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TECHNICAL PROGRESS REPORT

MHD SEED RECOVERY/REGENERATION - PHASE II
TRW APPLIED TECHNOLOGY DIVISION

SPONSORED BY: U.S. DEPT. OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER

CONTRACT NO: DE-AC22-PC79672

REPORT PERIOD - QUARTER ENDING MAY 29, 1992

TASK 1 - DESIGN, REFURBISH, OPERATE POTASSIUM FORMATE SYSTEM

Task 1 calls for the design, procurement, construction, and installation of the Seed Regeneration Proof-of-Concept Facility (SRPF) (Figure 1) that will produce tonnage quantities of recyclable potassium formate seed at a design rate of 250 lb/hr for testing in the channel at the CDIF while collecting data that will be used to upgrade the design of a 300 MW_t system. Approximately 12 tons of KCOOH (dry basis) as 70-75 wt% solution have been produced.

TASK 1.3 PRODUCTION OPERATION OF KCOOH POC UNIT

Dilute KCOOH Production Operations - March

The front end of the plant (potassium sulfate reaction and solids separation/washing units) was operated for five days in March. Most of the operations were conducted at a spent seed feed rate of 250 pounds/hour. A total of ~8,500 gallons of dilute KCOOH solution was generated containing approximately 2.6 tons of potassium formate (dry basis). The average KCOOH content of this solution was ~7 wt%. The design KCOOH solution concentration for the front end of the plant is 8.5 wt%.

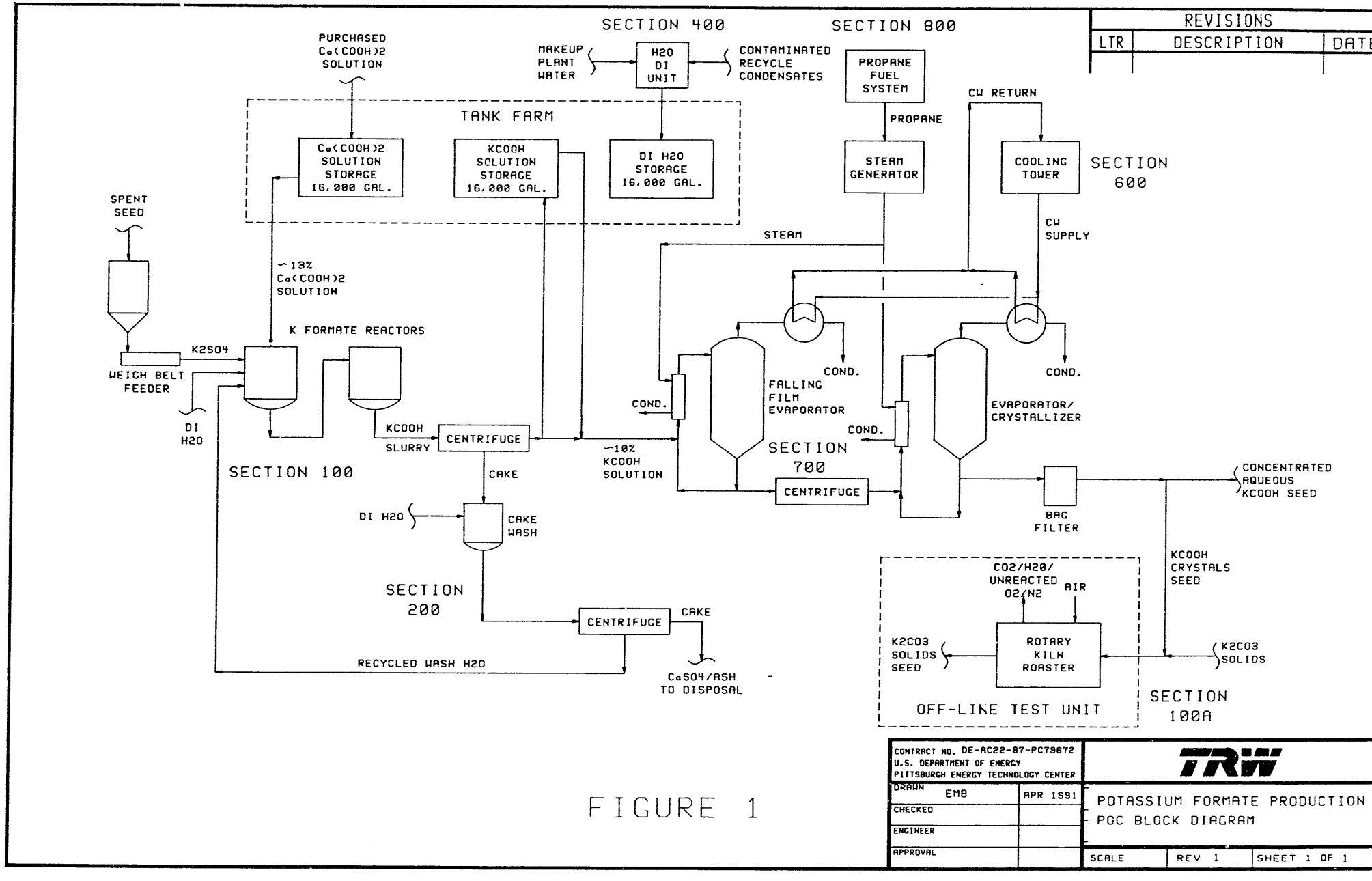
During three of the five test days in March, the spent seed material was spiked with sodium sulfate. In a full scale plant the sodium would enter the plant as an impurity with the coal ash. The purpose of adding sodium was to be able to track the sodium ions through the facility. No significant partitioning of the sodium relative to potassium was seen in the front end POC during these tests. During the other two test days, the wash water flow rate was reduced in an effort to increase the total dissolved solids in the dilute potassium formate solution that is then used as feed to the evaporator.

The facility is still configured to use horizontal reactor T-102 as a dissolve tank for the potassium sulfate seed only, while the gypsum-forming reaction takes place in vertical reactor T-104. That is, the only solids in reactor T-102 are any inert solids present in the seed and any undissolved K_2SO_4. The vertical geometry of T-104 was assumed to be better suited for handling solids. This configuration has solved the plugging problems associated with T-102 but may have moved the problem to T-104. The surfaces in reactor T-104 began to scale and the liquid level bubbler has plugged with solids on a couple of occasions. However, we have yet to have any major plugging problems in the level control valve in T-104.

Evaporator Operations - March

The evaporation unit was operated for a total of six days during March. Approximately 2.5 tons of potassium formate (dry basis) were processed through the evaporator and concentrated to >70 wt%. This material was allowed to settle and then decanted through a polishing bag filter into closed head drums for eventual shipment to the CDIF in Montana.

The evaporator plumbing is still configured for an interstage separation of the K_2SO_4 solids that precipitate in the first evaporator stage. That is, the centrifuge that was located downstream of the crystallizer is now located between the first evaporator stage and the crystallizer. There is



REVISIONS		
LTR	DESCRIPTION	DATE

FIGURE 1

CONTRACT NO. DE-AC22-87-PC79672 U.S. DEPARTMENT OF ENERGY PITTSBURGH ENERGY TECHNOLOGY CENTER	TRW
DRAWN EMB — APR 1991 CHECKED ENGINEER APPROVAL	POTASSIUM FORMATE PRODUCTION POC BLOCK DIAGRAM
SCALE	REV 1 — SHEET 1 OF 1

now a bag filter downstream of the crystallizer to remove any remaining solids (see Figure 1).

Dilute KCOOH Production Operations - April

The front end of the plant was operated for five days during April. The solids feed rate was increased from 250 pounds/hour to 290 pounds/hour during three of the test days. The plant appeared to handle the increased throughput without much difficulty but the accumulation of rust in reactor T-102 from the tote bins continued to cause problems. A total of ~7,600 gallons of dilute KCOOH solution was generated containing approximately 2.3 tons of potassium formate (dry basis). The average KCOOH content of this solution was ~7 wt%. The surfaces in reactor T-104 continued to scale.

Evaporator Operations - April

The evaporation unit was operated for a total of eleven days during April. Approximately 4.6 tons of potassium formate (dry basis) were processed through the evaporator and concentrated to >70 wt%. This material was allowed to settle and then decanted through a polishing bag filter into closed head drums for eventual shipment to the CDIF in Montana.

Summary of Production Operations

Production operations were completed during April with the production of more than twelve tons of regenerated seed (dry basis) as 70-75 wt% solution for shipment to the CDIF for use in channel tests.

For the purposes of the following discussion, the potassium formate production facility will be divided into two sections: 1) the 'front end' operation (Section 100 potassium sulfate reaction and Section 200 solids separation/washing) which is shown in the left side of Figure 1 and which produces dilute (~7 wt%) potassium formate solution, and 2) the two-stage evaporation unit (Section 700) which is shown in the right side of Figure 1 and which produces concentrated (>70 wt%) potassium formate.

The pertinent production figures for the dilute potassium formate production (front end) operations are given in Table 1. Approximately 35,000 pounds of Eastern spent seed from the UTSI CFFF were fed to the SRPF 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 thirty eight (38) single shift (8-hour) test runs. A total of 174 hours were logged with feeds flowing into the front end unit during the test runs. The balance of the test run hours, with no feeds into the unit, were utilized for startup and shutdown. Therefore, the "average" stream factor for the front end 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 typical spent seed feed rate achieved during production was ~250 pounds per hour. This was sufficient spent seed to produce ~200 pounds per hour of regenerated potassium formate seed (pure basis). The maximum potassium formate solution concentration achieved during production of the front end

TABLE 1. SRPF DILUTE POTASSIUM FORMATE UNIT PRODUCTION FIGURES

• Shakedown/Operations Time Period	9/91 thru 4/92	
• Total Number of Runs (Single 8-Hour Shift)	38	Average Stream Factor = 57%
• Total Stream Hours (Spent Seed Feed Into Unit)	174	
• Maximum Stream Factor Attained	85%	
• Total Pounds of Spend 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	
• Typical 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	

unit was ~7.5 wt%. On several occasions we 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 specific to the relatively small size of the piping and valving in our POC plant. It is possible that in a full scale plant we will be able to operate at higher potassium formate concentrations.

Many challenging mechanical problems were encountered during production operations. Foremost of these were the discharge of cake from the centrifuges (the dry gypsum/insoluble seed mineral matter tends to hang up in the ductwork) and the presence of large quantities of rust flakes (which play havoc with control valves) in the spent seed feed. Although we were successful in reaching our production goals, a number of challenging problems remain to be explained and resolved. Foremost among these are the observed formation of a pervasive gypsum scale in equipment and piping.

The pertinent production figures for the potassium formate concentration (evaporation) unit are given in Table 2. 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-two (32) single shift (8-hour) test runs. Maximum feed rate to the unit was ~6 GPM. Approximately 25,000 pounds of concentrated (70 to 75 wt%) potassium formate solution were produced in the unit. This regenerated seed solution has been packaged in about fifty 55-gallon drums for shipment to the CDIF in Butte, Montana for future use in channel tests.

Dilute Potassium Formate Production Unit Test Results

For front end 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 (~10%) in excess of stoichiometric to assure high sulfate conversion. Following the separation of the dilute potassium formate solution from the gypsum precipitate, a small amount of potassium carbonate was added to the formate solution. This was done to reduce the calcium content of this solution (by precipitating calcium carbonate), thereby reducing the potential for scale formation in the downstream formate concentration (evaporation) unit. Table 3 gives the stream analysis from a representative test run for the dilute formate solution after gypsum separation (by centrifugation) and then after addition of potassium carbonate and calcium carbonate separation (by filtration).

The front end operations were conducted in the temperature range of 60 to 70^{o}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. Indeed, no syngenite was found when an x-ray diffraction was run on the gypsum waste solids from the POC. The operations were conducted over a reactor residence time range of 50 to 100 minutes. High sulfate conversion was obtained over this entire range. 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 size of reactors currently being utilized.

TABLE 2. SRPF CONCENTRATED POTASSIUM FORMATE UNIT PRODUCTION FIGURES

• Shakedown/Operations Time Period	12/91 thru 4/92
• Total Number of Runs (Single 8-Hour Shift)	32
• Total Stream Hours	~200
• Maximum Stream Factor Attained	Not Applicable
• Maximum Feed Rate of Dilute Potassium Formate	~6 GPM
• Concentration of Potassium Formate Feed	5-7% KCOOH
• Concentration of Potassium Formate Product	70-75% KCOOH
• Total Pounds of Potassium Formate (Pure Basis) Produced	~25,000 lbs

TABLE 3. SRPF POC DILUTE POTASSIUM FORMATE PRODUCTION UNIT DILUTE FORMATE PRODUCT ANALYSIS

Ion in Solution	Dilute Formate After Gypsum Separation	Dilute Formate After Calcium Reduction
Potassium, wt%	3.12	3.56
Calcium, wt%	0.40	0.09
Formate, wt%	4.04	3.92
Sulfate, wt%	0.50*	0.48
Carbonate, wt%	--	0.04
Total Dissolved Solids, wt%	8.06	8.09

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

During a number of test runs, dry sodium sulfate was added to the formate reactor along with the spent seed. No significant partitioning of the sodium relative to potassium was seen in the front end POC during these test runs. Similarly, the small amount of chloride present in the calcium formate feed to the POC was not seen to partition as it was processed through the front end process units.

The solids waste product produced in the front end operations was relatively dry. These solids as discharged from a centrifuge contained ~0.2 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.

Concentrated Potassium Formate Production Unit Test Results

Approximately fifty (50) 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 70 to 77 wt%. The following range of concentrated seed impurity levels was seen:

	Wt. %
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 1.53-1.62. As noted above, 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 front end of the POC. Precipitated solids, consisting primarily of sulfates, are removed between the two stages of evaporation by a centrifuge. In a large scale unit, this material could be recycled to the front end of the plant for potassium recovery.

Although the concentrated regenerated seed that will be shipped to the CDIF contains 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 80-90 wt% potassium formate. This material was pumped from the second stage of the evaporator, operating at ~200^{o}F, into 55 gallon drums and then allowed to stand and cool. Upon cooling a large amount of potassium formate 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 the drums that are to be shipped to the CDIF. This regenerated seed solution (70-77 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^{o}C. However, since the regenerated seed is a saturated solution of potassium formate at ambient temperature, moderate reductions in temperature below ambient will reduce the solubility of potassium formate and cause a small amount of potassium formate to

precipitate from solution. Ambient temperature for the SRPF POC site at the time of drum filling was 10 to 20°C (50 to 68°F).

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.

Plant Activities - May

The long-term plant securing operations were started in May. Securing operations include both the front end units (potassium sulfate reaction and solids separation/washing) and the evaporator/crystallizer. The securing operations are expected to be completed in the next reporting period. Solid waste disposal activities will also begin in the next reporting period.

The potassium formate final product was transferred from epoxy lined steel drums to plastic drums. These drums will be weighed and labelled before they are shipped to the CDIF in Montana.

TASK 2 - DESIGN, CONSTRUCT, OPERATE THE CALCIUM FORMATE PRODUCTION POC

The objectives of Task 2 are to design and construct a POC unit (Figure 2) that will produce calcium formate from CO gas and lime slurry in a high pressure reactor system and to operate that POC unit to obtain data that will allow for low risk scaleup to larger sized systems. Since over two-thirds of the presently forecasted cost of seed regeneration is associated with this unit operation and the production of CO gas for reactor feed, verification of the process parameters for this operation is crucial to the MHD program.

TASK 2.1 DESIGN/CONSTRUCT CALCIUM FORMATE POC UNIT

Installation of plant interconnect plumbing continued during this reporting period.

Instrumentation

Instrumentation build-up for this task continued at a low level of effort during this reporting period. This subtask effort will increase upon completion of equipment installation when instrumentation wiring can be installed.

Documentation

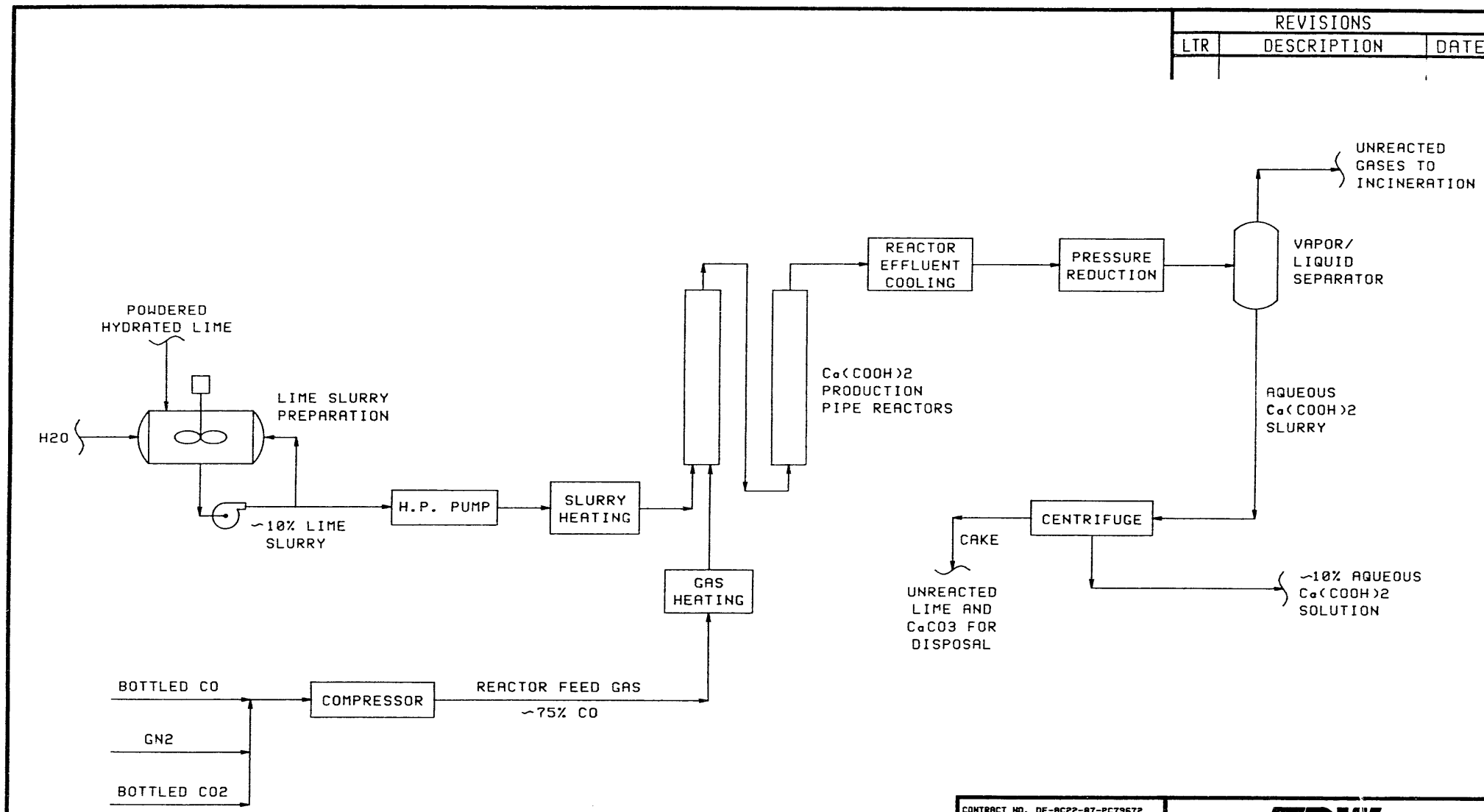
The following documents are currently under management review:

- Shakedown Test Plan
- Safety Hazard Analysis Report

Operating procedures for this unit are currently being written.

TASK 5 - PROGRAM MANAGEMENT AND REPORTING

The contract has been modified to extend the period of performance to June 30, 1993 and to add scope for Western seed studies.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~10% LIME SLURRY
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GAS HEATING
Ca(COOH)2 PRODUCTION PIPE REACTORS
REACTOR EFFLUENT COOLING
PRESSURE REDUCTION
VAPOR/ LIQUID SEPARATOR
UNREACTED GASES TO INCINERATION
AQUEOUS Ca(COOH)2 SLURRY
CENTRIFUGE
CAKE
UNREACTED LIME AND CaCO3 FOR DISPOSAL
~10% AQUEOUS Ca(COOH)2 SOLUTION
BOTTLED CO
GN2
BOTTLED CO2
COMPRESSOR
REACTOR FEED GAS
~75% CO
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FIGURE 2

TASK 6 WESTERN SEED STUDIES

Laboratory studies using "simulated" Western seed were started during this reporting period. Potassium carbonate and potassium sulfate were mixed in the ratio they are expected to be found in Western seed. Water was then added to this mixture in the amount mentioned in the literature that would dissolve only the carbonate. The resulting saturated solution is being analyzed to determine the ions present and thus to verify the literature and also confirm our analytical technique.

END

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