						
NA ₂ SO ₄	142.041					
NA ₂ CO ₃	105.989					
H ₂ O	18.015					
NACOOH	68.008					
KCOOH	84.116					
NAOH	39.997					
KOH	56.105					
TOTAL SOLIDS					852.40	0.00
LIQUIDS	MW					
K ₂ SO ₄	174.258	3187.60	3187.60			4040.00
NACOOH	68.008	1896.80	1896.80			1896.80
KCOOH	84.116	13435.50	13435.50			13435.50
H ₂ O	18.015	153724.70	19.00	153705.70		19.00
NA ₂ SO ₄	142.041	458.70	458.70			458.70
NAOH	39.997	0.30	0.30			0.30
KOH	56.105	2.00	2.00			2.00
TOTAL LIQUIDS		172705.60	18999.90	153705.70		19852.30
TOTAL		172705.60	18999.90	153705.70	852.40	19852.30
PERCENT SOLIDS						22.67%

water will be removed in the roasting operation which is highly exothermic. Figure 5-7 shows a flow diagram for the Option 2 Evaporation and Formate Roasting Section. The material balance is given in Tables 5-8A and 5-8B.

In Option 2 the evaporator bottoms (stream EK-2) are solidified and flaked on a water-cooled rotary drum flaker system. The flaked formate solids (stream EK-4) are conveyed and combined with recycle K_2CO_3 (stream EK-5) then fed to a direct fired rotary kiln (stream EK-6). The formate is the fuel for the roasting operation and the recycled carbonates provide a heat sink to protect from overheating and possible degradation of the product material. The conversion of formate to carbonate in air takes place at temperatures above $400^{\circ}C$, and at $500^{\circ}C$ almost complete conversion is accomplished in one hour or less. The rotary kiln system would be analogous to a commercial lime kiln where $CaCO_3$ is fed usually with coal for fuel producing CaO at temperatures around $1300^{\circ}C$. In this case the fuel is the $KCOOH$ and the inert material is the K_2CO_3 initially fed and formed from the fuel. Air is fed to the kiln (stream EK-7) at 200% of the stoichiometric amount for combustion. The kiln effluent (stream EK-9) at $500^{\circ}C$ now containing K_2CO_3 , Na_2CO_3 and sulfates is cooled in solids coolers typical of those used in the lime industry. The effluent stream is split to provide recycle (stream EK-10) to the kiln and the product (stream E-11) is combined with makeup potassium seed as K_2SO_4 (stream EK-12) to provide the regenerated seed material (stream EK-13) for recycle to the MHD system.

5.2.3.5 Steam/Water Balance

Table 5-9 outlines the steam and water requirements for the process. Six hundred (600) psig steam is generated in the reformer section when the hot synthesis gas is cooled in a waste heat boiler. A by-product credit is taken for this steam. One hundred seventy-five (175) psia and 150 psia steam is used in the evaporator and to preheat the feed to the calcium formate reactor, respectively. A net requirement of 15,700 lbs/hr of boiler feed water is required for the steam generated and used in the process. About 92,400 lbs/hr of process water is required, mostly because of cooling tower losses. A large amount of the process

EVAPORATION AND ROASTING
 K2CO3 PRODUCT
 DATE: OCT 6, 1988
 REV. 1
 TRW

Figure 5-7. Potassium Formate Evaporation/Roasting Block Flow Diagram

TABLE 5-8A. POTASSIUM FORMATE EVPORATION AND ROASTING MATERIAL BALANCE

POTASSIUM FORMATE EVAPORATION AND ROASTING SECTION

EVAPORATOR FEED:	FROM	KILN PARAMETERS:			
	FORMATE				
	REACTOR		% EXCESS AIR		200.0%
			FRACTION OF KILN PRODUCT TO RECYCLE		0.32
K2SO4	3187.6				
KCOOH	13435.5		CALCULATED RECYCLE TO FRESH FEED RATIO		0.36
NAOH	0.3		DELTA T IN KILN, DEG F	872	484 C
H2O	153724.7		T OUT	949	509 C
KOH	2.0				
NA2SO4	458.7				
NACOOH	1896.8				
			PRODUCT SEED:		
TOTAL	172705.6		K2SO4	4040.0	
			K2CO3	11040.0	
			INERTS	0.0	
DISS. SOLIDS CONC. AFTER EVAPORATOR		90.0%	NA2SO4	458.7	
MAKE UP K2SO4 SEED ADDED,LB/HR		852.4	NA2CO3	1478.5	
			TOTAL		17017.1

TABLE 5-8B. EVAPORATOR AND KILN MATERIAL BALANCE

STREAM		EK-1	EK-2	EK-3	EK-4	EK-5	EK-6	EK-7	EK-8	EK-9	EK-10	EK-11	EK-12	EK-13
DESCRIPTION		COMBINED		EVAPOR.	FLAKED	K2CO3	COMBINED	AIR	KILN	KILN	RECYCLE	REGENERATED		PRODUCT
		EVAP	EVAP	WATER	EVAP	RECYCLE	KILN	TO	VENT	SOLIDS	K2CO3	SEED	MAKEUP	SEED
		FEED	BOTTOMS	VENT	BOTTOMS	TO KILN	FEED	KILN		EFFLUENT			SEED	
SOLIDS	MW													
K2SO4	174.258				3187.60	1500.05	4687.65			4687.65	1500.05	3187.60	852.40	4040.00
K2CO3	138.205				0.00	5195.28	5195.28			16235.25	5195.28	11039.97		11039.97
INERTS					0.00	0.00	0.00			0.00	0.00	0.00		0.00
NA2SO4	142.041				458.70	215.86	674.56			674.56	215.86	458.70		458.70
NA2CO3	105.989				0.00	695.75	695.75			2174.21	695.75	1478.46		1478.46
H2O	18.015				2108.99	0.00	2108.99			0.00	0.00	0.00		0.00
NACOOH	68.008				1896.80	0.00	1896.80			0.00	0.00	0.00		0.00
KCOOH	84.116				13435.50	0.00	13435.50			0.00	0.00	0.00		0.00
NAOH	39.997				0.30	0.00	0.30			0.00	0.00	0.00		0.00
KOH	56.105				2.00	0.00	2.00			0.00	0.00	0.00		0.00
TOTAL SOLIDS					21089.89	7606.93	28696.82	0.00	0.00	23771.66	7606.93	16164.73	852.40	17017.13
LIQUIDS	MW													
K2SO4	174.258	3187.60	3187.60											
NACOOH	68.008	1896.80	1896.80											
KCOOH	84.116	13435.50	13435.50											
H2O	18.015	153724.70	2108.99	151615.71										
NA2SO4	142.041	458.70	458.70											
NAOH	39.997	0.30	0.30											
KOH	56.105	2.00	2.00											
TOTAL LIQUIDS		172705.60	21089.89	151615.71		0.00	0.00	0.00	0.00	0.00	0.00	0.00		
TOTAL GAS	MW	172705.60	21089.89	151615.71	21089.89	7606.93	28696.82	0.00	0.00	23771.66	7606.93	16164.73	852.40	17017.13
						KILN AIR:				VENT GAS:				
						MOLE %	MOLES	POUNDS	POUNDS	MOLES	MOLE %			
N2	28.013					79.00%	705.80	19771.79	19771.79	705.8	63.91%			
O2	31.999					21.00%	187.62	6003.52	3001.76	93.8	8.49%			
H2	2.016									0.0	0.00%			
H2O	18.015								3799.36	210.9	19.10%			
CO2	44.010								4127.56	93.8	8.49%			
TOTAL GASES						100.00%	893.41	25775.32	30700.47	1104.3	100.00%			

TABLE 5-9. STEAM AND WATER BALANCE

<u>600 psig Steam</u>	<u>lb/hr</u>
Generation	
Reformer	15,000
Use	0
<u>175 psia Steam</u>	
Generation	0
Use	
Evaporator	51,600
<u>150 psia Steam</u>	
Generation	0
Use	
Formate Reactor Preheater	3,750
<u>100 psig Steam</u>	
Generation	
Reformer	0
Use	0
<u>Boiler Feed Water</u>	
Use	
Reformer	15,300
Evaporator	51,600
Preheater	3,750
	<u>70,650</u>
Condensate Recovery	
Evaporator	51,600
Preheater	3,382
	<u>54,982</u>
Makeup BFW Requirement	15,668
<u>Process Water</u>	
Use	
Lime Slaker	54,426
Calcium Formate Wash Water	16,917
Potassium Formate Reactor	22,100
Potassium Formate Wash Water	71,981
Cooling Tower Makeup	93,560
	<u>258,984</u>
Recovery	
Evaporator	158,125
35 psia Flash Steam	5,351
15 psia Flash Steam	3,143
	<u>166,619</u>
Makeup Process Water Requirement	92,365
<u>Cooling Water Circulation</u>	
Reformer	165,000
Barometric Condenser	1,190,000
	<u>1,355,000</u>

water is recovered in the evaporator overhead stream. Very little water is lost with the solids from the process.

5.2.4 Major Equipment

The major equipment required by the Econoseed process for the regeneration of spent MHD seed material from a 300 MW_t plant is listed in Table 5-10. The code of accounts shown in Table 5-10 for reporting summary level costs is consistent with the DOE/NASA MHD Code. The major equipment for each code of accounts is shown along with a brief description of each equipment item, the major component material cost of each item delivered to the site, the balance of account materials delivered to the site (piping, concrete, steel, instruments, electrical, insulation, paint), and the installation cost which includes all unburdened field labor to install the equipment and erect the field materials. The sum of the major component material cost, the balance of account materials, and the installation cost is the total direct installed cost. An indirect construction cost is next added to the total direct installed cost to cover field supervision, payroll burden, tools, facilities, and engineering. The sum is the base erected cost. The major component material costs were obtained from various sources (equipment suppliers, the technical literature, previous TRW purchase requisitions for similar items, and internal TRW costing data). The cost of the Reducing Gas Generation Section, Account 317.61, was supplied by Fluor-Daniel, and the cost of the Evaporation System, Account No. 317.31, was supplied by Blaw-Knox. The costs of the equipment in these two areas were supplied as complete packaged units. The factors used to obtain the balance of account estimates, the installation costs, and the indirect costs were obtained from Guthrie (Reference 1). These factors are consistent with the EPRI-TAG guidelines (Reference 2).

5.2.5 Capital Costs

The capital costs of the battery limit Econoseed Seed Regeneration System were estimated consistent with EPRI-TAG methodology (Reference 2). Consequently, the capital costs of the system are expressed in terms of Total Plant Cost (TPC), Total Plant Investment

TABLE 5-10. MAJOR EQUIPMENT (\$1000)

ACCOUNT NO.	ACCOUNT TITLE	EQUIPMENT NO.	DUTY	MATERIAL COST		INSTALLATION COST	DIRECT INSTALLED	INDIRECT CONSTRUCTION	BARE ERECTED
				MAJOR COMPONENT	BALANCE OF ACCOUNT				
317.61	REDUCING GAS GENERATION			**	**	**	3600	800	4400
317.62	REACTION SECTION								
21	LIME SUPPLY SYSTEM								
	LIME SILO (1 WEEK)	CF-S-1	26,700 FT3	*	*	*	175	33	208
	LIME SILO (1 DAY)	CF-S-2	4000 FT3	*	*	*	63	12	75
	LIME CONVEYOR, PNEUMATIC	CF-CN-1	3 TPH	*	*	*	73	14	87
	LIME FEEDER, SCREW	CF-CN-2	3 TPH	*	*	*	54	10	64
22	LIME SLURRY								
	LIME DISSOLVER	CF-R-1	8'5" X 16'10" TT	42	43	41	126	30	156
	PUMP	CF-P-1	210 HP	214	150	145	509	122	631
	FIRST EXCHANGER	CF-E-1	6 MM BTU/H	29	20	18	67	16	83
	SECOND EXCHANGER	CF-E-2	3 MM BTU/H	16	11	10	37	9	46
23	SPENT SEED HANDLING								
	SPEND SEED SILO (3 DAYS)	KF-S-1	24,000 FT3	*	*	*	168	32	200
	SPENT SEED SILO (1 DAY)	KF-S-2	8000 FT3	*	*	*	79	15	94
	SPENT SEED CONVEYOR, PNEUMATIC	KF-CN-2	11 TPH	*	*	*	181	34	215
	SPENT SEED CONVEYOR, WEIGH BELT	KF-CN-1	10.5 TPH	*	*	*	175	33	208
	GRINDER	KF-G-1	10.5 TPH	20	1	1	22	4	26
	FEEDER, SCREW	KF-CN-3	10.5 TPH	*	*	*	50	10	60
24	SPENT SEED REACTOR								
	K2CO3 SILO (1 WEEK)	KF-S-3	400 FT3	*	*	*	20	4	24
	K2CO3 CONVEYOR, BELT	KF-CN-4	120 LB/H	*	*	*	10	2	12
	K2CO3 FEEDER, SCREW	KF-CN-5	120 LB/H	*	*	*	10	2	12
	KCOOH REACTOR	KF-R-1	9' X 18' TT	45	46	44	135	32	167
	MIXER	KF-M-1	17,400 GAL TANK	10	2	2	14	3	17
	SLURRY PUMP	KF-P-1	20 HP	5	4	3	12	3	15
25	CALCIUM FORMATE REACTOR								
	REACTORS (2)	CF-R-2	2' X 20' TT	62	64	60	186	45	231
	FIRST FLASH DRUM	CF-D-1	2'3" X 7' TT	11	11	11	33	8	41
	SECOND FLASH DRUM	CF-D-2	2' X 6' TT	10	10	10	30	7	37
	CENTRIFUGES (2)	CF-C-1,2	0.53 TPH CAKE	575	201	144	920	221	1141
	WASH DRUM	CF-D-3	5'3" X 10'5" TT	20	21	19	60	14	74
	PUMPS (4)	CF-P-2,3,4,5	50 TO 150 HP	10	7	7	24	6	30
	SOLIDS DISPOSAL	CF-D-4	0.5 TPH	20	3	2	25	5	30
26	SEED CLARIFICATION								
	CENTRIFUGES (3)	KF-C-1,2,3	9.4 TPH CAKE	1300	455	325	2080	499	2579
	WASH DRUMS (2)	KF-D-4,5	8' X 16' TT	62	64	60	186	45	231
	CENTRATE RECEIVER	KF-D-1	7'8" X 15'4" TT	30	31	29	90	22	112
	CENTRATE RECEIVERS (2)	KF-D-2,3	5'10" X 11'9" TT	44	45	43	132	32	164
	PUMPS (7)	KF-P-2 THRU 8	150 TO 350 HP	22	15	15	52	12	64
	MIXERS (2)	KF-M-2,3	6000 GAL TANKS	20	4	4	28	7	35
	SOLIDS DISPOSAL	KF-D-6	9.4 TPH	227	30	27	284	54	338
371.63	SEED CONCENTRATION AND OXIDATION								
31	EVAPORATION SYSTEM								
	EVAPORATOR/FLAKER	EK-EV-1	75.8 TPH STEAM	2580	305	305	3190	766	3956
	MISC. CONVEY, STORAGE EQUIPMENT	EK-CN-1	10.5 TPH BOTTOMS	*	*	*	374	71	445
317.65	REGENERATED SEED STORAGE	EK-S-1	8.5 TPH	*	*	*	178	34	212

* THE SOURCE FOR THE SILOS, CONVEYORS, AND SCREW FEEDERS ONLY PROVIDED INSTALLED COSTS

** FLUOR-DANIEL SUPPLIED ONLY DIRECT INSTALLED AND INDIRECT CONSTRUCTION COSTS

(TPI), and Total Capital Requirement (TCR). See Appendix A for EPRI-TAG terminology of capital cost components.

The major component material costs, the balance of account materials costs, the installation costs, the direct installed costs, the indirect construction costs, and the base erected costs from Table 5-10 were summed at the code of accounts summary level and are presented in Table 5-11.

An engineering services fee is next added. The engineering services fee includes the engineering and home office overhead and fee. With the exception of reducing gas generation, an engineering services fee of 10% of the bare erected cost was used based on Guthrie and EPRI-TAG guidelines. Fluor-Daniel provided the estimate for the engineering services fee for the reducing gas generation section.

EPRI-TAG guidelines use two types of contingencies: the project contingency and the process contingency. The project contingency is intended to cover the uncertainty in the cost estimate itself (such as the cost of additional equipment or other costs that would result from a more detailed design of a definitive project at an actual site), whereas the process contingency covers the uncertainty in the technical performance of the equipment, especially new technology. In both cases, the contingencies represent cost that are expected to occur.

Process contingency was selectively applied to the calcium formate reactor system at 25 percent of the direct installed cost, at 10% to the spent seed reactor, the lime slurry system and seed clarification system, and at 5% to the reducing gas generation system, lime supply system, spent seed handling system, evaporation system, and regenerated seed storage. The project contingency was estimate at 15% of the direct installed cost, engineering services fee, and process contingency. These values are in line with contingency percentages listed in EPRI-TAG (Reference 2).

TABLE 5-11. PLANT COST (\$1000)

		COST BASIS		MATERIAL COST			DIRECT	INDIRECT	BARE	CONTINGENCY			TOTAL
ACCOUNT				MAJOR	BALANCE OF	INSTALLATION	INSTALLED	CONSTRUCTION	ERECTED	ENGINEERING	PROCESS	PROJECT	PLANT
NO.	ACCOUNT TITLE	UNIT	QUANTITY	COMPONENT	ACCOUNT	COST	COST	COST	COST	SERVICES			COST (TPC)
317.61	REDUCING GAS GENERATION	EACH	*	*	*	*	3600	800	4400	1000	180	717	
317.62	REACTION SECTION												
21	LIME SUPPLY SYSTEM	EACH	*	*	*	*	365	69	434	43	18	64	
22	LIME SLURRY	EACH	*	301	224	214	739	177	916	92	74	136	
23	SPENT SEED HANDLING	EACH	*	20	1	1	675	128	803	80	34	118	
24	SPENT SEED REACTOR	EACH	*	60	52	49	201	46	247	25	20	37	
25	CALCIUM FORMATE REACTOR	EACH	*	708	317	253	1278	306	1584	158	320	263	
26	SEED CLARIFICATION	EACH	*	1705	644	503	2852	671	3523	352	285	523	
317.63	SEED CONCENTRATION/OXIDATION												
31	EVAPORATION SYSTEM	EACH	*	2580	305	305	3564	837	4401	440	178	627	
317.65	REGENERATED SEED STORAGE	EACH	*	*	*	*	178	34	212	21	9	31	
SUBTOTALS							13452	3068	16520	2212	1118	2517	22367

• SEE TABLE 5-10.

The sum of the bare erected cost, engineering services fee and the project and process contingencies is the Total Plant Cost (TPC). The TPC estimate of 22.4 million dollars is expressed in January 1988 dollars on an overnight construction basis.

In addition to the capital cost items listed in Table 5-11, there are additional cost items that must be included to arrive at the Total Capital Requirement for the Econoseed Regeneration System. The additional items are listed in Table 5-12.

The total plant cost (TPC) from Table 5-11 is at a single point in time and does not include the time value of money (interest, etc.) during the construction period. This TPC cost is converted to the total cash expended (TCE) which represents the amount of money that would have been spent for all labor, materials, and indirects at the time the plant goes into service. The procedure used to calculate the TCE includes de-escalating the components of the TPC back to the point of expenditure. The AFDC (Allowance for Funds During Construction) represents the interest paid on the cash expended during the construction period. The interest is accumulated and compounded until the plant goes into service. The total plant investment (TPI) is the sum of the TCE and AFDC. The TPI is expressed in mixed-year dollars accumulated at the same point in time as total plant cost (TPC).

For consistency, a uniform expenditure rate is assumed. For such a case, the total plant investment (TPI), total cash expended (TCE), and allowance for funds during construction (AFDC) can be calculated by multiplying the total plant cost (TPC) by the appropriate adjustment factors. Adjustment factors for converting TPC into TPI are given in EPRI-TAG (Reference 2) and are included in Appendix A of this report.

The adjustment factors used in this design assume a construction period of three years, an inflation rate of 6% per year, and an AFDC interest rate of 12.5% per year. Using these values, the Total Plant Investment (TPI) at the in-service date is 23.75 million dollars.

The Total Capital Requirement (TCR) includes all capital necessary to complete the entire project. This includes the TPI, prepaid royalties, preproduction (or startup) costs,

TABLE 5-12. TOTAL CAPITAL REQUIREMENT

	<u>\$1000</u>	<u>\$/KW*</u>	<u>\$/TON S**</u>
TOTAL PLANT COST (TPC)	22,367	223.67	2629.03
TOTAL CASH EXPENDED (TCE)	21,114	211.14	2481.80
INTEREST DURING CONSTRUCTION (AFDC)	2,639	26.39	310.23
TOTAL PLANT INVESTMENT (TPI)	23,754	237.54	2792.03
ROYALTY ALLOWANCE (0.5% OF TPI)	119	1.19	13.96
PREPRODUCTION COSTS	999	9.99	117.42
WORKING CAPITAL	1,971	19.71	231.67
INITIAL CATALYST AND CHEMICALS	0	0.00	0.00
LAND COST (10 ACRES @ \$7,750/ACRE)	78	0.78	9.11
TOTAL CAPITAL REQUIREMENT (TCR)	26,920	269.20	3164.20

* BASED ON 100 MWe NET

**PER TON OF SULFUR REMOVED PER YEAR

working capital, initial catalyst and chemical charges, and land cost. Prepaid royalties are taken at 0.5% of the TPI. Preproduction or startup costs are intended to cover preproject administrative costs, operator training, equipment checkout, changes in plant equipment, extra maintenance, and inefficient use of fuel and materials during plant startup. The preproduction costs are based on EPRI-TAG guidelines using fixed and variable operating costs, fuel costs, and TPI costs. Working or inventory capital covers the value of inventories of fuels, other consumables, byproducts, and spare parts. The working capital is based on the TPC costs and a fuel and consumable inventory of 60 days at full load capacity. The initial cost of any catalysts and chemicals contained in the process equipment (but not in storage, which is covered in inventory capital) is included in the initial catalyst and chemical charge. There is no initial catalyst and chemical charge for this process (see Table 5-12). Land costs are estimated at \$7,750/acre and include both the plant area and storage area.

The Total Capital Requirement (TCR) for the Econoseed System is 26.9 million dollars. The methodology used to determine this cost is consistent with EPRI-TAG. Each cost component of the TCR in Table 5-12 is also expressed in dollars per kW (net plant size) and dollars per ton of sulfur removed (tons per year at 65% capacity factor). The TCR is equivalent to \$269/kW and \$3164/ton sulfur removed.

5.2.6 Operating Costs

The operating costs and related maintenance expenses pertain to those charges associated with operating and maintaining the seed regeneration system. These costs and expenses are estimated on a first year basis in January 1988 dollars. The operating costs do not include the initial startup costs which were computed separately in Section 5.2.5 as part of the total capital requirement.

Operating costs, excluding consumables, according to EPRI-TAG are further divided into fixed and variable components. Fixed costs are essentially independent of actual capacity factor, number of hours of operation, or amount of energy produced, are generally expressed in \$/kW-yr. Variable costs are directly proportional to the amount of energy

produced and are referred to as incremental costs. They are generally expressed in mills/kWh.

The first year operating and maintenance costs are based on a plant capacity factor of 65%. The operating and maintenance costs are presented in Table 5-13. Costs in Table 5-13 are expressed in absolute dollars, dollars per kW-yr, mills per kWh, and dollars per ton of sulfur removed per year.

The operating labor cost is based on four shifts with a per shift requirement of four full time operators and a laboratory technician one half of the time. The first year operating labor charges are computed using an average labor rate of \$23.50/hr (including burden).

Based on EPRI-TAG guidelines, the annual maintenance costs are taken at 2.5 percent of the total plant investment. The maintenance costs are subdivided into maintenance labor (40%) and maintenance materials (60%). The administrative and support labor cost is an overhead charge taken as 30% of the operating and maintenance labor.

The operating labor, maintenance material and labor and other labor related costs, are combined and then divided into two components: 1) fixed O&M, which is independent of system operation, and 2) variable O&M, which is proportional to system operation.

The consumable operating costs presented in Table 5-13 are determined on a daily 100% operating capacity basis and adjusted to an annual plant operation basis equivalent to operating at 100% load for 65% for the year (plant capacity factor). The consumable operating costs consist of water, steam, chemicals, other consumables, and waste disposal. The consumable costs are incremental, directly proportional to the amount of power produced, and are also expressed in mills/kWh in Table 5-13. A consumable cost worksheet is presented in Table 5-14.

The total operating expenses for the Econoseed MHD seed regeneration process for a 300 MW_t plant are 6.65 million dollars for the first year.

TABLE 5-13. FIRST YEAR OPERATING AND MAINTENANCE COSTS

	\$1000	\$/KW-YR	\$/TON S
OPERATING AND MAINTENANCE COSTS			
OPERATING LABOR			
(4.5/SHIFT @\$23.50/PERSON HOUR INCLUDING BURDEN)	602	9.3	
MAINTENANCE LABOR (40% OF TOTAL MAINTENANCE COST)	238	3.7	
MAINTENANCE MATERIALS (60% OF TOTAL MAINTENANCE COST)	356	5.5	
ADMINISTRATIVE AND SUPPORT LABOR (30% OF OTHER LABOR)	252	3.9	
TOTAL OPERATION AND MAINTENANCE	1,448	22.3	170.2
FIXED O&M (FIRST YEAR)		14.5	\$/KW-YR
VARIABLE O&M (FIRST YEAR)		1.4	MILLS/KWH
	\$1000	MILLS/KWH	\$/TON-S
CONSUMABLE OPERATING COSTS*			
WATER	88	0.15	
STEAM	1,150	2.02	
CHEMICALS	1,268	2.23	
OTHER (LESS FUEL)	1,174	2.06	
WASTE DISPOSAL	318	0.56	
SUBTOTAL	3,998	7.02	469.9
FUEL	3,352	5.89	394.0
TOTAL CONSUMABLES	7,350	12.91	863.9
BY-PRODUCT CREDITS*	2,152	3.78	252.9
TOTAL FIRST YEAR OPERATING EXPENSES	6,646	11.67	781.2

* SEE TABLE 5-14.

TABLE 5-14. CONSUMABLE COST WORKSHEET

ITEM	QUANTITY		UNIT COST	INITIAL COST	DAILY COST	ANNUAL COST* (\$1000)
	INITIAL	/DAY				
WATER						
BFW (/1000 LB)	-	376	\$0.70	-	263	62
PROCESS WATER (/1000 GAL)	-	266	\$0.40	-	106	25
WATER SUBTOTAL				-	370	88
STEAM						
175 PSIA (/1000 LB)	-	1238	\$3.65	-	4519	1072
150 PSIA (/1000 LB)	-	90	\$3.65	-	329	78
STEAM SUBTOTAL				-	4847	1150
CHEMICALS						
LIME (TONS)	**	70	\$40.00	-	2800	664
K2CO3 (/100 LB)	**	29	\$36.00	-	1044	248
K2SO4 (TONS)	**	10	\$150.00	-	1500	356
CHEMICAL SUBTOTAL				-	5344	1268
OTHER						
NAT. GAS (MM BTU)	-	2826	\$5.00	-	14130	3352
IN PLANT POWER (kWh)	-	15840	\$0.06	-	950	225
OXYGEN (TONS)	***	80	\$50.00	-	4000	949
OTHER SUBTOTAL				-	19080	4527
WASTE DISPOSAL						
CACO3/CA(OH)2 (TONS)	-	13	\$8.35	-	109	26
FLYASH, K2SO4 (TONS)	-	13	\$8.35	-	109	26
GYPSUM (TONS)	-	225	\$5.00	-	1125	267
WASTE DISPOSAL SUBTOTAL				-	1342	318
BY-PRODUCTS						
FORMATE REACTOR OFFGAS (MM BTU)	-	358	\$4.00	-	1432	340
600 PSIA STEAM (/1000 LB)	-	360	\$5.50	-	1980	470
MEMBRANE SEPARATOR OFFGAS (MM BTU)	-	1415	\$4.00	-	5660	1343
BY-PRODUCTS SUBTOTAL				-	9072	2152
TOTAL				-	21911	5199

*AT 65% CAPACITY FACTOR

**(INCLUDED IN WORKING (INVENTORY) CAPITAL

***OXYGEN PLANT NOT PART OF SEED REGENERATION SITE

Using a capital recovery factor of 0.1546, the total cost of producing an equivalent amount of K_2CO_3 is 17.2 cents per pound (see Table 5-15). The 1988 price of K_2CO_3 was 35.5 cents per pound in bulk quantities (Reference 3). On a potassium basis, the cost of the Econoseed process is 23.6 cents per pound of potassium in the recycled seed (as compared to 62.7 cents per pound potassium based on the market value of K_2CO_3).

5.2.7 Phase I Alternate Cases

The base case discussed in the previous section has a natural gas partial oxidation unit and produces potassium formate as the product seed. However, the carbon monoxide needed by the calcium formate reactor can also be produced by a coal-fired partial oxidation (POX) unit. In addition, the regenerated seed product can be either potassium formate or potassium carbonate. As part of the Phase I design effort, three alternate cases were developed. These three cases (plus the base case) are:

- Natural gas POX unit and KCOOH seed product (base case)
- Natural gas POX unit and K_2CO_3 seed product
- Coal POX unit and KCOOH seed product
- Coal POX unit and K_2CO_3 seed product

In order to convert potassium formate to potassium carbonate, a rotary kiln is needed. The addition of a kiln does not affect the stream and water balance (Table 5-16); however, it adds four million dollars to the total plant cost (Table 5-17, Case 2 versus Case 1 and Case 4 versus Case 3), 4.4 million dollars to the total capital requirement (Table 5-17), and 0.12 million dollars per year to the operating expenses (Tables 5-18). Overall, the addition of a kiln increases the cost per equivalent pound of K_2CO_3 produced by 1.3 cents/lb (18.5 cents versus 17.2 cents, and 17.4 cents versus 16.1 cents, Table 5-18).

The conversion from a natural gas-fired POX unit to a coal-fired POX unit increases the capital requirement but decrease the operating expenses (Tables 5-16 through 5-18, Case 3

TABLE 5-15. COST OF PRODUCTION

TOTAL OPERATING EXPENSES (\$ MILLION/YR)	6.646
CAPITAL CHARGES @ 15.46% TCR (\$ MILLION/YR)	<u>4.162</u>
TOTAL AMORTIZED OPERATING COST (\$ MILLION/YR)	10.808
K ₂ CO ₃ EQUIVALENT (MILLION LBS/YR)	62.86
POTASSIUM IN RECYCLED SEED (MILLION LBS/YR)	45.89
TOTAL COST PER EQUIVALENT POUND	
K ₂ CO ₃ PRODUCED (CENTS/LB)	17.2
TOTAL COST PER LB POTASSIUM IN RECYCLED	
SEED (CENTS/LB)	23.6
PRESENT MARKET PRICE OF K ₂ CO ₃ (CENTS/LB)	35.5
PRESENT MARKET PRICE OF K EQUIVALENT (CENTS/LB)	62.7

TABLE 5-16. STEAM AND WATER BALANCE (KCOOH OR K₂CO₃ PRODUCT)

	Nat Gas POX lb/hr	Coal POX lb/hr
<u>600 psig Steam</u>		
Generation - Reformer	15,000	0
Use	0	0
<u>175 psia Steam</u>		
Generation	0	0
Use - Evaporator	51,600	51,600
<u>150 psia Steam</u>		
Generation	0	0
Use - Formate Reactor Preheater	3,750	3,750
<u>100 psig Steam</u>		
Generation - Reformer	0	10,900
Use	0	0
<u>Boiler Feed Water</u>		
Use	70,650	69,350
Condensate Recovery	54,982	54,982
Makeup BFW Requirement	15,668	14,368
<u>Process Water</u>		
Use	258,984	261,744
Recovery	166,619	166,619
Makeup Process Water Requirement	92,365	95,125
<u>Cooling Water</u>		
Circulation	1,355,000	1,395,000

TABLE 5-17. TOTAL CAPITAL REQUIREMENT FOR ALTERNATE CASES (\$1000)

ACCOUNT NO.	ACCOUNT TITLE	1	2	3	4
		NAT GAS POX KCOOH PROD	NAT GAS POX K2CO3 PROD	COAL POX KCOOH PROD	COAL POX K2CO3 PROD
317.61	REDUCING GAS GENERATION	4,400	4,400	9,100	9,100
317.62	REACTION SECTION				
21	LIME SUPPLY SYSTEM	434	434	434	434
22	LIME SLURRY	916	916	916	916
23	SPENT SEED HANDLING	803	803	803	803
24	SPENT SEED REACTOR	247	247	247	247
25	CALCIUM FORMATE REACTOR	1,584	1,584	1,584	1,584
26	SEED CLARIFICATION	3,523	3,523	3,523	3,523
317.63	SEED CONCENTRATION/OXIDATION				
31	EVAPORATION SYSTEM	4,401	4,401	4,401	4,401
33	OXIDATION REACTOR	0	3,149	0	3,149
317.65	REGENERATED SEED STORAGE	212	212	212	212
	TOTAL BARE ERECTED COST	16,520	19,669	21,220	24,369
	ENGINEERING SERVICES	2,212	2,527	3,112	3,427
	PROCESS CONTINGENCY	1,118	1,246	1,323	1,451
	PROJECT CONTINGENCY	2,517	2,967	3,298	3,748
	TOTAL PLANT COST (TPC)	22,367	26,409	28,953	32,995
	TOTAL CASH EXPENDED (TCE)	21,114	24,930	27,332	31,147
	INTEREST DURING CONSTRUCTION (AF)	2,639	3,116	3,416	3,893
	TOTAL PLANT INVESTMENT (TPI)	23,754	28,046	30,748	35,040
	ROYALTY ALLOWANCE (0.5% OF TPI)	119	140	154	175
	PREPRODUCTION COSTS	999	1,095	1,066	1,162
	WORKING CAPITAL	1,971	1,991	1,233	1,253
	INITIAL CATALYST AND CHEMICALS	0	0	0	0
	LAND COST (10 ACRES @ \$7,750/ACRE)	78	78	78	78
	TOTAL CAPITAL REQUIREMENT (TCR)	26,920	31,350	33,279	37,708

TABLE 5-18. FIRST YEAR ANNUAL OPERATING COST COMPARISON FOR ALTERNATE CASES (\$1000/YR)

	1	2	3	4
	NAT GAS POX KCOOH PROD	NAT GAS POX K2CO3 PROD	COAL POX KCOOH PROD	COAL POX K2CO3 PROD
OPERATING AND MAINTENANCE COSTS				
OPERATING LABOR	602	602	602	602
MAINTENANCE LABOR	238	280	307	350
MAINTENANCE MATERIALS	356	421	461	526
ADMINISTRATIVE/SUPPORT LABOR	252	265	273	286
TOTAL OPERATION AND MAINTENANCE	1,448	1,568	1,643	1,764
CONSUMABLE OPERATING COSTS				
WATER	88	88	83	83
STEAM	1,150	1,150	1,150	1,150
CHEMICALS	1,268	1,268	1,268	1,268
OTHER (LESS FUEL)	1,174	1,174	759	759
WASTE DISPOSAL	318	318	334	334
SUBTOTAL	3,998	3,998	3,594	3,594
FUEL	3,352	3,352	709	709
TOTAL CONSUMABLES	7,350	7,350	4,303	4,303
BY-PRODUCT CREDITS	2,152	2,152	966	966
TOTAL FIRST YEAR OPERATING EXPENSES	6,646	6,766	4,980	5,101
CAPITAL CHARGES @ 15.46% TRC	4,162	4,847	5,145	5,830
AMORTIZED OPERATING COST	10,808	11,613	10,125	10,931
TOTAL COST PER EQUIVALENT POUND K2CO3 PRODUCED	17.2 CENT/LB	18.5 CENT/LB	16.1 CENT/LB	17.4 CENT/LB
TOTAL COST PER K IN RECYCLED SEED	23.6 CENT/LB	25.3 CENT/LB	22.1 CENT/LB	23.8 CENT/LB

versus Case 1 and Case 4 versus Case 2). The savings in operating costs for a coal-fired unit (due mostly to fuel savings) more than offset the increase capital expenditures on a cost of K_2CO_3 basis. Conversion to a coal-fired POX unit decreases the cost per equivalent pound of K_2CO_3 produced by 1.1 cents/lb (16.1 cents versus 17.2 cents and 17.4 cents versus 18.5 cents).

Table 5-19 summarizes some of the important economic criteria for the four cases studies. Total capital requirements (TCR) are given as 1988 dollars, \$/kW (based on 100 MW_e, i.e. a 33% overall efficiency), and \$/ton sulfur removed. Annual operating costs are added to a capital charge equal to 15.46% of TCR to give a total amortized operating cost for each case. The amortized operating cost is then presented based on several different criteria. The total cost per pound equivalent of K_2CO_3 is the amortized operating cost divided by the total annual production of K_2CO_3 in the seed (or K_2CO_3 equivalent of the KCOOH in the seed). Also given is the amortized cost per pound equivalent of potassium in the seed. This includes the potassium in K_2SO_4 as well as the potassium in K_2CO_3 which both make up the criteria for 1.5% K in the MHD channel. A third criteria is the cost per pound of total seed produced which is the amortized operating cost divided by the annual total weight of seed produced. The total weight here contains sodium salts and other contaminants as well as the potassium salts that make up the product seed which are recycled. Finally, the amortized operating costs in Table 5-19 are given as mills/kWh based on 100 MW_e and a 65% capacity factor.

5.2.7.1 *Cost of Power*

The cost of power for each of the four cases studied are shown in Table 5-19. The total annual amortized cost for each case is the sum of the annual operating costs plus a capital charge equal to 15.46% of the total capital requirement (TCR). The cost of power for each case in mills/kWh is based on 100 MW_e and the 65% capacity factor. From Table 5-19 the cost of power ranges from 17.8 mills/kWh for the coal-fired POX unit producing KCOOH (Case 3) to 20.4 mills/kWh for the natural gas POX unit producing K_2CO_3 solid seed (Case 2).

TABLE 5-19. ECONOMIC COMPARISONS FOR ALTERNATE CASE STUDIES

ECONOMIC CRITERIA	CASE 1 (BASE CASE) NAT GAS POX KCOOH SEED	CASE 2 NAT GAS POX K ₂ CO ₃ SEED	CASE 3 COAL POX KCOOH SEED	CASE 4 COAL POX K ₂ CO ₃ SEED
CAPITAL INVESTMENT:				
Total Capital Requirement, \$ Millions	26.9	31.4	33.3	37.7
Total Capital Requirement, \$/kW	269	314	333	377
Total Capital Requirement, \$/ton S Removed	3,164	3,687	3,917	4,434
OPERATING COSTS:				
Annual Operating Expenses, \$ Million/Yr (O&M, Consumables, Credits, etc.)	6.65	6.77	4.98	5.10
Capital Charges @ 15.46% TCR, \$ Millions/Yr	4.16	4.85	5.15	5.83
Total Annual Amortized Cost, \$ Millions/Yr	10.81	11.61	10.13	10.93
Total Cost per Lb Equivalent K ₂ CO ₃ , cents/lb	17.2	18.5	16.1	17.4
Total Cost per Lb K in Recycle Seed, cents/lb	23.6	25.3	22.1	23.8
Total Cost per Lb of Seed (Mixture of Salts)	11.1	12.0	10.4	11.3
Total Annual Amortized Cost, mills/kWh (Based on 100 MW _e @ 65% Capacity Factor)	19.0	20.4	17.8	19.2

5.2.7.2 *Potential Process Improvements*

There are several areas in the Econoseed process where process improvements and changes may show significant lowering of capital and operating costs. Some of the improvements in costs have been shown in comparisons of the cases studies. The use of a coal POX unit for CO generation and producing a formate liquid seed material rather than K_2CO_3 offers potential savings. Other potential cost saving modifications that require investigation are:

- The use of first stage MHD combustor gases as a source for CO in the calcium formate reactor eliminating the POX unit. This would entail drawing a slip-stream from the combustor and gas conditioning for use in the calcium formate reactor. The MHD combustor would increase in size slightly to provide this gas.
- Using a capacity factor higher than 65% for the seed regeneration plant would reduce the plant size and the capital investment. Chemical plants are typically operated at a higher on-stream factor (~80%).
- The cost estimates presented contain rather high contingency factors that could probably be reduced after POC testing when design parameters become better defined. This could lead to a potential capital savings up to about 10%.
- The design cases presented assume an addition of K_2CO_3 or $KCOOH$ as seed that would capture 100% of the sulfur from the coal. If this assumption was eased to 90% capture to equal typical FGD design assumptions, there would be a 10% reduction in the amount of seed regenerated from K_2SO_4 to $KCOOH$. This would reduce operating costs especially of the calcium formate reactor section and the CO gas generation section. The most significant savings would be a 10% fuel savings for CO generation.
- The countercurrent washing of solids such as $CaSO_4$ in the potassium formate reactor section has not been optimized. There is a potential to reduce the number of centrifuge stages for dewatering and washing while still providing adequate solids washing by the use of more recycle wash water. Since the centrifuges are high cost items to the process, significant capital savings might be realized.

5.2.8 Phase II Alternate Cases

Early in the Phase II program several additional alternate cases were developed in order to guide the design of the POC units and the Western seed laboratory studies. When the

process design for a 300 MW_t MHD system using high sulfur Illinois No. 6 coal was developed as part of the Phase I Seed Regeneration program (see Section 5.2.7), it was recognized that critical differences in the seed regeneration process might exist for a system using Western coal due to the lower sulfur content. The Econoseed process as configured for Eastern seed does not take advantage of the lower sulfur content of Western coal, and thus the processing costs for a Western coal system would be about the same as those for a higher sulfur Eastern coal. However, if the method described in Section 4 of this Final Report for separation of the carbonate from the sulfate in the spent seed is used on low sulfur Western coal, considerable cost savings can be realized. Assuming the spent seed contains about 2:1 (wt) carbonate to sulfate, the calcium formate required for the reaction can be reduced by two-thirds, equally reducing the requirement for CO gas generation. The potassium carbonate solution from the carbonate/sulfate separation is evaporated to recover the seed material as a solid or slurry (if the formate and carbonate are mixed before feeding the evaporator). In either case, the amount of water evaporated is reduced since the carbonate solution contains about 35% dissolved solids while the usual solution from the potassium formate system contains no more than 10% dissolved solids.

Several seed regeneration cases were investigated early in the Phase II program in order to show the potential capital and operating cost savings that might be realized if this method for pre-separation of carbonate and sulfate from Western coal spent seed were developed. Table 5-20 presents the results of that investigation for five cases, including both Eastern and Western coals. All cases in Table 5-20 use a natural gas-fired POX unit for CO generation.

A 40% overall efficiency was assumed for the MHD systems presented in Table 5-20 versus a 33% overall efficiency used in the process design developed during the Phase I program. Case 1 in Table 5-20 is similar to the Phase I Case 1 in Tables 5-17 through 5-19 with the major difference being the difference in overall efficiency (40% versus 33%). This change (among others) lowered the cost for seed regeneration from 21.3 mills/kWh to 15.8 mills/kWh.

TABLE 5-20. COMPARISON OF PROCESS ECONOMICS FOR EASTERN AND WESTERN
COAL SEED REGENERATION

BASIS:

300 MWt MHD SYSTEMS @ 40% OVERALL EFFICIENCY

95% THEORETICAL COMBUSTION AIR

AIR ENRICHED TO 35% O₂

SLAG REJECTION- 70%

65% CAPACITY FACTOR

CASE	1	2	3	4	5
COAL:					
COAL TYPE	ILL #6	ILL #6	ILL #6	MONTANA	MONTANA
ASH CONTENT	12.52%	12.52%	12.52%	13.06%	13.06%
SULFUR CONTENT	3.62%	3.62%	3.62%	1.10%	1.10%
SEED:					
WT % K IN CHANNEL	1.5%	1.5%	1.17%	1.5%	1.5%
CO ₃ (equivalent) / S RATIO	1:1	1.29:1	1:1	3.95	3.95
SEED TYPE	FORMATE/ SULFATE	FORMATE	FORMATE	FORMATE	FORMATE/ CARBONATE
PROCESS ECONOMICS					
TOTAL CAPITAL REQMENT,(TCR) \$, millions	\$26.9	\$30.0	\$26.2	\$29.9	\$18.2
TCR - \$/KWe NAMEPLATE	\$224	\$250	\$218	\$249	\$152
OPERATING COSTS:					
DIR. OPER. COST, \$, Million	\$6.6	\$7.7	\$6.5	\$7.3	\$3.3
CAPITAL CHARGE- 15.5% TCR	\$4.2	<u>\$4.6</u>	<u>\$4.0</u>	<u>\$4.6</u>	<u>\$2.8</u>
TOTAL AMORTIZED OP COSTS	\$10.8	\$12.4	\$10.5	\$11.9	\$6.1
OPERATING COSTS, \$/LB K Based on total seed circ.	\$0.24	\$0.27	\$0.30	\$0.26	\$0.13
TOTAL OPERATING COST,mills/kwh	15.8	18.1	15.4	17.5	9.0

Case 1 in Table 5-20 is for an Illinois No. 6 coal where the recycled seed is processed to contain a formate/sulfate mixture at a seed loading of 1.5% K. Case 1 is the new base case design. The cost for Case 1 is 15.8 mills/kW-hr. Case 2 is similar to Case 1 except the recycled seed is processed to contain all potassium formate at a seed loading of 1.5% K. In this case there is a slight excess of potassium carbonate for sulfur capture resulting in a stoichiometric molar ratio of $\text{CO}_3(\text{equivalent})\text{:S}$ of about 1.3:1 (versus 1:1 for Case 1). Case 2 produces seed at a cost of 18.1 mills/kW-hr. Case 3 is similar to Case 2 except that the seed circulation rate is reduced to the theoretical stoichiometry for sulfur capture resulting in seed loading of 1.17% K. The cost for Case 3 is 15.4 mills/kW-hr.

The costs shown for Case 1 (15.8 mills/kW-hr) indicate that a savings of up to 10% in capital and operating costs might be realized for Eastern coal if the recycled seed is processed to contain a formate/sulfate mixture instead of all potassium formate at a seed loading of 1.5% K (see Case 2, 18.1 mills/kW-hr). The costs shown for Case 3 (15.4 mills/kW-hr) also indicate that a savings of up to 10% in capital and operating costs might be realized for Eastern coal if the seed loadings were reduced to 1.17%, just meeting the requirement for sulfur capture.

Case 4 uses a Western coal with seed loading at 1.5% without using any methods for separation of the carbonate from the sulfate. In this case, the recycled seed contains almost four times the amount of potassium formate required for sulfur capture and the process is operated the same as in Case 2. The cost for Case 4 is 17.5 mills/kW-hr. Comparison of Cases 2 and 4 indicate that the capital and operating costs for Western and Eastern coal systems are about the same if methods for removing the excess unreacted carbonate from the spent seed are not employed before feeding the seed to the Econoseed process.

Case 5 is also a Western coal case except that the proposed method for separating the carbonate from the sulfate in the spent seed is employed. Case 5 is very promising with cost at about 9 mills/kW-hr, which is about one-half the costs projected for Cases 2 and 4 (18.1 and 17.5 mills/kW-hr). This is due mainly to the reduction in size of both the calcium formate reactor system and the partial oxidation system producing CO gas for the calcium

formate unit. Additional savings are realized in a reduced evaporation load. The total capital requirement data is also presented in graphical form in Figure 5-8, which clearly shows the cost savings of Case 5.

Figure 5-9 shows how the cost of low sulfur Western coal seed regeneration varies with the overall efficiency of the MHD system. As can be seen, both the capital and operating cost portion of the cost of seed regeneration are affected by the overall efficiency of the MHD system.

Figure 5-10 shows the range of amortized seed regeneration costs based on the sulfur content of the coal for 300 MW_t systems. The upper range of costs represents the cases where all of the spent seed is processed to potassium formate. The lower range of costs represent those cases where the conversion of spent seed is based on the stoichiometry required for 100% sulfur capture. In those cases for low sulfur coal, a separation of K₂CO₃ from K₂SO₄ is made. For the high sulfur coal, only the portion of the spent seed required for sulfur capture is processed allowing a portion of the K₂SO₄ to be recycled without processing.

Comparisons of process economics for seed regeneration have been made against those of flue gas desulfurization, the logical choice for sulfur control technology if seed regeneration were not used. Figure 5-11 shows the cost of seed regeneration for the five cases studied versus annual SO₂ reduction compared to published costs for FGD systems. From Figure 5-11 it can be seen that seed regeneration shows favorable processing costs compared to FGD systems at the lower end of annual sulfur reduction. Figure 5-12 shows a similar comparison based on boiler size. Based on Figure 5-12, the costs of seed regeneration are lower than those of FGD systems at comparable boiler sizes. Even if the seed regeneration costs were extrapolated to larger sizes, the costs would be competitive with those of the FGD systems. From this it can be concluded that from the standpoint of sulfur control, seed regeneration offers the lowest cost control method besides the added benefit of providing potassium ions to the MHD channel.

Figure 5-8. Breakdown of Total Capital Requirement for 300 MW_t MHD Seed Regeneration System

Figure 5-9. Cost of Low Sulfur Western Coal Seed Regeneration Versus Overall MHD System Efficiency

Figure 5-10. Cost of Seed Regeneration Versus Percent Sulfur in Feed Coal

Figure 5-11. FGD and Seed Regeneration Costs Versus SO₂ Reduction

Figure 5-12. FGD and Seed Regeneration Costs Versus Boiler Size

5.2.9 Summary of Phase I Design Criterion

5.2.9.1 *Percent Recovery and Regeneration of Potassium*

The Econoseed process is capable of almost complete recovery of potassium from both the flyash seed and slag seed recovered from MHD systems. In addition, the potassium recovered can be regenerated almost completely to KCOOH or K_2CO_3 if necessary. In the design presented here, about 6% of the potassium feed to the channel is lost through intentional purges of slag and flyash seed to limit the buildup of contaminants such as sodium and chlorine.

Even without the need to control the buildup of contaminants in the seed, it would be advisable to discard the slag seed. Figure 5-13 shows the overall percent recovery of potassium possible if the slag seed is discarded and only the water soluble flyash seed is processed in the seed regeneration plant. Figure 5-13 is based on a model that evaluated the potential recovery of potassium from the system if only the soluble seed fraction is processed. The model is based on the slag rejection in the MHD combustor and the level of potassium in the slag seed component. For this design, a baseline of 70% slag rejection and 10% by weight potassium in the slag seed was assumed. This is consistent with slag samples analyzed and demonstrated performance of the combustor. Under those conditions, about 98.6% recovery could be attained if only the flyash seed were processed.

From Figure 5-13 it can be seen that higher combustor slag rejection and lower potassium content in the slag seed lead to even higher potential recovery of potassium from the flyash seed component.

The potential recovery of 98.6% of the potassium loses importance in the 300 MW_t design presented here, since a 6% loss of potassium must be taken to limit contaminant buildup in the recycled seed.

WATER SOLUBLE SEED RECOVERY VS SLAG REJECTION & %K IN SEED SLAG

Figure 5-13. Water Soluble Seed Recovery Versus Slag Rejection in Combustor and Percent Potassium in Seed Slag

5.2.9.2 Limit of the Buildup of Impurities

The limiting of the buildup of impurities in the seed is accomplished by a continuous purge of a portion of the spent seed from the MHD system representing about 6% of the potassium recycled as seed. The main source of contaminants such as sodium, chlorine and other potentially soluble salts that would continue to buildup and recycle with the seed is the coal mineral matter. Another source, although smaller, is makeup chemicals such as K_2CO_3 and lime. Section 5.2.2.2 discusses the means of controlling sodium (and thus other contaminants from the coal ash) buildup in the recycled seed. Essentially, the sodium is allowed to build to a level where a continuing purge of some seed material removes in a steady-state manner the incoming contaminants. For this study, a level of 1 part sodium to about 10 parts potassium on a weight basis was assumed. At this level no detrimental effects to the MHD system are expected and the contaminant levels can be controlled with acceptable losses of potassium. If higher sodium to potassium levels were acceptable for channel injection, a lesser purge rate and lower potassium losses would be incurred. Lower sodium to potassium levels would of course lead to higher purge requirements and higher potassium losses.

5.2.9.3 Impact on System Performance and Subsequent Economics

Since the seed regeneration process is not a stand alone facility but part of an overall, complex MHD power plant, the economics of seed regeneration cannot be evaluated without considering the impact of overall system economics. As an example, the production of a potassium formate seed versus a potassium carbonate seed is clearly more economic for the seed regeneration process. Potassium formate as seed, though, may not give the same performance and economics for the MHD system. Preliminary studies by TRW show that $KCOOH$ seed gives conductivities slightly higher than K_2CO_3 seed at 1.5% K seed loading and even greater conductivity at higher seed loading (1.5 to 1.8% K). See IOC MHD-ITC-165 and Figure 5-14 on the following pages.

Subject	Date	From
Comparison of the Effect of Potassium Carbonate versus Potassium Formate on MHD Channel Conductivity	10 October 1988 MHD-ITC-165	S. M. Myrick
	cc	Location/Phone
Bob Myers	R. Braswell M. Bauer T. Fitzgerald D. Grove G. Ogle A. Solbes	01/1171 - 55900

Potassium Carbonate (K_2CO_3) and Potassium Formate ($KCOOH$) are two types of seeding particles widely discussed for MHD channel use. Figure 4.9 compares the theoretical mid-channel conductivity of K_2CO_3 and $KCOOH$ at global oxygen to fuel equivalence ratios (ϕ) of .90 and .95. The solid curves represent the baseline $\phi=.90$ condition, while the dashed lines are for the reference case, $\phi=.95$. The unsymboled curves are for K_2CO_3 while the curves with square symbols represent $KCOOH$. The baseline of $\phi=.90$ is chosen because it is the most efficient condition when the entire MHD system is considered (including components downstream of the channel) according to commercial MHD power plant conceptual design¹. Other baseline assumptions include: Western coal (Montana Rosebud), 50 MW thermal throughput, volumetric $N/O=.85$, 8% combustor heat loss, 85 psia combustor pressure, and oil-fired vitiation to 1200° F. Both seed types are injected in solid form. These run conditions reflect conditions for the prototypical power train being installed at CDIF. However, the relative position of these four curves would not be expected to change appreciably over the range of pressures, preheats, heat losses and N/O ratios encompassing prototypical and retrofit operation. These assumptions result in inputs into a NASA thermodynamic equilibrium code which calculates the theoretical conductivity of the gas stream at the mid-channel supersonic area ratio, 2.37.

Figure 1 clearly shows that for all levels of potassium, $KCOOH$ produces higher mid-channel conductivity than K_2CO_3 . At the nominal potassium level of 1.5%, baseline conductivity is .25 mho/m higher with $KCOOH$. The primary difference between these seed types which causes the disparity in conductivity is that the reaction breaking down K_2CO_3 into ionic potassium is endothermic, while the reaction for $KCOOH$ is exothermic. The dashed curves at $\phi=.95$ also show a higher conductivity for $KCOOH$, as well as a shift in maximum conductivity to higher percent potassium levels.

1. Design Definition Document, Conceptual Design of a Coal-Fired MHD Retrofit - Cormette; MHD Development Corporation.

Figure 5-14. Theoretical Mid-Channel Conductivity Versus Percent Potassium in Total Mass Flow

5.2.9.4 Major Reaction Sequence

The major reactions for the production of potassium formate and potassium carbonate from spent K_2SO_4 seed are:

Reactions 1 and 4 were successfully carried out under various conditions as part of the Phase I laboratory program. Reaction 2, the production of calcium formate in a pressure reactor was demonstration as part of the Phase II POC program. Reaction 3, the slaking of lime, is a well established, industry proven, and commonly used reaction. In the Econoseed process, low concentrations of $Ca(OH)_2$ in water are used, making the slaking process even less severe than commonly used in industry.

The chemicals used in the process are readily available industrial chemicals. For CO gas, the raw material is fuel either coal or natural gas. Calcium formate requires lime as a raw material. Lime is a readily available, inexpensive commodity chemical available from many sources both in the U.S. and abroad. The only other chemical requirements are K_2SO_4 and/or K_2CO_3 for potassium makeup to replace the system losses. About 2500 tons/year K_2SO_4 and 350 tons/year K_2CO_3 are required. Both potassium salts are produced in large quantities in the U.S.

5.2.9.5 Potentially Hazardous Process Conditions

The process does not pose any unusual safety, health or environmental hazards. The chemicals used are essentially nonhazardous with the exception of the intermediate CO gas used for the intermediate calcium formate production. Precautions in design and operation commonly used in chemical and refining industries would be required to contain the CO gas

in a safe and nonhazardous manner. The waste products would be essentially gypsum, free of sulfites, that can be landfilled directly and slag seed that is water insoluble also allowing for landfill.

The process does have processing equipment operating at elevated temperatures and pressures and rotating equipment such as pumps, conveyors, centrifuges and rotary kilns. This equipment is common to the chemical industry and although potential hazards exist these are negated through design and operating procedures.

5.3 EFFECT OF EASTERN SEED POC TEST DATA AND WESTERN SEED LABORATORY STUDIES ON ENGINEERING DESIGN FROM PHASE I OF THE PROGRAM

5.3.1 Calcium Formate Production Unit

5.3.1.1 *Potential Sources of Carbon Monoxide*

TRW found during the operation of the calcium formate proof-of-concept production unit that, given the necessary reactor operating conditions (pressure, temperature, residence time and lime/CO stoichiometry), it is possible to feed a gas to the calcium formate reactor that contains as little as 40% (volume basis) carbon monoxide and still achieve ~100% conversion of the carbon monoxide. This finding opens the door for the utilization of potentially inexpensive sources of carbon monoxide. In the 300 MW_t seed regeneration conceptual plant design prepared in Phase I of the program (see Section 5.2), TRW had assumed that the feed gas to the calcium formate reactor would require a carbon monoxide content of ~80%. Therefore, a fairly complicated and relatively expensive route to carbon monoxide production was selected. That is, a natural gas POX (partial oxidation) unit was selected for the production of a carbon monoxide containing gas.

Natural gas is combusted with oxygen in the POX unit to produce a gas that is nitrogen free. The raw gas from the POX unit is cooled (and scrubbed free of soot residue) and then processed in a membrane-type separator to separate the hydrogen and carbon dioxide content of the gas from the carbon monoxide. The resulting product gas contains ~80% carbon

monoxide. The carbon monoxide production unit is the single most expensive component in the seed regeneration plant. In the Phase I design, this unit accounted for $\sim 30\%$ of the total capital cost of the seed regeneration plant. In fact, subsequent (1992) conversations with licensors of the POX technology led TRW to conclude that a POX unit, particularly at the small scale required to support a 300 MW_t seed regeneration unit, would be considerably more expensive than our initial estimate. Aside from a relatively high capital cost, the POX unit, with its requirement for natural gas and oxygen, also accounts for $\sim 50\%$ of the daily consumable operating costs of the seed regeneration plant.

If a less concentrated carbon monoxide gas can be efficiently utilized, there are less costly alternatives to a natural gas POX unit as the source of carbon monoxide for calcium formate production. In this regard, the first stage (the slagging stage) of the MHD coal combustor should be considered as a possible source of carbon monoxide. This stage is operated at a stoichiometry (ϕ) of 0.55, and the gas issuing from it has a significant carbon monoxide content. A small slip stream (perhaps 2 to 5% of the total stream) of this gas could be drawn from the combustor at this location and quenched immediately to freeze the carbon monoxide content close to its value in the 3000°F+ environment of the first stage. The quenched gas could then be compressed to the high pressure (1250 psig) required by the calcium formate production unit. The pressurized gas would be processed through an acid gas removal unit for removal of carbon dioxide and the small amount of H₂S present before being fed to the calcium formate reactor. This processing scheme, to this point, would offer some obvious cost savings when compared to the generation of carbon monoxide by natural gas partial oxidation. First, an entire stand alone natural gas partial oxidation unit has been eliminated for probably the relatively small incremental increase in cost incurred by enlarging the first stage of the MHD combustor to handle a 2 to 5% increase in total throughput. Second, coal, a cheap fuel, has been substituted for natural gas, a more expensive fuel, as the source of carbon monoxide. This should result in a significant savings in both plant capital and operating costs.

Some process detriments will be incurred when utilizing the first stage combustor gas as a source of carbon monoxide. A high carbon monoxide content (80 mole %) gas can be

produced for the calcium formate reactor via a natural gas POX unit since the oxidant used in the POX unit is 95% oxygen. Thus, the major constituents in the POX effluent gas (in addition to CO) are hydrogen and carbon dioxide, both readily separated from carbon monoxide. In contrast, a probably 35 to 40 mole percent carbon monoxide gas will be produced for the calcium formate reactor if a slip stream is taken from the first stage of the MHD combustor. The oxidant used in the first stage combustor of first generation MHD plants will likely be enriched air. Thus, the major constituent of the combustion gas (in addition to CO) is nitrogen. Nitrogen and carbon monoxide are not easily separated. However, based on work performed in the calcium formate POC unit (see Section 3.4.2 of this Final Report), the effect of reducing the carbon monoxide content of the feed gas to the calcium formate reactor will be mainly the requirement of an increased reactor temperature, and perhaps an increased reactor residence time, to achieve a given carbon monoxide conversion. This will result in a small increase in the cost of the calcium formate production unit. However, the net impact of replacing the natural gas POX unit with the first stage of the MHD combustor as a source of carbon monoxide is likely to be a significant decrease in both the capital and operating cost of a seed regeneration plant.

5.3.2 Potassium Formate Production Unit

5.3.2.1 *Separation of the Spent Seed into its Component Fractions Prior to Seed Regeneration with Calcium Formate*

The seed regeneration POC program (as described in Sections 2 and 3 of this Final Report) was directed towards the processing of high sulfur spent seed (consisting of K_2SO_4 and coal ash) produced from high sulfur Eastern coal. In the case of lower sulfur Western coals, the spent seed will be reduced in sulfur content (potassium seed will likely be required in the channel in excess of that required for sulfur capture), and therefore will consist of a mixture of K_2SO_4 , K_2CO_3 and coal ash. The seed regeneration process scheme tested in the POC program could be utilized on Western seed as is, converting both the K_2SO_4 and K_2CO_3 to the $KCOOH$ seed form by reaction with calcium formate. However, the K_2CO_3 is already a viable fresh seed material and can be reused as is, without the need for regeneration (with its associated processing cost), if it can be separated from the K_2SO_4 in the spent seed. A

reduction in the amount of seed that requires regeneration (for rejection of sulfur, coal ash and impurities such as chloride) directly affects the cost of seed regeneration and, therefore, the cost of MHD power production.

5.3.2.1.1 Once-Through Processing Scheme

TRW devised a once-through processing scheme for the separation of the spent seed into its K_2CO_3 and K_2SO_4 fractions. Western seed laboratory studies (as described in Section 4.2 of this Final Report) were conducted to verify the feasibility of performing the proposed separation.

A process flow schematic for the proposed seed separation scheme is depicted in Figure 5-15. An accompanying material balance is given in Table 5-21. A spent seed containing K_2CO_3 : K_2SO_4 respectively in a 0.826:1 weight ratio and also 20 wt% insoluble coal ash was selected for this example. The spent seed, stream 1, is contacted in a dissolver vessel at ambient temperature (25°C) with the minimum quantity of water, stream 2, needed to completely dissolve the K_2CO_3 in the spent seed. The equilibrium solubility data available for the K_2CO_3 - K_2SO_4 - H_2O system (Table 5-22) indicates that ~14% of the seed K_2SO_4 will go into solution with the K_2CO_3 . The effluent slurry from the dissolver, stream 3, is processed in a centrifuge. The centrate, stream 4, is a relatively dilute (~16 wt%) K_2CO_3 solution also containing ~3 wt% K_2SO_4 . The cake from the centrifuge, stream 5, consists of ~86% of the K_2SO_4 in the spent seed and all the insoluble coal ash in the spent seed. The centrifuge cake will also contain some surface moisture. For the purposes of this example, it was assumed that the cake would contain 0.2 lbs of moisture per lb of dry cake. Since the moisture is a dilute K_2CO_3 solution, approximately 5% of the K_2CO_3 in the spent seed reports with the cake.

The Western seed laboratory studies that were performed (see Section 4.2 of this Final Report) verified the equilibrium solubility data for the K_2CO_3 - K_2SO_4 - H_2O system that are reported in the literature. The studies also indicated that equilibrium could be achieved in a seed dissolver in a relatively short period of time (~15 minutes).

Figure 5-15. Process Flow Schematic of Separation of K₂CO₃ and K₂SO₄ in Spent Seed - Once-Through System

TABLE 5-21. MATERIAL BALANCE FOR SEPARATION OF K_2CO_3 AND K_2SO_4 IN SPENT SEED
ONCE-THROUGH SYSTEM

STREAM NO.	1	2	3	4	5
DESCRIPTION	SPENT SEED ¹	DISSOLVER H ₂ O	CENTRIFUGE FEED	K ₂ CO ₃ SOLUTION	K ₂ SO ₄ CAKE ²
K ₂ CO ₃ , lbs	36.2		36.2	34.3	1.9
K ₂ SO ₄	43.8		43.8	5.9	37.9
ASH	20.0		20.0	---	20.0
H ₂ O	---	176.4	176.4	167.1	9.3
TOTAL, lbs	100.00	176.4	276.4	207.3	69.1

¹ MATERIAL BALANCE BASIS = 100 POUNDS OF SPENT SEED.

² ASSUMES THAT CENTRIFUGE CAKE CONTAINS 0.2 LBS MOISTURE PER POUND DRY CAKE.

TABLE 5-22. PERCENT OF K_2SO_4 DISSOLVED IN WATER VERSUS K_2CO_3 : K_2SO_4 RATIO IN FEED AT 25°C¹

SPENT SEED K_2CO_3 : K_2SO_4 (wt)	CARBONATE SOLUTION (@100% K_2CO_3 DISSOLVED) ² K_2SO_4 : K_2CO_3 (wt)	PERCENT OF FEED K_2SO_4 DISSOLVED ²	TOTAL DISSOLVED SOLIDS IN EQUILIBRIUM SOLUTION ² WT %
0.21:1	1.18:1	24.94%	12.0
0.48:1	0.52:1	25.15%	14.3
0.82:1	0.17:1	14.08%	19.2
1.49:1	0.065:1	9.62%	24.7
2.06:1	0.009:1	1.77%	35.3
2.45:1	0.0006:1	0.15%	48.63
5.12:1	0.002:1	0.91%	45.18

¹ MINIMUM AMOUNT OF WATER IS USED WHICH WILL DISSOLVE 100% OF THE K_2CO_3 . REMAINING SOLID PHASE IS K_2SO_4 .

² CALCULATED FROM K_2CO_3 - K_2SO_4 - H_2O SYSTEM SOLUBILITY DATA (@25°C) PRESENTED IN MELLOR'S COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY, VOLUME II, PAGE 1914.

A number of possible improvements to the separation process as described above were suggested by the results of the laboratory studies. One possibility would be to contact the seed with less than the minimum amount of water required for complete dissolution of the K_2CO_3 in the seed. The study results suggested that even at a considerable reduction in the quantity of dissolve water utilized, most of the seed's K_2CO_3 content will still go into solution. As an example (for an experiment conducted on a seed containing K_2CO_3 : K_2SO_4 at a 0.589:1 weight ratio), it was found that when using $\sim 63\%$ of the minimum water required for complete K_2CO_3 dissolution, approximately 95% of the K_2CO_3 would still go into solution (see Section 4.2.2). The reduced water usage however had a significant effect on the K_2SO_4 dissolved. When using $\sim 65\%$ of the minimum water for complete K_2CO_3 dissolution, the fraction of seed K_2SO_4 also taken into solution was reduced by a factor of two-thirds. Thus a more concentrated K_2CO_3 solution (which will require less downstream water evaporation) containing less K_2SO_4 is produced by allowing a relatively small amount of seed K_2CO_3 to remain undissolved.

Another possible improvement to the separation process as described above would be to operate the dissolver at greater than ambient temperatures. The study results indicate that as the dissolver temperature is increased, the minimum amount of water required for complete K_2CO_3 dissolution decreases and the fraction of K_2SO_4 that goes into solution with the K_2CO_3 also decreases. As an example (for an experiment conducted on a seed containing K_2CO_3 : K_2SO_4 at a 0.48:1 weight ratio), it was found that as the temperature of dissolution was increased from 25°C to 60°C, the minimum water required for complete K_2CO_3 dissolution decreased by a factor of about two-thirds (see Section 4.2.3). At the same time, the fraction of K_2SO_4 taken into solution with the K_2CO_3 decreased by a factor of about two-thirds. Thus increasing the temperature of seed dissolution results in a more concentrated K_2CO_3 solution (which will require less downstream water evaporation) containing a reduced amount of K_2SO_4 . Both the K_2CO_3 solution and the K_2SO_4 cake from the dissolver will be subsequently processed in units operating at elevated temperatures (70+°C). Therefore, if these streams are preheated in the dissolution step, no overall energy penalty is incurred.

5.3.2.1.2 Processing Scheme with Internal Recycle

The literature solubility data for the K_2CO_3 - K_2SO_4 - H_2O system (and the laboratory studies) indicate that the lower the K_2CO_3 : K_2SO_4 ratio in the seed feed, the greater the minimum amount of water needed for complete K_2CO_3 dissolution, and the greater the fraction of K_2SO_4 that goes into solution with the K_2CO_3 (Table 5-22). That is, for a once-through dissolver system, the separation will become less sharp and the K_2CO_3 solution produced will become increasingly dilute, as the K_2CO_3 : K_2SO_4 ratio in the spent seed decreases. In order to overcome this seed composition effect and to produce a sharp separation of the spent seed into its fractions and concentrated K_2CO_3 solutions regardless of the composition of the spent seed, a process scheme was conceptualized that utilizes an internal recycle. Experiments subsequently conducted in the Western seed laboratory study verified the feasibility of the proposed scheme.

A process flow schematic for the proposed seed separation scheme is depicted in Figure 5-16. An accompanying material balance is given in Table 5-23. A spent seed containing K_2CO_3 : K_2SO_4 respectively in a 0.826:1 weight ratio and also 20 wt% insoluble coal ash was selected for this example. The spent seed, stream 1, is contacted in a dissolver vessel at ambient temperature (25°C) with recycled solids-free dissolver solution, stream 3, in the proportions shown in Table 5-23. When these streams are combined in these proportions, the effect will be to create a dissolver inventory containing K_2CO_3 : K_2SO_4 respectively in a 5.12:1 weight ratio. At this K_2CO_3 : K_2SO_4 ratio, if the minimum quantity of water, stream 2, needed to completely dissolve the K_2CO_3 in the spent seed is added to the dissolver, the equilibrium solubility data available for the K_2CO_3 - K_2SO_4 - H_2O system (see Table 5-22) indicates that <1% of the system's K_2SO_4 will be in solution. The effluent slurry from the dissolver, stream 4, is processed in a centrifuge. The centrate from the centrifuge is collected in a tank. A fraction of the centrate, stream 3, is then recycled to the dissolver. The balance of the centrate, stream 7, is sent to an evaporator/crystallizer for recovery of its K_2CO_3 content. This centrate stream is a concentrated (~45 wt%) K_2CO_3 solution containing <0.1 wt% K_2SO_4 . The cake from the centrifuge, stream 5, consists of ~99.9% of the K_2SO_4 in the spent seed and all the insoluble coal ash in the spent seed. The

Figure 5-16. Process Flow Schematic of Separation of K₂CO₃ and K₂SO₄ in Spent Seed - Recycle System

TABLE 5-23. MATERIAL BALANCE FOR SEPARATION OF K_2CO_3 AND K_2SO_4 IN SPENT SEED RECYCLE SYSTEM

STREAM NO.	1	2	3	4	5	6	7
DESCRIPTION	SPENT WESTERN SEED ¹	DISSOLVER H_2O	RECYCLE K_2CO_3 SOLUTION	DISSOLVER EFFLUENT	K_2CO_4 CAKE ²	CENTRATE	SULFATE-FREE K_2CO_3 SOLUTION
K_2CO_3 , lbs	36.20	--	189.80	226.00	5.75	220.25	30.45
K_2SO_4	43.80	--	0.34	44.14	43.75	0.39	0.05
ASH	20.00	--	--	20.00	20.00	--	--
H_2O	--	44.00	230.71	274.71	6.99	267.72	37.01
TOTAL, lbs	100.00	44.00	420.85	564.85	76.49	488.36	67.51

¹ MATERIAL BALANCE BASIS = 100 POUNDS OF SPENT SEED.

² ASSUMES THAT CENTRIFUGE CAKE CONTAINS 0.2 LBS MOISTURE PER POUND DRY CAKE.

centrifuge cake will also contain some surface moisture. For the purposes of this example, it was assumed that the cake would contain 0.2 lbs of moisture per lb of dry cake. Since the moisture is a concentrated (45%) K_2CO_3 solution, approximately 15% of the K_2CO_3 in the spent seed remains with the K_2SO_4 . This compares to a figure of $\sim 5\%$ for a once-through dissolution system (see Table 5-21). A process scheme for recovering this K_2CO_3 is discussed in Section 5.3.2.2 this Final Report.

In summary, by employing an internal recycle it is possible to control the K_2CO_3 : K_2SO_4 ratio in the dissolver system and thereby obtain a sharp separation of the seed into its component fractions (and also produce a concentrated K_2CO_3 solution) regardless of the K_2CO_3 : K_2SO_4 ratio in the spent seed. Figure 5-17 is a plot of the required recycle/spent seed flow ratio as a function of the K_2CO_3 : K_2SO_4 ratio in the spent seed. The recycle/spent seed ratio was calculated for two cases. In one instance, the dissolver contents were specified to be controlled at a K_2CO_3 : K_2SO_4 ratio of 5.12:1 (weight), resulting in a ~ 45 wt% K_2CO_3 solution (containing < 0.1 wt% K_2SO_4). A second case was calculated in which the dissolver contents were specified to be controlled at a K_2CO_3 : K_2SO_4 ratio of 2.06:1 (weight), resulting in a ~ 35 wt% K_2CO_3 solution (containing 0.3 wt% K_2SO_4).

5.3.2.1.3 Chloride Rejection

The spent seed will contain chloride from the coal processed in the MHD power plant. Chloride is an impurity that if allowed to build up in the spent seed could potentially shorten channel life (increased corrosion) and/or degrade channel performance (decreased plasma conductivity). During the Western seed laboratory studies (see Section 4.2.5 of this Final Report), it was found that in the range of seed chloride content investigated, the chloride partitions with the K_2CO_3 during the seed dissolution process. That is, when using the minimum amount of water necessary for complete dissolution of the K_2CO_3 in the spent seed, greater than 95% of the chloride in the spent seed also goes into solution. Therefore, if the chloride level in the spent seed is to be controlled, the chloride must be rejected at high efficiency from the K_2CO_3 solution produced in the seed dissolution step. A number of processing schemes to accomplish this were devised and are discussed in Section 5.3.3.

Figure 5-17. Effect of K₂CO₃:K₂SO₄ Ratio in Spent Seed on System Recycle

5.3.2.2 Separation of K_2CO_3 (and Chloride) from Wet K_2SO_4 Cake

It was mentioned in Section 5.3.2.1 that the K_2SO_4 cake from the K_2CO_3/K_2SO_4 separation step (seed dissolution) would be wet with moisture containing K_2CO_3 (and chloride). In most instances no undissolved chloride will remain with the K_2SO_4 cake. However, if a very high chloride coal is utilized in the MHD power plant, it is possible that the K_2SO_4 cake could include undissolved chloride (KCl). This situation can be avoided by relaxing the sharpness of the K_2CO_3/K_2SO_4 separation in the seed dissolution step. Instead of producing a 45 wt% K_2CO_3 solution in this step (containing <0.1 wt% K_2SO_4), a 35 wt% K_2CO_3 solution could be produced (containing 0.3 wt% K_2SO_4). The more dilute solution has a greater potential for solubilizing the chloride in the spent seed and is therefore less likely to leave undissolved chloride in the K_2SO_4 cake.

A process scheme was devised for removal of the dissolved K_2CO_3/KCl and undissolved KCl from the wet K_2SO_4 cake. This scheme is depicted in Figure 5-18. An experiment was conducted as part of the Western seed laboratory study to verify the feasibility of the process. A material balance for the process, based on laboratory data, is given in Table 5-24. The balance is based on a K_2SO_4 cake containing 0.25 lbs of moisture per lb of dry cake. The cake moisture consists of a ~ 45 wt% K_2CO_3 solution (also containing ~ 2 wt% KCl). Approximately 50% of the chloride in the wet cake is assumed to be undissolved KCl. The wet cake is reslurried with a relatively small amount of water (the resulting slurry contains ~ 32 wt% solids) to wash K_2CO_3 and KCl from the cake. It was determined that the amount of K_2SO_4 that dissolved in the reslurry solution was approximately equal to the quantity of K_2CO_3 (plus KCl) in the wet cake feed. This means that $\sim 13\%$ of the K_2SO_4 went into solution. The effluent from the reslurry tank is fed to a centrifuge. The centrifuge cake, which is now relatively pure (99.5 wt%) K_2SO_4 (and based on laboratory data contains <0.1 lbs of moisture per lb of dry cake) is sent to the potassium formate reactor for regeneration. The centrate, containing ~ 12 wt% total dissolved solids, will undergo further processing to separate the solid fractions.

Figure 5-18. Process Flow Schematic of Removal of K₂CO₃/KCl from Wet K₂CO₃ Cake

TABLE 5-24. MATERIAL BALANCE FOR REMOVAL OF K_2CO_3/KCl FROM WET K_2SO_4 CAKE

STREAM NO.	1	2	3	4	5
DESCRIPTION	WET K_2SO_4 CAKE ¹	WASH WATER	SLURRY TO CENTRIFUGE	WASH SOLUTION	WASHED K_2SO_4 CAKE
K_2SO_4 , lbs	79.1		79.1	9.6	69.2
K_2CO_3	9.0		9.0	8.7	0.3
KCl	0.9		0.9	0.9	0.03
H ₂ O	11.0	132.2	143.2	138.5	4.7
TOTAL, lbs	100.0	132.2	232.2	157.7	74.2

¹ MATERIAL BALANCE BASIS = 100 POUNDS OF WET K_2SO_4 CAKE.

A possible process scheme to accomplish this is depicted in Figure 5-19. An accompanying material balance is given in Table 5-25. In this instance, since the solution contains a relatively high proportion of K_2SO_4 (and KCl) relative to K_2CO_3 , it should be possible to evaporate the solution to the extent that pure K_2SO_4 (or a mixture of K_2SO_4 and KCl) is crystallized from the solution, leaving a concentrated K_2CO_3 solution (still containing some KCl) that is essentially K_2SO_4 -free. In this particular case, it was assumed that the solution is processed in an evaporator/crystallizer operating at the triple point for the K_2CO_3 -KCl- K_2SO_4 - H_2O system at 75°C. According to the literature (Seidell's "Solubilities of Inorganic and Metal-Organic Compounds," Fourth Edition, Volume II, page 87 (Teeple, 1929)), the saturated solution at the triple point at this temperature will contain 55.93 wt% K_2CO_3 , 2.18 wt% KCl and a 'trace' of K_2SO_4 . Therefore, at the triple point virtually all the K_2SO_4 and ~60% of the KCl will have precipitated from solution. The crystals can then be washed with the minimum amount of water necessary to redissolve the KCl. If this is performed at a temperature of 35°C, less than 1% of the K_2SO_4 crystals will go into solution with the KCl. Literature (Teeple, 1929) equilibrium data indicates that the saturated solution produced in the KCl dissolver will contain 27.4 wt% KCl and 1.2 wt% K_2SO_4 . The slurry from the KCl dissolver is separated in a centrifuge. The solids-free centrate is a concentrated KCl solution that is a chloride reject stream from the plant. The K_2SO_4 cake from the centrifuge is sent to the potassium formate reactor for regeneration.

5.3.2.3 Potassium Formate Evaporator Impurities Rejection

During operation of the potassium formate POC evaporation unit, it was observed that solids precipitated from solution as the dilute formate solution was concentrated. In particular, the sulfate salts were removed to very low concentrations in the final formate product. Sulfate concentration in the ~70 wt% potassium formate product ranged from 0.01 to 0.03 wt%. The evaporator feed contained on average ~0.4 wt% sulfate. Since a concentration factor in excess of 10 was achieved in the evaporator, ~4 wt% sulfate in the final product would be expected if no sulfate had precipitated in the evaporator. Based on the observed sulfate values, it appears that >99% of the sulfate has precipitated during the evaporation process. It should be mentioned that the final formate product was sampled for

Figure 5-19. Process Flow Schematic of Removal of K_2SO_4 from K_2SO_4 Cake Wash Solution

TABLE 5-25. MATERIAL BALANCE FOR REMOVAL OF K_2SO_4 FROM K_2SO_4 CAKE WASH SOLUTION

STREAM NO.	1	2	3	4	5	6	7
DESCRIPTION	K_2SO_4 CAKE WASH SOLUTION	EVAPORATED H_2O	CONCENTRATED K_2CO_3/KCl SOLUTION	K_2SO_4/KCl CRYSTALS ¹	DISSOLVE H_2O	KCl REJECT STREAM	K_2SO_4 CAKE TO $KCOOH$ UNIT ¹
K_2SO_4 , lbs	9.60		---	9.60		0.03	9.57
K_2CO_3	8.70		8.70	---		---	---
KCl	0.90		0.34	0.56		0.56	---
H_2O	138.50	131.94	6.56	---	1.46	1.46	---
TOTAL, lbs	157.70	131.94	15.6	10.16	1.46	2.05	9.57

¹ For the purposes of this example, the effect of the relatively small amount of surface moisture which would be carried on these crystals was ignored.

analysis after it had been allowed to cool from a process temperature of $\sim 200^{\circ}\text{F}$ to ambient temperature. It is likely that the sulfate solubility in the concentrated formate at process temperature is somewhat higher than that measured at ambient temperature. However, even if the ambient sulfate solubility were increased by a factor of ten at the elevated temperature, a very unlikely scenario, sulfate rejection in the formate evaporator would still be $>90\%$. (Note: In a commercial MHD seed regeneration plant, the potassium formate seed would be evaporated to $>90\%$ concentration. It is likely that the more closely the potassium formate product approaches the anhydrous condition, the more its sulfate solubility will be depressed.)

The fact that most of the sulfate in the dilute feed to the potassium formate evaporator precipitates during the evaporation process, and can be removed between evaporation stages or after the final evaporation stage, means that it is not necessary to get complete conversion of the sulfate (to insoluble gypsum) in a single pass through the potassium formate reactor. The sulfate salts, of potassium and calcium, that precipitate during evaporation can be recovered and recycled to the formate reactor for a second pass at conversion to insoluble gypsum. It was observed that the upper limit to sulfate removal from the spent seed on a single pass through the formate reactor is dictated by the solubility of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the dilute formate solution. The solubility was determined to be $\sim 0.4 \text{ wt}\% \text{ CaSO}_4$ ($\sim 0.28 \text{ wt}\% \text{ sulfate}$). If the dilute formate solution from the formate reactor is assumed to contain $7.5 \text{ wt}\% \text{ potassium formate}$, approximately 6.5% of the sulfate in the spent seed will remain in solution, even at complete conversion of the K_2SO_4 in the spent seed to gypsum, due to the gypsum solubility in the solution.

Sulfate solids precipitated in the formate evaporator can be recycled to the formate reactor. The gypsum in these solids will not dissolve in the reactor solution (since the dilute formate solution in the reactor is already saturated with CaSO_4) but instead will report with the gypsum centrifuged from the reactor effluent slurry. Any K_2SO_4 solids precipitated in the formate evaporator and recycled to the formate reactor will have a second chance for conversion to potassium formate (and gypsum). This conversion should take place as long as sufficient calcium formate is added to the formate reactor to react with all soluble sulfate

salts in the spent seed to the formate reactor. Thus, recycling formate evaporator sulfate precipitate to the formate reactor offers a means of obtaining complete conversion and removal of the sulfate in the spent seed feed to the reactor.

5.3.3 Chloride Rejection from Spent Seed

As was discussed in 5.3.2.1 above, the chloride in the spent seed was observed to dissolve in the K_2CO_3 solution produced during the selective dissolution of the seed into its K_2CO_3 and K_2SO_4 fractions. A number of process schemes were devised to effect the removal of the chloride from the K_2CO_3 solution before recycling the K_2CO_3 seed to the MHD channel. Two process schemes were proposed: one scheme to be employed for a 'low' chloride spent seed and the other for a 'high' chloride spent seed. Both process schemes have as their end products: 1) pure $K_2CO_3 \cdot 1.5H_2O$ crystals for recycle to the MHD channel, and 2) KCl crystals or a concentrated KCl solution for waste disposal (or sale). The feasibility of the individual processing steps in each of the processing schemes was successfully verified at laboratory scale as part of the Western seed laboratory studies (see Section 4.3 of this report).

5.3.3.1 *Process Scheme for Chloride Rejection from 'Low' Chloride Spent Seed*

In this scheme, chloride will be rejected from the plant in a multi-step fractional crystallization unit. A 'low' chloride spent seed is defined as one which will, after K_2CO_3/K_2SO_4 separation in a selective dissolution unit, result in a chloride-containing K_2CO_3 solution having a 'low' KCl: K_2CO_3 ratio. Specifically this ratio is defined as being less than that at the double salt point (solution saturated with both KCl and K_2CO_3) at the operating temperature of the evaporator/crystallizer which constitutes the first processing step in the chloride rejection processing scheme. The process scheme for chloride rejection for a 'low' chloride spent seed is depicted in Figure 5-20. An accompanying material balance is given in Table 5-26.

The K_2CO_3 solution feeding the unit is assumed to have been generated in a spent seed selective dissolution unit (provided with an internal recycle for a sharp K_2CO_3/K_2SO_4

Figure 5-20. Process Flow Schematic of K_2CO_3/KCl Separation Unit for 'Low' Chloride Spent Seed

TABLE 5-26. MATERIAL BALANCE FOR K₂CO₃/KCl SEPARATION UNIT
'LOW' CHLORIDE SPENT SEED

STREAM NO.	1	2	3	4	5	6	7	8	9
DESCRIPTION	FRESH FEED	EVAPORATED H ₂ O	WET CAKE	CENTRATE	WET CAKE	RECYCLE CENTRATE	ADDED H ₂ O	WET CAKE	RECYCLE CENTRATE
<u>AS LIQUID</u>									
K ₂ CO ₃ , lbs/hr	2223	--	160	638	23	238	--	1	399
KCl	23	--	7	26	--	4	--	--	6
H ₂ O	2716	2503	78	313	22	217	269	1	364
Subtotal, lbs/hr	4962	2503	245	977	45	459	269	2	769
<u>AS SOLID</u>									
K ₂ CO ₃ , lbs/hr	--	--	2062	--	377	--	--	--	--
KCl	--	--	--	--	22	--	--	16	--
H ₂ O	--	--	403	--	74	--	--	--	--
Subtotal, lbs/hr	0	0	2465	0	473	0	0	16	769
TOTAL, lbs/hr	4962	2503	2710	977	518	459	269	18	769

separation). This solution is assumed to have a K_2CO_3 content of 44.8 wt% and a KCl content of 0.46 wt% ($KCl:K_2CO_3$ ratio of 0.0103:1). This solution, stream 1, is fed to a K_2CO_3 crystallizer operating at a temperature of 124°C. Water, stream 2, is continuously evaporated from the solution in sufficient quantity to cause K_2CO_3 to crystallize from solution (as $K_2CO_3 \cdot 1.5H_2O$). The chloride concentration of the mother liquor in the crystallizer is maintained at just below the double salt point, (2.68 wt% KCl and 65.33 wt% K_2CO_3 for a $KCl:K_2CO_3$ ratio of 0.0410:1), by controlling the quantity of K_2CO_3 crystallized, to avoid coprecipitation of KCl with the K_2CO_3 . The slurry produced in the crystallizer is centrifuged. The solids, stream 3, are $K_2CO_3 \cdot 1.5H_2O$ crystals containing some residual moisture and are available for recycle to the MHD channel.

The solids-free mother liquor, stream 4, is cooled to 20°C and fed to a K_2CO_3/KCl crystallizer. This stream, upon cooling, becomes supersaturated in both K_2CO_3 and KCl. Given sufficient time, both K_2CO_3 and KCl will precipitate from solution until the 20°C double salt point (0.8 wt% KCl, 51.9 wt% K_2CO_3) is reached. The resulting slurry is centrifuged for removal of solids ($K_2CO_3 \cdot 1.5H_2O$ and KCl), stream 5. The solids-free mother liquor, stream 6, with a $KCl:K_2CO_3$ ratio of 0.0154:1, is recycled to the K_2CO_3 crystallizer. The $K_2CO_3 \cdot 1.5H_2O$ and KCl cake, stream 5, is mixed with the minimum amount of water, stream 7, necessary to just completely dissolve the K_2CO_3 content of the cake at a temperature of 20°C. The resulting saturated solution will be at a concentration corresponding to the double salt point (0.8 wt% KCl, 51.9 wt% K_2CO_3). Although all of the K_2CO_3 in the solids feed goes into solution, only ~25% of the KCl content of the solids feed will be taken into solution. The slurry from the K_2CO_3 dissolver will be filtered for removal of the undissolved KCl solids, stream 8. The filtrate, stream 9, with a $KCl:K_2CO_3$ ratio of 0.0154:1 will be recycled to the K_2CO_3 crystallizer.

This process scheme as shown rejects chloride from the K_2CO_3 solution at an efficiency of ~70%. Approximately 30% of the chloride in the feed solution is recycled back to the MHD channel in the surface moisture (assumed 0.1 lb of moisture per lb of dry crystals) on the wet $K_2CO_3 \cdot 1.5H_2O$ crystals removed in the K_2CO_3 crystallizer, stream 3. This will result in only a modest buildup of chloride in the channel (to a value only ~45% greater

than for once-through seed operation) and subsequently in the K_2CO_3 solution from the spent seed selective dissolution step. The incremental KCl in the K_2CO_3 crystallizer feed solution, due to the chloride in the recycled seed, will be removed at 100% efficiency in passage through the chloride rejection process (the chloride content of the $K_2CO_3 \cdot 1.5H_2O$ crystals recycled to the MHD channel is not dependent on the chloride content of the feed solution to the K_2CO_3 crystallizer).

Chloride is rejected in this scheme without a simultaneous loss of seed. The KCl crystal reject stream, stream 8, contains K_2CO_3 in its surface moisture that is $<0.05\%$ of the K_2CO_3 in the spent seed.

5.3.3.2 Process Scheme for Chloride Rejection from 'High' Chloride Spent Seed

A 'high' chloride spent seed is defined as one which will, after K_2CO_3/K_2SO_4 separation in a selective dissolution unit, result in a chloride-containing K_2CO_3 solution having a 'high' KCl: K_2CO_3 ratio. Specifically this ratio is defined as being greater than that at the double salt point (solution saturated with both KCl and K_2CO_3) at the operating temperature of the evaporator/crystallizer which constitutes the first processing step in the chloride rejection processing scheme. The process scheme for chloride rejection for a 'high' chloride spent seed is depicted in Figure 5-21. An accompanying material balance is given in Table 5-27.

The K_2CO_3 solution feeding the unit is assumed to have been generated in a spent seed selective dissolution unit (provided with an internal recycle for a sharp K_2CO_3/K_2SO_4 separation). This solution is assumed to have a K_2CO_3 content of 43.7 wt% and a KCl content of 3.0 wt% (KCl: K_2CO_3 ratio of 0.0686:1). This solution, stream 1, is fed to a KCl crystallizer operating at a temperature of 70°C. (Note: 70°C was selected for this example. A higher operating temperature can be employed if the vacuum level required in the crystallizer is too low at 70°C.) Water, stream 2, is continuously evaporated from the solution in sufficient quantity to cause KCl to crystallize from solution. The K_2CO_3 concentration of the mother liquor in the crystallizer is maintained at just below the double salt point, (2.00 wt% KCl, 56.06 wt% K_2CO_3), by controlling the quantity of KCl

Figure 5-21. Process Flow Schematic of K₂CO₃/KCl Separation Unit for 'High' Chloride Spent Seed

TABLE 5-27. MATERIAL BALANCE FOR K₂CO₃/KCl SEPARATION UNIT
'HIGH' CHLORIDE SPENT SEED

STREAM NO.	1	2	3	4	5	6
DESCRIPTION	FRESH FEED	EVAPORATED H ₂ O	WET CAKE	CENTRATE	CENTRATE	WET CAKE
<u>AS LIQUID</u>						
K ₂ CO ₃ , lbs/hr	9,125	--	17	9,108	8,540	308
KCl	626	--	--	327	132	5
H ₂ O	11,143	4,318	13	6,812	7,785	283
Subtotal, lbs/hr	20,894	4,318	30	16,247	16,457	596
<u>AS SOLID</u>						
K ₂ CO ₃ , lbs/hr	--	--	--	--	--	4,699
KCl	--	--	299	--	--	372
H ₂ O	--	--	--	--	--	918
Subtotal, lbs/hr	0	0	299	0	0	5,989
TOTAL, lbs/hr	20,894	4,318	329	16,247	16,457	6,585

TABLE 5-27. MATERIAL BALANCE FOR K₂CO₃/KCl SEPARATION UNIT
'HIGH' CHLORIDE SPENT SEED (CONTINUED)

STREAM NO.	7	8	9	10	11	12
DESCRIPTION	ADDED H ₂ O	WET CAKE	CENTRATE	EVAPORATED H ₂ O	WET CAKE	CENTRATE
<u>AS LIQUID</u>						
K ₂ CO ₃ , lbs/hr	--	16	4,991	--	653	4,439
KCl	--	--	77	--	27	182
H ₂ O	3,363	14	4,550	8,190	323	2,174
Subtotal, lbs/hr	3,363	30	9,629	8,190	1,003	6,795
<u>AS SOLID</u>						
K ₂ CO ₃ , lbs/hr	--	--	--	--	8,439	--
KCl	--	300	--	--	--	--
H ₂ O	--	--	--	--	1,648	--
Subtotal, lbs/hr	0	300	0	0	10,087	0
TOTAL, lbs/hr	3,363	330	9,629	8,190	11,090	6,795

crystallized, to avoid coprecipitation of K_2CO_3 with the KCl. This case is similar to that discussed above in Section 5.3.3.1 for 'low' chloride spent seed except that the double salt point is now approached from the KCl-rich side (in contrast to the K_2CO_3 -rich side approach for the 'low' chloride spent seed case). The result is that, in this 'high' chloride spent seed case, KCl is initially crystallized from solution. The slurry produced in the crystallizer is centrifuged. The solids, stream 3, are KCl crystals which can be disposed of as a waste product (or possibly sold).

The solids-free mother liquor, stream 4, is cooled to 20°C and fed to a K_2CO_3 /KCl crystallizer. This stream, upon cooling, becomes supersaturated in both K_2CO_3 and KCl. Given sufficient time, both K_2CO_3 and KCl will precipitate from solution until the 20°C double salt point (0.8 wt% KCl, 51.9 wt% K_2CO_3) is reached. The resulting slurry is centrifuged for removal of solids ($K_2CO_3 \cdot 1.5H_2O$ and KCl), stream 6. The solids-free mother liquor, stream 5, with a KCl: K_2CO_3 ratio of 0.0154:1, is fed to a K_2CO_3 crystallizer.

The $K_2CO_3 \cdot 1.5H_2O$, KCl cake, stream 6, is mixed with the minimum amount of water, stream 7, necessary to just completely dissolve the K_2CO_3 content of the cake at a temperature of 20°C. The resulting saturated solution will be at a concentration corresponding to the double salt point (0.8 wt% KCl, 51.9 wt% K_2CO_3). Although all of the K_2CO_3 solids feed goes into solution, only ~25% of the KCl content of the solids feed will be taken into solution. The slurry from the K_2CO_3 dissolver will be filtered (or centrifuged) for removal of the undissolved KCl solids, stream 8. This stream can be disposed of as a waste product (or possibly sold).

The filtrate, stream 9, with a KCl: K_2CO_3 ratio of 0.0154:1 will be fed to a K_2CO_3 crystallizer. The K_2CO_3 crystallizer is operated at a temperature of 125°C. Water, stream 10, is continuously evaporated from the solution in sufficient quantity to cause K_2CO_3 to crystallize from solution (as $K_2CO_3 \cdot 1.5H_2O$). The chloride concentration of the mother liquor in the crystallizer is maintained at just below the double salt point (2.68 wt% KCl, 65.33 wt% K_2CO_3 for a KCl: K_2CO_3 ratio of 0.0410:1), by controlling the quantity of K_2CO_3 crystallized, to avoid coprecipitation of KCl with the K_2CO_3 . The slurry produced in the

crystallizer is centrifuged. The solids, stream 11, are $K_2CO_3 \cdot 1.5H_2O$ crystals containing some residual moisture and are available for recycle to the MHD channel. The solids-free mother liquor, stream 12, with a $KCl:K_2CO_3$ ratio of 0.0410, is recycled to the K_2CO_3/KCl crystallizer.

The process scheme as shown rejects chloride from the K_2CO_3 solution at an efficiency of $\sim 95\%$. Chloride is rejected in this scheme with little loss of seed. The KCl crystal reject streams (stream 3 plus stream 8) contain K_2CO_3 in their surface moisture that is $\sim 0.4\%$ of the K_2CO_3 in the spent seed.

5.4 REGENERATED SEED FORM

The regenerated seed form for the first commercial MHD power plant is likely to be a mixture of potassium carbonate and potassium formate. It was observed in a crude experiment conducted as part of the Western seed laboratory studies (see Section 4.5 of this Final Report) that this mixture will likely be a pumpable slurry at elevated temperatures ($>250^\circ F$). No quantitative data on the hydraulic characteristics of this slurry was collected.

5.4.1 Long Term Seed Storage

In a commercial MHD power plant it will be necessary to provide on-site capacity for several days of seed storage. This requirement will be dictated by the need to allow independent MHD plant operation when the seed regeneration plant is temporarily inoperative and to provide an uninterrupted seed supply during minor seed regeneration plant forced outages. It is not practical to provide tankage for storage of a large quantity of mixed seed (formate/carbonate). As mentioned above, this seed mix will be in the form of a slurry. Therefore, this seed mix would have to be maintained in a constant state of agitation, a difficult task in large capacity tankage. In addition this seed mix would have to be stored hot ($>250^\circ F$) to avoid freezing into a solid mass.

TRW recommends that the long term seed storage inventory consist of ~ 70 wt% potassium formate. This material is a solids-free liquid at ambient ($20^\circ C$) temperature that

can be easily stored in large tanks without a requirement for heating or agitation (although some heating may be necessary if the storage tanks are located out-of-doors or in a non-heated environment). If the formate evaporation unit is still operable when the seed regeneration plant is temporarily shutdown, the ~70% formate solution from storage can be concentrated to ~95% (normal formate seed concentration) in this unit before being injected into the MHD system. If the formate evaporation unit is not operable, the ~70% potassium formate solution could be injected into the MHD system as is. Calculations show that the amount of water in the channel will increase by only about 5 to 6% when a 70% formate solution is used instead of a 95% formate solution. For short periods of time, this is likely to be acceptable. Most of the water in the channel comes from combustion of the hydrogen in the feed coal, not from the recycled seed. Since the 70% potassium formate solution that would be stored in the long term storage system is not the typical concentration produced by the formate evaporator, it would have to be produced ahead of time such as during initial startup or during off-line operation of the formate evaporator.

References

1. Guthrie, Kenneth M., Process Plant Estimating Evaluation and Control, Craftsman Book Company, 1974.
2. TAGTM - Technical Assessment Guide, Volume 1: Electricity Supply-1986, Electric Power Research Institute, EPRI P-4463-SR, Volume 1, Special Report, December 1986.
3. Chemical Marketing Reporter, 1988.

6. SUMMARY OF PROGRAM ACCOMPLISHMENTS

The Department of Energy-sponsored MHD Seed Regeneration program resulted in the following:

- The design, construction and successful operation of a Proof-of-Concept (POC) Econoseed seed regeneration plant. The POC unit was operated for a total of ~200 hours with a spent seed feed derived from Eastern coal operation at UTSI's CFFF. The spent seed, primarily K_2SO_4 (plus a small fraction of coal mineral matter), was successfully regenerated to a potassium formate seed form at a rate of up to 200 pounds per hour. This was accomplished at a high (~97%) sulfate rejection efficiency and with a high (>99%) potassium recovery. Approximately 21,000 pounds (pure basis) of potassium formate seed was produced as a concentrated (~75%) aqueous solution. This seed material was shipped to MSE's CDIF for channel tests. The engineering data base required for scaleup of the Econoseed process to commercial size was collected during operation of the POC.
- The design, construction and successful operation of a Proof-of-Concept (POC) calcium formate production unit. This POC unit was operated for ~100 hours and demonstrated the feasibility of generating calcium formate (the chemical reagent used in the Econoseed process) via a new synthesis route from the relatively inexpensive raw materials, carbon monoxide and lime. The POC unit was operated over a matrix of process conditions (pressure, temperature, reaction time). A number of combinations of test conditions resulted in carbon monoxide conversions in excess of 90%. Calcium formate (in aqueous solution at concentrations of up to ~13%) was produced at rates as high as 50 pounds per hour (pure basis). The engineering data base required for scaleup of a calcium formate production unit to commercial size was collected during operation of the POC.
- The completion of laboratory studies which demonstrated the feasibility of a process scheme proposed for the separation of the potassium carbonate (K_2CO_3) and

potassium sulfate (K_2SO_4) fractions that constitute the spent seed likely to be derived from low sulfur Western coal (and even from moderate sulfur level Eastern coals). Since K_2CO_3 is a fresh seed material for the channel, there is no need to regenerate this component. Therefore, a modification of the Econoseed process to allow the K_2CO_3 to be separated from the K_2SO_4 prior to regeneration of the spent seed could result in a significant reduction in the cost of seed regeneration, hence a reduction in the cost of MHD-produced power.

- The completion of laboratory studies which demonstrated the feasibility of a process scheme proposed for the rejection of chloride from spent seed. Chloride partitions with K_2CO_3 in the K_2CO_3/K_2SO_4 separation step and can subsequently be separated from the K_2CO_3 by fractional crystallization. If the coal-derived chloride is not efficiently rejected from the spent seed, it has the potential to buildup in the seed upon recycle and could corrode the channel and also decrease plasma conductivity.
- The preparation of conceptual flow drawings and material balances for commercial-scale seed regeneration processing units for separation of the K_2CO_3 and K_2SO_4 fractions of spent seed and for seed chloride rejection. These conceptual designs were based on literature data as well as the findings of TRW's laboratory studies. These unit operations should next be conducted at Proof-of-Concept (POC) scale to accumulate the engineering data base necessary for the design of commercial-scale plants.

APPENDIX A

EPRI-TAG¹

¹ TAGTM - Technical Assessment Guide, Volume 1: Electricity Supply-1986, Electric Power Research Institute, EPRI P-4463-SR, Volume 1, Special Report, December 1986.

Section 3

COST-ESTIMATING PREMISES

3.1 INTRODUCTION

This section presents and discusses the definitions and methods for treating the economic variables that are a part of most cost estimates for new and existing power-generating technologies. EPRI is most concerned with comparing the relative economic advantages and disadvantages of new technologies rather than the absolute cost of a specific technology. Therefore, the main emphasis is on consistency in both the economic premises presented here and the design premises that were presented in Section 2. Since one set of premises cannot cover all possible situations, the Planning and Evaluation Division staff should be consulted in cases where special definitions are required.

3.2 COST ESTIMATE

The cost estimate includes both capital and operating costs along with fuel requirements and other consumables whose cost may vary with time. The cost estimate is generally computed as though the technology is in a "mature" state of development. Extra facilities that will be needed for demonstration or first commercial plants are not normally included in the cost estimates in the Technical Assessment Guide.

3.3 CAPITAL INVESTMENT BASIS

The capital cost components are shown in Table 3-1. The definitions for the capital cost components are presented in the following sections.

3.4 TOTAL PLANT COST

The total plant cost (TPC) is developed on the basis of instantaneous construction (also called overnight construction) and is expressed in December (of a reference year) dollars. For new studies, the reference point to be used is December of the previous year. The adjustments to express the total plant investment (TPI) at the plant in-service or startup date are presented in Section 3.5.1.

The TPC is the sum of the following:

1. Process capital
2. General facilities capital
3. Engineering and home office fees
4. Project contingency
5. Process contingency

These items are discussed in the following sections. Table 3-2 gives a recommended format for the cost breakdown for the TPC.

3.4.1 Process Capital

Process capital is the total constructed cost of all on-site processing and generating units, including all direct and indirect construction costs. All sales taxes must be included where applicable. As shown in Table 3-2, the process capital cost is to be divided into major plant sections (e.g., fuel storage, combustion systems, emission-control systems, generators). The specific section breakdown should be agreed upon with the EPRI project manager who is responsible for the study. In addition, the total process capital for each plant section should be broken down into factory materials, field materials, field labor, and indirect field costs.

3.4.2 General Facilities

The capital cost of the general facilities is to be given explicitly. General facilities include roads, office buildings, shops, laboratories, etc., and are generally in the range of 5% to 20% of the process capital cost. Fuel, chemical, and by-product storage systems are to be included in the process capital costs and are not part of the general facilities. The cost basis for the general facilities will be established by the contractor with the concurrence of the EPRI project manager. Sales taxes must be included where applicable.

3.4.3 Engineering and Home Office Overhead Including Fee

An estimate is to be included of the engineering and home office overhead and fee that is considered representative of the type of plant in the study. These fees may be included in the process capital and general facility capital costs if the

contractor's cost-estimating system incorporates estimates of these fees as a part of the equipment costs. The capital cost summary tables must indicate where these fees have been included. For these fees, 7% to 15% of the process capital is typical.

3.4.4 Contingencies

EPRI uses two types of contingencies: the project contingency and the process contingency. The project contingency is intended to cover the uncertainty in the cost estimate itself, whereas the process contingency covers the uncertainty in the technical performance of the equipment. In both cases, the contingencies represent costs that are expected to occur.

3.4.4.1 Project Contingency. The project contingency is a capital cost contingency factor that covers the cost of additional equipment or other costs that would result from a more detailed design of a definitive project at an actual site. Table 3-3 presents guidelines for relating the project contingency to the level of design-estimating effort. Thus, by specifying the project contingency, the level of design-estimating effort can be defined, or vice versa. The contingency factors developed for each plant section should be shown explicitly.

3.4.4.2 Process Contingency. The process contingency is a capital cost contingency factor applied to a new technology in an effort to quantify the uncertainty in the technical performance and cost of the commercial-scale equipment. The following guidelines are provided to aid in assigning process contingency allowances to various sections of the plant.

<u>State of Technology Development</u>	<u>Percentages of Installed Section Cost</u>
New concept with limited data	40% and up
Concept with bench-scale data available	30% to 70%
Small pilot plant data (e.g., 1 MW) available	20% to 35%
A full-size module has been operated (e.g., 20-100 MW)	5% to 20%
The process is used commercially	0% to 10%

The process contingency should be given separately for each major plant section, as shown in Table 3-2.

3.5 TOTAL CAPITAL REQUIREMENT

The total capital requirement (TCR) includes all capital necessary to complete the entire project. These items include:

1. The total plant investment (TPI) at the in-service date. TPI includes an allowance for funds used during construction (AFUDC).
2. Prepaid royalties
3. Preproduction (or startup) costs
4. Inventory capital (fuel storage, etc.)
5. Initial chemicals and catalyst charges
6. Land

These items are discussed in the following sections.

3.5.1 Total Plant Investment (TPI) at the In-Service Date

The TPI at the in-service date includes escalation of construction costs and AFDC (sometimes called interest during construction) over the construction period. TPI is computed from the TPC (where the TPC is expressed on an "overnight" or instantaneous construction basis) as follows:

From the plant construction expenditure schedule, the amount of money spent during each year of construction is determined and referred to as E_j . For consistency, E_j is assumed to be spent at the end of the year. E_j is expressed in December (reference-year) dollars.

$$\text{Therefore, } TPC = \sum_{j=1}^N E_j \quad (3-1)$$

Where N is the total construction time in years.

To determine the actual money as spent over a construction period that ends in December (reference year), the costs are de-escalated back in time as follows:

The total cash expended, TCE, which is expressed in mixed-year dollars, is computed as shown below:

$$TCE = \frac{E_1}{(1+e_a)^{N-1}} + \dots + \frac{E_{N-2}}{(1+e_a)^2} + \frac{E_{N-1}}{1+e_a} + E_N \quad (3-2)$$

Once the money is spent, interest charges are accumulated as part of the AFDC at an interest rate, i , that is equivalent to the weighted cost of capital. The accumulation of all costs at the reference year is shown in the following time diagram.

Hence,

$$TPI = E_1 \left(\frac{1+i}{1+e_a} \right)^{N-1} + \dots + E_{N-1} \left(\frac{1+i}{1+e_a} \right) + E_N \quad (3-3)$$

AFDC can be computed directly as:

$$AFDC = \frac{TC}{P} - TCE \quad (3-4)$$

where TPI and TCE are computed from Equations 3-2 and 3-3.

For the case where the construction expenditure rate is assumed to be uniform, $E_1=E_2=E_j=TPC/N$, the following can be derived:

$$TPI \text{ (Dec. reference year)} = TPC \text{ (Dec. reference year dollars)} \times AF_{tpi} \quad (3-5)$$

$$\text{Where } AF_{tpi} = \frac{1}{N} (1 + Z + Z^2 + \dots + Z^{N-1}) = \frac{Z^N - 1}{(Z - 1)N} \quad (3-6)$$

$$Z = \frac{(1+i)}{(1+e_a)} \quad (3-7)$$

i = weighted cost of capital (interest cost for spent funds)

e_a = the apparent annual escalation rate for the plant equipment (generally e_a is assumed to be equal to the annual inflation rate, e_i , for capital equipment)

N = Construction period in years

TPC = Instantaneous total plant cost in December (reference-year) dollars

TPI = Total plant investment, including AFDC, at an annual interest rate of i and an annual escalation rate of e_a for a hypothetical December (reference year) in-service date. This is equivalent to an in-service date of January of the year following the reference year.

Sample Calculation IV in Section 6 of Volume 3 gives an example of the above calculation. Idealized construction periods for several types of power plants are shown in the following tabulation.

<u>Idealized Time Required For Construction (N)</u>	<u>Example of Plant Type</u>
6 years	Nuclear
5 years	Pulverized coal-fired (1000 MW unit)
4 years	Pulverized coal-fired (Single 500 MW unit)
3 years	Pulverized coal-fired (Single 200 MW Unit)
2 years	Oil-fired combined cycle (250 MW unit)
1 year	Combustion turbine (75 MW unit)

The periods shown in the above table are idealized in that no allowance is included for externally caused delays such as regulatory delays or labor strikes. Actual construction times may be somewhat longer. The construction times for new technologies should be estimated in a manner consistent with the data in the above table.

Adjustment factors for converting TPC into TPI for plants with a uniform rate of capital expenditures are given in Section B.5.8 in Appendix B. For consistency, a uniform expenditure rate should be assumed for new technologies unless an estimate of the actual expenditure rate is available.

3.5.2 Prepaid Royalties

Some new technologies may have royalty charges on portions of the plant. These royalty charges, if known, must be included in the capital requirement. For proprietary processes with an uncertain royalty, a value of 0.5% of the process capital is recommended.

3.5.3 Preproduction Costs

The preproduction costs are intended to cover operator training, equipment checkout, major changes in plant equipment, extra maintenance, and inefficient use of fuel and other materials during plant startup. For EPRI purposes, the preproduction costs are estimated as follows:

1. One month fixed operating costs (operating and maintenance labor, administrative and support labor, and maintenance materials).

2. One month of variable operating costs (consumables) at full capacity, excluding fuel. (These variable operating costs include chemicals, water, and other consumables plus waste disposal charges.)
3. Twenty-five percent of full-capacity fuel cost for one month. This charge covers inefficient operation that occurs during the startup period.
4. Two percent of total plant investment (TPI). This charge covers expected changes and modifications to equipment that will be needed to bring the plant up to full capacity.
5. No credit for by-products during startup.

The method for computing the operating costs needed for the above preproduction cost estimate is given in Section 3.6.1.

3.5.4 Inventory Capital

The value of inventories of fuels, other consumables, and by-products is capitalized and included in the inventory capital account. The inventory capital is estimated as follows:

<u>Type of Plant</u> <u>(See Section 2.2)</u>	<u>Nominal</u> <u>Capacity Factor</u>	<u>Fuel and Consumable</u> <u>Inventory Days at</u> <u>Full Load (100% Capacity)</u>
Baseload	65%	60
Intermediate	30%	30
Peaking	10% (or less)	5

Prices for fuel and consumables are given in Appendix B.

An allowance for spare parts of 0.5% of the total plant cost should be included.

3.5.5 Initial Catalyst and Chemicals Charge

The initial cost of any catalyst or chemicals contained in the process equipment (but not in storage, which is covered in inventory capital) is to be included.

3.5.6 Land

Although land costs vary and are site-specific, a nominal cost for land is to be included and is given in Table B3-1 of Appendix B.

3.6 OPERATING COSTS

Operating costs are to be estimated for a year of normal operation and presented in December (reference-year) dollars. The costs also will be computed on a 10-year and a 30-year levelized basis (see Section 1).

Operating costs are divided into fixed, variable, and consumable costs. All operating costs are subject to inflation. Fixed operating costs are essentially independent of actual capacity factor, number of hours of operation, or amount of energy produced, and are generally expressed in \$/kW-yr. Variable operating costs and consumables are directly proportional to the amount of energy produced and are referred to as incremental costs. They are generally expressed in mills/kWh.

3.6.1 Fixed and Variable Operating Costs

Fixed operating costs include the following:

1. Operating labor
2. Maintenance (may also have a significant variable component)
3. Overhead charges

These items are discussed in the following sections.

3.6.1.1 Operating Labor. An estimate is to be made of the number of operating jobs (OJ) that are required to operate the plant. The operating labor charges (OLC) are then computed using the average labor rate (ALR), as follows:

$$OLC = \frac{(OJ \times (ALR) \times (8760 \text{ hr/yr}))}{(\text{Net capacity of plant in kW})} = \$/kW\text{-yr} \quad (3-8)$$

The ALR includes payroll burden and is given in Table B3-1 in Appendix B.

3.6.1.2 Total Maintenance Costs. Annual maintenance costs for new technologies are often estimated as a percentage of the installed capital cost of the facilities. The percentage varies widely, depending on the nature of the processing conditions and the type of design. The ranges shown are representative.

<u>Type of Processing Conditions</u>	<u>Maintenance Percentage of Total Plant Capital Cost/Yr^a</u>
Corrosive and abrasive slurries	5 to 10 (& higher)
Severe (solids, high-pressure and temperature)	3 to 6 (& higher)
Clean (liquids and gases only)	1.5 to 4
General facilities and steam electrical systems	1.0 to 3

^aMinimum capital cost plants will generally experience maintenance costs at the high end of the range.

Maintenance costs can be developed separately for different sections of the plant. Maintenance cost estimates should be separately expressed as maintenance labor and maintenance materials. A maintenance labor/materials ratio of 40/60 may be used for this breakdown if other information is not available. The maintenance costs estimates will be developed by the contractor with concurrence of the EPRI project manager.

3.6.1.3 Overhead Charges. The only overhead charge to be included in power plant studies is a charge for administrative and support labor, which is taken as 30% of the operating and maintenance labor.

General and administrative expenses are not included.

3.6.2 Breakdown of Operating Costs into Fixed and Variable Components

From utility experience, baseload plants tend to have a relatively high fixed component of operating cost, whereas peaking and intermediate plants have a relatively high variable component. To break the operating costs computed in Section 3.6.1 into fixed and variable components, it is assumed that the portion of operating costs that is fixed is equal to the expected nominal capacity factor for the plant, which is given in Section 2.2 (65% base, 30% intermediate, and 10% peaking). The balance of the cost is assumed to be variable. An example of the calculation is shown below:

Example 3-1: Given a generating unit with a 65% capacity factor and a total O&M (the sum of operating labor, total maintenance, and overhead) of \$24/kw-yr, determine the breakdown between fixed O&M and variable O&M costs.

$$\text{Fixed O\&M} = (0.65)(24) = 15.6 \text{ \$/kW-yr}$$

$$\begin{aligned} \text{Variable O\&M} &= \frac{(1 - 0.65)(24) \text{ \$/kW-yr (1000 mills/\$)}}{0.65 (8760 \text{ hrs/yr})} \\ &= 1.5 \text{ mills/kWh} \end{aligned}$$

It is important to emphasize that all operating costs are subject to inflation and that "fixed" merely implies that the cost is not a function of the amount of energy generated.

3.6.3 Consumables

Consumables include water, chemicals, and other items that are consumed in proportion to energy output. The cost to be used for these items is given in Table B3-1 of Appendix B.

3.6.4 By-product Credits

By-product credits (if any) are based on values given in Table B3-1 of Appendix B.

3.6.5 Fuel Costs

Appendix B contains all fuel cost data. Recommended fuel costs for coal types included in Section 2, Tables 2-1, 2-2, and 2-3 are given in Table B4-1 of Appendix B. Costs for other coals are also given in Appendix B. Petroleum-based fuel price projections are given in Table B4-8, and uranium price projections are given in Table B4-7 in Appendix B.

Table 3-1

COMPONENTS OF CAPITAL COST

Table 3-2

EXAMPLE FORMAT FOR TOTAL PLANT COST DETAIL
(December 19__ dollars)

<u>Plant Section</u>	<u>Factory Materials</u>	<u>Field Materials</u>	<u>Field Labor</u>	<u>Indirect Field Costs</u>	<u>Sales Tax</u>	<u>Total</u>	<u>Engrg & Home Office Ov'hd & Fee</u>	<u>Contingencies</u>		<u>Total Plant Cost</u>
								<u>Process</u>	<u>Project</u>	
Coal Storage										
Coal Handling										
Coal Combustion										
(etc.)										
Totals	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>
(Process Capital)						A				
General Facilities	<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>	B				
Totals							C	D	E	F

Example Total Plant Cost

Summary
\$/kW

Process Capital
General Facilities
Engrg & Home Office Ov'hd & Fee
Project Contingency
Process Contingency
Total Plant Cost

A
B
C
D
E
F

Table 3-3

DESIGN AND COST ESTIMATE CLASSIFICATIONS

Item	Design/ Estimate Description	Project Contingency Range ^{a)}	Design Information Required	Major Equipment	Cost Estimate Basis Other Materials	Labor
Class I	Simplified	30% to 50%	General site conditions, geographic location & plant layout. Process flow/operation diagram. Product output capacities	By overall project or section-by-section based on capacity/cost graphs, ratio methods, and comparison with similar work completed by the contractor, with material adjusted to current cost indices and labor adjusted to site conditions.		
Class II	Preliminary	15% to 30%	As for Type Class I plus engineering specifics, e.g.: Major equipment specifications. Preliminary P&I flow diagrams.	Recent purchase costs (including freight) adjusted to current cost index.	By ratio to major equip. costs on plant parameters.	Labor/material ratios for similar work, adjusted for site conditions and using expected average labor rates.
Class III	Detailed	10% to 20%	Complete process design. Engineering design usually 20%-40% complete. Project construction schedule. Contractual conditions and local labor conditions.	Firm quotations adjusted for possible price escalation with some critical items committed. Pertinent taxes & freight included.	Firm unit cost quotes (or current billing costs) based on detailed quantity take-off.	Estimated man-hour units (including assessment) using expected labor rate for each job classification.
Class IV	Finalized	5% to 10%	As for Class III, with engineering essentially complete.	As for Class III, with most items committed.	As for Class III, with material on approximately 100% firm basis.	As for Class III, some actual field labor productivity may be available.

^{a)}Expressed as a percentage of the total of process capital, engineering and home office fees, and process contingency.

- First Commercial Service - This item is an estimate of the earliest date that a commercial-size plant could be put into operation. The first commercial service date estimate is usually based on adding the idealized construction time plus an allowance for design time to the "Available for Commercial Orders" date.
- Plant Capital Costs - This heading gives the basis for the cost estimate in terms of the number of units included in the plant. The various components of the capital cost are shown in Table 3-1 in Section 3.
- Total Plant Cost - This entry gives the total plant cost (TPC) at a single point in time and does not include the time value of money (interest, etc.) during the construction period. Capital cost estimates expressed at a single point in time are often referred to as instantaneous or overnight construction costs.
- Total Cash Expended - The total cash expended (TCE) is expressed in mixed-year dollars accumulated over the construction period. It represents the amount of money that would have been spent for all labor, materials, and indirects at the time the plant goes into service. The calculation procedure is shown in Section 3.5.1. The procedure includes de-escalating the components of the TPC back to the point of expenditure.
- AFDC - AFDC (Allowance for Funds During Construction) represents the interest paid on the cash expended during the construction period. This interest is accumulated and compounded until the plant goes into service. A procedure for computing the AFDC charges is shown in Section 3.5.1.
- Total Plant-Investment - The total plant investment (TPI) is the sum of TCE and AFDC. TPI is expressed in mixed-year dollars accumulated at the same point in time as total plant cost. The calculation procedure is discussed in Section 3.5.1. An example of the calculation is given in Sample Calculation IV in Section 6.5 of Volume 3. For cases where the expenditure rate is uniform, total plant investment (TPI), total cash expended (TCE), allowance for funds during construction (AFDC) can be calculated by multiplying total plant cost (TPC) by the appropriate adjustment factor (AF) from the following tabulation.

Idealized Construction Time (years)	Adjustment Factors ^(a)		
	AF(TPI)	AF(TCE)	AF(AFDC)
1	1.0	1.0	0.0
2	1.03	0.972	0.058
3	1.062	0.944	0.118
4	1.096	0.918	0.178
5	1.130	0.893	0.237
6	1.167	0.869	0.298
7	1.204	0.845	0.359
8	1.243	0.823	0.420

^(a) Based on 6.0%/yr cost escalation and 12.5%/yr AFDC interest rate.

From the preceding tabulation:

$$\begin{aligned} \text{TPI} &= \text{TPC} \times \text{AF}(\text{TPI}) \\ \text{TCE} &= \text{TPC} \times \text{AF}(\text{TCE}) \\ \text{AFDC} &= \text{TPC} \times \text{AF}(\text{AFDC}) \end{aligned}$$

- Startup, Inventory, and Land - These costs are based on representative costs for startup, fuel and other inventory, and land, as discussed in Sections 3.5.3 through 3.5.6 of Volume 1. The amount of fuel inventory is based on the expected capacity factor of the plant.
- Total Capital Requirement - This item represents all capital costs that would go into the rate base on a hypothetical January 1985 in-service date. Since the technology may not be available until a much later point in time, the total capital requirement should be multiplied by the appropriate cost escalation factor for a future in-service date.
- Operation and Maintenance Costs - Development of the operation and maintenance costs is described in Section 3.6 of Volume 1. Costs are expressed at the same point in time as the total capital requirement and represent the costs for a normal year of operation. The extra cost associated with plant start-up in the first year are included in the total capital requirement discussed above. Incremental costs are broken down into variable and consumable components. Consumables such as water and limestone are computed directly from the plant material balance. The variable component primarily represents variable maintenance and is estimated from an algorithm incorporating the expected capacity factor of the plant.
- Net Heat Rate - The heat rate is the amount of fuel energy (in Btus) needed to produce one kWh (net) of electricity. The heat rate is based on the higher heating value (or gross heating value) of the fuel. The part-load heat rate is an estimate of the actual heat rate at part load and is not an incremental heat rate.
- Unit Availability - The availability definitions are given in Section 4 of Volume 1. The availability estimates are based on mature plants and are likely to be significantly more optimistic than the initial experience with first-of-a-kind plants.
- Duty Cycle - Based on the plant cost and operational characteristics, the most probable duty cycle is shown. The duty cycle definitions are further discussed in Section 2.2 of Volume 1.
- Minimum Load - An estimate of the minimum load from which the plant could be ramped up to full load in a reasonable time (one hour or less) is given.
- Preconstruction, Licensing, and Design Time - Time periods for the preconstruction activities depend on local regulations and conditions. The time period shown is intended to be a reasonable approximation. Actual times may range from one-half to two times the value shown.

Appendix B

LIST OF ACRONYMS/ABBREVIATIONS

TABLE B-1. LIST OF ACRONYMS/ABBREVIATIONS

AA	Atomic Absorption
AFDC	Allowance for funds during construction
CDIF	Component Development and Integration Facility
CFFF	Coal-Fired Flow Facility
CSTR	Continuously stirred tank reactor
DI	Deionized
EP	Extraction Procedure
FGD	Flue gas desulfurization
GM	Gravimetric analysis
GPH	Gallons per hour
GPM	Gallons per minute
IC	Ion chromatography
KCOOH	Potassium formate
MHD	Magnetohydrodynamics
MSE	Mountain States Energy, Inc.
NDIR	Non-Dispersive Infrared Analyzer
PC	Personal Computer
PID	Proportional, Integral, Derivative
POC	Proof-of-Concept
POX	Partial Oxidation
PSIG	Pound per square inch gauge
PVC	Polyvinylchloride
RCRA	Resource Conservation Recovery Act
SCF	Standard cubic feet
SCFD	Standard cubic feet per day
SCFM	Standard cubic feet per minute
TCE	Total cash expended
TCR	Total Capital Requirement
TDS	Total dissolved solids
TGA	Thermogravimetric analysis
TPC	Total Plant Cost
TPD	Tons per day
TPI	Total Plant Investment
TT	Titration
UTSI	University of Tennessee Space Institute

End Date

2/10/95