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# THE ECONOSEED PROCESS FOR MHD SEED REGENERATION: PROGRESS AND NEW DEVELOPMENTS

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## ABSTRACT

Design and construction of the third crucial facility project comprising the DoE Proof of Concept (POC) Program is currently underway. Design is complete, equipment is on order, and plant modifications are underway for a plant to regenerate spent seed from Illinois #6 coal to potassium formate for recycle at a rate that supports a 4 to 5 MWt MHD system. New laboratory and literature data indicate that it may be possible to reduce regeneration requirements for systems using low sulfur western coal. In this case, it may be possible to separate the unreacted potassium carbonate in spent seed from western coals from the potassium sulfate used for sulfur capture thus avoiding the complete reprocessing of the spent seed to potassium formate. This processing operation will require the installation of an additional dissolver and separator at the POC plant but engineering assessments indicate a potential for up to 50% savings in seed regeneration costs for western coal systems. Status of the POC facility, laboratory and engineering data on the potential regeneration improvements for western coals, and economic comparisons of seed regeneration options for both western and eastern coals will be discussed.

## INTRODUCTION

The block flow diagram for the TRW Econoseed MHD Seed Regeneration Process is shown in Figure 1. Spent seed recovered as potassium sulfate or unreacted excess potassium carbonate, reacts with calcium formate in aqueous solution producing potassium formate and gypsum. The reactor effluent is dewatered to separate the gypsum and mineral matter from the regenerated seed solution and the solution is concentrated to anhydrous potassium formate in a forced circulation evaporator. The calcium formate used in the reaction is produced by the reaction of carbon monoxide gas with lime slurry in a continuous pressure contactor. The CO for this reaction can be produced via partial oxidation of natural gas or, for larger units, by coal gasification. The concentrated potassium formate can be used as the MHD seed material allowing for liquid injection of the molten salt into the channel at temperatures of about 150 deg. C. If necessary, the potassium formate can be converted to potassium carbonate by oxidation in a rotary kiln furnace. The processing steps have been successfully demonstrated at bench scale and work is underway to demonstrate the process at POC scale under DoE Contract DE-AC22-87-PC79672.

## PROOF OF CONCEPT MHD SEED REGENERATION PLANT

The design of the POC plant for the reaction of spent seed with calcium formate solution is now complete and purchase orders have been placed for materials and equipment. Modification of TRW's Multi-use Energy Test Facility to accommodate the new equipment is now underway and equipment installation will commence as delivery is completed. The plant is designed to process seed recovered from the UTSI CFFF tests using Illinois #6. Approximately 18 tons of spent seed from the November 1989 tests at CFFF has been loaded into tote bins and delivered to TRW. Additional spent seed will be delivered as testing continues at CFFF. The plant will produce up to 250 lb/hr of potassium formate seed material and deliver tonnage quantities for regenerated seed tests at CDIF. Presently the schedule for plant completion and the start of shakedown testing is February 1991 followed by plant operations starting in April 1991.

The process flow diagrams (PFD) for the reaction of spent seed with calcium formate solution and the separation of the potassium formate solution from the gypsum solids is shown in Figures 2 and 3. Spent seed from tote bins is fed continuously to a dissolver tank where it is contacted with aqueous calcium formate solution producing potassium formate and gypsum solids. The reactor effluent is fed to a centrifuge where the gypsum is separated from the aqueous potassium formate solution.

The gypsum solids are water washed and reseparated in another centrifuge to remove residual potassium formate, and the wash centrate is used as water makeup to the reactor. The centrate from the first centrifuge is the dilute potassium formate product feed to the evaporator system. Figure 4 shows the PFD for the evaporation system where the potassium formate solution is concentrated to anhydrous or highly concentrated solution which becomes the regenerated seed product. The evaporator is a forced circulation crystallizer system that can be operated to remove the formate seed product as crystals or as a slurry of crystals and highly concentrated solution. For delivery of seed to CDIF for testing, the product form will be a concentrated solution of potassium formate that will allow for feeding the seed by liquid injection. For the purpose of collecting scaleup data for retrofit systems, the product will be removed from the evaporator as anhydrous crystals. The POC plant will also allow for the testing of a system to produce potassium

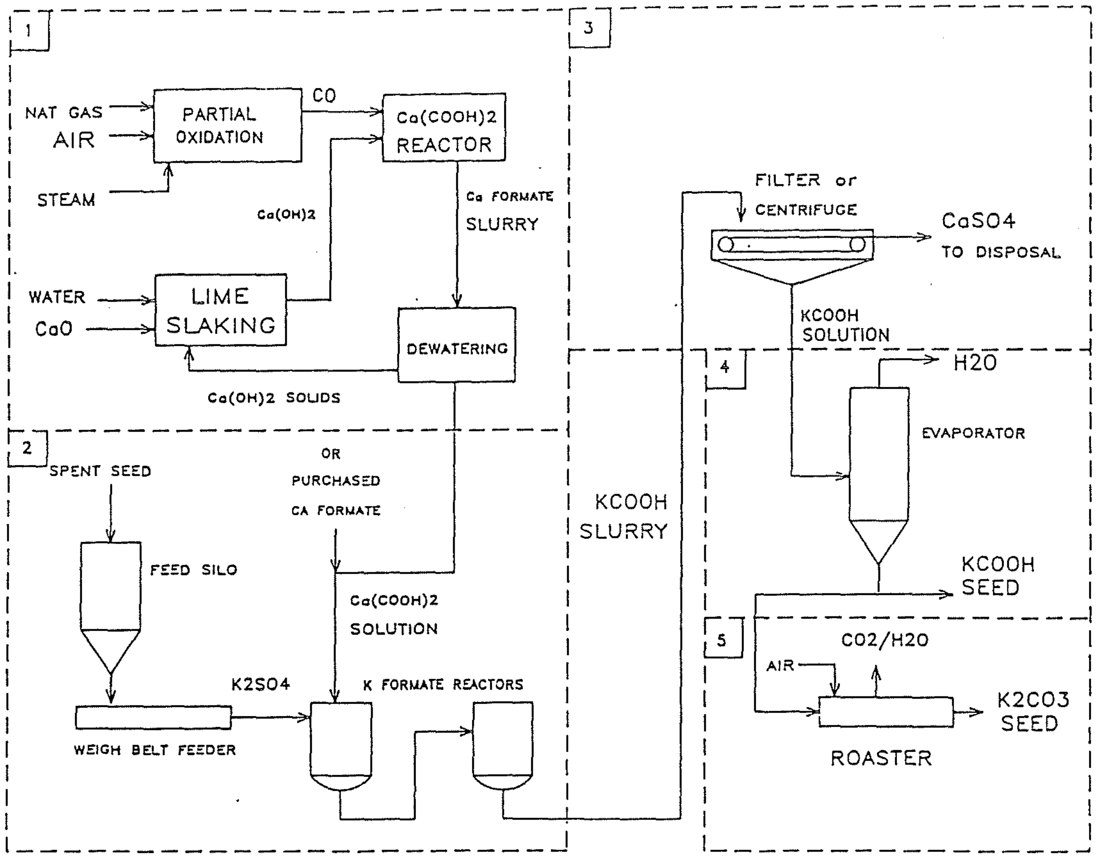


Figure 1. Econoseed Block Flow Diagram

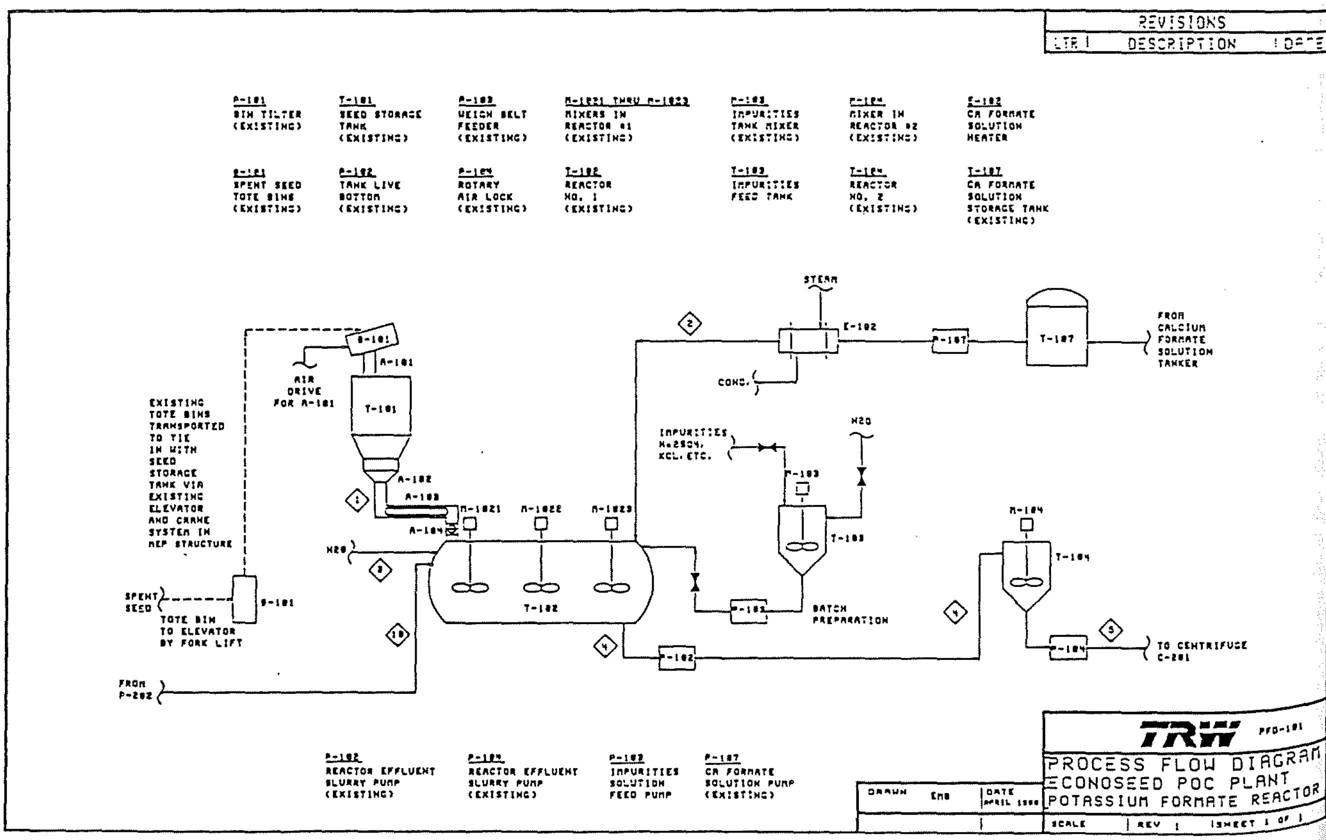


Figure 2. Process Flow Diagram - Potassium Formate Reactor

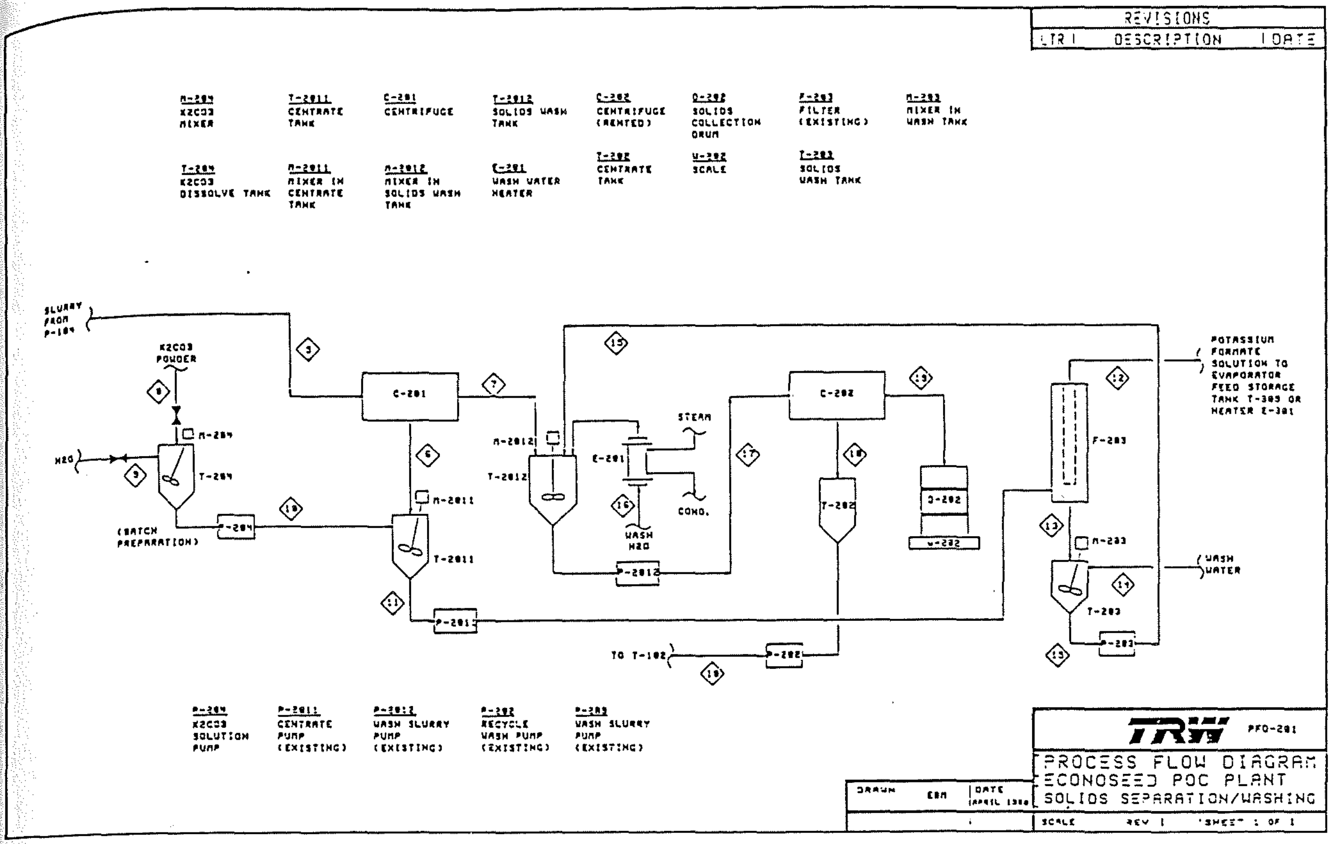


Figure 3. Process Flow Diagram - Solids Separation/Washing

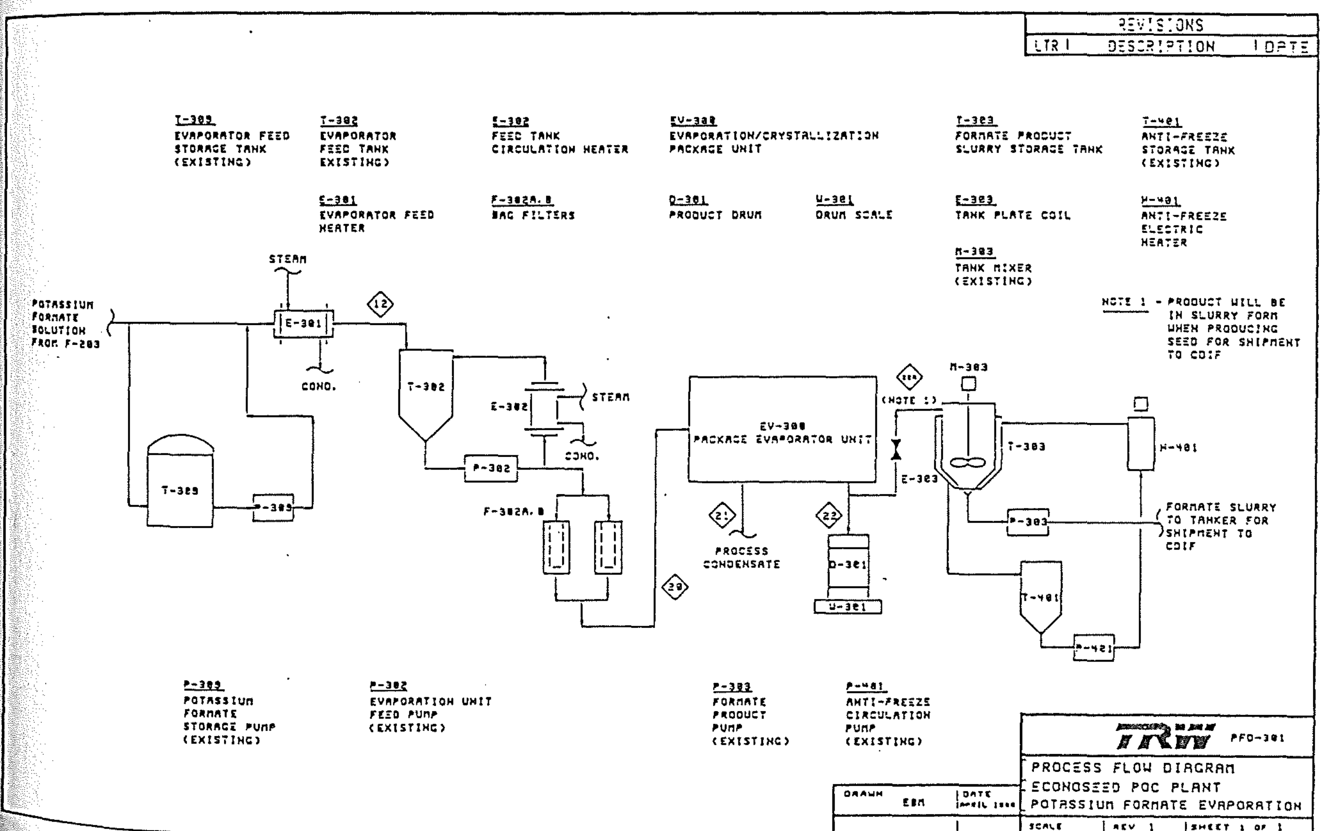


Figure 4. Process Flow Diagram - Potassium Formate Evaporation

carbonate from the potassium formate crystals. The PFD for the rotary kiln roasting system to oxidize the formate to carbonate is shown in Figure 5. This testing will be conducted in an existing system modified to feed the formate solids to the rotary kiln and react with air at about 500 deg. C.

The demonstration of the calcium formate production from carbon monoxide and lime slurry will be conducted at the POC plant offline from the potassium formate reactor section. The design of this system will commence in the fourth quarter of FY 1990 and operations are planned for the fourth quarter of FY 1991. The calcium formate POC system will be designed to produce up to 50 lbs/hr Ca(COOH)2 and will provide scaleup data for reactor sizing for retrofit applications.

## SEPARATION OF POTASSIUM CARBONATE SULFATE IN SPENT SEED FROM WESTERN COALS

Due to the lower sulfur content of western coals, the spent seed recovered when using Montana Rosebud coal 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 stoichiometric molar ratio of carbonate to sulfur is equal to almost 4:1. Under the same conditions (1.5% K) for an eastern coal (Ill #6) the stoichiometric molar ratio is equal to only 1.29:1. The spent seed in the western coal case contains about 2/3 potassium carbonate and 1/3 potassium sulfate on a weight basis. If this spent seed is fed to the seed regeneration process all of the sulfate and carbonate must be converted to formate via the reaction with calcium formate in order to recycle the seed 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. From the standpoint of seed regeneration, the processing costs are essentially the same for a low sulfur western coals as for the higher sulfur coal. 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.

There is data in the literature (Ref. 1) indicating that for solid mixtures of potassium carbonate and sulfate where the weight ratio of CO3:SO4 is 2:1 or greater, differences in the solubilities of the two salts might allow for a suitable separation of the sulfate from the carbonate. Table 1 shows the literature data for the system K2CO3-K2SO4-H2O at 25 deg C. The potassium carbonate is more soluble than the sulfate in the mixed system especially where the ratio of carbonate to sulfate in the original complex (recovered seed) is greater than 2:1. This means that the spent seed could be dissolved in a limited amount of water to dissolve the potassium carbonate leaving essentially all of the K2SO4 and mineral matter undissolved. The saturated carbonate solution could be evaporated and recycled to the MHD system after separating the solids from the solution. The solids would then be fed to the

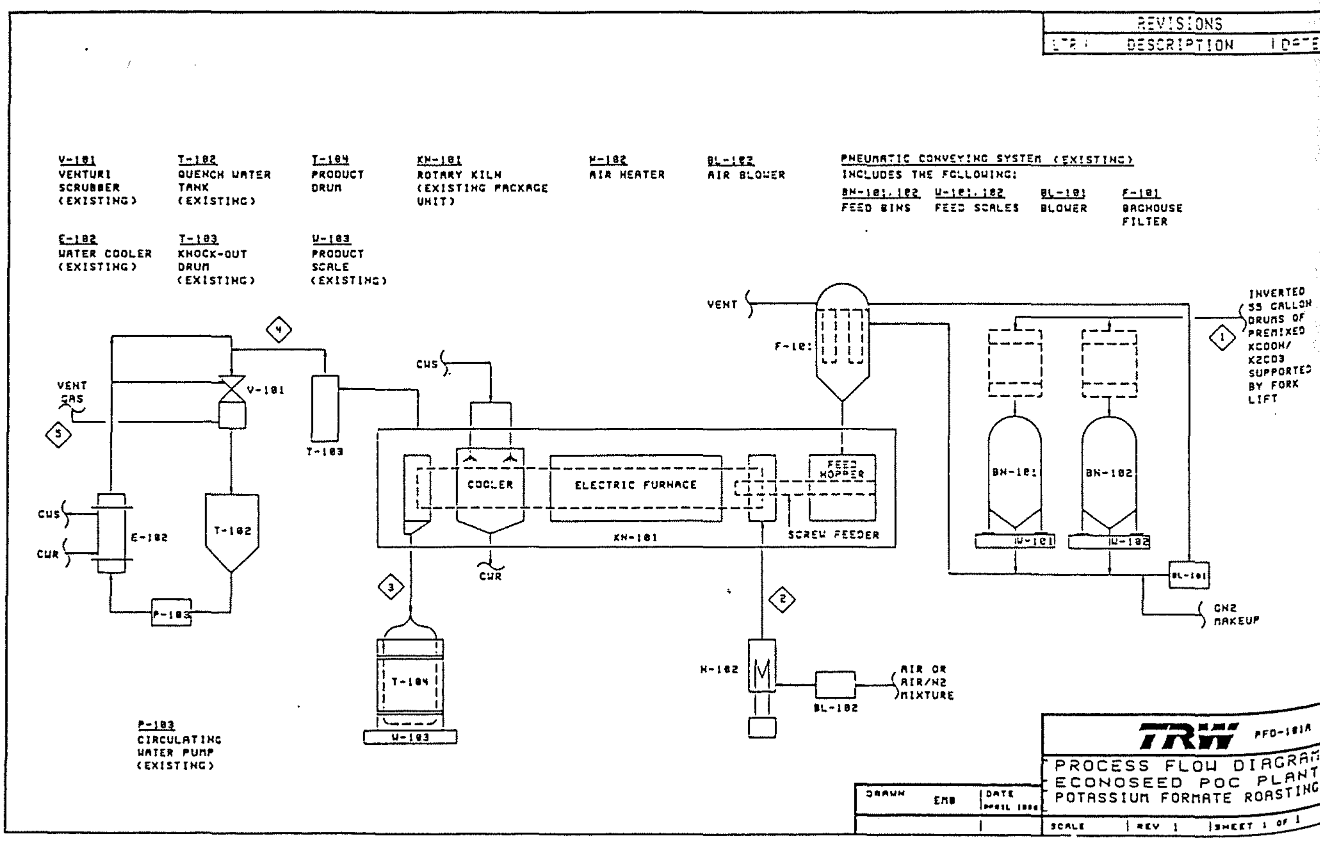


Figure 5. Process Flow Diagram - Potassium Formate Roasting

Econoseed process for conversion to formate. The regenerated potassium formate seed would then be mixed with the recovered potassium carbonate for seed recycle.

TABLE 1. SOLUBILITY RELATIONSHIPS IN THE SYSTEM K2SO4-K2CO3-H2O AT 25 DEG C.

| ORIGINAL COMPLEX | | SAT'D SOLUTION | | DENSITY | SOLID PHASE |
|---|---|---|---|---|---|
| WT% K2SO4 | WT% K2CO3 | WT% K2SO4 | WT% K2CO3 | | |
| ---- | ---- | 10.7 | ---- | 1.083 | K2SO4 |
| 21.8 | 4.6 | 6.5 | 5.5 | 1.103 | K2SO4 |
| 17.2 | 8.3 | 4.9 | 9.4 | 1.122 | K2SO4 |
| 17.1 | 14.1 | 2.8 | 16.4 | 1.17 | K2SO4 |
| 13.7 | 20.4 | 1.5 | 23.2 | 1.23 | K2SO4 |
| 14.8 | 30.1 | 0.3 | 35.0 | 1.348 | K2SO4 |
| 16.6 | 40.6 | 0.03 | 48.6 | 1.465 | K2SO4 |
| 8.1 | 41.5 | 0.08 | 45.1 | 1.506 | K2SO4 |
| 8.4 | 51.6 | 0.03 | 52.8 | 1.557 | K2SO4 • K2CO3*1.5 H20 |
| ---- | ---- | ---- | 52.8 | 1.557 | K2CO3*1.5 H2O |

REFERENCE 1

This modification to the Econoseed Process would require the addition of several processing steps such as dissolvers and solid-liquid separators but would substantially reduce the size of the calcium formate reactor and CO gas generation systems which would more than offset the added cost.

TRW has conducted one laboratory experiment using spent seed to confirm the literature data on the mixed seed system. Using spent seed samples from Illinois #6 coal provided by UTSI, potassium carbonate was added to adjust the ratio of carbonate to sulfate to about 2.1:1. This represents the ratio expected if a Montana Rosebud were used as the coal feed. To the mixed sample enough water was added to saturate the solution with respect to the carbonate. The solution was then filtered and analyzed. Table 2 shows the results of that experiment for two different ratios of carbonate to sulfate. The resulting concentrations of sulfate and carbonate closely coincide with the literature data showing promise for a method of separating the carbonate from sulfate from western coal spent seed. Although this data represents only a single experiment, there is evidence that further investigation of this method is warranted. Presently, the TRW seed regeneration program is only under contract to conduct studies at POC scale for seed samples generated from Illinois #6 coal but samples of spent seed from western coals will be collected by UTSI during 1991 that could be made available for POC testing if this is deemed important to establish a data base for seed regeneration scaleup to retrofit MHD systems.

TABLE 2. TRW LABORATORY SOLUBILITY DATA K2SO4-K2CO3-H2O AT 25 DEG C.

| ORIGINAL COMPLEX | | SAT'D SOLUTION | |
|---|---|---|---|
| WT% K2SO4 | WT% K2CO3 | WT% K2SO4 | WT% K2CO3 |
| 14.41 | 29.93 | 0.82 | 30.27 |
| 16.99 | 14.02 | 3.28 | 16.24 |

## PROCESS ECONOMICS FOR SEED REGENERATION USING EASTERN AND WESTERN COALS

A process design, capital cost estimate, and estimate of operating costs for a MHD system using Illinois #6 coal was performed as part of the Phase I Seed Regeneration program. At that time 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 quantity of seed used for a western coal system would provide almost three times the stoichiometric amount of formate for sulfur capture resulting in a spent seed containing more potassium carbonate than potassium sulfate. Although the Econoseed Process will regenerate the mixed seed to potassium formate, it requires the same quantity of calcium formate reactant that would be required if the spent seed were all potassium sulfate. The process does not take advantage of the lower sulfur coal and the processing costs for a western coal system are about the same as those for a higher sulfur eastern coal. A method for separation of the sulfate from carbonate in the spent seed could capitalize on the use of low sulfur western coal. Assuming the spent seed contains about 2:1 carbonate to sulfate, the carbonate could be dissolved in a solution forming about 35% potassium carbonate and separated from the undissolved potassium sulfate and mineral matter. The solid K2SO4 and mineral matter is then fed to the Econoseed plant and processed in the normal manner. The advantage with this method is that the calcium formate required for the reaction is reduced to one-third, equally reducing the requirement for CO gas generation. The potassium carbonate solution from the original 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 any 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 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 3 gives the results of that investigation for four cases. Case 1 is the base case design for an Illinois #6 coal where 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 about 1.3:1. Case 2 is similar to Case 1 except that the seed circulation rate is reduced to the theoretical stoichiometry for sulfur capture resulting in seed loading of 1.17% K. Case 3 uses a western coal with seed loading at 1.5% K without using any methods for separation of the carbonate in excess for sulfur capture. In this case the recycled seed contains almost a 4:1 ratio of potassium formate required for sulfur capture and the process is operated the same as in Case 1. Case 4 is also a western coal case except that the method for separating the carbonate from the sulfate in the spent seed described above is employed. Comparison of Cases 1 and 3 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

## TABLE 3. COMPARISONS OF PROCESS ECONOMICS FOR WESTERN AND EASTERN COAL SEED REGENERATION

BASIS:
300 MWt MHD SYSTEMS
95% THEORETICAL COMBUSTION AIR
AIR ENRICHED TO 35% O2
SLAG REJECTION- 30%
65% CAPACITY FACTOR

| CASE | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| COAL: | | | | |
| COAL TYPE | ILL #6 | ILL #6 | MONT ROSEBUD | MONT ROSEBUD |
| ASH CONTENT | 12.52% | 12.52% | 13.06% | 13.06% |
| SULFUR CONTENT | 3.62% | 3.62% | 1.10% | 1.10% |
| SEED: | | | | |
| WT % K IN CHANNEL | 1.5% | 1.17% | 1.5% | 1.5% |
| CO3 (equivalent) / S RATIO | 1.29:1 | 1:1 | 3.95 | 3.95 |
| SEED TYPE | FORMATE | FORMATE | FORMATE | FORMATE/ CARBONATE |
| PROCESS ECONOMICS | | | | |
| TOTAL CAPITAL REQMENT,(TCR) $, millions | $30.0 | $26.2 | $29.9 | $18.2 |
| TCR – $/KWe NAMEPLATE | $300 | $262 | $299 | $182 |
| OPERATING COSTS: | | | | |
| DIR. OPER. COST, $, Million | $7.7 | $6.5 | $7.3 | $3.3 |
| CAPITAL CHARGE– 15.5% TCR | $4.6 | $4.0 | $4.6 | $2.8 |
| TOTAL AMORTIZED OP COSTS | $12.4 | $10.5 | $11.9 | $6.1 |
| OPERATING COSTS, $/LB K Based on total seed circ. | $0.27 | $0.30 | $0.26 | $0.13 |
| TOTAL OPERATING COST,mills/kwh | 22.0 | 18.6 | 21.2 | 10.9 |

process. The potential for cost savings are promising for Case 4, where the spent seed was separated prior to processing. The capital cost in Cases 1 and 3 is more than 50% higher than those projected for Case 4. 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 operating costs for Case 4 are approximately one-half those for Cases 1 and 3, producing seed at about 11 mills/kwh.

The costs shown for Case 2 indicate that a savings of up to 10% in capital and operating costs might be realized for eastern coal if the seed loading were reduced to 1.17% K, just meeting the requirement for sulfur capture.

### CONCLUSIONS

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 DoE sponsored seed regeneration program offers opportunity to refine and develop that process to reduce the risk and costs associated with the recycle of seed. The potential for significantly reducing the costs for seed regeneration for western coals lies with the development of methods for separation of the excess unreacted carbonate seed prior to treatment with calcium formate. The methods described offer that potential and should be further investigated and developed at POC scale to provide a full database for design of larger systems.

### ACKNOWLEDGEMENT

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