A Process for Cleaning and Removal of Sulfur Compounds From Hot Low-BTU Fuel Gas

Part I: Process Development Unit
Design and Construction

Part II: Pilot-Plant Experience

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June 1979

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SUMMARY

Most current research in high-temperature gas cleaning is concerned with the use of various filters for particle removal and with the use of solid absorbants for sulfur compound removal. Pacific Northwest Laboratory (PNL), in a departure from this approach, has developed a unique process that uses liquid (molten) salt scrubbing both for particle agglomeration and removal and for extraction of sulfur compounds. A Process Development Unit (PDU) has been designed and constructed to demonstrate this process. The work reported herein concerns this design and construction phase of work.

This PDU features unit operations never previously attempted at such extremes of temperature (700° to 730°C) and with molten salts as a working fluid. The process utilizes a venturi scrubber to circulate the molten salt, thereby eliminating failure-prone mechanical pumps. The venturi produces a fully entrained dispersion of the molten salt in the hot fuel gas. The dispersed salt droplets avidly extract sulfur compounds from the gas and adhere to and collect particles.

The salt is de-entrained in a simple knockout drum. The gas then passes through two bubble-cap trays flowing counter-current to regenerated salt. A packed-bed de-entrainer removes the residual salt from the gas. A portion of the salt is bled off for particle removal. The sulfur extraction capacity of the salt is then restored by reaction with steam + carbon dioxide to yield H_2S -rich gas (feed to a Claus sulfur converter). The regenerator is also a bubble-cap tray column.

The PDU was constructed using 304 SS and 304-L SS pipe and equipment made corrosion resistant by an aluminizing treatment ("pack-alonizing process"). An exception was the venturi scrubber: because of extremely erosive conditions, the venturi scrubber and areas of the venturi exhaust just downstream of the throat were formed of high-purity alumina as a liner for this "alonized" steel part.

A full-scale plant would utilize sensible heat in the incoming gas to maintain required process temperatures. In a small PDU this is not feasible, and all pipe and equipment was electrically heated and fully insulated.

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Electrically heated auxilliary equipment for preheating steam-carbon dioxide and for preheating air required in a heat exchanger used for salt cooling was provided. This array of electrical loads required sophisticated controls and power supplies.

Long runs of pipe (30 to 32 ft) expanded up to 5 in. when heated from ambient to operating temperatures. Extreme care was required in making up flanges and in supporting pipe and equipment so as to accommodate this movement.

This PDU was operated in a series of short runs over a period of about one year, and successfully demonstrated salt regeneration and extraction of sulfur compounds to design levels. Particle removal and salt de-entrainment was highly efficient, and gas approaching the "moving target for turbine quality gas" was produced. Gas was supplied by PNL's fixed-bed gasifier operating on coke and on Wyoming sub-bituminous coal. A detailed analysis of this operating history is provided in Part II of this report.

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A PROCESS FOR CLEANING AND REMOVAL OF SULFUR
COMPOUNDS FROM HOT LOW-BTU FUEL GAS
PART I: PROCESS DEVELOPMENT UNIT DESIGN AND CONSTRUCTION

INTRODUCTION

Low-BTU gas from coal offers one of the more promising methods of using coal for electric power production in an economical and environmentally acceptable manner. Favorable economics derive from the combined cycle concept, with its potential for enhanced Carnot cycle efficiency. Control of environmentally noxious emissions depends upon cleaning the gas. Conventional technology exists for this, provided the gas is cooled to ambient temperatures. The challenge lies in hot fuel gas cleaning, which allows optimum utilization of the energy available in the coal.

Pacific Northwest Laboratory (PNL) has been developing a hot fuel gas cleaning process that utilizes liquid scrubbing with a molten salt. In work begun under Office of Coal Research sponsorship, a process devised in the laboratory was partially demonstrated at Process Development Unit (PDU)-scale. A venturi scrubber and de-entrainer was successfully operated to verify laboratory sulfur recovery data and to demonstrate efficient particle agglomeration and collection. This work demonstrated that a vertically oriented venturi scrubber would function both as a co-current flow contactor and as a device with which to circulate the salt. This eliminated the need for a mechanical pump or gas lift for salt circulation. The venturi scrubber operated on low-BTU gas produced by the PNL fixed-bed gasifier operating on metallurgical coke.

During the transition from OCR to ERDA (now DOE) the project went unfunded for about a year. Work has been resumed under DOE's Fossil Energy Directorate. The work reported here outlines details of the design and construction of a PDU with fully continuous processing capability. Details of its operation and of data generated will appear in Part II of this report.

I. PROCESS DESCRIPTION

BASIC CHEMISTRY

Hydrogen sulfide, accompanied by minor amounts of COS, is the principal sulfur compound resulting from air-steam gasification of high-sulfur coal. Its removal from fuel gas by contact with the scrubbing liquid is the result of the reaction:

where

M = Na, K, or Li (in which case $n = 2$) or

M = Ca ($n = 1$).

The equilibrium constant for reaction (I-1) is given by:

$$K = \frac{a_{M_nS}}{a_{M_nCO_3}} \cdot \frac{f_{CO_2} \cdot f_{H_2O}}{f_{H_2S}}. \quad (I-2)$$

The equilibrium H_2S concentration cannot be accurately predicted from this equation because the activities a_{M_nS} and $a_{M_nCO_3}$ have not been measured.

It is reasonable to assume that the liquid phase activities can be approximated by mole fractions and that the fugacities of gaseous components can be approximated by partial pressures. Then, since

$$p = XP, \quad (I-3)$$

where

p = partial pressure,

X = mole fraction, and

P = total pressure,

equation (I-2) becomes:

$$K' = P \cdot \frac{X_{M_nS}}{X_{M_nCO_3}} \cdot \frac{X_{H_2O} \cdot X_{CO_2}}{X_{H_2S}}, \quad (I-4)$$

where all non-idealities have been absorbed into K' . With one caveat this equation can be utilized to evaluate K' from experimentally measurable quantities. With mixtures of carbonates it is not possible to determine how $S^{=}$ in the salt is combined. It was necessary to make an assumption concerning the relative reactivity of the alkali cations. For mixtures of (Li, K, Na)₂CO₃ it was assumed they were equally active. When CaCO₃ was present it was assumed that the reaction exclusively formed CaS.

The results of laboratory evaluation of the temperature dependence of K' have been reported, but for convenience the graphic summary of these data is reproduced in Figures I-1 and I-2.⁽¹⁾⁽²⁾ In Figure I-1 experimental data for the molten eutectic mixture Li₂CO₃ (43.5 mole%), Na₂CO₃ (31.5 mole%), and K₂CO₃ (25.0 mole%) in reaction with H₂S is compared with data of Koszegi and Rosen.⁽³⁾ Their data is for the reaction of H₂S with solid Na₂CO₃ and K₂CO₃. The data for the molten eutectic with K' computed on the assumption that all cations are equally active plots below and parallel to Koszegi and Rosen's data for solid Na₂CO₃. Curiously, if K' is computed with the assumption that Na ions are the only active cations, then the data for the molten mixtures plot almost on the dashed line for Na₂CO₃(s).

The data in Figure I-1 show that the ternary alkali carbonate eutectic would be a suitable extractant for H₂S. Multi-stage extraction would be required for all but the highest temperatures to attain >90% sulfur removal.

Equilibrium constants for the reaction of solid CaCO₃ with H₂S were calculated from thermodynamic data of Rosenquist.⁽⁴⁾ As shown in Figure I-2, this curve lies well above the curve for Na₂CO₃(s) defined by data of Koszegi and Rosen and well above the experimentally derived curve for the molten eutectic. Unless the activity of Ca⁺² ion is somehow suppressed,

FIGURE I-1. Reaction of H_2S with the Molten $(Li, Na, K)_2$ Eutectic Compared with Data of Koszegi and Rosen

FIGURE I-2. Reaction of H₂S with Molten Salts Containing CaCO₃

its addition to the alkali carbonate eutectic should result in improved extraction of H_2S .

The curve (Figure I-2) defined by open circles illustrates data obtained with salt mixtures to which 15 to 19 mole% CaCO_3 had been added. In calculating K' , reaction was assumed to be exclusively with CaCO_3 to form CaS . At low sulfur loadings and at low temperatures this was an accurate assumption. It becomes highly inaccurate, however, when most of the Ca^{+2} ions have been consumed (and at higher temperatures) and when competition with Na^+ ions occurs. These data predict that at temperatures of from 700°C to 850°C efficient extraction of H_2S can be achieved in a single stage.

Carbonyl sulfide is produced by the PNL gasifier at concentrations in the range of $\sim 0.02\%$. It is removed from the gas stream by reaction with CaCO_3 in accordance with the equation:

The equilibrium constants for this reaction computed from thermodynamic data of Rosenquist are compared with those for reaction (I-1) in Table I-1.⁽⁴⁾ It is clear from these data that COS should be extracted even more efficiently than is H_2S .

TABLE I-1. Comparison of Thermodynamically Derived Reaction Constants for Reaction of $\text{CaCO}_3(\text{s})$ with $\text{H}_2\text{S}(\text{g})$ and $\text{COS}(\text{g})$

<u>Temp, $^\circ\text{C}$</u>	<u>(H_2S)</u>	<u>(COS)</u>
400	0.15	66.9
500	5.1	735
600	22.7	1508
700	63.7	3125
800	312.5	-
900	909	-
1000	4000	-

Reactions I-1 and I-5 are reversible. Melts containing CaS (and M_2S) can be stripped of their sulfur content by contact with steam and CO_2 at concentrations exceeding the equilibrium values. From the temperature dependence of these reactions, it is clear that regeneration proceeds most favorably at lower temperatures. Laboratory data confirmed that efficient regeneration of the sulfur extracting capacity of the melts is feasible.⁽¹⁾⁽²⁾

PDU-SCALE DEMONSTRATION IN BATCH MODE

A practical scrubber for hot fuel gas must not only remove sulfur compounds but must also reduce particle concentrations to extremely low levels. A venturi scrubber is a highly efficient device for particle removal, and was the choice for installation in a PDU designed to scrub fuel gas generated by PNL's fixed-bed coal gasifier. Design, construction,⁽¹⁾ and operation⁽²⁾ of this PDU configured in batch mode has been described, but for convenience of review, salient features are described here.

The process flow diagram is illustrated in Figure I-3, with stream flows tabulated in Table I-2. The design basis for sizing the venturi throat was a gas flow in the range 50 to 75 SCFM, which would allow the PNL gasifier to operate well below its capacity. Since the PNL fixed-bed gasifier will not yield gas at temperatures near $700^{\circ}C$ or higher, this modest flow also allowed for design of a preheater of reasonable size.

A unique feature of the design called for operation of the venturi in vertical orientation. This allowed the venturi to double as a pump to circulate the molten salt. Referring to Figure I-3, gas was fed to the gas preheater, where its temperature could be adjusted and controlled to within a few degrees of the preselected run temperature. The H_2S content of the gas leaving the preheater could be enriched by gas from cylinders if desired. It then flowed to the throat of the venturi scrubber, where it encountered molten salt. Violent shearing forces produced by contact of the rapidly accelerating gas with the liquid salt converted the bulk liquid to a dispersion of fine droplets (mean droplet size computed to be 116 microns in diameter). This process was complete before the gas left the throat area. It produces such

FIGURE I-3. Schematic Flow Diagram of Molten Salt Scrubber De-Entrainer Operation

TABLE I-2. Mass Balance Calculations: Raw Gas Flow Rate 50 SCFM; Salt Feed Tank, 20 gal; CaCO_3 Concentration, 20 Mole%

[illegible]

high rates of mass transfer that extraction of sulfur compounds may be virtually complete within this element of volume, as shown by Eckman and Johnstone⁽⁵⁾ in studies of SO₂ extraction with NaOH(aq). With vertical orientation the dispersion was carried via a 2-in. exhaust line (sized to ensure a climbing film along the pipe wall) to a packed-bed de-entrainer that removed the entrained salt, allowing it to return to the venturi feed tank. The cleaned gas flowed to a burner for disposal.

In this first-ever attempt to utilize a venturi scrubber with a molten salt as a working fluid, all effort was focussed upon sulfur removal, particle removal, salt loss measurement, and mechanical operation of the venturi both as a pump and as a co-current flow contactor. Batch regeneration capability was provided, but regeneration could not be performed in conjunction with extraction. The process therefore was not fully demonstrated. Data was obtained at modest expenditure that confirmed laboratory data on H₂S extraction.^(a) Measurements of salt losses and particle concentrations confirmed that design criteria were being met. The stage was now set for design and construction of a modified PDU configured to operate in fully continuous mode.

PROCESS DEVELOPMENT UNIT, FULLY CONTINUOUS PROCESS CONFIGURATION

Operation of the PDU in batch mode provided opportunity for evaluation of various construction features to be utilized in the new PDU. Some were improved upon as a result of this experience.

Materials Problems

A very limited test program at PNL led to use of "alonized" 304 SS (or 304-L). This material proved generally satisfactory during batch operation of the PDU, so the new PDU was designed so as to permit use of the "pack-alonizing" process for corrosion protection of all pipe, vessels, and fittings.

(a) Reviewed in Part II of this report.

The "pack-alonizing" process produces a protective diffusion layer consisting of FeAl , FeAl_2 , and FeAl_3 intermetallic compounds at the surface. This layer has a thickness of no more than 5 to 10 mils. It provides protection against corrosion by sulfide ions that aggressively attack nickel-base alloys. This protection fails at temperatures above 750°C , where pitting and undercutting of the diffusion layer occurs.

During operation of the PDU in batch mode, "alonizing" failed to protect the venturi throat area as a consequence of erosion. In the new PDU the venturi configuration was produced by a ceramic liner that proved resistant to corrosion-erosion effects, but which was somewhat vulnerable to thermal shock.

Fittings and Valves

Grayloc flange assemblies were used in lines carrying liquid salt. These were generally satisfactory, but small leaks occasionally resulted that caused problems. Spiral-wound grafoil or equivalent gaskets were completely satisfactory in sealing standard flanges on lines where gas or gas-salt dispersions were carried.

Valves were a serious problem, and no completely satisfactory solution evolved from this work. Bellows-sealed needle valves used in early operation of the PDU were installed initially. These were available only in small sizes and had a tortuous flow passage 3/16 in. in dia that was easily plugged or obstructed. Run disruptions caused by plugging of these valves were so serious that the valves were considered completely unsatisfactory. They were replaced by suitably modified gate valves, which are a "full opening" type valve more resistant to plugging but less suitable for flow control. Flow control did become a serious problem.

Trace Heating

All pipes and vessels in this PDU require heating. Kanthal wire heater coils on ceramic supports were used for this requirement. Were cost no impediment, these would have been powered and controlled by zero phase angle firing, silicon control rectifiers. Instead, solid-state, proportioning-band controllers and magnetic contactors (relays) were used. Type K thermocouples for controls were peened into pipe and vessel walls and shielded from direct

exposure to the trace heaters with Kaowool paper. Numerous spare thermocouples were installed in addition to those required for control.

Facilities

At the start of the remodeling program PNL provided new supporting facilities, including a building and fenced cement slab. The PNL gasifier and auxiliaries (steam generator, blower, conveyor, and secondary combustor and stack) were moved to this facility, known as the Chemical Engineering Laboratory (CEL). Elements of the PDU in batch configuration were also moved.

This building provides sanitary facilities, soft water, high-pressure air, and process water to the adjacent slab. In addition, it provides an air-conditioned space for installation of sensitive analytical and control instrumentation.

The installation is served by fire alarm circuitry and is monitored around the clock by PNL's security patrol. Janitorial and trash removal services are provided.

Process Design Basis

In the continuing evolution of this molten salt scrubbing process it was decided to strive for a design that tends toward an economic optimum and which will provide data sufficient for scale-up, process optimization, and economic evaluation. Very little existing equipment was discarded.

The process is designed to remove sulfur compounds from low-BTU fuel gas at temperatures up to 725⁰C (limited by performance of materials). The system was designed for flows of up to 75 SCFM with removal of >90% of the sulfur compounds and with production of a gas containing <0.001 grains/SCF of particles 2 to 6 microns in diameter. The use of mechanical pumps for circulating the molten salt was avoided.

Major process variables are listed below, together with a qualitative description of the effect of changes in these variables. Where appropriate, the design basis value of the variable is discussed.

Inlet Gas Sulfur Content

As the inlet gas sulfur content increases, the regenerant gas H_2S concentration, the regenerated salt sulfur content, and the product gas sulfur content all tend to increase. If the product gas sulfur content is to be held constant despite an increase in the inlet gas sulfur content, this can be accomplished through some combination of increased salt flow, increased regenerant gas flow, reduced regeneration temperature, or an increase in the number of absorption and regeneration stages.

For the purpose of the present design, the inlet H_2S concentration was set at 1.30%. This is roughly twice the concentration typically obtained by air gasification of high-sulfur coals, and is near the upper limit for oxygen gasification of such coals.

Outlet Gas Sulfur Content

This is a dependent variable and is proportional to the inlet gas sulfur content. It decreases with increased salt flow, decreases with increasing number of extraction stages, and decreases as the sulfur content of salt from the regenerator is reduced. Increased salt flow requires greater regeneration efficiency (increased number of regeneration stages, lower regeneration temperature, or increased steam + CO_2 flow).

For design purposes the outlet H_2S concentration was set at 0.045%. This is the equivalent of less than 1/2 of the present EPA limit for SO_2 emissions from plants burning solid fuels (based on 150 BTU/SCF in the product gas and a standard of 1.2 lb $SO_2/10^6$ BTU). This represents a removal efficiency of 96.5%.

Regenerator Temperature

The regeneration reaction is exothermic and the position of the equilibrium is increasingly favorable at lower temperatures. Lowering the temperature for regeneration reduces the steam + CO_2 requirement and allows production of a gas of higher H_2S content. Decreased regeneration temperatures, however, require larger salt-cooling capacity and/or installation of inter-stage cooling. In addition, increased heat input is required to reheat the

salt to the absorption temperature. There is, of course, a low limit for the regeneration temperature due to the freezing point of the salt.

The pure ternary eutectic mixture of Li_2CO_3 , Na_2CO_3 , and K_2CO_3 melts at 394°C . Tests with Na_2S substituted for all of the Na_2CO_3 show adequate liquidity at 500°C . It seems reasonable to expect, however, that ash constituents solubilized by the salt may act to raise the freezing point of the mixtures. For design purposes, a salt temperature of 550°C was assumed at the regenerator inlet and the column was assumed to operate adiabatically. Provision was also made for cooling the top stage of the regenerator.

Extractor Temperature

The extraction reaction is endothermic and the position of the equilibrium is increasingly favorable to extraction of sulfur compounds at higher temperatures. Higher temperatures result in increased corrosion-erosion of materials. A practical upper limit for the "alloyed" steels to be used here appears to be about 750°C . For purposes of this design calculation a temperature of 700°C was selected.

Number of Theoretical Stages in Regenerator and Absorber

The number of theoretical stages in the extractor sets an upper limit on the regenerator outlet H_2S concentration (assuming gas product purity is fixed). An increase in the number of extraction stages allows attainment of a predetermined product gas purity despite an increase in the sulfur content of the extracting salt. This increased sulfur content, in turn, allows an increase in regenerant outlet gas H_2S concentration or a reduction in the number of regeneration stages. An increase in the ratio of extractor to regenerator stages will also result in decreased salt flow rates--a consequence of higher salt loading.

Because of the higher temperature and higher gas flow rate in the extraction section, it is anticipated that extraction stages will be more expensive than regenerator stages. In the present design, the number of extraction stages has been reduced somewhat by increasing the number of regeneration stages. This also lowers the regeneration gas flow rate.

Regeneration Gas Rate and Composition

The regeneration gas (67% steam + 33% CO_2) rate is increased when the ratio of extractor to regenerator stages increases...a consequence of lowered sulfur content in the salt. The rate is also increased either by increased liquid flow rate, by increased regeneration temperature, or by a reduction in the number of stages.

Since the cost of regeneration gas can be substantial, it is important to minimize its use. It is also desirable to produce a gas high in H_2S concentration as feed to a Claus process. For design purposes, the regenerator off gas has been specified at 12% H_2S (prior to steam condensation...which yields 30% H_2S after steam is condensed).

Liquid Flow Rate

Liquid flow to the regenerator and extractor is small in comparison to the gas flow--a consequence of the salt's high capacity for extraction of sulfur compounds. The required flow would be insufficient for efficient particle removal in the venturi scrubber, so a substantial recycle flow is utilized. The recycle stream does not pass through the regeneration or the extraction columns. The recycle stream carries the sulfur extracted by the co-current flow contact in the venturi scrubber. For design purposes, the recycle flow rate was set at 3 l/min.

Particle Removal

Particle removal (from the salt) was accomplished by means of a bleed stream. If the salt is the eutectic mixture of alkali carbonates, it can be freed of particles by dissolving the bleed salt in water, filtering to remove insoluble matter, and evaporating to effect crystallization of the mixed carbonates. This may be possible with salts containing calcium, but will probably be more difficult because of the low solubility of CaCO_3 .

Particle loading in gas entering the venturi scrubber depends on the characteristics of the gasifier and any precleaning equipment (cyclones, etc.) in use. Insufficient data were available to specify a bleed rate required, though it was anticipated to be very low.

Figure I-4 illustrates the flow diagram for the process that involved from these design criteria. Stream flows are shown in Table I-3.

As illustrated in Figure I-4, raw gas from PNL's fixed-bed gasifier enters the venturi scrubber, where the gas is accelerated to 300 ft/sec (or more) in the throat area. Salt also enters the venturi in the throat area and is dispersed into a fine mist by energy transferred from the gas phase. This dispersion is lifted to the de-entrainer, where the majority of the salt coalesces to a bulk liquid phase. A portion of the de-entrained salt flows through a cooler and on to a regeneration column, where it is contacted

FIGURE I-4. PNL Hot Fuel Gas Desulfurization and Cleaning Process Flow Diagram

TABLE I-3. Design Basis Process Stream Properties for Continuous Hot Gas Cleaning
(Basis 75 SCFM Feed Gas 1.3% H₂S)

Stream	Temp., °C	Pressure, psig	Flow Rate, lb-mole/hr					Salt Phase Sulfur
			Flow Rate H ₂ + CO + N ₂	CO ₂	H ₂ S	H ₂ O	Salt	
1	750	2.25	10.5	0.63	0.164	1.25	0	0
2	700	1.5	10.5	0.75	0.046	1.37	8.56	1.167
3	700	1.33	10.5	0.75	0.046	1.37	(a)	(a)
4	700	1.33	--	--	--	--	7.32	0.998
5	700	1.33	10.5	0.75	0.046	1.37	7.32	0.998
6	700	1.33	--	--	--	--	1.24	0.169
7	550	1.33	--	--	--	--	1.24	0.169
8	600	1.0	--	--	--	--	1.24	0.011
9	110	1.0	--	0.49	--	0.98	--	--
10	500	1.0	--	0.49	--	0.98	--	--
11	580	0	--	0.332	0.158	0.822	--	--
12	700	0.75	--	--	--	--	1.24	0.011
13	700	1.29	--	--	--	--	1.24	0.052
14	700	0	10.5	0.79	0.006	1.41	--	--
15	700	2.25	--	--	--	--	8.56	1.05

(a) Salt carryover in stream 3 is considered part of stream 4.

counter-currently with a steam + CO₂ mixture. This treatment converts sulfur compounds in the salt to gas phase H₂S, which may subsequently be converted to sulfur in a Claus process.^(a) The regenerated salt flows on to the fresh salt makeup tank where it is reheated and fed to the top of the absorption column. Here the clean salt again encounters gas flowing from the de-entrainer and additional sulfur compound extraction occurs, this time in counter-current flow. Salt leaving this column flows to the venturi feed tank.

A packed-bed de-entrainer sits on top of the extraction column. The de-entrainer consists of a shallow bed (18 in. deep) of 1/2-in. aluminum oxide rings similar to Rashig rings, but of the type produced by Carborundum Corporation for catalyst supports.

Two additional items could have been provided but were not: 1) a salt bleed recovery and recycle system, and 2) a polishing filter. The use of a venturi and subsequent gravity flow sequence for salt circulation is a choice that eliminates salt filtration as a process step. Without a mechanical pump, the pressure for filtration is not available. The other option is to take off a bleed stream at a rate sufficient to maintain a constant particulate level in the salt and to avoid operating problems. A salt bleed recovery system was designed and is described in detail in the Appendix.

The venturi scrubber is designed to remove 99% of particles 4μm or larger. The probable level of salt droplet carryover could be estimated on the basis of data obtained during batch mode operation of the PDU. It appeared that somewhat more than an order of magnitude improvement in particle scrubbing and salt carryover would be required to meet turbine specifications. It did not appear likely that packed-bed de-entrainer performance could be sufficiently improved to attain this goal. A demister or some sort of backup polishing filter might be required.

(a) PNL is not required to demonstrate this conversion step. After condensation of steam, H₂S was burned and disposed of with other stack gas.

This is a difficult problem. At the planned operating temperature of 700°C, soot (carbon) deposition can occur as a consequence of the reverse Boudouard reaction, (I-6):

This reaction can become troublesome if the gas is relatively dry and the contribution of the steam-carbon reaction is reduced. Taking all equilibria into account, it is clear that a slight lowering in temperature or reduction in moisture or CO₂ content can lead to soot formation. If this should occur while the gas is flowing through an efficient particulate filter, it would tend to blind rapidly.

Conditions can be controlled so that soot deposition is reduced or eliminated if sufficient attention is directed to operation of the gasifier. Water injection in the region above the gasification zone has proved effective in operation of the PNL gasifier. Increasing operating temperatures is another effective method of controlling soot deposition.

The problem of particle filtration is compounded by lack of agreement on what the specification for turbine-quality gas should be. It appears, however, that inlet gas to a turbine must contain <1 mg/M³ with no particles larger than some critical size--probably in the range of 2 to 10 μm.⁽⁶⁾ This specification is close to the quality usually ascribed to ambient air (i.e., 10⁻¹ mg/M³) and if realistic, may rule out hot fuel gas cleaning as a viable option. With the back-up filter described later, a gas with 37 mg/M³ was produced with no particles larger than 6 μm. Though preliminary in nature, this result may be indicative of the performance to be anticipated from particle filters of practical design.

II. EQUIPMENT DESIGN DETAIL

VENTURI SCRUBBER

Operation of the PDU in batch mode demonstrated the effectiveness of a venturi scrubber for salt circulation, particle removal, and extraction of sulfur compounds. The design of this venturi is illustrated schematically in Figure II-1, and details of the design calculations are given in reference 1.

This venturi scrubber was found to be structurally unsound at the point where the salt inlet side arm was welded to the throat constriction. In addition, severe corrosion-erosion effects were observed in the throat area and in the exhaust just downstream of the throat. The protective "aluminizing" layer was severely pitted and undercut in these zones after only 7 to 8 hours' operating time.

For the remodeled PDU the venturi was redesigned, incorporating a liner of high-purity, high-density Al_2O_3 to resist corrosion-erosion effects and to shape the venturi throat and exhaust parts. As shown in Figure II-2, the liner is made in two sections. The section which defines the throat rests on a shoulder of aluminized steel. The other section stacks above this and is secured by a retaining ring.

Originally the salt inlet orifice was a 1/4-in.-dia x 1-in.-long hole entering the venturi just below the shoulder upon which the alumina liner rests. The salt inlet line of 1-in. schedule 40 pipe was welded in place so the 1/4-in. inlet hole was tangential to the circumference of the inside of the pipe and was on the bottom side. The hole was placed at the bottom of the pipe so that the pipe could be completely drained.

This design proved to be adequate structurally, but the venturi inlet orifice constantly plugged and in early runs was often the cause of unscheduled shutdowns. In the earlier design, the salt inlet line funneled smoothly down to a 3/16-in. opening. Here the 1/4-in. opening was a hole an inch long at the bottom of a slightly sloping pipe. Solids settling in this pipe would pile up against the sharp shoulder around and above the 1/4-in. hole. Eventually, particles that lodged in this area obstructed salt flow. It was finally necessary to ream the 1/4-in. x 1-in. hole to 1/4 in. at the inlet side (for

FIGURE II-1. Schematic of Venturi Scrubber (Early Design)

FIGURE II-2. Design of Venturi Scrubber for PDU Startup Configuration

flow control) and to 1/2 in. on the outlet side. Further, an access hole immediately opposite the 1/2-in.-dia outlet was provided so that a poker could be inserted to remove obstructing solids. This configuration of the venturi scrubber is shown in Figure II-3. It was necessary to resort to the use of a poker to restart salt flow on a number of occasions.

The alumina liner eliminated the corrosion-erosion problems. The liner was replaced once, simply because other work on the unit was in progress. It had a few cracks in it, but was otherwise intact. The replacement liner failed during the course of a run; it broke up, and fragments were carried up the 2.5-in. exhaust line to the coarse de-entrainer. Some of these lodged in such a way that they obstructed this line at a point where it entered the coarse de-entrainer. As a result, the pressure drop became so great that the venturi could not be operated.

It appears the liner failed as a consequence of thermal cycling. Salt gets between the liner and the metal surfaces and freezes, bonding the liner and metal together. On further cooling the metal shrinks faster than the liner; on reheat, the metal expands faster. After a number of cycles, severe damage results.

This venturi was operated at a higher gas flow rate than was used in tests with the older design. With a flow of 75 SCFM the equation of Nukiyama and Tanasawa predicts a mean salt droplet size of 60 μm (vs 116 μm at 50 SCFM).⁽⁷⁾ This should yield slightly better particle agglomeration and sulfur compound extraction into the salt phase. The pressure drop across the venturi will be slightly greater because of the increased salt flow through the 1/4-in.-dia orifice (viz a viz 3/16-in. used earlier) as well as to the higher gas flow rate. This led to a decision to use a 2.5-in. exhaust line in preference to a less costly 2-in. line to reduce the pressure drop in this 30 ft-long section.

COARSE DE-ENTRAINER

The coarse de-entrainer is an alonized 304-L SS vessel, 42 in. tall, with an I.D. of ten inches. It was designed as a knockout drum for the removal of

FIGURE II-3. Final Modification of Venturi Scrubber

most of the salt from the high-velocity gas stream. A baffle plate was provided for impingement of salt droplets to improve separation. This plate was to be located directly below the high-velocity gas inlet. Unfortunately, it was not positioned correctly during fabrication, so the gas stream does not impinge on the plate. It was decided to use the coarse de-entrainer as-is, rather than to delay the project for refabrication of the plate in the correct location. The coarse de-entrainer performance proved satisfactory during operation of the PDU.

The coarse de-entrainer is positioned at the high point in the system. From it, salt flows by gravity to the regenerator and subsequently to the extractor. Salt flow to the regenerator is only a fraction (10 to 50%) of the total salt recirculated by the venturi. The balance of the salt overflows a weir in the coarse de-entrainer and flows down the recycle salt line to the venturi feed tank. Salt that has been regenerated and then flows through the extractor rejoins the recycle salt in the venturi feed tank. As its name implies, this tank holds the salt that feeds the venturi, thus starting the cycle again.

The venturi feed tank is an alonized 304 SS vessel that is 46 in. high and has a 10-in. I.D. It is the storage reservoir for the venturi feed salt. The salt from the extractor and the recycle salt combine in this vessel before being fed to the venturi scrubber. This vessel also had a tall standpipe in it; when the liquid reaches the level of this standpipe it overflows into a catch tank and is removed from the system. Upon discovery of the valve plugging problem (described later) it was decided to install a short, hooded standpipe in this tank. The standpipe was placed in the port from the venturi feed tank to the venturi feed line. This provides a salt-filled dead space in which suspended solids can settle. The standpipe was fabricated with a 6-in. pipe cap in a bell arrangement. Salt entering the venturi feed tank had to change direction of flow twice before flowing out. This helped eliminate foreign solid particles from the salt in the venturi feed line.

EXTRACTION AND REGENERATION COLUMN DESIGN

The extraction and regeneration columns were designed to provide intimate contact between gas and salt phases. Salt, low in sulfur content from the regenerator, flows counter to the fuel gas in the extractor, where it reacts with and removes sulfur from the fuel gas. The salt then flows to the venturi scrubber, where it picks up additional sulfur before returning to the regenerator. These multiple contacts allow production of a spent salt high in sulfur loading. This is desirable to maintain a low liquid flow and to allow production of a product gas from the regenerator high enough in H_2S to permit subsequent conversion to sulfur in a Claus plant.

From the beginning it was clear that the PDU should be capable of operating somewhere near the economically optimum conditions. What those conditions were was not known. However, it appeared that a low liquid rate was desirable to reduce energy used for reheating the lean salt from the regenerator, and that a high concentration of H_2S was required in the regenerator product gas to reduce steam and CO_2 consumption and to allow subsequent conversion to sulfur in a Claus plant. Reducing the liquid flow rate will typically allow production of a more concentrated regenerator product gas at the expense of additional extraction and/or regeneration stages required to maintain product fuel gas purity.

For the design basis conditions (i.e., 700°C extraction, 1.3% inlet H_2S , 5% CO_2 and 10% H_2O in producer gas) the minimum theoretical liquid flow is 0.61 lb-mole/hr (220 ml/min) when using the ternary salt composition. The salt flow rate used for column design was 1.24 lb-mole/hr (450 ml/min). Calculations show that at this flow rate the design basis specifications can be met with a modest number of extraction and regeneration stages.

Another option that should be considered is the use of a single extraction stage (e.g., a single venturi). Operation in this mode requires a substantial increase in the liquid flow rate. This results in a reduced sulfur loading in the salt, so it is much more difficult to produce a high H_2S concentration in the regenerator product gas. It would not be possible to produce a regenerator product gas containing 12% H_2S and still meet the fuel gas

specifications when extracting at 700°C and regenerating at 550°C. However, calculations indicate that this would be possible if the extraction temperature were increased to ~800°C. Because of the inherent simplicity of this mode of operation, it would probably be preferred at the higher end of the operating temperature range.

Extraction and Regeneration Column Design Details

The extraction column design is based on a nominal gas flow rate of 75 SCFM and an operating temperature of 700°C. A product gas containing no more than 0.045% H₂S and an inlet gas of 0.37% H₂S is assumed.^(a) The salt entering the column will contain 0.009 mole-fraction alkali sulfide and should exit at a mole-fraction of 0.042, at which concentration it flows into and mixes with recycle salt to be returned to the venturi inlet. The 700°C equilibrium curve and the venturi and extractor operating lines are shown in Figure II-4. The extractor requires 1.5 equilibrium stages. Salt flow rate is 0.0206 lb-mole/min (~450 ml/min).

The regeneration column inlet and outlet salt contains 0.136 and 0.009 mole-fraction alkali sulfide, respectively. The inlet gas is 67% H₂O and 33% CO₂ and the outlet gas contains 12% H₂S.

Heat of reaction cannot be neglected in designing the regenerator. A tray-by-tray calculation was made taking the following assumptions into account:

- regenerant gas enters at 500°C
- salt enters at 550°C
- the heat of reaction is 25 kcal/g-mole
- operation is adiabatic
- the average temperature of the gas leaving each plate is assumed to be equal to that of the salt on the plate.

(a) It should be noted that partial extraction of H₂S from gas entering the venturi at 1.30% H₂S has been achieved before the gas enters the extractor.

FIGURE II-4. Equilibrium Curve at 700°C and Venturi and Extractor Operating Lines

The calculation then proceeds by simultaneously solving the heat balance, mass balance, and equilibrium relations for each theoretical stage. This calculation indicates that three theoretical stages are sufficient to provide the required regeneration efficiency. The maximum salt temperature inside the column is predicted to be 617°C, and the outlet salt will be at 600°C. The required regeneration gas rate is estimated to be 8.8 SCFM; however, the column has been sized to allow operation at slightly more than twice this flow rate.

In designing both the extractor and regenerator it has been assumed that the chemical reaction is essentially instantaneous--i.e., that mass transfer is rate-controlling. Equilibrium data (Figure II-4) were those determined in laboratory studies of the behavior of the $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic system.⁽¹⁾ It was assumed, as indicated by the data, that the Na_2CO_3 was the active species for reaction with H_2S .

A number of different types of contactors are in common use for gas scrubbing. Several types were considered for this application, including columns with random-dumped packing, bubble-cap tray columns, sieve tray columns, spray towers, baffle-plate columns, venturi scrubbers, and Doyle scrubbers. In selecting a contactor one must consider the very low ratio of liquid-to-gas flow that characterizes this process. Because of the low liquid rate, a packed column is a poor candidate for the extractor. The regenerator, on the other hand, operates at the same liquid rate but at about an eighth of the gas flow rate, so a packed column might be feasible for the regenerator. Unfortunately, packed columns operate efficiently only over a narrow range of gas flow rates. This flow must offer resistance to liquid flow without reversing the liquid flow--a condition known as flooding. In order to study the desired range of gas flow rates and salt flows, it might be necessary to provide several columns of different diameters and packing sizes.

Bubble-cap tray columns provide considerable flexibility and maintain high efficiency over a wide range of liquid and gas flow rates. A large amount of test data has been published on their operating characteristics, allowing fairly reliable design without extensive preliminary development work. Their major disadvantages are high pressure drop and relatively complex (and costly) fabrication problems.

Sieve tray columns tend to weep at low liquid flow rates, and the small plate perforations may plug when the liquid contains suspended solids.⁽⁸⁾ Spray towers would be difficult to operate because of the low liquid head available. Also, erosion and plugging of small nozzles could be a problem. The Doyle scrubber is designed primarily for particle removal;⁽⁹⁾ however, it could also provide efficient sulfur compound absorption because of the intimate gas-liquid contact it provides. A series of venturi scrubbers could also be used. The venturi scrubber provides high stage efficiency, but produces a fairly large gas pressure drop. A total of three venturi scrubbers would be required. One was employed in the PDU to attain the necessary salt circulation. It was felt that operation of the PDU would generate sufficient data regarding the performance of a venturi to permit design of a cascade of

multiple venturi scrubbers, and that the project objectives would be better served by using a different type of contactor to provide the additional two extraction stages required. Two bubble-cap trays were provided for this purpose.

The regenerator was designed with a short packed-bed de-entrainment section above the top bubble-cap tray. By lengthening this section and by providing a suitable salt inlet line (which can be blanked off when not in use) this packed section could be used as a packed column. To do so, the center section of bubble-cap trays would be removed and the packed section would bolt directly to the bottom section. Because of problems with plugging of the bubble caps and downcomers, the trays were eventually removed and approximately 3 ft of packing installed to allow operation as a packed column.

Tray Efficiency

A number of empirical correlations have been published for estimating tray efficiencies. Unfortunately these concern systems which are quite different from that under consideration here and can hardly be expected to apply. Theoretical relations were used to estimate tray efficiencies. The relations proposed by Geddes indicate a Murphree vapor efficiency of 95.7% in the regenerator and >99% in the extractor.⁽¹⁰⁾ Those proposed by Bakowski predict 78.5% for the regenerator and 98.8% for the extractor.⁽¹¹⁾ In calculating the number of stages required, the more conservative estimates have been used. These high efficiencies are in agreement with laboratory data taken in a bubbler contactor. Data obtained during operation of the system were not sufficient to determine actual tray efficiencies; however, the flat gas concentration profiles observed indicate that the efficiency is high.

Liquid Entrainment

In a bubble-cap column the gas stream may entrain a small amount of liquid, carrying it up the column. This has the effect of reducing the efficiency of the column. The extent of entrainment was estimated using two methods given by Perry.⁽⁷⁾ Both are in essential agreement (eq. 18-19 and Figures 18-19C) indicating that approximately 11% of the gross liquid flow through the extractor will be entrained and carried from the bottom stage to

the top stage. This entrained liquid causes the effective vapor efficiency of the top stage to be reduced from 98.8% to 88%. Assuming the same amount of liquid entrained from the knockout drum, the efficiency of the bottom plate will also be reduced to 88%. For the regenerator the entrainment is predicted to be less than 2% of gross liquid flow, reducing effective gas phase tray efficiency from 78.5% to 77.4%.

Determination of Actual Number of Stages Required

A tray-by-tray calculation indicates that with a tray efficiency of 77.4%, four actual regeneration stages are required. Because of various uncertainties and extrapolations necessary in the calculations, the regenerator was provided with eight actual stages. In addition, provision was made for cooling the liquid phase on the top stage, where maximum heat generation occurs.

Equilibrium considerations led to prediction of 1.5 equilibrium stages needed for the extractor. This is in addition to the venturi. With a vapor efficiency of 88%, two actual stages are required.

Column Design Details

The extraction column shown in Figure II-5 is a 10.75-in.-O.D. cylinder (10-in. schedule 40 pipe) containing two bubble-cap trays with four 2.875-in.-O.D. caps per tray. The downcomer weir extends 3.25 in. above the tray and provides 2 in. of static liquid seal. Fifteen slots (0.25 in. wide x 0.75 in. high) are cut into each cap. The gas riser has a 1.9-in. O.D. (1.5-in. schedule 40 pipe) and the downcomer has a 1.315-in. O.D. (1-in. schedule 40 pipe). Spacing between trays is 19.375 inches. With outlet connections included, the column has an overall height of 76.31 inches. It was fabricated in two sections using 10-in., 150-lb flanges to connect the two sections. A similar flange connects the upper half section to the de-entrainer.

The regeneration column shown in Figure II-6 contains eight bubble-cap trays in a 6.625-in.-O.D. cylinder (6-in. schedule 40 pipe). Each tray holds two bubble caps. Nine slots (0.25 in. wide x 0.5 in. high) are cut into each cap. The gas riser has a 1.315-in. O.D. (1-in. schedule 40 pipe) and the downcomer weir extends 1.4 in. above the plate.

The cap slots have been sized to provide gas velocities within the range recommended by Davies,⁽¹²⁾ e.g.:

$$\rho_g^{-0.5} \cdot 3.4 < V_{\text{slot}} < 12 \cdot \rho_g^{-0.5}, \quad (\text{II-1})$$

where V_{slot} is the velocity of the gas coming through the slot (in ft/sec) and ρ_g = gas density (in lb/ft³). The limits for the two columns are:

Regenerator: $23 \text{ ft/sec} < V_{\text{slot}} < 81 \text{ ft/sec}$
 @ Design flow, $V_{\text{slot}} = 31 \text{ ft/sec}$

Extractor: $25 \text{ ft/sec} < V_{\text{slot}} < 90 \text{ ft/sec}$
 @ Design flow, $V_{\text{slot}} = 57 \text{ ft/sec}$.

Pressure Drop and Flooding

Pressure drop in the columns results mainly from contraction losses in the riser, losses due to flow reversal in the cap, resistance to flow in the cap slots, and the pressure caused by the liquid seal above the slots. Methods for estimating these losses are given by Peters and Timmerhaus.⁽¹³⁾ Results of this estimate are given in Table II-1. These estimates are in good agreement with normal pressure drops measured with the columns operating properly.

If the pressure imposed across a tray exceeds the height of the downcomer, the liquid will not flow down the downcomer. This condition is known as flooding. As evident from Table II-1, the design basis is well below flooding in both units when they are operating properly. In practice it was found that both columns did flood. Flooding of the extractor was caused by failure of the trays to prime. If full gas flow was started through the column before starting the liquid flow, gas blowing up the downcomer would prevent liquid from flowing down. Once a sufficient liquid layer was established on the tray below, a liquid seal would form, stopping the gas flow up the downcomer and allowing proper operation. Failure of a tray to prime was indicated by a continual increase in the pressure drop across the tray caused by a continued buildup of liquid. When this was encountered it was remedied by simply shutting off the gas flow momentarily to allow a liquid seal to form.

TABLE II-1. Pressure Drop in Regenerator and Extractor

Source	Extractor (Flow 75 SCFM, 700°C)		Regenerator (Flow 8.85 SCFM, 630°C)	
	ΔP , psi	ΔP , in. liq	ΔP , psi	ΔP , in. liq
Riser and Cap	0.0785 (Per Tray)	1.087 (Per Tray)	0.0382 (Per Tray)	0.53 (Per Tray)
Slot Blow	0.0498	0.69	0.0274	0.38
Liquid Seal	<u>0.1444</u>	<u>2</u>	<u>0.0361</u>	<u>0.50</u>
Total	0.2727	3.777	0.102	1.41

Fortunately, this operating characteristic of the extractor was discovered in shakedown tests using water, and because of this it never caused any serious problem when operating with molten salt. The regenerator flooded on several occasions, causing serious process upsets and equipment damage. Flooding of the regenerator was traced to: 1) accumulation of solids in the risers and in the annulus between the riser and cap, causing the pressure drop across the tray to greatly exceed that for a clean riser and cap, and resulting in liquid being forced up the downcomer; 2) solids accumulation in the downcomers, which prevented proper draining; and 3) a frozen drain line at the bottom of the column. In several instances flooding of the column resulted in molten salt being blown out the top of the column. This salt froze in the unheated line, creating a plug impervious to gas flow and with a consistency similar to concrete.

Packed-Column Stripper

Because of continuing problems with plugging and flooding of the stripper, the bubble-cap trays were cut out and approximately three feet of dumped packing was installed. Alumina cylinders approximately 1/2 in. in O.D. x 5/8 in. long with a 1/4-in.-dia hole through the center were used as packing. This packing was considered to be a more open structure and to be more resistant to plugging than was the bubble-cap tray column.

Column Operability and Performance

This topic is treated in detail in Part II of this report; however, in general it can be stated that mechanical operation of the extraction column

was about as expected. The column occasionally required priming when starting or restarting liquid flow, but otherwise it operated with no problems. The regenerator, on the other hand, was a frequent cause of problems. In early runs the regenerator flooded several times, causing major process upsets. Because of numerous problems with other parts of the PDU, it was not until run C-9 that sufficient operating data was obtained to pinpoint the location and cause of the problem. Plugged bubble caps on the 6th tray (from the bottom) were causing liquid to be forced up the downcomer. It appears that these caps were partially plugged from the start with residual aluminum oxide powder from the corrosion-proofing treatment. This powder, together with additional solids from the salt, combined to form a solid plug. Attempts to remove the plug with nitric acid, steam, and water were unsuccessful; therefore, the center section of the column was removed and the regenerator operated with only four trays in runs C-10 through C-15. In runs C-11 and C-12 the shortened column operated without problems. In runs C-13 through C-15 plugging and flooding problems were again encountered. After run C-15 the trays were cut out and replaced with packing. This change created an opportunity for inspection of the column internals and disclosed a buildup of solids (possibly corrosion products) inside the risers, caps and downcomers. The packed column used in run C-16 was only operated briefly, and little information was gained on its operability or performance.

Efficient extraction of H_2S and regeneration of the salt were demonstrated in the extractor and regenerator, respectively. However, it was not possible to verify the theoretical models used in designing the columns. This was due to difficulties encountered in establishing and maintaining the desired liquid flow rate. In runs where successful operation of the columns was achieved, the liquid flow rate was almost continually changing and was typically much higher than desired.

PACKED-BED DE-ENTRAINER

During operation of the PDU in batch mode, the packed-bed de-entrainer consisted of a column 32 in. high x 12.5 in. in dia. This column was packed

to a depth of 15 in. with 1-in.-dia ceramic (Al_2O_3) balls. The packing was supported on a wire screen of 1-in. mesh made of 1/4-in.-dia stainless steel wire. The de-entrainer had a calculated removal efficiency of 90% for particles 3.5 μm in dia and >99% for droplets of 10 μm dia and larger.⁽¹⁾ The product gas from this de-entrainer contained a particulate loading of 0.0422 grains/SCF (149 mg/M^3).

During operation of the PDU in continuous mode, the packed-bed de-entrainer was re-packed with a hollow cylindrical material. This material exhibits a lower pressure drop because of its higher packing void fraction. Particle collection was enhanced because of the smaller packing diameter. The packing material was 5/8-in.-dia x 5/8-in.-long cylinders with a 1/4-in.-dia hollow center. These cylinders, originally manufactured as a gas reforming catalyst carrier, are composed of Al_2O_3 (98.5%) with small amounts of SiO_2 , Fe_2O_3 , and Na_2O . Cylinders with two different firing temperatures were used. One set of cylinders was fired at 2700°F and the other at 3200°F. The high-fired material was of higher density than the lower-fired cylinders. There were no signs of chemical attack by either the salt or the producer gas on either type of packing material. This packing was supported as described earlier, but two layers of the 1-in. ceramic balls were placed on the wire screen first to prevent the cylinders from falling through.

Demister (Filter)

The head space above the ceramic packing within the packed-bed de-entrainer vessel measures 12.5 in. in I.D. x 17 in. high. This space can be utilized for tests of various demister or filter configurations. During operation of the PDU in batch mode, part of this space was filled with rolls of stainless steel screen. The rolls were about 3/4 in. in dia x 3 in. long, and were fabricated from screen of 50 and 20 mesh.

The rolls were simply dumped into the head space above the 1-in.-dia ceramic ball packing then in use. Rolls of the 20 mesh screen formed a layer 10 in. deep. This was covered with a 4-in.-deep layer of rolls from the 50 mesh screen.

This material did not resist exposure to the hot reducing gas too well. During portions of Run No. 6 the screen was exposed to gases as hot as 860°C

with a H_2S content of 2750 ppm. This is a severely corrosive condition, and when the de-entrainer vessel was subsequently opened it was found that the rolls of screen had partly disintegrated and were covered with a soot deposit.

The rolled screen demister was effective in reducing the particulate burden in the clean gas. Without the screen demister, the de-entrainer alone yielded a gas with 0.0422 grains/SCF (149 mg/M^3). With the demister in place, the product gas contained a particle burden of 0.0245 grains/SCF (56 mg/M^3). Clearly, significant improvement in gas quality may result from use of a properly designed demister or filter.

Tests of a prototype filter assembly were conducted during run C-13. The filter material was an experimental material furnished by 3M Company, and it consisted of a loosely woven ceramic felt about 1/8 to 3/16 in. thick and about 3-1/2 to 4 in. wide. Enough of this material was furnished to cover a stainless steel hardware screen (approximately 1/8-in. mesh) formed into a cylinder 7 in. in dia x 12 in. high. Only the walls of the cylinder were covered by the filter media. One end of the cylinder was welded to a circle of sheet stainless 7 in. in diameter. The other end was welded to the edge of a 7-in.-dia hole in a circle of sheet metal 16 in. in diameter. The 16-in.-dia sheet metal circular piece centered properly within the bolt circle of the flange on top of the de-entrainer and was securely clamped in place between two gaskets when the flange was assembled.

Just before assembly, a cover of 20 mesh stainless screen was wired in place over the ceramic filter material. The resulting filter exhibited an area of 264 in.^2 , and during run C-13 filtered a total of 45,000 SCF (208,035 CF) of fuel gas. The filter blinded almost immediately with soot. This was remedied by increasing the temperature and the water content of the gas. The filter was beginning to blind and exhibit excessive pressure drop at the end of the run. Though effective, it was obviously much too small in area for extended operation. The product gas contained 0.016 grains/SCF (37 mg/M^3). Further details of performance are given in Part II.

SALT COOLER

Regeneration of the extraction capacity of the salt by contact with steam + CO₂ in excess of equilibrium concentration is favored by reduced temperatures. Isothermal extraction-regeneration is possible, but at the expense of excessive steam consumption. In the present flowsheet, extraction is at (nominally) 700°C and regeneration is at 550°C. A salt cooler that will cool the salt to a temperature lower than 550°C is desirable.

Design of this cooler turned out to be more of a problem than was anticipated. Available heat transfer data indicates that the heat transfer coefficient of the solid salt (in pure conduction) is about an order of magnitude higher than that of the liquid salt. The calculations implied that if a coolant such as air is used at a significantly lower temperature than the freezing point of the salt, complete solidification of the salt would be difficult to prevent. Pre-heating the coolant air sufficiently to avoid this problem reduces the ΔT and increases the area of heat transfer surface required. With counter-current flow of salt and air, and with a jacketed 1.5-in. pipe through which a 470 ml/min salt flow is established, calculations indicate that 31 ft of pipe is required to cool this salt 200°C, (assuming a 450°C freezing point).

In part, this result arises from operation with laminar flow. It would be helpful if turbulent flow could be achieved, but this would require a very small diameter. In order to promote turbulence in the salt flow it was decided to pack the 1.5-in. pipe. Some rather brief laboratory experiments were performed using water as the fluid being cooled. It was found that the convective heat transfer coefficient for the fluid side could be approximately doubled by packing the tube.

Figure II-7 shows the position of the salt cooler that connects the coarse de-entrainer to the regenerator. Preheated air was used to cool salt, which was flowing through 1.5-in. pipe. The three long, straight sections of the salt cooler were jacketed, and the cooling air was applied only in these sections. The jacket (not shown in Figure II-7) was made of 16-gauge sheet stainless steel. End fittings were formed to fit loosely around the 1.5-in. pipe. These fittings were packed with "Kaowool" insulation and secured with a

FIGURE II-7. Elevation Drawing Showing Location of Equipment and Piping

clamp to hold the slight air pressure. Trace heaters were installed where possible on unjacketed portions of the salt cooler and over the jacket on the last leg of the salt cooler. These trace heaters were used for heatup and to help prevent inadvertent salt freezing. A total of 19 ft of jacketed 1.5-in. pipe was provided for heat exchange. The lowest leg (5.5 ft) of this was packed with 1/2-in. ceramic (Al_2O_3) balls to promote turbulence in the salt flow.

For the salt cooler to perform as designed, 470 ml/min of salt was to be cooled 150°C to 200°C by a counter-current flow of about 40 SCFM of air that had been preheated to approximately 400°C . Unfortunately, because of salt flow control problems (discussed later) the salt flow through the salt cooler was from three to eight times the rate of the design flow most of the time it was in operation. However, during operation in run C-12 the salt cooler became partially plugged, thus restricting salt flow. A heat balance on the salt cooler showed that the salt flow rate at this time was approximately 350 ml/min. The salt temperature was lowered by 100°C during this period of operation to an average temperature of 610°C . The cooling air flow rate was 35.5 SCFM, and its inlet temperature averaged 580°C . A reduction in the inlet temperature of the cooling air would provide a driving force that would allow the salt stream to be cooled further, but the salt cooler became completely plugged and flow was lost before this could be accomplished.

The cooling air for the salt cooler was used to heat the salt cooler during heat-up and to maintain it at operating temperature during periods when there was no salt flow through the salt cooler. It was found that the air had to be maintained at 600° to 650°C during these periods in order to prevent cold spots at bends and other shapes for which heating elements were not available. Therefore, when salt flow was started to the salt cooler the air preheater had to be backed down so that the air inlet temperature to the salt cooler could be lowered to the desired operating temperature. Thus, salt flow had to be sustained over a long period of time for the salt cooler to reach steady-state operation at design conditions. Because of problems with flow

control, operation of the regeneration column, and plugging in the salt cooler, this type of operation was not achieved.

In run C-11 the salt cooler operated continuously for eight hours. The salt flow at this time was calculated to be 2000 to 4000 ml/min. During this period of operation the air was brought up to 40.5 SCFM at an inlet temperature of 450°C. Due to the high salt flow rate the salt was cooled by only 35°C. Later in run C-11 the salt cooler was operated at 2000 to 4000 ml/min salt flow and 50 SCFM air flow with an inlet temperature of 450°C. During this period of operation the salt temperature was decreased by 45°C. This shows that the salt cooler did not have enough heat transfer area to adequately cool the salt at this flow rate. The salt cooler would cool the salt enough for efficient regeneration at design flow rates, but did not provide adequate cooling for salt flow rates that were four to eight times the design basis.

SALT MAKEUP TANK AND REHEATER

The salt makeup tank and reheater (upper tank) was used to melt the salt during heatup for each run. Any fresh salt required during a run was added through a small lock hopper and brought up to operating temperature in this tank. The regenerated salt also drained to this tank for reheating to the extractor operating temperature.

The upper tank is a 30-gal round-bottom vessel made of alonized 304 stainless steel. A 24-in. pipe cap was welded to the top of the tank to provide a gas seal. Openings in the pipe cap were provided for salt addition, salt sampling, a pressure relief valve, a salt inlet line from the regenerator, and a spare port for use if needed. A drain line from the bottom of the upper tank provided the salt feed for the extraction column. The upper tank is heated by a 40 kW electric resistance furnace. A liner made of Inconel-600 protects the furnace elements in case of failure of the upper tank. The tank itself has a lip around its top. It hangs on the liner by this lip and is free to expand or contract as it is heated or cooled.

During operation of the PDU a standpipe was fabricated and installed in the upper tank. The standpipe was similar to and performed the same function as the one previously described for the venturi feed tank. A 4-in. pipe cap was used to make the bell for this standpipe. The upper tank performed without incident during operation of the PDU.

EMERGENCY SALT STORAGE TANK

The emergency salt storage tank (lower tank) was located directly below the venturi scrubber. In case of a process interruption, such as loss of gas flow or flooding of the venturi scrubber, the salt feeding the venturi scrubber would drain into the lower tank. This would prevent salt from backing up into the gas preheater, where it could do considerable damage to heating elements. The lower tank is heated by a 35 kW electric resistance heater. The tank, furnace, and liner assembly are similar to that described for the upper tank, except that there is no drain line in the bottom of the lower tank. The liner for the lower tank is fitted with 5/8-in. studs that match holes drilled into the tank lid. A gas seal for the lower tank is provided by bolting the lid on via these studs over a spiral-wound gasket.

During run C-11 the lower tank furnace tripped its breakers and had to be shut down. It was found to have one shorted and two open elements. Connective wiring was revised to allow continued operation of the furnace at about 67% of rated power, which was adequate.

During run C-11 this furnace was off during much of the run. This led to an insidious problem which surfaced during the next run. With this furnace off, sections of pipe below the venturi orifice--including a 3-in. tee and, below this, a 6-in. slide valve--all run cool. These normally heat by radiation and conduction from this big furnace. Whenever gas flow to the venturi was bypassed, however, these parts cooled down because no hot gas was flowing. These factors combined to produce a cold spot on which salt could freeze. Each time flow to the venturi was stopped, a small amount of salt that has been climbing up the wall of the venturi exhaust line flowed back down and into the tank in this large furnace. The cold spot caused some of

this to freeze, and a plug began to form between the venturi orifice and the lower tank.

During run C-12 it was decided to jettison about 75 lb of salt to the lower tank. This was to be done by allowing salt flow to the venturi in the absence of gas flow. With no gas flow, the venturi would flood and salt would flow to the lower tank. As described above, the flow path to the lower tank had become partially plugged and the flowing salt built up sufficient head to flow up the 3-in. gas inlet line and into the gas preheater. Fortunately, the amount of salt that took this route (no more than 5 or 6 lb) was insufficient to reach the heating elements in this unit. The gas preheater was off and the presence of salt at the outlet of the gas preheater was sensed by the control thermocouple at that point.

Salt which accumulated in the lower tank could be removed through a 1-in. pipe that went in through the lid and down to the bottom of the tank. The tank could be pressurized with CO_2 to force the salt out. It was collected in a 55-gal drum and held for disposal.

PIPING

Alonizing

All piping and equipment that would contain salt was alonized. Alonizing produces an aluminum-rich diffusion layer on treated surfaces. This diffusion layer is approximately 10 mils thick. Iron-aluminum compounds are formed in this layer that are highly resistant to oxidation and chemical attack. The piping and equipment used in the PDU were coated by the "pack-cementation" process.⁽¹⁴⁾ In this process the material to be coated is packed with the coating agent in a retort. The coating agent, a carrier, and an inert powder (to prevent sintering) are packed around all surfaces to be coated. The retort is then placed in a vacuum, sealed, and heated to the reaction temperature. It is held at the reaction temperature a sufficient length of time for the coating to be formed. After cooling to room temperature, the pack powder is brushed off and the treated item is ready for use. Overall length on any piping element was restricted to 10 ft because of furnace size for the alonizing process.

Any modification to alonized piping or equipment items would destroy the protective diffusion layer. Therefore, upon completion of fabrication all piping runs and vessels were preassembled to check for dimensional accuracy. Any corrections required were made prior to alonizing.

Gasketing

High operating temperature and the corrosive nature of the salt presented a sealing problem at piping and piping-to-vessel connections. It was decided to use Grayloc connections for all lines carrying a continuous molten salt phase. This connection was developed for use at extreme temperatures or pressures. It is an external clamp-type connection with a metal-to-metal seal as shown in Figure II-8.⁽¹⁵⁾ It was found that the joints performed adequately when extreme care was taken in making them up. The sealing surface had to be completely free of salt or other foreign material when a connection was made. Also, pipefitters had to be certain that all bolts in the clamp were tightened to specified torque values. If improperly tightened, the connection would leak when heated to operating temperature. It was also found that whenever

FIGURE II-8. Standard Grayloc Assembly

possible, the connections should be oriented horizontally. If a leak occurred in a vertically oriented connection the salt ran down the pipe and shorted out all the heater elements contacted. In the horizontal arrangement only insulation below the leak was affected, with only occasional failure of adjacent heaters.

Piping runs that carried gas or salt-in-gas dispersions were connected using standard raised-face flanges. It was decided to use spiral-wound gaskets for these lines because of the extreme operating temperature. The spiral-wound gaskets consisted of a 347 stainless steel winding with "grafoil" packing and a solid outer ring. The outer ring made the gasket self-aligning and provided radial strength. Grafoil is an all-graphite product with good high-temperature operating characteristics.

During operation of the PDU a leak was detected at only one flanged connection. Upon inspection it was discovered that this flange had failed because of improper makeup, and not as a result of gasket failure. Overall, success was experienced with spiral-wound gaskets in flanged connections.

Support

Figure II-7 shows the support structure and major piping runs in the PDU. The 2.5-in. venturi exhaust line is approximately 30 ft long. Upon heating to operating temperature this line will expand nearly 5 inches. Therefore, the support for this line has to be able to move so that the line will not be stressed to the failure point. The upper end of this line is connected to the coarse de-entrainer, which will also move.

To accommodate growth of the venturi exhaust line, the coarse de-entrainer is supported by constant rate supports. Figure II-9 shows the constant rate supports and how they are attached to the mounting bracket for the coarse de-entrainer. These supports are compression spring mechanical devices, which yield a constant supporting force at all positions throughout its travel. They are sized so that they carry the weight of the coarse de-entrainer, one half of the venturi exhaust line, and one half of the 4-in. recycle salt and gas return line. Weight estimates included pipe, salt, heater elements, and insulation. The 4-in. recycle salt and gas return line would also grow about

FIGURE II-9. Constant Rate Supports to Which Pipe and Coarse De-Entainer Are Attached

5 in. on heat-up. As shown in Figure II-9, this line runs parallel to the venturi exhaust line. These two lines were heated and cooled at the same rate to prevent stress caused by differential thermal expansion. Alarm features on temperature monitoring equipment would alert operators if a section of heaters on one of these lines failed. The operator could then shut down a corresponding section on the other line. Additional spring-type supports were used on the venturi, on the recycle salt and gas return line near the bend leading to the venturi feed tank, and on the salt cooler.

Stresses in all pipe runs and vessels have been analyzed for thermal and deadweight loadings using the Swanson Analysis Code ANSYS. This code is extremely well-suited to piping analysis. Specific piping components and supports can be modeled exactly from its wide-element library. The code is noted by many authorities as the industry standard for sophisticated structural analysis.

To maximize system integrity, two basic criteria for piping stresses were considered. The first criteria is that primary stress (i.e., stress caused by deadweight and external loads) be kept below approximately one-fifth yield strength at operating temperature. Material strength at 730⁰C was estimated at about 11 ksi. Deadweight loading primary stress intensities nominally calculated by the ANSYS program were therefore kept below 2000 psi.

The secondary stress criteria for thermal loading was two-pronged. Secondary stresses from thermal loading are self-relieving for ductile materials--a fact long recognized by established piping codes. What this means is that the stresses calculated on the basis of elastic analysis can exceed the elastic limits of the material for certain loadings without the integrity of the system being compromised in any way. A system will, in fact, shake down to where it is cycling completely elastically under thermal expansion loadings if elastically-calculated stresses are kept below twice the high-temperature yield strength of the material. The system will "relax" itself. For this reason a combined maximum stress intensity limit was set at approximately 1.5 times the high-temperature yield strength of the material. The second prong of this secondary stress criteria deals with the stresses in the 2.5- and

4-in.-long vertical risers. These runs, being very long, displace significantly due to thermal expansion, driving the coarse de-entrainer vessel nearly 5 inches. For these reasons it was decided to limit maximum stress intensity caused by combined loading in these runs to approximately one-half the high-temperature yield stress. These values seem to indicate fairly high stress values, but they are the combination of direct stresses and peak nominal bending stresses. The vast majority of the stresses indicated in the piping were caused by pipe and elbow flexure accommodating length changes, and do not reflect direct tensile or compressive stresses resulting from restraint. Direct stresses were carefully monitored so that large loads would not be transmitted to the support structure. For example, direct stress in the vertical runs was adjusted to be less than 100 psi under combined loading. The constant rate supports and spring hangers described earlier were selected from standard equipment as a result of this analysis.

System Integrity

During operation of the PDU few problems were experienced that were a result of piping system failure. In two instances, however, 1-in. lines did fail. Examination of the failed lines disclosed that both ruptured from internal pressure. The pressure in these lines was a result of uneven heatup. A section of pipe would contain melted salt while still being plugged at both ends by frozen salt. Expansion forces exceeding the yield strength of the pipe could be generated, causing the pipe to rupture. Upon discovery of this problem the heatup procedure was modified. The piping system was held at the melting point of the salt long enough to ensure that cold spots were eliminated.

VALVES

The availability of flow control valves for operation at 700°C is quite limited. A "Nupro" series "V" bellows valve was used during operation of the PDU in batch mode. The same valve was specified for use during operation of the PDU in continuous mode. During the initial runs of the PDU in continuous mode the Nupro valves were constantly plugging. A black sludge that appeared

to be a mixture of corrosion products and residue from the alonizing process caused the plug. Figure II-10 shows a cross section of salt in the venturi feed line after a run. The white area is the normal appearance of the clean salt. The black area is the sludge that was plugging the Nupro valves. The Nupro valves have a 1/4-in.-dia, "Z"-shaped flow path, as shown in Figure II-11. Because of this it was decided that these valves would not be adequate, and new valves had to be found. A full-opening 1-in. gate valve was found that could be appropriately modified. In utilizing these valves, control of flow at the low salt flow rates (600 ml/min) would be sacrificed for the ability to open them to the full pipe diameter. If salt flow was lost because of plugging at the valve, the foreign material that caused the plug could be washed away by momentarily opening the valve to full open. Modifications to these valves involved: 1) bonnet extension so that the stem packing gland could be kept cool, and 2) addition of a port to the bonnet so that a CO₂ purge could be installed. The purge helped keep the stem packing gland cool and maintained a positive pressure in the bonnet with respect to the salt phase. This prevented salt from backing up into the bonnet and freezing around the stem. These valves did not plug as the Nupro valves did, but as anticipated, control of salt flow at the design rates was a problem. During normal operation these valves were opened 1/4 to 1/2 turn, but frequently had to be opened 3 to 4 turns to clear away foreign material.

It was decided to install the new valves without first having them alonized. This decision was made because of the time delay that the program would have experienced while waiting for the valves. Without the protective coating the valves were subject to attack by the salt. The gates and seats on these unprotected valves corroded so that they would not stop salt flow, and the valves had to be replaced once during subsequent operation.

SALT FLOWMETERS

Flowmeters that can withstand an environment of 700°C molten salt are not available at present. An attempt at development of such a device was made. The flow meters were to be used in the regenerator and extractor drain

FIGURE II-10. Cross Section of Venturi Feed Line, 2X

FIGURE II-11. Schematic Showing Flow Pattern in Bellows-Sealed Needle Valve

lines. The bottom of each column was a reservoir to which a siphon tube was connected to form a drain. The salt would accumulate in the bottom of a column until the level was high enough to start the siphon action. When the column emptied the flow would stop and the fill cycle would start again. By knowing the volume of salt drained per cycle and the number of cycles, an average flow rate could be calculated over a period of time. Instantaneous flow rates would not be available from this type of meter. The siphons were sized so that they would cycle about six times per hour at design flow rates. The number of cycles/time would be measured by a gamma-ray densitometer.

The output from the densitometer would be recorded on a roll chart recorder, thus providing a permanent record. The gamma sources were sized so that a measurable amount of gamma radiation could be detected by a Geiger-Mueller tube located on the opposite side of the column when the column was empty. When the reservoir was full of salt, the amount of radiation reaching the detector would be reduced. A switch in the detector housing was

open or closed, depending upon the amount of radiation the Geiger-Mueller tube was detecting. A power source attached to this switch provides recorder input.

Unfortunately, during operation of the PDU the data acquired from these flow meters was not reliable. The siphons operated correctly at times, but most of the time they did not. It was found that the siphons did not break properly, and that upon completion of a cycle the salt would continue to flow through the siphon tube instead of stopping. The rate of salt flow through the siphon tube would be approximately equal to the rate at which it entered the reservoir. Therefore, no further cycles would be detected.

Plugging problems were experienced with the siphon tubes. In order for the siphon action to occur, the siphon tube I.D. had to be relatively small (these were approximately 0.45 in.). As a result, they would plug during operation. When it was decided that these flowmeters were not going to function properly the siphon tubes were replaced with 1-in. pipe.

PURGE GAS SYSTEM

An inert gas purge system was required for three reasons:

1. to prevent mixing of combustible gases with air;
2. to prevent salt, moisture, or tar from entering certain lines; and
3. to protect the gas heater from overheating when producer gas was not flowing through the heater.

The location of the purges and their specific functions are as follows:

- Upstream of the gas heater. The gas heater required purge gas flow to prevent damage to its elements while bringing it to operating temperature or while bypassing producer gas. A carbon dioxide purge upstream of the gas heater also displaced air in the extraction section of the PDU prior to initiation of producer gas flow, thus eliminating the possible formation of explosive gas mixtures. Purge gas flow to the heater was manually controlled using a 1/4-in. ball valve.
- On the gasifier lock hopper. This dual purge system served two functions. It eliminated air from the hopper during coal/coke loading operations and eliminated combustible gases from the hopper prior to opening

the hopper to the atmosphere. The purge gas was vented to the secondary burner. This purge, used to control the atmosphere within the lock hopper, was controlled by a switch in the conveyor controls which activated a solenoid valve. After loading operations ceased this purge exhaust valve was closed. Another CO_2 purge to the lock hopper continued at 50 SCFH. This prevented tars and producer gas from leaking into the hopper. The purge was increased to 150 SCFH while operators were placing or removing the seal plate from the top of the lock hopper. Flow was measured by a 0-150 SCFH rotameter.

- On pressure ports on the extraction column, regenerator column, venturi feed tank, producer gas lines, and annubar differential pressure flow sensors. Carbon dioxide, metered through rotameters at approximately 0.5 SCFH, was required to prevent salt, moisture, and/or tar from accumulating in pressure sensing lines and gas sampling lines. When a gas sample was being drawn from a port where a purge was located, that purge had to be stopped until gas sampling was finished.
- On the gasifier tar collection system. A carbon dioxide purge was connected to the tar receiving drum to displace air from the drum prior to draining tar into the drum. The possibility of forming flammable gas mixtures was avoided by using the purge. Purge flow was manually controlled using a ball valve, and was vented to the secondary burner.
- On the modified molten salt gate valves. After run C-5 the Nupro bellows valves were replaced by 1-in. stainless steel gate valves on the venturi feed line, the extractor feed line, and the salt cooler. Carbon dioxide purges on the stems of these valves were required to prevent salt from entering. Salt could freeze in the stem or damage the packing if no purge was present. These purges were metered through 0-10 SCFH rotameters at approximately 1-2 SCFH.

Carbon dioxide was chosen over nitrogen as a purge gas because of the large requirement of the regenerator. Here, CO_2 requirements were of the order of 22 lb/hr. By contrast, the requirements for continuous purges at the ΔP sensors and gasifier lock hopper were about 2 lb/hr. Additional CO_2 was required intermittently (gas heater and startup purges, coal feeding cycles

of the lock hopper, and tar drum). Carbon dioxide also acts to suppress dissociation of carbonate salts, and where CaCO_3 is present this is highly desirable to prevent formation of CaO , which has limited solubility. Nitrogen can strip CO_2 from the salt, causing CaO to precipitate.

A 6-ton refrigerated storage tank for CO_2 storage was leased to supply requirements. This was kept filled by vendor-owned tanker trucks.

AIR PREHEATER

Air was the medium chosen to cool the salt in the salt cooler. The air blower at the PDU had adequate capacity to supply the required air flow. However, air had to be heated above 395°C in order to prevent salt from freezing. An air preheater was designed and built to supply hot air to the salt cooler.

Design calculations for the salt cooler showed 40 SCFM of preheated air were required to cool 470 ml/min of molten salt. The design criterion for the air preheater was twice the calculated flow, or 80 SCFM. The energy required to heat 80 SCFM of air from 15°C to 400°C is about 60,000 BTU/hr or 17.5 kW.

Heat transfer calculations for an 8-in. pipe packed with 1-in. stainless steel pall rings produced an average heat transfer coefficient of $12.9 \text{ BTU/hrft}^2\text{F}$ based on the temperature difference between the pipe wall and the bulk gas. Assuming a constant heat capacity for air, the driving force (wall temperature minus bulk gas temperature) is constant along the length of the heater. Estimating a ΔT of 29°C (53°F), the required heater length was 4 ft. Trace heaters to cover 4 ft of 8-in. pipe provided 21.6 kW at 208 V. The power available was 1.2 times the power required to heat 80 SCFM of air to 400°C .

The pressure drop of air from the blower, through a control valve, through a packed-bed preheater, and through the annulus of the salt cooler was estimated. Results showed that the 5-psig supply could produce the required air flow.

The air preheater resulting from this design consisted of a 4-ft-long x 8-in.-dia pipe of 304-L stainless steel. The heater was packed with 1-in. stainless steel pall rings. Distributor plates (1/2-in. stainless steel) at each end of the heater held the packing in and provided uniform flow throughout the cross section. Extensions on the distributor plates supported the unit. Air entered and left the preheater through 2-in. pipes. Figure II-12 shows the preheater. After construction, the preheater was mounted on Level 3 of the structure. Heaters and insulation were installed and wiring was completed.

Prior to installation of the trace heaters on the PDU, it was decided to abandon most of the heaters on the salt cooler and use air from the air preheater to heat the salt cooler. Calculations showed that the air preheater as designed could heat air to higher temperatures at a reduced flow rate. Operation of the air preheater during startup produced 600°C air at a rate of 36 SCFM.

Using air to heat the salt cooler during a startup was quite slow, especially when salt was frozen in the cooler. By monitoring the temperature of the air exiting the salt cooler it was possible to determine when the salt was melted. When salt flow to the regenerator was established, operators reduced the control temperature on the air preheater so that the salt could be cooled.

STEAM SUPERHEATER AND STEAM-CO₂ PREHEATER

Steam and CO₂ were required to feed the regeneration column. Carbon dioxide was supplied from the refrigerated tank previously described and was metered to the column with a float-type rotameter. Steam was supplied by the steam generator, which also furnished the steam requirement for the gasifier. The generator had a 50 lb/hr capacity and supplied 15 psig steam.

Saturated steam flow is difficult to measure, so a superheater was designed to allow flow measurement of superheated steam by a differential pressure flow meter. There were other reasons for superheating the steam,

FIGURE II-12. Air Preheater With Heaters Attached

e.g.: 1) steam would not condense when mixed with cool CO_2 before entry into the steam- CO_2 preheater, and 2) heat losses in lines might have caused entry of wet steam into the steam- CO_2 preheater operating at 550°C --resulting in uneven flow to the regenerator. Both CO_2 and steam flows could be manually regulated with needle valves.

The design basis for the steam superheater was: 18 lb/hr saturated steam, outlet temperature 204°C (400°F). The heat requirement was 1692 BTU/hr or 0.5 kW. The calculated average heat transfer coefficient was 5.1 BTU/hrft²°F in a 1-in. stainless steel pipe, based on the ΔT between the pipe wall and the bulk gas. For 8.5 ft of heated length, the ΔT was 82°C . Trace heaters of this length could provide 9.0 kW at 208 V, or 18 times the actual power required. It would have been possible to have a shorter heater with less capacity, but it would have operated with a higher ΔT . The steam superheater performed as expected. The pipe wall near the end of the superheater was maintained at 300°C , and 200°C steam was produced at flows less than the design rate.

Superheated steam combined with CO_2 and flowed to the steam- CO_2 preheater. This heater raised the gas temperature to 550°C .

The design basis of the steam- CO_2 preheater was: 18 lb steam/hr at 204°C , 22 lb CO_2 /hr at -1°C , and a maximum outlet temperature of 600°C . The energy requirement was 11,200 BTU/hr or 3.3 kW. For these conditions the average heat transfer coefficient was 5.0 BTU/hrft²°F using a heater 8 in. in dia and packed with stainless steel pall rings. For a ΔT (wall temperature minus bulk gas temperature) of 29°C , the heater needed to be 2 ft long. Trace heaters for this length provide 13.7 kW at 240 V, or 4.2 times the design heat requirement.

The steam- CO_2 preheater was built with the same design as the air preheater. The length, however, was shortened to 2 ft. The inlet side had a 3/4-in. flanged port for superheated steam and a 3/4-in. nipple for CO_2 . The outlet was a 1.5-in. flanged port. This heater was filled with 1-in. stainless steel pall rings. Figure II-13 shows the steam- CO_2 preheater on Level 3 of the structure before heaters were placed on it.

FIGURE II-13. View of the Steam-CO₂ Preheater Before Trace Heaters Were Installed

The pipe wall temperature of the steam-CO₂ preheater was controlled at 650°C in most cases. The gas leaving the heater was 550°C at a maximum. This preheater did not perform as well as the air preheater for two reasons:

- steam-CO₂ rates were often below the design rates, so a lower heat transfer coefficient resulted in a higher ΔT ; and
- steam most likely entered the preheater at less than 204°C (design condition) due to heat loss in the line between the superheater and the preheater.

During run C-8 salt entered the steam-CO₂ preheater because of flooding in the regeneration column. After this run the heater was cleaned by circulating dilute nitric acid through it. To prevent this from occurring again, a check valve was added to the 1.5-in. line between the regenerator and the steam-CO₂ preheater.

A steam vent valve was added to the superheated steam line just before the steam-CO₂ preheater after run C-8. The vent line made it possible to warm up the line between the steam superheater on ground level and the steam-CO₂ preheater on Level 3 without steam flow to the regeneration column. This vent line was used during startup periods, or when steam flow to the regenerator was not desired.

III. ELECTRICAL EQUIPMENT

HEATER CIRCUIT DESIGN

From the onset of PDU design it was recognized that vessels, columns, and most of the process piping would have to be covered with electric heaters to create and maintain the desired operating temperatures. To a considerable degree, dimensions of pipe and equipment were adjusted to assure compatibility with commercially available electric heaters. The latter consisted of coiled Kanthal resistance wire embedded in ceramic half or quarter cylindrical shells and covered with potting cement. The maximum temperature rating was 1205°C.

In some instances, the intricate shape of parts to be covered precluded the use of ceramic-supported heater coil. In such cases, beaded nichrome resistance wire was substituted. This wire could be wrapped with the coils touching to yield high watt density, or loosely (eg., with 1-in. to 2-in. spacing) to produce moderate heating. Due to their curvature, the siphons below the extraction and regeneration columns were wrapped with this wire. The sample ports on these columns were also heated with beaded wire heaters, and the regenerator product gas line was heated with loosely wound coils to prevent steam condensation.

Twenty seven circuits were required for the trace heating. These were operated from 115-V, 208-V, or 240-V transformers described below. In addition to the trace heating, the system electrical loads included the two large salt tank heaters, the gas preheater, the steam generator, the air blower, the coal/coke conveyor, the CO₂ refrigerator-compressor, and various control and lighting circuits. The supporting laboratory also drew power from the main transformer.

With exception of the trace heating, the circuits powering the equipment mentioned above were of proven design used in the earlier version of the PDU. No problems were experienced with this circuitry. There were problems with the trace heating circuits. Almost all of the heaters used were designed for operation at 230 volts. This being the case, electrical engineers tended to provide a 230-V supply with appropriate transformer and switchgear components.

As it turned out, the heat loads were such that most of the pipe and equipment could probably have been heated with 1/3 to 1/2 of the available voltage. Exceptions would include the air and steam-CO₂ preheaters, which were being driven hard.

Because of the nature of the control system described below, when a controller called for heat the heaters came on under full power. They were well insulated and rapidly came to a high temperature. In the smaller sizes, where the mass of ceramic was low and the object to be heated was small, the heaters tended to overshoot the control point temperature and numerous heater failures occurred. This problem was eventually solved by installing variable transformers in those circuits involving small heaters and operating the circuits at 100 to 110 volts.

Beaded heaters failed frequently, as they were not suited for this application. Possibly the use of heavier gauge, less brittle wire would have helped reduce frequent heater failures.

TRANSFORMERS

A city-owned transformer provided a 480-V, 225-KVA supply to the PDU. The maximum 15-min demand observed during the entire period of PDU operation was 192 KVA. This transformer fed a 480-V circuit breaker panel that supplied power to:

- the steam generator
- the salt tank furnaces
- the air blower
- the gas preheater
- the coal/coke conveyor
- the CO₂ refrigerator-compressor.

A 240-V, 75-KVA transformer that had been used in the original PDU to power trace heating was again used for this purpose and to provide power to the Athena solid-state proportioning controllers. It also supplied power to a Chromolox air heater to preheat gasifier inlet air above 212°F to prevent inlet steam condensation.

A 208-Y, 120-V, 225-KVA transformer was procured to add capacity in the 208-V range. It was used exclusively to power trace heater circuits.

CONTACTORS AND SUBPANELS

Each trace heater circuit had a main breaker and a magnetic contactor. The larger circuits were divided into subcircuits on additional circuit breaker panels. The subcircuits, either on 20- or 30-amp breakers, decreased the wire size needed in the run between the contactors and the heaters. They also provided for continued safe operation of unaffected portions of a circuit if a single subcircuit had a short to ground. All contactors and subpanels were in outdoor, drip-proof enclosures and were mounted on flexsteel supports. Figure III-1 shows the array of contactors and subpanels. The 208-V, 225-KVA transformer is at the extreme rear. The curious pattern was caused by shadows. The cabinet in the right foreground (not installed) contains the Athena solid-state proportioning controllers. Controls for the two large tank furnaces appear in the left edge of the photo.

CONTROL SYSTEM

A variety of control systems were utilized for operation of the trace heaters, furnaces, gas heaters, etc. All of the trace heaters were controlled by solid-state proportioning on-off controllers. Type K thermocouples were used as sensors. These controllers actuate magnetic reactors that close to permit flow of power to the heaters. With an array of 27 active circuits an immediate problem was encountered on startup, when electrical noise generated upon closure of a large magnetic reactor fed back through the controllers to actuate other magnetic reactors. The resulting chatter kept the magnetic reactors cycling at a rate that would soon destroy the silver contacts. It was necessary to install filters across the magnetic reactors to eliminate the noise signal. Once these were in place, the magnetic reactors operated normally and with no contact failures.

Air flow control to the air preheater on the salt cooler was by a thermocouple sensor monitoring the salt temperature out of the salt cooler.

FIGURE III-1. Transformer, Switchgear, and Wireway Installation

The thermocouple signal actuated a proportioning controller, which operated a motor-driven butterfly valve in the air supply line.

As it turned out, salt flow through the salt cooler was both intermittent and variable. Air flow was usually pre-set to a suitable level (with the flow controller disconnected) and changed only as conditions warranted.

The large tank furnaces were controlled by separate solid-state proportioning controllers, but here two thermocouples and controllers were provided. One controller and thermocouple was utilized for set point control, with the control thermocouple protected by a "well" extending into the salt tank so as to sense the salt temperature. The other controller was used for over-temperature protection of the furnace, with its thermocouple positioned near the furnace elements.

The gas preheater was controlled by a zero-phase-angle firing silicon control rectifier. Type K thermocouples were used for both outlet gas temperature sensing (for set point control) and for over-temperature protection (near the heating elements).

In addition to controls for the resistance heating loads, controls were provided for operation of the secondary burner and the Redler drag chain conveyor. The function of controls for these units has been described previously.⁽¹⁾

TEMPERATURE MEASUREMENT

Temperature sensing was done using Type K thermocouples. The Athena solid-state proportioning controllers gave readouts of all of the control thermocouples. It was not sufficient, however, to rely upon a single temperature measurement to define the temperature of a pipe section 8 ft long. Supplementary thermocouples were positioned on all pipe and vessels, and their signals were printed out using a Fluke 60-channel digital data logger. This instrument was specially modified to provide over-temperature printout in red ink on all channels, and to provide over-temperature protection in the form of red printout plus circuit interruption on eight channels. The latter were used for protection of major process vessels and column segments.

IV. CONSTRUCTION AND ASSEMBLY

Design, procurement, subcontracting and assembly of the PDU has been aided by certain management tools. Activities essential to the program were outlined in Precedence Diagram format--Figures IV-1 and IV-2. Boxes are shown containing a descriptive title of the task. Numbers above the title identify the cost center, and numbers below the title are actual or estimated man-hours required for task performance. Boxes shown with crosshatching identify tasks which lie along a critical path. The boxes are not done to scale (in relation to time), though the position of the end closure of a box along the time scale represents a schedule that was adhered to as closely as possible.

Program Evaluation and Review Techniques (PERT) diagrams were also utilized to analyze details of some of the more complex tasks (e.g., the preliminary assembly and disassembly of pipe and equipment in February 1977). This task could not begin until the remodeled support structure had been fabricated and assembled. It could not be completed until all pipe and equipment being fabricated under subcontract was received, (scheduled for delivery by 2/15/77). The PERT technique disclosed this schedule could not be met with such a late start because of insufficient manpower. A schedule slippage of about a month occurred because of late equipment delivery and the resulting manpower crunch.

Additional schedule slippage occurred when the alonizing consumed more time than estimated. Final assembly, especially installation of trace heaters, also consumed more time than expected. This work was delayed by unseasonably heavy August rains. Shakedown runs scheduled for 8/1/77 did not actually get underway until 11/14/77.

SUPPORT STRUCTURE

The only portion of the original PDU support structure that was retained in the remodeled version was the base, with its first deck at 10 ft above grade. Three new working levels were fabricated and installed on top of the original base at elevations of 17 ft, 25 ft, and 32 ft above grade. Working space on each level was 9 ft x 10 ft, except for the top level, which was 11 ft x 12 feet.

Because it was convenient to do so during this construction work, the large furnace used to heat the salt makeup tank was installed on the second level above grade. A 20-ft extension was also added to the secondary burner stack. Figure IV-3 is a photo showing the remodeled support structure and the extended stack. The gasifier, with its conveyor, is visible to the right. The low structure at the left is a small gasifier used in biomass conversion studies.

This structure is quite tall for its base width. Analysis by the Applied Engineering section disclosed it was adequate to withstand applied 20-psf ($\sim 100\text{m/hr}$) wind stresses. The deadweight design is conservative as to floor beam spans and column loadings, with 100-psf loads on all gratings.

EQUIPMENT AND PIPING

Most pipe and equipment were to be alonized and were pre-assembled to check dimensional accuracy and fit. Photographs were taken to document the progress in this work. Figure IV-4 shows the exit piping on the venturi feed tank and the venturi feed line connecting with the venturi scrubber. This configuration of the venturi feed line was considered necessary to permit stress relief, but a line with fewer bends would have been easier to heat properly. The 1.5-in. line at the bottom of the venturi feed tank is an extension of a 24-in. standpipe within the tank. This was later connected to an overflow receiver capable of withstanding the .3 to 5-psig pressure within the system and the impact of molten salt at 700°C . Overflowing salt was allowed to freeze in this unheated receiver. The receivers were fabricated from 6-ft lengths of 8-in.-dia schedule 10 SS pipe, and were discarded along with their contents of solidified salt. The remaining 6-in.-long stub of 1-in. pipe at the base of the tank was a spare for use in draining the tank.

The open hub on the venturi feed line was provided to accommodate the probe of a salt flowmeter. This was installed, but was removed when it failed to function properly. The probe acted like a "cold finger," and contributed to problems of maintaining salt flow in this line.

BATTELLE-NORTHWEST "HOT FUEL GAS CLEANING" CODE

- 1. ENERGY AND WASTE TECHNOLOGY
- 2. ENGINEERING DEPARTMENT - STRUCTURES AND MECHANICAL
- 3. FACILITIES ENGINEERING - DESIGN AND DRAFTING
- 4. CRAFT SERVICES
- 5. PROCUREMENT AND ADMINISTRATIVE

FIGURE IV-2. Program Plan, Procendence Diagram (contd)

FIGURE IV-3. Process Development Unit Support Structure and Stack

FIGURE IV-4. View of Venturi Feed Line and Bottom of Venturi Feed Tank

The coarse de-entrainer and connections to the 2.5-in venturi exhaust line and the 4-in. gas return line can be seen in Figure IV-5. This tank and much of the weight of the 2.5-in. and 4-in. lines are floating on constant rate supports. The flange cover for this tank is also penetrated by a 1-in. line

FIGURE IV-5. Coarse De-Entrainer and Connecting Piping

which was later fitted with a ball valve and a CO₂ purge system for taking salt samples. The floor grid visible here is the fourth and uppermost level, and is 32 ft above grade.

Figure IV-6 shows the top of the venturi feed tank and its mounting bracket. The 4-in. gas return line (from the coarse de-entrainer) comes across the floor grid and enters the venturi feed tank on the left side just below the lid flange. The 4-in. jumper connecting the extraction column (left rear) to the venturi feed tank is clearly visible. The lid of the venturi feed tank is also penetrated by a 1-in. line subsequently fitted for salt sampling. A stub with a 1/2-in. graylock hub is visible on the 4-in. gas return line. The siphon which drained the reservoir at the base of the extraction column was subsequently connected here. Mounting brackets at the base of the extraction column are also visible in this picture. This floor grid is the first level above grade and was part of the original PDU.

From a more distant vantage point, Figure IV-7 shows the two sections of the extraction column topped by the packed-bed de-entrainer. The 3-in. line connecting the packed-bed de-entrainer to the secondary burner had not been installed when this picture was taken. The weight of the extraction column was carried by the base support bracket, visible in Figure IV-6. The column and packed-bed de-entrainer could expand upward. A bracket at the point where the column passed through the second level floor grid permitted this expansion but prevented tilting or swaying motions. There was a bellows in the 3-in. line to the secondary burner that also accommodated this movement. The 4-in. jumper to the venturi feed tank is clearly visible.

The large furnace visible at ground level at the center of the picture contains the emergency salt storage tank, a tank 24 in. in dia by 24 in. deep used in the original PDU. The tall cylindrical object to the right is the gas preheater.

Portions of the regeneration column and the salt cooler are shown in Figure IV-8. A spool piece containing the regenerator flow control valve remains to be installed between the regeneration column and the salt cooler. The latter is shown before the sheet steel cooling jackets were in place. The 1/2-in.-dia standpipe on the salt cooler (near the position of the missing spool piece) was provided for installation of a ceramic-sheathed thermocouple,

FIGURE IV-6. View Showing Top of Venturi Feed Tank and 4-in. Jumper to the Extraction Column

FIGURE IV-7. Extraction Column (Lower Left) Topped by the Packed-Bed De-Entrainer

which monitored the salt temperature as it flowed out of the salt cooler. This floor grid is the third level, at 25 ft above grade. The air preheater (for the salt cooler) and the steam-CO₂ preheater were also installed on this level after the photo was taken.

FIGURE IV-8. View of Portion of the Salt Cooler and Upper Section of the Regeneration Column

Figure IV-9 shows the 24-in.-dia pipe cap that is welded to the 24-in.-dia x 24-in.-deep salt makeup tank, which is to be heated by the large furnace shown here. The base section of the 6-in.-dia regeneration column is visible to the upper right. This picture shows the small lock hopper attached

FIGURE IV-9. Salt Makeup Pot with 24-in. Pipe Cap^(a)

^(a) Lock hopper for salt addition is shown.

to the 8-in. flange in the center of the cap. This was provided to permit additions of up to 10 lb of salt without causing process upsets. The siphon leg and pressure-equalizing lines connecting the regeneration column to this tank are not yet installed. During PDU operation, this tank operates at the same pressure as the regeneration column. If the tank were opened to permit salt additions, the steam-CO₂ flow to the regenerator would vent, causing regenerator upset. As it turned out, it was usually possible to find times for salt addition when the regenerator was not operating.

Figure IV-9 shows how the Inconel furnace liner has buckled. This has no effect on PDU operation, but is an example of poor design. Buckling is caused by the sharp temperature gradient from the inner to the outer edge of the cover.

ELECTRICAL

Installation of the 208-V, 225-KVA transformer, the circuit breakers, the magnetic reactors, the screwcover wireway, and the flexsteel frames was done by subcontractor personnel. Crafts personnel from PNL completed installation and wiring of trace heaters and control circuits. Trace heater installation and wiring presented a unique problem. No codes exist governing such an installation. It is fortunate that good electrical engineering and experienced electrician's craft personnel were available.

Before the pipe and equipment could be covered with electric heaters, thermocouples for both temperature measurement and heater control had to be installed. Type K thermocouples were used. The thermocouple junction was inserted into a small hole drilled into the pipe or vessel wall. The edges of the hole were then peened with a punch against the junction to secure it in place. The junction was then covered with a 1/8-in.-thick strip of Kaowool paper taped in place with glass tape to reduce exposure to direct radiation from the heaters. Ceramic beading was used to insulate the thermocouple wire within heated spaces. The thermocouples were installed in pairs - i.e., on opposite sides of a pipe and with beaded sections emerging through the insulation (and labeled). Only one was connected to a lead wire (the other was a spare). About 100 such pairs were installed.

Great care was required in installation of electric heaters on pipe and equipment to protect against accidental shorting. The potting cement covering the heater coils proved to be very fragile when the heaters were previously unused. (It hardens and becomes strong when heated to high temperatures). It also was readily washed away by water, as occurred during an unexpectedly heavy rain.

To protect against accidental shorting, the elements were held away from the pipe walls by two layers of 1/8-in.-thick Kaowool paper placed near the ends of the elements. Small pieces of MgO brick were used as separators between elements and to stand off the elements from flanges or metal support tabs. The elements were secured to the pipe by adjustable stainless steel clamps. Figure IV-10 shows a view of the air preheater with heaters installed (and wrapped in plastic for temporary weather protection). The steam-CO₂ preheater is visible in the foreground.

Element lead wires were insulated with ceramic beads over a distance sufficient to bring the lead through the insulation (8 to 10 in.). The lead wires were then clamped together in the appropriate series-parallel wiring configuration and labeled. Once covered with insulation there is no way to tell to which heater a lead wire connects. This was done because it proved to be much easier to install insulation before these short lengths of lead wire were connected to the appropriate circuits.

In general, the reliability of these electric heaters was a direct function of their sizes: the larger the heater, the more reliably it functioned. This may be due in part to the fact that heavier wire was used in the larger heaters, and it did not become as brittle when heated. Light gauge lead wire on smaller heaters became so brittle that it parted if disturbed only slightly. It proved almost impossible to do maintenance work on heated lines without fairly extensive heater replacement as part of the task.

It was determined that many of the small heaters, though rated for 230-V service, were being over-driven at this voltage. The circuits were initially revised to reduce the applied voltage to 208-V on most of the small heaters.

FIGURE IV-10. View of Air and Steam-CO₂ Preheaters

When this did not suffice, the circuits on critical lines (such as the venturi feed line and the upper tank drain line) were reduced with variable transformers to 100 volts. The venturi feed line circuit was split into two circuits in such a way that the half circular heaters on one side of the line were on one circuit and the other half were on the other circuit. With this expedient, a single heater failure would not force a shut down. The heavily insulated lines could readily be brought to operating temperature with the reduced voltage.

The beaded heaters proved to be poorly suited to this application. They failed repeatedly and required frequent repair. Possibly heavier gauge heater wire would have helped reduce failures.

INSULATION

In anticipation that considerable maintainance would be required on the PDU, it was necessary to utilize a type of insulation which could easily be removed and then replaced. The insulation would have to be resistant to temperatures prevailing on the back side of the trace heaters and be chemically inert--i.e., it should yield no noxious products on exposure to process streams or conditions, and should present a resistant surface to wet weather.

High-density Kaowool (8 lb/ft^2), which comes in rolls (24 in. wide and about 1.5 in. thick), satisfied all but the last requirement--that of weather resistance. It was possible to paint or trowel on a weather-resistant coating material known to the trade as "vicryl mastic." This withstood the surface temperatures, which ranged from 40°C in winter to 68°C in summer, and protected the underlying Kaowool from moisture penetration.

Kaowool lends itself to application over irregular shapes and sizes. The major task of insulating all pipe and equipment was among the last tasks performed and was accomplished by subcontractor personnel. An insulation thickness of 4 in. was determined from heat flux calculations to be adequate for most items. Only 1 in. was required for the salt cooler and the steam superheater. Molded calcium silicate (1.5 in. thick) was used on the regenerator product gas line, the steam- CO_2 line, the air line, and the steam line.

PROCESS INSTRUMENTATION

Differential pressure gauges were major aids in assessing plant performance. In the extraction section these gauges were used to measure pressure drop across the venturi scrubber and across the trays in the extraction column. They provided immediate indication that salt flow to these units was established. In the regeneration column these gauges measured the pressure drop across the top tray and across combinations of two trays for the remainder of the column. Overall pressure drop across the entire regeneration column was also measured.

Fuel gas flow and steam flow rates were measured using "annubar" flowmeters. These are a pitot tube primary flow measurement device. Carbon dioxide, H₂S spike gas, and water injection flow rates were all measured with float-type rotameters of various kinds.

The pressure sensors and flow metering devices required installation of numerous small lines. The valves and connections all had to be checked and monitored for leaks as time went on. Some of these are shown in Figure IV-11. (The minihelics in this panel proved unsatisfactory and were eventually replaced by magnehelics, which tolerate a higher static pressure.)

FIGURE IV-11. Panel Showing Pressure Gauges and Connections

V. SAMPLING AND ANALYSIS

The PDU has been fitted with an elaborate gas sampling system, a schematic of which is shown in Figure V-1. Samples G-1 and G-2 are taken upstream and downstream, respectively, of the gas preheater. Samples taken at G-2 will reflect the effect of H₂S cylinder gas additions. Samples G-1 and G-2 pass through water-cooled condensers and can be valved to any of the gas chromatographs or to the infrared analyzers.

The G-3 sample is the final product gas sample. It is taken at a point between the packed-bed de-entrainer and the secondary burner. Unlike the G-1 and G-2 samples, it feeds through the multiposition valve to the Carle or Hewlett-Packard gas chromatographs.

The V-1 sample is taken from the head space in the de-entrainer. It is in equilibrium with salt which, at steady state, contains the highest sulfur content of any in the system. This gas sample gives a good indication of how the venturi is performing. It, too, feeds through the multiposition valve to the gas chromatographs.

The extraction column has been fitted with three gas sampling points: A-0, below the bottom tray; A-1, above the bottom tray; and A-2, above the top tray. These samples feed through steam-cooled condensers fabricated with Inconel-600 tubing in contact with the sample. These connect to Teflon tubing, which routes the sample through the multiposition valves to either the Carle or Hewlett-Packard gas chromatographs.

There are five sample points on the regeneration column. Numbering from bottom to top these are: S-1, above the bottom tray; S-3, above the third tray; S-5, above the 5th tray; S-7, above the 7th tray; and S-8, above the top tray. These samples also pass through steam-cooled condensers and into Teflon lines leading to the multiposition valves through which they feed to either gas chromatograph.

The sample probes entering the extraction and regeneration columns are visible in Figures II-5 and II-6. These perform a multiple function. The probes were fabricated of schedule 80, 3/8-in. pipe. A cross-shaped connector was threaded on the end, as shown in Figure V-2. A ceramic thermocouple well

FIGURE V-2. First Sample Probe Design

gas was turned off to take a sample, and salt would find its way into tubing connections and freeze. Both sample lines and ΔP sensors were rapidly rendered inoperative. The ceramic sheaths also failed as a result of thermal cycling.

To correct this problem, the ceramic thermocouple sheaths were removed and replaced with stainless steel-sheathed thermocouples. In addition, the cross fitting was replaced with the arrangement shown in Figure V-3. Beaded heaters were wrapped around this assembly, which provides a reservoir for collection of molten salt carried out of the column. This reservoir should drain, allowing salt to return to the column as soon as purge gas flow was resumed. The only failures experienced with this sampler configuration were the consequences

FIGURE V-3. Improved Sample Probe Design

of severe flooding conditions in the columns that caused over-filling of the reservoir spaces. In such cases, salt found its way into small lines, where it froze.

Salt samples were taken from reservoir spaces such as the coarse de-entrainer, the venturi feed tank, and the salt makeup tank. The sampler configuration is shown in Figure V-4. Samples were taken by plunging a steel rod into the salt and allowing the adhering salt to freeze as the rod was withdrawn. The brittle salt could be chipped off the rod and collected.

The head space in these vessels contained a toxic and combustible gas, so the sampler was fitted with a CO₂ purge gas inlet. The procedure was to turn on the purge gas, insert the rod through the cap and push it in to the ball valve, and then open the ball valve. The rod could then be pushed all the way to the bottom of the tank. When the rod was withdrawn, the ball valve would be closed before the rod was removed through the cap. By this procedure, the rod acted to restrict gas flow out past the ball valve, where dilution by purge gas occurred.

MULTIPOSITION VALVES

As the gas samples left the samplers described above, they were cooled by steam in condensers fabricated from Inconel-600 tubing. The samples then flowed through Teflon tubing to a multiposition valve made by Scanivalve Corp. All sample lines converged on this valve. Two steam-traced Teflon lines carried samples from this valve to either of two gas chromatographs within the building. A vacuum pump provided the driving force to move the sample from its point of origin through the multiposition "sample valve" and into the gas chromatograph sample loop. Sample collection was thus completely automated except for operation of purge gas valves.

ANALYTICAL INSTRUMENTATION

Three gas chromatographs and two infrared analyzers were available for gas analyses. The infrared analyzers provided analyses of the CO and CO₂ content of G-1 or G-2 samples. The information was useful in appraising the performance of the gasifier.

FIGURE V-4. Salt Sample Entry Port Configuration

Carle's basic gas chromatograph model was used for analysis of water vapor. Any and all samples could be routed to this instrument.

A Carle Series-S Analytical Gas Chromatograph with factory-installed multicolumn and factory-programmed valve switching sequence was used for H₂S (high-range) and multicomponent analyses. This instrument was interfaced to the Spectra-Physics SP-4000, described below, and to the associated printer plotter.

A Hewlett-Packard 5700A Gas Chromatograph with a flame photometer detector was used for low-level H_2S and COS analyses. This unit was also interfaced to the Spectra Physics SP-4000 and had its own accessory printer plotter. The flame photometer detector is selectively sensitive to phosphorous and sulfur compounds that exhibit chemiluminescent photoemission. With band-pass filters and sensitive photomultipliers, this detector gives a specificity ratio of 30,000 to 1 for sulfur to nonsulfur compounds. The instrument calibration covered a range from 10 ppm to 9900 ppm H_2S .

The Carle and Hewlett-Packard gas chromatographs were interfaced to a Spectra-Physics 4000 multichannel data system. This is a microprocessor specifically designed for chromatography. It provides complete programs for data acquisition, post-run calculations, reporting, and instrument control. The SP-4000 Central Processor can control up to 16 gas chromatographs. This was a most powerful tool; it provided output by component name in volume percent (or ppm) so that plant operators could tell at a glance what the samples contained. The Hewlett-Packard G.C. was programmed to produce H_2S and COS analyses at 10-min intervals (which included time for line purges). This is a near approach to "real time, on-line" analysis.

Two isokinetic sampling probes have been provided for inlet and product gas particle sampling. These can be connected to Emission Parameter Analyzers and to Anderson-2000 impingers. The latter allow particle collection and sizing.

VI. SAFETY EQUIPMENT

The PDU was constructed out in the open, with no enclosing walls or roof, so as to ensure maximum ventilation. By this means it was sought to minimize the hazard from unexpected leaks of fuel gas containing CO, H₂S, and coal tars. Any leak would produce a buoyant plume, due to its elevated temperature, which would diffuse away.

In earlier operation of the PDU, which operated at only 1 to 2 psig, gas leaks invariably were accompanied by autoignition. At the higher pressures expected for operation of the remodeled PDU, calculations showed that cooling resulting from expansion would not be sufficient to prevent autoignition⁽⁷⁾ but in one instance, experience was to the contrary. It became necessary to drill out the G-2 sample port, which had plugged with salt. Gas escaping from the port could readily be ignited, but would not autoignite.

A greater hazard exists if the leaking gas does not autoignite and reveal its presence. The gas plume is likely to be invisible and must be sensed by instruments provided for this purpose. Three H₂S sensors were provided. One was mounted on the gasifier support frame about 10 ft above grade, another on the PDU at 10 ft above grade, and a third on the PDU about 17 ft above grade and near the regeneration column. These sensors were connected to instruments within the supporting laboratory made by Bullard Manufacturing Co. after a design by International Sensor Technology, Inc. The instruments were set to alarm at 10 ppm H₂S and triggered a loud alarm bell.

Carbon monoxide was sensed with a Mine Safety Appliances Model 701 sensor. This unit would detect 5 to 10 ppm CO and was set to alarm at 50 ppm with a loud claxon. This unit operated on a 115-V A.C. supply. A long cord was used to allow moving it about for occasional surveys.

Scott Air Packs, a type of self-contained breathing apparatus, were made available and all personnel were trained in their use. In addition, small MSA breathing units for use in atmospheres containing up to 1% CO were available. Standard protective gear such as face masks, dust masks, asbestos gloves and aprons, coveralls, and work gloves of all types were in good supply.

Personnel from PNL's Atmospheric Sciences Department provided assistance in assessing plume behavior from the stack or from leaks. This assessment disclosed that stack plume touch-down would never be a problem. Leaks would have to be of catastrophic nature to be of concern, and would only be of concern if they occurred at or near ground level.

VII. HAZARDS ANALYSIS

Prior to startup of the PDU it was necessary to prepare a detailed safe operating procedure and a hazards analysis. PNL's Safety Review Committee was convened (comprised of senior staff and including two retired Laboratory Directors) and project management was subjected to detailed interrogation and comment on the hazards analysis and safe operating procedures. Operation was approved, and over a course of a year's time only one minor injury to personnel occurred. Even this could have been avoided, had proper protective clothing been worn. (a)

(a) Bare arms of an employee were splattered with drops of molten salt, causing minor burns.

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APPENDIX

REMOVAL OF PARTICLES AND DISSOLVED IMPURITIES FROM THE SALT

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REMOVAL OF PARTICLES AND DISSOLVED IMPURITIES FROM THE SALT

The sulfur extracting capacity of the salt can be regenerated by contact with steam- CO_2 in equipment specifically designed for this. Other impurities that accumulate in the salt, however, are not so easily removed. The most obvious method of control of such impurities is a bleed stream and the incremental addition of fresh salt.

With Li_2CO_3 @ 93¢/lb, K_2CO_3 @ 19¢/lb, Na_2CO_3 @ 3¢/lb, and CaCO_3 @ 1¢/lb it will be desirable to recover and recycle Li_2CO_3 and K_2CO_3 . Sodium carbonate and CaCO_3 cannot be economically recovered.

The chemical properties of these compounds and of the associated impurities requires the use of aqueous processing techniques for their purification and recovery. The design of a system for effecting the transition from a molten salt phase to an aqueous solution phase must take account of the serious problem of physical vapor explosions, or so-called "superheat limit explosions," which occur when a molten salt is added to an aqueous phase. Because of the excellent heat transfer afforded by the intimate mixing of two liquids, vapor can be generated at a high rate. Under some conditions this may be accompanied by violent pressure pulses and shock waves, which have proved to be fairly destructive in a number of instances.

Several theories have been proposed to explain the mechanism of vapor explosions. One of the most plausible involves a triggering mechanism initiated by collapse of the vapor film separating the hot and cold liquids. The collapse of the vapor film corresponds to the well known transition from film to nucleate boiling. If the hot liquid is dispersed in a cold liquid, the droplets of hot liquid will initially be coated with a film of vapor produced by vaporization of the cold liquid. As the hot liquid droplet cools the heat transfer rate becomes insufficient to maintain a continuous vapor film. When

this occurs the film will collapse, allowing direct contact of the two liquids. Within a very short time following the collapse of the vapor film a sudden increase in vapor generation rate occurs and shock waves may be generated by the expanding vapor. This is accompanied by shattering of the droplets, greatly increasing the surface and further increasing the vapor generation rate.

One theory holds that because of the lack of nucleation sites at the liquid-liquid interface, the cold liquid can be heated far above its normal boiling point. When the superheat limit or homogeneous nucleation temperature is reached, the liquid suddenly flashes. Because of the almost instantaneous conversion of liquid to vapor, shock waves may be generated. For a significant explosion to occur, a relatively large mass of liquid must be present.

In Kraft furnace operation, the molten "smelt" at $\sim 1500^{\circ}\text{F}$ is quenched and dissolved in an aqueous liquor ("green liquor"). It is common practice to shatter the molten smelt stream with a steam jet or a spray of green liquor. This breaks the molten salt into small droplets that impinge on the surface of the liquor in the quench tank. Numerous small explosions result, but the mass of material involved is maintained below dangerous levels. Various data are available which indicate that if the cold liquid is maintained at or near its boiling temperature, the probability of explosions is markedly reduced. In the design selected for the salt quencher-dissolver (below), the feature of hot liquid shattering and the use of near-boiling colder liquids are employed.

In the proposed design shown in Figure A-1, salt flowing through a heated nozzle impinges on a trough.^(a) The bulk salt stream flowing off the edge of the trough is blasted into droplets by liquid sprays of filtered salt solution. The salt/water slurry cascades over baffles that permit further cooling and dissolution of salt before the mixture falls into the boiling liquor reservoir below. Salt droplets washed off the baffle plates should be at or near

(a) The reader should note that while a conceptual salt "bleed" recovery system was designed, authority to proceed with construction and operation was not granted (nor requested) because of program termination.

FIGURE A-1. Schematic of Quencher-Dissolver

their solidification temperature by the time they impact the boiling liquid reservoir. Salt phase and aqueous phase flow rates that lead to smooth operation must be determined experimentally. It may be desirable to change the number and configuration of baffle plates.

The proposed salt separation and recovery process takes advantage of the differences in solubility of the carbonates and bicarbonates. Sodium and potassium carbonates have relatively high solubilities and should be completely dissolved during the salt cooling and quenching step. Calcium carbonate and Li_2CO_3 will remain associated with aqueous insoluble solids. The pH of this solution will be of the order of 9.5 to 10.0, which is sufficient to precipitate heavy metals as basic carbonates.

Figure A-2 is a simplified schematic flow diagram of the proposed separation and recovery process. Table A-1 shows stream flows identified by numbers in diamond-shaped indices of Figure A-2.

Stream 5 consists of precipitated solids that combine with suspended solids removed from stream 3. These are digested in a carbonator to dissolve lithium carbonate as LiHCO_3 , which is several times as soluble as the normal carbonate. After solids removal, the LiHCO_3 solution is decarbonated by steam/air stripping to precipitate Li_2CO_3 , which is removed by filtration.

The liquids from the primary centrifugation (stream 3), rich in Na_2CO_3 and K_2CO_3 , can be carbonated to the bicarbonates, which are much less soluble than the carbonates (contrast to $\text{Li}_2\text{CO}_3/\text{LiHCO}_3$). After removal of precipitated NaHCO_3 and KHCO_3 the liquid phase is recycled to the quencher-dissolver. This liquid phase will also contain soluble silica in such forms as sodium orthosilicate. To prevent buildup of this material in the system a portion of this recycle stream will have to be rejected as a waste stream. More detailed development of this recovery scheme has been deferred for the moment.

FIGURE A-2. Schematic Flow Diagram; Salt Bleed Recovery

TABLE A-1. Stream Flows, lb/lb of Salt Bleed, (Cf. Figure A-2)

Stream No.	Temp., °C	H_2O	CaCO_3	Li_2CO_3	K_2CO_3	Na_2CO_3	$\text{KHCO}_3^{(a)}$	$\text{NaHCO}_3^{(a)}$	$\text{LiHCO}_3^{(a)}$
1	700	-	0.20	0.26	0.26	0.26	-	-	-
2	35	1.47	Trace	-	-	-	0.48	0.04	0.01
3	100	1.47	Trace	0.01	0.74	0.30	-	-	-
4	100	0.6	-	-	-	-	-	-	-
5	35	-	0.20	0.26	0 ^(b)	0 ^(b)	-	-	-
6	100	4.3 ^(c)	Trace	0.03	2.2	0.9	-	-	-
7	20	10.4	Trace	-	-	-	-	-	0.57
8	20	10.4	Trace	0.31	-	-	-	-	-
9	20	-	0.20	-	-	-	0 ^(b)	0 ^(b)	0 ^(b)
10	20	0.6	-	-	-	-	-	-	-

(a) Weight corrected to equivalent carbonate basis.

(b) Assumed 100% recovery.

(c) Estimate based on 10:1 total coolant:salt ratio.

A PROCESS FOR CLEANING AND REMOVAL OF SULFUR
COMPOUNDS FROM HOT LOW BTU-FUEL GAS
PART II: PILOT-PLANT EXPERIENCE

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SUMMARY

In an extension of research on high-temperature gas cleaning, Pacific Northwest Laboratory (PNL) has developed an unique process that uses molten salt scrubbing both for particle removal and for removal of sulfur compounds. A Process Development Unit (PDU) has been designed and constructed to demonstrate this process. The work reported here is concerned with the operating experience and data generated during 16 runs conducted over a period of about a year. Reference should be made to Part I of this report for details of design and construction of the PDU.

The PDU was operated in a series of short runs using fuel gas supplied at 75 SCFM by PNL's fixed-bed gasifier. It was anticipated that characteristics of this gasifier would limit the runs to 5 to 6 days' duration, but operating problems forced termination of the runs before the gasifier became a limiting factor.

Efficient extraction of sulfur compounds (H_2S and COS) was demonstrated. Product gas ranged from 20 ppm to about 250 ppm sulfur (total) with recovery dependent upon inlet gas sulfur content and salt sulfur loading. Extraction of sulfur compounds was found to follow thermodynamic theory and conformed to predictions based on earlier laboratory data. Data obtained was not sufficient, however, to confirm the theoretical models used in detailed design of the extraction (and regeneration) columns. This was due to difficulty in establishing and maintaining steady liquid flow rates. Particle removal by the packed-bed de-entrainer resulted in gas containing 149 mg/m^3 . A polishing filter used in run C-13 reduced this to 37 mg/m^3 .

The extraction section (comprised of a venturi scrubber, knock-out drum or coarse de-entrainer, two-tray bubble-cap column, and packed-bed de-entrainer) gave serious operating problems in early runs. Small salt flow control valve passages and the 1/4-in.-dia venturi salt inlet orifice plugged frequently and caused run terminations. These problems were partly problems of operational scale and were never completely eliminated, but were solved to the extent that run termination never resulted as a consequence of plugging of equipment in the extraction section after run C-8.

The regeneration section (comprised of a salt cooler, a 6-in.-dia 8-tray bubble-cap column, and accessory CO_2 and steam supply and preheat systems) demonstrated efficient regeneration of the extraction capacity of the salt. This section, however, gave very serious operating problems. Because of numerous difficulties with other parts of the PDU, it was not until the mid-point of the program that these problems were traced to plugged risers in the column caused by Al_2O_3 derived from the "pack-alonizing" process of corrosion-proofing. Removal of the section containing the plugged risers allowed efficient operation of the regenerator (with the 4 remaining trays). Because of difficulty with salt flow control, the regeneration column could not be operated at design temperatures and, in consequence, H_2S concentrations in the regenerator product gas were lower than the design basis by about a factor of 10.

Serious operating problems resulted from the presence of iron, which occurred as an impurity in the salt. Iron was introduced from corrosion of equipment upstream of the PDU and from corrosion of unalozed parts. At high sulfur concentrations, Fe competed with CaCO_3 for reaction with sulfur and formed compounds, e.g. $3\text{M}_2\text{S} \cdot 4\text{FeS}$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$), which were high-melting and of limited solubility in the molten salt. These created serious plugging problems at small orifices or flow passages and were especially troublesome in the regeneration section, which operated at lower temperature than did the extraction section. Unfortunately, it was not until post-run examination of the PDU was complete that it was realized that intrusion of iron was from equipment upstream of the PDU. Iron derived from coal or coke would be trivial in amount. Corrosion product iron was insufficient to account for the levels of iron present.

This report concludes with a section covering simple modifications to the plant that would have substantially improved operability. Making these changes would have delayed completion of the program and would have required funding not then available.

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A PROCESS FOR CLEANING AND REMOVAL OF SULFUR
COMPOUNDS FROM HOT LOW-BTU FUEL GAS
PART II: PILOT-PLANT EXPERIENCE

INTRODUCTION

Development of a molten salt scrubbing process for hot fuel gas cleaning began with laboratory experiments in 1973.⁽¹⁾ These defined the nature of the molten salt system, identified useable materials for construction, and yielded data for the equilibrium extraction of H_2S as a function of temperature. On the basis of these experiments, a Process Development Unit (PDU) which employed a venturi scrubber/packed-bed de-entrainer configuration was constructed. The venturi was operated in vertical orientation. The fully dispersed salt was carried up the venturi exhaust line to a de-entrainer positioned so that the de-entrained salt would return by gravity-induced flow to the venturi feed tank from which it originated. By this expedient, no failure-prone mechanical pump was required to circulate the molten salt.

PNL's fixed-bed gasifier was operated on metallurgical coke to supply 50 to 70 SCFM of low-BTU fuel gas to the venturi scrubber. Supplemental H_2S was added to the fuel gas from a cylinder source.

Only the extraction section of a fuel gas cleaning process was tested at PDU scale.⁽²⁾ Three short runs disclosed:

- >90% removal of H_2S and COS ,
- removal of particles to yield a product gas containing only 56 mg/M^3 (of which 1/3 was entrained salt),
- that efficient circulation of salt by means of a venturi scrubber was feasible,
- that 304 SS protected by a coating of aluminum-iron intermetallic compounds produced by the "pack-alonizing process" appeared suitable for construction.

With this modest success the decision was made to proceed with design and construction of a PDU configured for fully continuous operation. The design and construction phase of this work has been reported in Part I of this document. The work reported here concerns details of operation of the remodeled and redesigned PDU and presentation and analysis of the very considerable amount of data generated in sixteen runs.

I. PROCESS DESCRIPTION

FLOWSHEET AND DISCUSSION

For efficient extraction of sulfur compounds it is necessary to ensure intimate contact of fuel gas with the molten salt. This process utilized multistage scrubbing: 1) a cocurrent flow contact in a venturi scrubber, and 2) two stages of countercurrent flow contact in a bubble-cap tray column. The venturi scrubber produced a dispersion of salt droplets entrained in the gas phase with a mean droplet size calculated to be $60\text{ }\mu\text{M}$. Such a dispersion is not only effective for extraction of sulfur compounds (due to the high rate of mass transfer) but is highly efficient in agglomeration and collection of particles. In addition to sulfur compounds, the molten salt would extract halogens and volatile metals and nonmetals. Ammonia removal would occur only as a consequence of thermal dissociation. Water vapor will not be extracted. Tar and oil removal will be accomplished through processes of pyrolysis and alkali carbonate catalyzed reaction of resulting char with water and CO_2 .

To some it may appear the problem of gas cleaning has been further complicated by producing a dispersion of salt in the gas phase. Most of the salt coalesces as it slows in passage through the coarse de-entrainer vessel (Figure I-1) which is positioned at the highest point in the process. Small droplets which fail to coalesce here are carried by the gas down a 4-in. line to the head space of the venturi feed tank, where again the flow rate slows. From here the gas passes upward counter to a flow of regenerated salt in a 10.75-in.-dia, two-tray extraction column (with four bubble caps per tray). The gas can entrain salt as it passes upward through this column because the velocity through the slots in the caps is fairly high (70 to 80 ft/sec). A packed-bed de-entrainer is, therefore, positioned immediately above the top tray of the column. The gas flowing through the packing in the de-entrainer loses entrained salt through processes of inertial impaction. (The packing was a 15-in.-deep layer of Al_2O_3 hollow cylinders $5/8$ in. in dia x $5/8$ in. long with a $1/4$ -in.-dia center hole).

Salt being fed to the top tray of the extraction column is regenerated salt. It is not entirely sulfur-free, and since the gas and salt phase sulfur concentrations are equilibrium controlled,^(a) the product gas sulfur concentration is highly dependent upon efficient operation of the regeneration column.

The latter is a 6-in.-dia x 11-ft-long bubble-cap tray column containing 8 trays with two caps per tray. Preheated steam and CO₂ flowed upward through the column counter to the down-flowing salt phase. The regenerated salt leaving this column flowed to the 30-gal salt makeup tank, where it blended with the contents of that vessel. At steady state the sulfur content of this salt would be that of the regenerated salt.

As mentioned above, the regenerated salt flowed to the top tray of the extraction column and down to the lower tray, picking up more sulfur from the upflowing gas. The salt continued to the venturi feed tank and was dispersed by the venturi scrubber and carried to the coarse de-entrainer. By this time its sulfur content had increased still further as a result of contact with dirty gas entering the venturi. Most of the salt (90%) recycled to the venturi feed tank to again be dispersed in the venturi and collected at the coarse de-entrainer. Additional sulfur accumulates in the salt as recycle continues until the salt and gas phases come to equilibrium with respect to sulfur content.

The recycled salt flowed from the coarse de-entrainer via a standpipe which fixed the volume of salt held up in the coarse de-entrainer. No recycle flow occurred until this vessel filled to the level of the standpipe. In addition to the recycle flow, a much smaller stream flowed from the bottom of the coarse de-entrainer through a salt cooler to the regenerator. This flow was actuated and controlled by a valve positioned between the salt cooler and the regeneration column.

Effectiveness of regeneration increases as the temperature decreases, with the limit, of course, being the freezing point of the salt. The salt

(a) Confer Part I of this report, Section I.

mixture does not exhibit a sharp freezing point, but becomes viscous as solid separation occurs. It is probable that 550°C is the minimum practical regeneration temperature.

The cooled salt entered above the top tray of the regenerator. At this point the salt contains the highest sulfur content of any in the system. It is in equilibrium with the gas emerging from the regenerator, so this gas also has the highest H₂S content. This is the regenerator product gas. It too flowed to the secondary burner for combustion and disposal. With a fuel gas containing 1.3 v/o H₂S, the steady-state regenerator product gas should contain 12% H₂S (before steam condensation) if design conditions (temperature and flow rate) can be met.

Figure I-2 is a photo which illustrates the completed PDU as it appeared in early December of 1977. The structure at the right is the PNL gasifier. The secondary burner and stack are at the left rear.

SUMMARY OF OPERATING EXPERIENCE

The PDU was operated in a series of 16 short runs with a total operating time of 744 hours. The PNL gasifier operated for approximately 670 hr and was fueled with a total of 25,880 lb of coke and 4005 lb of sub-bituminous coal. An additional 800 lb of charcoal was required for starting.

On-stream efficiency of the molten salt scrubber was low. The venturi operated with salt flow for a total of 94 hours. The extraction and regeneration columns operated with salt flow for 51.5 and 60.2 hr, respectively. Details of this operating history are summarized in Table I-1.

Coke and sub-bituminous coal were low-sulfur fuels. To simulate gasification of high-sulfur coals, H₂S cylinder gas was metered to the PDU during portions of runs C-5, C-12, C-14 and C-15.

The extraction section of the PDU consistently performed in accordance with theory and met or exceeded design requirements with respect to sulfur compound removal. Because of the relatively small scale of operation, the 1/4-in.-dia venturi orifice frequently plugged. Again, because of scale, control of salt flow to levels of a liter/min or lower was difficult, and the control valves frequently plugged.

FIGURE I-2. Photo Showing the Completed PDU and Associated PNL Equipment

TABLE I-1. Summary of Test Runs

Run	Start Date	Duration (hr)	Gasifier (hr)	Fuel Charged (lb)	Venturi Oper. Time (hr)	Extr'n Col. Oper. Time (hr)	Regen. Col. Oper. Time (hr)	Reason for Shutdown	Comments
C-1	11/14/77	34	34	1800 coke	0	2.1	0	PUD power failure	• Gasifier did not consume more than 50% of fuel charged
C-2	11/17/77	20	20	800 coke	0.5	0.5	0	Plugged venturi feed valve	
C-3	11/29/77	19.5	--		1.0	--	1.8	Plugged venturi feed valve	• Operation with air to circulate the salt
C-4	12/6/77	25	--		1.5	1.5	1.2	Plugged venturi feed line or orifice	• Operation with air to circulate the salt
C-5	12/16/77	72	72	2500 coke 1600 coal	14.7	5.3	6.2	High ΔP , slushy salt	• This was the last test, using the ternary alkali carbonate eutectic salt
C-6	2/13/77	33	26	1530 coke	3.5	0.75	0.25	Plugged venturi orifice	• First run using ~20 mole% CaCO_3 in the ternary eutectic salt
C-7	2/27/77	22	12	800 coke	4.5	1.0	0	Gas preheater failed	• Cold entering gas caused severe soot deposition and high ΔP in venturi exhaust line
C-8	4/11/77	48	48	1600 coke	5.5	2.5	1.0	Regen. flooded	• Flooding salt overflowed to plug numerous lines and equipment
C-9	4/26/77	39	36	1000 coke 200 coal	1.0	0.5	2.0	Trace heater failure on extrac-tion col. feed line	• C-9 established that the regen. column was definitely plugged and required repair
C-10	5/22/78	16	16	800 coke	0	0	0	Venturi feed line failure	
C-11	6/5/78	74	69	2300 coke 1400 coal	20	13	13.4	Trace heater failures	• Low iron contamination reduced salt plugging problems
C-12	6/25/78	82	77	3350 coke 250 coal	14.5	5.5	9.5	Salt cooler plugged	
C-13	7/16/78	21	26	800 coke 300 coal	6.1	3.0	3.5	Polishing filter blinded	• Erratic salt flow occurring
C-14	8/13/78	48	44	1800 coke	6.2	4.7	2.5	Extr'n column feed line failure	• New valves caused sporadic flow difficult to control. Regenerator siphon caused plugging problems
C-15	8/20/78	94	94	3400 coke	12.0	8.8	12.0	Regen. column plugged	• High iron content of salt renders operation difficult
C-16	9/10/78	96	96	3400 coke	3.0	2.3	4.3	Extraction column feed valve plugged	
TOTALS		744	670	25880 coke 4005 coal	94	51.5	60.2		

Plugging problems were not easily remedied. The venturi orifice was finally fitted with an opening through which a poker rod could be inserted. This solved the problem; however, more frequent recourse to this expedient was required than was desired.

Plugged valves, lines, or columns were frequent causes of shutdowns or run terminations. Heating and/or pressurizing with CO₂, or even with high-pressure air, was sometimes effective in restoring flow in plugged lines.

Impurities in the salt were the major cause of plugging; iron was by far the worst offender. Ash and char merely contributed to the problem by collecting with iron-bearing precipitates. For the most part, iron entered as a tramp impurity derived from the gas preheater calrods and from mild steel piping between the gas preheater and the gasifier. Iron derived from coal ash particles was of no consequence.^(a) The quantities of iron involved were too large to be accounted for by corrosion effects, which were minimal.

The iron impurity contributed to improper operation in a physical sense, and when present in large amounts affected the chemistry of the process. It enhanced extraction of sulfur compounds and inhibited regeneration of the salt. Its compounds were particularly prone to precipitation in cooler zones, and thus caused serious problems in proper operation of the salt cooler and regenerator.

The regeneration column gave serious trouble in early runs and was found to have plugged risers at tray number 6. The plug was a consequence of the "pack-alonizing" treatment, which left insoluble Al₂O₃ in the risers. This tray is within a blind segment of the column and its condition was not detected in early shakedown and calibration tests.

Removal of this segment of the regeneration column reduced the number of trays from 8 to 4, but permitted successful operation of the regeneration column in subsequent runs. It was never possible to operate the regenerator

(a) Calculation indicates the iron derived from entering particulate matter is only 25 g for the total 90 hr of venturi operation for each percent of Fe in the particles, nominally about 1%.

at the design salt flow or design temperature, however, so product gas with the desired high H_2S content was not produced. Regeneration temperatures were generally from 75°C to 100°C above the design temperature of 550°C and salt flows were generally from 2 to 5 times the design flow. Salt flow and temperature are related in that high flow to the salt cooler, which is in series flow with the regenerator, causes the cooling capacity to be exceeded.

Data obtained during runs C-11 and C-12 indicated that the regenerator performed somewhat better than theoretical calculations indicated it should. This may have been due to side reactions producing some SO_2 which was not analyzed for. The side reactions would diminish in significance at the design temperature.

The mechanical operability of the regeneration column was unsatisfactory. This small column has clearances of no more than $1/8$ in. between the caps and risers. This aperture was easily plugged. Access to the internals of small columns such as this for sampling and for taking pressure drop measurements is difficult. This is especially true when a liquid molten salt is present. Any salt which enters access lines will freeze and block further use. It was often necessary to operate the column without the aid of all of the installed sensors and sampling points.

This PDU was difficult to maintain or to modify in any way. All pipe connections were buried beneath insulation; pipe and equipment were covered with fragile trace heaters. If a line was plugged with a substance foreign to the system and not molten at temperature, the line usually had to be dismantled and cleared or replaced. Such a situation often entailed complete rebuilding of the trace heating and insulation.

Small heaters on 1-in.-dia lines were especially vulnerable and were a frequent cause of outages. Large trace heaters on the other hand, on 2-1/2 in. or larger pipe and equipment, rarely failed or caused problems.

Few valves are available for use at temperatures of 700°C or higher. Still fewer can tolerate molten carbonates containing sulfide ion. Valving for control of salt flow was a continuing and troublesome problem and no satisfactory solution was achieved.

SPECIFICS OF RUNS 1 TO 16 INCLUSIVE

Run C-1 disclosed limitations of the trace heater controls which required installation of electrical noise filters to correct. Run C-2 through C-4 disclosed the first appearance of tramp iron impurity and its serious effect on process operability by causing plugging problems. Before run C-5, stand-pipes were installed in the salt makeup tank and venturi feed tank to provide a volume in which impurities could settle. Old salt was drained and replaced with fresh before startup. These measures helped, but did not prevent plugging problems.

Run C-5 yielded significant data on the performance of the extraction section using the ternary alkali carbonate salt mixture with no CaCO_3 added. Very high sulfur recovery was demonstrated; however, the operating time was insufficient to reach steady-state conditions where recoveries would be closer to 90%.

Operation of the regeneration column was sporadic and subject to severe flooding. This was a consequence of the plugged riser on tray 6, which was not pinpointed until run C-9 was completed.

Run C-5 was terminated when the salt became viscous due to accumulation of impurities. At the time it was erroneously concluded that the PDU was being corroded excessively by the alkali carbonate mixture, and in subsequent runs 20 mole% CaCO_3 was added to the salt as a corrosion inhibitor.

Runs C-1 through C-5 conclusively showed that the bellows-sealed needle valves for salt flow control were unsatisfactory. For if these plug there is no way to unplug them without shutting down and dismantling the line. The valves can then be freed of salt by a combination of a torch to melt out most of the salt and acid to remove the remainder.

Prior to run C-6 the needle valves were replaced with suitably modified gate valves. These would plug when pinched down to limit flow, but could be opened wide for a moment to release the obstruction and then reclosed to limit the flow. These markedly reduced the incidence of plugging problems at valves, but were poor devices with which to carefully meter small salt flows.

The samplers on the extraction and regeneration columns were modified to reduce fouling by the salt. This improvement helped, but the samplers were not immune to the effects of severe flooding.

Most of the old salt was drained, and salt containing 20 mole% CaCO_3 was added. This was done to suppress the sulfide ion activity and to reduce the corrosivity of the salt. Runs C-6 and C-7 were the first made with salt containing CaCO_3 . Run C-6 had to be terminated when the venturi orifice plugged. This was found to be due to the presence of black, iron-bearing solids. Despite the change out of most of the salt, it isn't possible to completely eliminate these iron-bearing solids, which are held in tank heels and on extraction and regeneration column trays.

Run C-7 was made following modification of the gate valve in the venturi feed line. The gate was slotted on the downstream side so that purge gas, which keeps the valve stem free of salt, would force salt through the venturi orifice and out of the line. In addition, a 1/8-in.-dia hole was drilled to intersect the 1/4-in.-dia x 1-in.-long venturi salt inlet orifice at its midpoint. This was fitted with a CO_2 purge line, including a flowmeter. This purge is designed to keep the orifice free of salt or to allow salt plugs to be blown out. No plugging problems with the venturi salt feed system occurred during run C-7, but as it turned out, this was not a satisfactory solution because the orifice continued to plug in later runs. Run C-7 was terminated when the gas preheater failed, causing cold gas to enter the scrubber. This produced severe soot deposition, forcing a shutdown.

Both run C-6 and C-7 gave very high sulfur removal efficiency. Product gas sulfur burdens remained in the 100 to 200 ppm range. The regeneration column was operated for only a very brief period in run C-6 before shutdown occurred. Salt flow to the regenerator could not be established in run C-7.

Prior to run C-8, new calrod heaters were procured and installed in the gas preheater. Run C-8 disclosed that the CO_2 purge inlet to the venturi orifice and the slotted gate valve did not suffice to prevent plugging of the venturi orifice. It plugged twice, once upstream and once downstream of the point where the purge enters the orifice. After run C-8 the 1/4-in.-dia x 1-in. orifice was reamed so it tapered from a 1/2-in. dia at the outlet to a

1/4-in. dia at the inlet (for flow control), and a port for use of a poker was installed. Thereafter, it was always possible to restore flow to the venturi orifice, with but a brief shutdown while by-passing gas.

During run C-8 the regeneration column flooded severely. The operating data indicated the column may be defective. The seriousness of flooding may have been aggravated by a frozen siphon through which salt exits the column and by poor flow control at the salt feed gate valve.

Salt overflowed and filled the 1.5-in. H_2S exhaust line over a length of about 30 feet. The salt reached and damaged the ceramic burner block in the secondary burner. Salt also backed into the steam- CO_2 preheater, which is an 8-in.-dia x 24-in.-long, pall-ring-packed heat exchanger. Salt backed through this unit and filled about 20 ft of the 1-in.-dia steam supply line.

To effect repairs, salt-filled lines were simply replaced with newly fabricated lines. The steam- CO_2 preheater was cleaned with aqueous HNO_3 and water. A new burner block was installed in the secondary burner. Finally, all sample and ΔP sensor lines were cleaned.

To limit damage should flooding recur, a trap was fabricated for installation between the column and H_2S exhaust line. A check valve was also installed between the column and the steam- CO_2 preheater.

As in runs C-6 and C-7, the extraction section gave good recovery during run C-8. Overall sulfur recoveries in the 94% to 97% range were obtained.

Run C-9 was made solely for the purpose of pinpointing the problem with the regenerator. Data obtained indicated the risers on either tray 6 or 7 were plugged. The column is assembled in three segments. The middle segment containing the affected trays was removed, stripped of trace heaters, and sectioned on a lathe. Tray 6, a blind section, was found to have risers plugged with Al_2O_3 derived from the "pack-alonizing" treatment.

The two remaining segments of the column were joined to yield a regenerator with four trays. This was deemed adequate for process demonstration purposes.

During run C-9 trace heaters on the venturi feed line failed repeatedly, causing serious delay in the run. The reason for this became evident during

run C-10, when it was discovered that the venturi feed line had cracked and was leaking salt, which destroys the trace heaters. It was necessary to shut down run C-10 and replace the failed portion of the line. No data was obtained. The line failed due to expansion of liquid salt trapped between plugs of still-solid salt. This occurs during heating sequences. The line was bulged at a number of points.

From an operating standpoint run C-11 was the most successful run made. Simultaneous operation of all systems was achieved for periods up to 8 hr, at which point shutdown to refuel the PNL gasifier was necessary. While continuous operation was achieved over fairly long periods, it was not possible to maintain steady salt flow rates to the extraction and regeneration columns. In addition, salt flows to the regenerator substantially exceeded the design basis and this limited regenerator performance.

During the early part of the run the gasifier was putting out a gas so low in moisture and CO_2 that soot deposition in the venturi exhaust line became a problem. To remedy this a water injection port was installed in the gasifier to allow water injection onto the top of the bed. This solved the soot problem, but the high moisture content of the gas (30 to 40%) reduced the sulfur recovery efficiency in accordance with the thermodynamics of the extraction reaction. Some channeling of the bed in the gasifier also occurred, causing CO_2 concentrations to increase. Even with high moisture and CO_2 content, the extraction section maintained product gas sulfur concentrations in the 100 to 200 ppm range or below.

The regenerator performed better than predicted from equilibrium data obtained in the laboratory. This is not as bad as worse performance, but it still requires explanation, and the result is attributed to side reactions that become increasingly important at higher temperatures. The regenerator operated at 75 to 100 degrees above the design temperature, which seriously reduced its effectiveness. This was the result of high salt flow rates that exceeded flows the salt cooler could effectively cool. Run C-11 was forced to shut down when trace heaters on the salt cooler failed and replacements were found to have been damaged in shipment.

Run C-12 was marred by a number of operational mishaps. After the salt cooler was repaired run C-12 was started. All systems had been operating simultaneously for about 4.5 hr when the extraction column flooded and plugged all of the samplers and ΔP sensor lines. This was the first and only time this occurred. It was caused by excessive salt flow, which actually overfilled the venturi feed tank and backed salt into the extraction column faster than it could flow out. This damage was repaired the following day. In attempts to jettison excess salt in the venturi feed tank (to the lower catch tank) salt overflowed to the 3-in. line from the gas preheater, and this line had to be repaired. Fortunately, no salt contacted the heaters in the gas preheater, which was off. The run was finally resumed after several hours' delay and continued over about an 11-hr period, but with somewhat irregular operation of all units. Hydrogen sulfide cylinder gas was added to hurry the approach to equilibrium sulfur concentrations in the salt.

Very high water injection rates to the gasifier led to moisture contents of up to 50% at times. This reduced the inlet sulfur in the gas to only about 150 ppm. Moderate extraction of sulfur was still observed. When H_2S cylinder gas was added the inlet sulfur concentration increased to 1150 ppm and the venturi outlet gas increased rapidly to 1000 ppm. Product gas samples remained below 200 ppm over the 90- to 100-min period of cylinder gas addition, but were beginning to increase (from 90 to 185 ppm) during this interval. Shutdown of the run was forced when the salt cooler plugged and could not be re-opened.

Regenerator performance was sufficient to maintain low average sulfur concentrations in the salt phase. The salt was initially quite clean, so sulfur concentrations in the regenerator product gas remained low.

Run C-13 was designed to test a polishing filter for particle and salt mist control. Gas coming off the packed-bed demister has a particle burden on the order of 150 mg/M^3 of which up to 1/3 may be salt fume. During run C-13 a small filter cartridge placed in the void above the packing in the de-entrainer reduced the particle burden to 37 mg/M^3 . Alkali metals

comprised about 21% of this total. This filter was too small and was beginning to blind when problems with the regenerator forced a decision to shut down.

Gas flow was routed to the scrubber before the gas preheater and scrubber units were up to temperature and the filter began to blind with soot. As a result, salt flow to the venturi could not be maintained adequately. Moreover, when salt flow to the extraction column was valved on, the pressure required to force gas through the filter was higher than that due to the liquid head and salt and gas blew back into the salt makeup tank. The bell-shaped standpipe in this tank was blown out of the exit line at the bottom of the tank. This allowed high-iron-bearing sludge to flow to the extraction column later.

By initiation of water injection to the gasifier and by raising extraction side temperatures to 730°C the filter was cleared and operation of all systems was achieved after 15:00. Operation continued until 19:30 when the regenerator appeared to have plugged.

Run C-13 gave good data on extraction behavior and limited data on regenerator performance. Feed gas sulfur concentration was only about 250 ppm and in most cases this was reduced to 150 to 220 ppm. High moisture content in the gas prevented more efficient extraction.

Run C-14 was initiated after the PDU was given a thorough cleaning with aqueous HNO_3 , water, and steam. All units were cleaned with exception of long runs of pipe (2.5-in. venturi exhaust and the 4-in. gas-salt return line). Significant amounts of black flakes high in iron and highly magnetic were flushed from the system.

Run C-14 was started on 8/7/78 but was shut down after a serious salt spill occurred when the venturi feed valve failed to restrict salt flow. All salt flow control valves were replaced and the run was resumed on 8/14/78. Very high sulfur recovery was observed as a result of the use of clean salt. Cylinder gas was used to increase the H_2S content of the feed gas. The regenerator flooded severely on two occasions. It was starting to yield good performance when it flooded the second time, probably due to poor flow control

with the new gate valves. Run C-14 was terminated when a crack developed in the line between the salt makeup tank and the extraction column feed valve.

Run C-15 was essentially a continuation of run C-14 (following repairs). The new gate valves performed badly during this run. They leaked continually, so salt losses from the process became a problem and salt additions of considerable magnitude were required.

Iron contamination was also a problem and occurred concurrently with fresh salt additions, which is further evidence that iron is entering the PDU from equipment upstream. Corrosion does not occur with sufficient seriousness to account for so much iron in such a short time span.

Data obtained during run C-15 indicated the extraction efficiency was higher than theory predicts. The additional extraction was evidently due to iron. Regenerator product gas was lower in H_2S than theory predicts, and the high iron content was again responsible.

The run was terminated when the regenerator plugged. Post-run examination of the regenerator confirmed that most of the risers and some of the downcomers were plugged. At the flange joining the two segments of the column (a cool spot), a large cluster of salt was found. In general this was high in iron and of higher melting point than the bulk salt phase.

Run C-16 was initiated after converting the regenerator to a packed column. The trays were cut out and the column welded back together to yield a 6-in.-dia column packed to a depth of 4 ft with Al_2O_3 cylinders 5/8 in. in dia x 5/8 in. long with a 1/4-in.-dia axial hole.

Unfortunately, run C-16 was plagued with so many problems due to plugged lines (partly the result of trace heater failures) that salt flow was very sporadic. Steady operation was not achieved for periods sufficient to evaluate the performance of the packed column.

A bubble-cap tray column holds up sufficient salt that production of H_2S due to the regeneration reaction continues if salt flow is briefly interrupted. The packed column, on the other hand, holds up very little salt and must be operated at a steady rate to gain reliable data. This was not achieved during run C-16.

In sections to follow data obtained in all of the runs is presented in detail. In general the format for data presentation starts with a run summary followed by experimental data and discussion. A chronological history of the run is also given for the benefit of readers concerned with detail.

II. PLANT SHAKEDOWN

RUNS C-1 THROUGH C-4

Run C-1 was initiated on 11/15/77 and was the first attempt to operate the PDU. The gasifier was started early on this date and was producing good quality fuel gas by 10:30 to 11:00. Salt flow to the extraction column was initiated with only CO₂ purge gas flowing. Pressure drops indicated both trays had sealed off properly and the gamma-ray densitometer indicated the siphon reservoir had filled. Gas flow was then valved to the scrubber and attempts were made to initiate salt flow to the venturi. Salt overflowed the standpipe in the venturi feed tank before this could be accomplished and salt feed to the extraction column had to be valved off. Efforts were still in progress to initiate salt flow to the venturi when a fuse blew in the Richland PUD high-voltage line, causing loss of one phase and necessitating an emergency shutdown. A motor on a high-pressure air compressor within the supporting laboratory single-phased and burned out, but this was the only damage sustained.

The power outage was caused by failure of the Richland PUD to act on a request for proper line fusing, but would probably not have occurred had the heater controls operated properly. When the heaters were brought up to the set temperature there was excessive chatter in the magnetic reactors that feed power to the trace heaters. Electrical noise was feeding through the controllers to actuate a dozen or more reactors at a time. These abnormal power surges probably caused the fuse to blow. Electrical filters installed across terminals of the magnetic reactors corrected this problem.

Run C-2 was initiated on 11/17/77, and this time the heaters came to temperature with normal control operation. The run was delayed for several hours when the drag chain conveyor broke down and had to be repaired. Flow to the venturi scrubber was initiated without difficulty, but after only about 10% of salt had been transferred to the coarse de-entrainer salt flow to the venturi stopped and could not be restarted. It was necessary to terminate the run.

Upon disassembly of the venturi feed line to determine the cause of flow disruption it was found that a plug of black, high-melting material was obstructing the bellows-sealed needle valve. This valve has a 1/4-in.-dia Z-shaped flow passage, which is easily plugged.

To reduce staff requirements and costs, runs C-3 and C-4--initiated on 11/29/77 and 12/6/77, respectively--were conducted using preheated air to circulate the molten salt. Considerable difficulty was again experienced in initiating and maintaining reliable salt flow, and the difficulty was traced to heavy solids settling in the venturi feed line.

To ameliorate the problem,hooded standpipes were installed in the salt makeup tank and venturi feed tank to provide a place for solids to settle out. Before starting run C-5, the salt was drained and replaced to get rid of as much debris as possible. These steps helped, but did not eliminate plugging problems.

RUN C-5

Summary

Run C-5 began on December 16, 1977 and continued for three days. Dirty salt from earlier runs was drained and replaced with clean salt prior to starting. Standpipes were installed in the venturi feed tank and makeup tank to allow heavy solids a place to settle out. This modification substantially reduced, but did not eliminate plugging problems. The system was initially started using preheated air in place of fuel gas. When salt flow had been established to all system components, the gasifier was started and the run proceeded using the gasifier product gas. All equipment was operated with salt flow; however, simultaneous operation of the extractor and regenerator was not achieved. The venturi operated with salt flow for approximately 15 hr, the extractor for 5 hr, and the regenerator for 2 to 3 hours. Throughout the run problems were encountered in establishing and maintaining salt flow. These problems were caused by cold spots in salt transfer lines, by frozen valves, and by solids which collected at the valve ports and at cold spots.

Significant data were obtained on gas cleaning performance of the venturi and extractor. These units performed about as expected. Because of intermittent and sporadic salt feed, no significant data was obtained on regenerator performance. Early in the run the regeneration column flooded. This resulted in plugging of the regenerator off-gas line and several sampling and pressure sensor lines with frozen salt. Removing the plug from the off-gas line caused a substantial delay in the run; the plugged sampling lines resulted in reduced data acquisition and uncertain operation of the regenerator during the balance of the run.

Late in the run the pressure drop across the system (and particularly across the extraction column) began increasing, and it appeared that the salt was becoming slushy or viscous. Salt flow could not be established at the venturi, and the extractor/packed-bed demister unit began vibrating excessively. At this point it was decided to terminate the run.

Subsequent analysis of salt samples showed a high concentration of both iron and carbon in the salt. Either of these could have contributed to the slushy consistency of the salt. In later runs, when high system pressure drop developed, it was found that humidification of the fuel gas reduced the problem, indicating that it was probably caused by carbon deposition from the gas. The solid material plugging the valve ports was found to be very high in iron content, which was interpreted as indicating that plugging problems were caused primarily by corrosion products. The high iron content of the various salt samples indicated a much higher corrosion rate than experienced in the earlier batch tests. Calcium carbonate had been added to the salt in those earlier tests, and it was concluded that the calcium might have a corrosion-inhibiting effect. Runs made after C-5 used the ternary (Li, Na, K)₂CO₃ eutectic with approximately 20% CaCO₃ added. No data was obtained which conclusively indicated that corrosion was reduced by CaCO₃.

Performance of the Extraction and Regeneration Sections

Significant data were obtained on sulfur removal performance during the second and third operating periods. After operation with air to circulate the salt (first operating period) the second operating period (using fuel gas)

extended from 03:10 to 05:02 on 12/18/77. These operating periods refer to periods when salt flow to the venturi was essentially continuous.

Figure II-1 illustrates the gas phase sulfur concentrations ($H_2S + COS$) at various times. In the second operating period the inlet gas G-1 (before the gas preheater) and G-2 (between the gas preheater and the venturi scrubber) gave values ranging from about 210 to 310 ppm. The first venturi outlet (V-1) sample (taken before salt flow was established) shows 218 ppm in agreement with G-1 and G-2. The V-1 samples decreased steadily thereafter, as full salt flow was established to a low of 45 ppm.

Salt flow to the extraction column was started at 03:20 and continued until 05:20. The A-2 sample taken at 03:18, which measured 84 ppm sulfur, was taken just a fraction too soon to reflect the effect of fresh salt addition. But the A-1 sample at 03:42 showing only 22 ppm shows this effect, as do the A-0 and A-2 samples taken at 04:14 and 05:31. The G-3 sample taken at 06:17 reflects the buildup of sulfur in static salt within the extraction column and packed-bed de-entrainer. This sample was taken about an hour after salt flow to the extraction section was suspended. Figure II-1 shows that samples can be analyzed at a rate of about 3 samples per hour. This is not as fast as was anticipated, but with more experience the analytical staff may improve on this.

Table II-1 shows the recoveries obtained. The average COS content of the inlet gas was about 38% of the total. The values for the inlet gas shown were read from the curve for times which correspond to the V-1 or other sample to be compared. Sulfur recovery at the venturi increased with time to a maximum of 79%. The first sample at 02:58 was taken before salt flow was established. During the 30 min or so until the next sample was taken the tank level readings in the salt makeup tank went down 0.75 in., indicating 5ℓ had been removed, which is not sufficient to fill the coarse de-entrainer to the level of the standpipe (when recycle flow would start). This is a flow of only 240 ml/min. By 03:52 there was 10 in. of salt in the coarse de-entrainer, but no recycle flow will occur until the level reaches 11.5 in., so the sample at 04:01 also reflects a low flow estimated to be on the order of 370 ml/min (average).

FIGURE II-1. Performance of the Extraction Section During the Second and Third Operating Periods

TABLE II-1. Extraction Section Performance, 2nd Operating Period
02:44 to 06:17 (12/7/77), Run C-5

Venturi Scrubber (only)						
Time	Inlet Gas	V. Gas Sample			% Sulfur Removal	
	ppm S	COS, ppm	H ₂ S, ppm	S, ppm		
02:58	203	47	171	218	0 ^(a)	
03:31	204	16	115	131	36	
04:01	205	10.5	92	102	50	
04:25	208	10	57	67	68	
05:19	217	10	35	45	79	
05:58	225	11	44	55	76	

Venturi Scrubber and Extraction Column						
Time	Inlet Gas	Sample Point	COS, ppm	H ₂ S, ppm	S, ppm	% Sulfur Removal
	ppm S					
03:18	203	A-2	12	72	84	59
03:42	204	A-1	9	13	22	89
04:14	205	A-0	10	15	25	88
05:31	219	A-2	9	11	20	91
06:17	233	G-3	16	19	35	85

(a) Values read from the curve, Figure II-1, at the indicated times.

(b) No salt flow.

By 04:25 full recycle salt flow should have been established and the recovery had increased to 68%. The recovery reached 79% at 05:19 just before salt flow was valved off. The sample at 05:58 was taken just after salt flow was valved off. Efficient extraction continued for a short period, with the system behaving like a wetted wall contactor.

After salt flow was started to the extraction column at 03:20, the samples taken above and below the lower tray and above the top tray ranged

from 20 to 25 ppm sulfur. This additional extraction over and above that achieved with the venturi scrubber was due to the use of relatively clean salt.

The sulfur content of the salt at the start of the run was measured at 345 ppm. A material balance calculation indicates this should have increased to about 800 ppm by the end of this second operating period. The concentration at the V-1 sample point would be slightly higher than average--the concentration at the extraction column feed entry slightly below the average.

The equilibrium H_2S concentrations in the gas phase corresponding to 345 ppm and 800 ppm sulfur loadings are 14 ppm and 30 ppm, respectively.^(a) These values compare well with the measured gas analyses, indicating that the performance of the extraction section was about as anticipated from theory.

During the third operating period the venturi was operated for nearly six hours beginning at 23:03 on 12/17/77. The extraction column was operated for two brief periods beginning at 22:35 and again at 23:29. Additional H_2S was added to the feed gas in order to obtain data at higher sulfur loadings.

Figure II-1 also shows data for the third operating period. During this period H_2S cylinder gas was added to increase the rate of sulfur accumulation in the salt. The scrubber was operated without supplemental H_2S addition until 01:30. During this period, as shown in Table II-2, sulfur removal at the venturi outlet peaked at 87%, then dropped to 81%. During this time samples taken above the top and bottom trays in the extraction column were showing only 22 and 21 ppm sulfur--i.e., a recovery of 97%. There was no salt flow to the extraction column when these samples were measured.

After addition of H_2S cylinder gas the sulfur content of the venturi outlet increased, reaching a maximum of 585 ppm at 03:20. Between 04:00 and 05:00 the extraction efficiency at the venturi suddenly increased. There appears to be no reason to expect such behavior.

(a) This calculation assumes the average measured CO_2 concentration of 14 mole% and an estimated water content of 3 mole%.

TABLE II-2. Extraction Section Performance, 3rd Operating Period
21:00 (12/17/77) to 05:30 (12/18/77), Run C-5

Venturi Scrubber Only						
Time	Inlet Gas ppm S	V. Gas Sample			% Sulfur Removal	Remarks
		COS, ppm	H ₂ S, ppm	S, ppm		
23:33	740	76	121	197	73	
24:02	705	10	85	95	87	
00:28	650	10	93	103	84	
00:49	560	10	95	105	81	
02:00	2350	125	158	283	88	Cyl. H ₂ S added
02:30	2550	90	260	350	86	
03:20	3000	95	490	585	81	
04:22	3800	85	434	519	86	
04:44	3800	84	235	319	92	

Venturi Scrubber and Extraction Column							
Time	Inlet Gas ppm S	Sample Point	COS, ppm	H ₂ S, ppm	S, ppm	% Sulfur Removal	Remarks
00:15	680	A-2	9	13	22	97	
00:38	605	A-1	9	11	21	97	
01:03	505	A-0	11	36	47	91	
02:44	2700	A-2	13	24	37	99	Cyl. H ₂ S added
05:02	3800(est)	G-3	105	203	308	92	

Only one sample (A-2) was taken in the extraction column during the period of supplemental H₂S addition. It contained 13 ppm COS and 24 ppm H₂S, which represents approximately 99% recovery. At the time this sample was taken, salt flow to the extraction column had been off for over 2 hours. Extraction can continue after salt flow is turned off because the trays hold about 6% of salt, or a total of 25 to 30 pounds. The venturi outlet gas is so dilute with respect to sulfur compounds that it does not load the salt in the column very fast.

A salt sample taken from the salt makeup tank at 02:00 (12/18/77) contained 1000 ppm sulfur. It should be in equilibrium with gas containing 25 ppm sulfur (8.9 mole% CO_2 and 4 mole% H_2O). This is good agreement with the 24 ppm H_2S measured at A-2 44 min later.

At 02:59 (12/18/77) a salt sample taken from the coarse de-entrainer was found to contain 1.6 w/o sulfur. This should be in equilibrium with venturi outlet gas containing 460 ppm H_2S . The V-1 sample at 02:30 contained 350 ppm H_2S and the one at 3:20 contained 585 ppm H_2S , for an average of 468 ppm H_2S . Salt samples taken were always too few in number, but as was the case during the second operating period, the data obtained during the third operating period are in excellent agreement with predictions from theory.

During the second operating period no data was obtained as a result of attempts to operate the regeneration column. Salt flow to this column was initiated at 03:50 (12/17/77), but before the column could be successfully lined out salt overflowed via the H_2S exhaust line and froze in this line. This prevented further attempts to operate the regeneration column at the time and some 8 to 10 hr were required to unplug this line and ready the column for renewed operation. This work delayed the start of the third operating period.

Attempts to start the regenerator during the third operating period were not successful. Salt flowed to the column very briefly but it was determined that the siphon through which the salt flows to the salt makeup tank was plugged because of heater failure. This required suspension of salt flow to the column until repairs could be made.

Experimental difficulties mounted rapidly during the fourth operating period (07:00, 12/18/77 to 02:00, 12/19/77). Salt flow to the regenerator was initiated at 07:25 (12/18/77). Salt flow to the venturi was initiated at 08:33, but salt flow to the extraction column could not be started. Both the venturi feed tank and the coarse de-entrainer emptied and all salt accumulated in the salt makeup tank behind the balky valve to the extraction column.

Salt flow to the extraction column was finally achieved at 15:15 and the flow control valve promptly froze open. Flow to the venturi scrubber could

not be obtained, and some 30 lb of salt overflowed the standpipe in the venturi feed tank and was lost before the valve to the extraction column was finally closed. Salt flow to the venturi was finally achieved at 18:30 and maintained until 19:20, but it was necessary to shut down and charge the gasifier at this time.

Gas flow to the scrubber was resumed at 20:00 and irregular salt flow to the venturi was obtained at 20:30 and maintained until 21:00. Figure II-2 shows gas sample analyses obtained from about 19:25 to 24:00 (12/18/77). The V-1 sample at 20:44 shows the effect of this brief pulse of salt to the venturi. It contained 79 ppm COS and 26 ppm H₂S (105 ppm sulfur). With the inlet gas estimated from the curve at 460 ppm sulfur, this V-1 sample indicates a recovery of 77%.

The V-1 samples at 20:28 and 21:22 were measured when no venturi salt flow was present. At such times the gas composition should be nearly the same as at G-1 (or G-2).

At 22:36 H₂S cylinder gas was added but no analysis at G-2 was obtained until 23:45 (2350 ppm sulfur). The cylinder gas addition was suspended at 23:50.

The A-2 sampler was the only one still operative in the extraction column. Flow of salt to this column consisted of no more than an occasional spurt so the results obtained at this sample point have little significance and are extremely variable.

The final product gas samples yield results ranging from 110 to 260 ppm sulfur during this period. These show no consistent trend. When the inlet gas with cylinder H₂S addition is compared with the G-3 samples, the recoveries indicated are in the range 89% to 95%. This is a little better than might be expected, considering the troubles experienced with salt flow.

A salt sample taken from the venturi feed tank at the conclusion of the run assayed 1.56 w/o sulfur. This salt would yield an equilibrium gas phase concentration of 1397 ppm H₂S. The coarse de-entrainer, sampled the following morning, contained salt with 1.75 w/o sulfur, and here the corresponding equilibrium value for the gas is 1659 ppm H₂S. The venturi

FIGURE II-2. Extraction Section Performance During the Fourth Operating Period

outlet (V-1) sample measured at 23:15 gave a value of 1173 ppm H_2S + 94 ppm COS. At this time H_2S cylinder gas was being added to yield a scrubber inlet feed composition of 2350 ppm. There was question whether salt flow to the venturi was occurring at 23:15, but the result on the V-1 sample seems to indicate there was some flow.

In general, the extraction performance was better than predicted from theory. This may be due to accumulations of iron as an impurity in the salt, which reacts to form FeS. The latter appears to have only limited solubility in the salt and probably is not uniformly distributed. For this reason it is difficult to make quantitative corrections for the effect of Fe. Iron would tend to improve performance of the extraction section and detract from performance of the regeneration column.

It would be reasonable to assume that the serious problems with maintenance of salt flow were due to solids accumulating in the salt. The run was terminated when the extraction column and packed-bed de-entrainer assembly began to vibrate excessively. It appeared the salt was thick and slushy at this point. Subsequent analyses disclosed the salt was contaminated severely with carbon, believed to result from soot deposition derived from decomposition of CO. High iron concentrations may also have contributed to the solids burden.

CHRONOLOGICAL RUN DESCRIPTION RUN C-5

08:00 to 18:00 December 16, 1977

Five hundred pounds of salt was mixed, charged to the salt makeup tank, melted, and brought to a temperature of 1320°F by 14:30. All trace heaters were brought up close to predetermined set points. The secondary burner was started and the gasifier slide valves and conveyor tested and found ready to operate. Sample lines and pressure sensor lines were leak-tested and found to be okay. A supply of coke was transferred from the stockpile to a point near the conveyor using a small front-end loader.

18:00 to 06:00 December 16-17, 1977

First Operating Period

At 20:30, operation was started using air to circulate the salt. Immediate salt flow to the extraction column at 0.89 ℓ /min was observed by tank level measurements on the salt makeup pot, but flow to the venturi scrubber was slow and the venturi feed tank overflowed at the standpipe at 21:10. Flow to the extraction column had to be valved off. The ΔP at the venturi was 1.25 to 1.4 psi, indicating some flow. The course de-entrainer had been filling and showed 8 ℓ at 21:20. This would indicate an average flow through the venturi of about 160 ml/min. If this is subtracted from the 890 ml/min through the extraction column, the net inflow to the venturi feed tank was 730 ml/min, which is sufficient to fill the venturi feed tank to the point of overflow in 38 min--or about the elapsed time at which overflow was noted.

In the interval from 21:20 to 21:30 the level in the course de-entrainer increased to 10.5 in. (13 ℓ) indicating flow to the venturi had increased to 500 ml/min and was increasing (as shown by ΔP readings). Flow was now initiated to the regeneration column and also to the adsorption column. It was found possible to balance the flow into and out of the salt makeup pot, which is required for smooth, steady operation of the system, but the flows could be balanced only for short periods.

Difficulty was experienced in getting reliable ΔP readings across the trays in the regeneration column. It was believed some of these small lines may have become plugged with salt from earlier testing. In any case, all systems were in simultaneous operation and it was decided to proceed with operation on fuel gas.

Second Operating Period

At 01:00 the charging of 1000 lb of coke to the gasifier was completed, and at 02:40 preparations to initiate salt flow were complete. At 03:15 salt flow to the venturi was valved on and ΔP readings indicated full salt flow was established almost immediately. At 03:20 flow to the extraction column was initiated and tank level readings indicated immediate flow response at 0.64 ℓ /min.

At 03:50 attempts were made to start the regeneration column. Soon after starting salt flow, the pressure at the bottom of the column began rising. To the operators it appeared the regeneration column had plugged and steam-CO₂ flow to this column was shut down when pressures reached 6 psig. Flow to the extraction column was valved off about 04:30, and with the venturi still operating all salt collected in the salt makeup tank by 05:30.

Analyses of product gases and gas samples taken throughout the extraction column showed COS and H₂S concentrations in the range of 9 to 12 ppm each. Inlet H₂S and COS concentrations were measured at 135 ppm and 99 ppm, respectively. This inlet H₂S concentration is low and is the result of the early stage in operation of the gasifier. The overall sulfur recovery during this period of operation averaged about 90%.

06:00 to 18:00 December 17, 1977

The gasifier was continued in operation via the bypass line while efforts were made to locate the obstruction in the regeneration column. By measuring pressure drops from point to point along the column it was soon discovered that the column itself was not plugged, but that the exit line was plugged. Sometime later the actual plug (about 1 $\frac{1}{2}$ of frozen salt) was located by the laborious process of disassembling the line. This salt was chipped and washed out of the line, which was then reassembled--a process that required about 8 to 10 hours' work.

At the time it was believed that salt had been blown out the top of the column by gas flow surges caused by liquid water being injected into the steam-CO₂ preheater, which normally operates at about 650°C. While this may have been the problem, later experience suggests that an internal plug in the regenerator may have been the primary cause. In the remainder of run C-5 and in later runs, efforts were made to ensure that condensate was never injected into the steam-CO₂ preheater.

It was also discovered that one of the heaters on the regenerator siphon had failed, and this was spliced for temporary repair. Efforts were made to get all sample lines and ΔP sensor lines to the regenerator cleared, but these efforts were only partly successful.

At 16:30, 800 lb of coke and 200 lb of sub-bituminous coal were charged to the gasifier, and by 18:00 the PDU was again ready to operate.

18:00 to 06:00 December 17-18, 1977

Efforts were continued to clear lines to the regenerator sample and pressure sensors, and 30 lb of fresh salt was added to the salt makeup tank to compensate for inadvertent losses resulting from overflow at the venturi feed tank.

Third Operating Period

At 22:30 salt flow was initiated to the venturi, and a few minutes later to the extraction column, with immediate flow response. During the next hour salt flow to the extraction column seemed somewhat variable, and it was necessary to open and reset the valve to this column frequently. At 24:00 the salt feed to the extraction column was turned off.

At 01:30 pure H_2S cylinder gas was added, bringing the inlet H_2S concentration to 2355 ppm (from 504). Salt continued to circulate in the venturi/coarse de-entrainer loop to allow buildup of sulfur compounds in the salt phase. At 04:00 salt flow to the regenerator was started using only CO_2 as a strip gas. The steam flow to the superheater was erratic, and no steam was admitted to the column until the condition could be corrected. At 05:02 salt flows were shut down and gas flow bypassed to permit addition of coal to the gasifier. By 05:30 400 lb of coke and 400 lb of coal had been added.

During the period from 22:30 to 05:00 a continuous effort to analyze as many gas samples as possible was in progress. The results are reported in Table II-2, p. II.26. Unfortunately, sampling difficulties prevented getting data on the effect CO_2 strip gas has upon salt flowing through the regeneration column. The exact nature of the difficulty being encountered was not clear at the time, but proved later to be frozen salt obstructing flow in sample lines.

Between 05:02 and 05:30, 400 lb of coal and 400 lb of coke were added to the gasifier.

06:00 to 18:00 December 18, 1977

Dry steam was available to the regeneration column, which was started up with steam flow followed by salt flow and, finally, by CO₂ flow. Startup of the regeneration column was achieved at 07:42 after minor difficulties in starting salt flow were overcome.

After considerable difficulty in establishing flow to the venturi (it was necessary to apply a torch to the stem of the venturi feed valve) flow was achieved about 08:20. This was just in time to prevent the feed supply to the regeneration column from being exhausted.

At 08:33 attempts were made to initiate salt flow to the extraction column (which in turn supplies the venturi scrubber) but no flow could be obtained. As efforts were continued, the reservoir of salt in the venturi feed tank emptied and flow to the venturi slowed and finally stopped. In turn, the reservoir of salt in the course de-entrainer, normally kept filled by the venturi scrubber, drained through the salt cooler and through the regeneration column to the salt makeup tank. Thus, all of the salt inventory collected in the salt makeup tank behind this recalcitrant valve.

Efforts to unplug this valve finally succeeded about 15:30 and, as if to add insult to injury, the valve froze in the open position as salt crept up into the bellows and froze around the stem. Immediate steps were taken to open the valve to the venturi scrubber, but for unknown reasons, flow to the venturi scrubber could not be established immediately. Some salt was lost at the venturi feed tank overflow standpipe before the valve from the salt makeup tank to the extraction column could be reclosed.

To this point (16:30) operating difficulties had accumulated to the point where run termination was being seriously contemplated. The venturi ΔP gauge was beginning to indicate a trickle of salt flow, and as the next shift came on it was decided the run would be terminated unless the venturi would start within a few hours. Within a half hour it did start.

18:00 to 06:00 December 18-19, 1977

Fourth Operating Period

At 18:30 flow to the venturi scrubber was achieved and was maintained until 19:15, when flow was valved off to permit charging coal to the gasifier. At 20:30 1000 lb of sub-bituminous coal had been charged to the gasifier and flow of salt to the venturi scrubber re-established. The venturi was continued in operation while efforts were directed at starting salt flow to the regeneration column. Sporadic flow to this column was obtained starting at 23:25, and was continued with moderate success until 01:00, when gas flow was bypassed.

Meanwhile, at 23:15 H_2S cylinder gas flow was started and allowed to flow into the venturi scrubber section until 23:53. Flow to the absorber was never initiated except for one brief pulse just after the H_2S cylinder gas was turned off.

The pressure drop across the venturi scrubber and extraction column began increasing and eventually exceeded 4 psig with no liquid flow. The extraction column began vibrating badly, as though the gas was being forced through a pool of mud. Addition of fresh salt to the extraction column reduced the pressure drop somewhat, but only temporarily. Gas flow was bypassed, and tank levels and salt samples were taken. When taking the coarse de-entrainer level it was noticed that the salt had turned to a thick, viscous slush. At this point it was decided to shut down. Analysis of salt samples indicated that carbon and iron were probably the cause of changes in the salt consistency.

III. CORROSION PROBLEMS

SUMMARY OF OBSERVATIONS

With the very first series of shakedown tests of the PDU, elements typical of corrosion products derived from PDU construction materials accumulated in the salt at an alarming rate. These were subsequently found to derive from equipment upstream of the PDU. The alonized steels of which the PDU was constructed performed exceptionally well. A few minor instances of corrosion-erosion effects and of crevice corrosion were noted. Severe pitting attack was observed in a 1-in.-dia line that had been overheated. "Unalonized" valves, standpipes, and pipe sections suffered severe corrosion.

PRIOR EXPERIENCE

Laboratory screening studies identified "alonized" steels as one of the most promising of materials for PDU construction.⁽¹⁾ Alonized 304SS was used in construction of the venturi scrubber/packed-bed de-entrainer. It was never possible to detect the presence of corrosion product elements in the molten salt during operation of this plant. Visual inspection of vessels and piping at the conclusion of these operations also failed to disclose evidence of corrosion, with one exception. The throat area of the venturi scrubber and portions of the exhaust section just downstream of the throat were severely pitted. The "alonizing" was undercut and had suffered severe corrosion-erosion after a total of only 7 to 8 hours' operation. Clearly, alonized steel would be unsuitable for use in this service in a PDU designed for prolonged operation.

PDU OPERATION EXPERIENCE

For the remodeled PDU a venturi scrubber was designed which utilized a ceramic liner to form the venturi configuration (Figure III-1). This design proved completely resistant to the corrosion-erosion effects that had so drastically affected the "alonized" steel venturi scrubber. The high-purity Al_2O_3 ceramic did fracture as a result of thermal cycling. For the most

FIGURE III-1. Design of Venturi Scrubber for PDU Startup Configuration

part these were hairline cracks which were not serious, but during run C-15 the liner broke up and its fragments were ejected via the 2.5-in. venturi exhaust line. They lodged in a bend in this line near the point of entry into

the coarse de-entrainer, and together with particulate matter constricted flow to the point where shutdown became necessary.

The ceramic liner was fabricated in two sections, which slipped into the metal spool piece and rested on a shoulder just above the salt inlet port. A metal washer was inserted above the ceramic to take up space between the liner and the flange above it and to secure the liner so that the frictional drag of the gas would not cause it to move.

This washer suffered what appears to be severe crevice corrosion effects, which destroyed the "aluminumizing." Figure III-2 shows the bottom surface of this severely corroded item. The top surface is relatively uncorroded by comparison, though it does show pitting of sufficient severity to penetrate the "aluminumizing." Corrosion of this item was disclosed when it became necessary to replace the damaged ceramic liner.

During early shakedown runs--in fact, during the very first run--significant levels of what appeared to be corrosion product elements appeared in the molten salt. As it turned out these were derived from severely corroding mild steel pipe connecting the gasifier to the gas preheater. This pipe was scaling and flaking badly. The 321SS-sheathed elements in the gas preheater were also corroding severely and flaking away. The reducing gas environment and high surface temperature of the sheath is the most severely corrosive condition that exists in the array of equipment in place. The gas preheater was not anticipated to serve for long periods. It failed during run C-7. The sheathed heaters were replaced, and during runs C-8 through C-12 salt phase assays remained low in iron and other corrosion product elements. The levels were much lower than those which were obtained prior to this replacement.

Following run C-9 it was determined that the regeneration column was plugged at tray No. 6. The column was disassembled and the center section removed. This was cut open to reveal the 6th tray, and it was found that the annular space between the caps and risers were plugged with alumina derived from the "pack-aluminumizing" process.⁽³⁾

FIGURE III-2. Retaining Ring: Example of What Appear to be Crevice Corrosion Effects

Inspection of all regeneration column internals exposed during this operation disclosed that little if any corrosion had occurred. No pitting nor undercutting of the protective alonizing was disclosed. A slight discoloration of the surface seemed to be the only effect.

Prior to run C-13, the packed-bed de-entrainer was opened to allow installation of a filter assembly. The ceramic packing was removed, inspected, and found essentially unaffected by its exposure. The vessel walls were smooth and showed no evidence of pitting nor of undercutting of the alonizing layer. The vessel lid and the short curving section of 3-in. pipe which connects to the product gas outlet line was similarly unaffected. The gasket on the flange was of high-temperature asbestos paper (1/8-in. thickness). It had held very well, but had to be replaced each time the flange was disassembled and reassembled. This gasket is exposed only to cleaned product fuel gas.

At the conclusion of the tests, the major process vessels were opened, cleaned with nitric acid and water, dried, and carefully inspected. Some surface etching was evident, but in no instance was there evidence of severe pitting or undercutting of the alonizing layer.

Standpipes had been installed in the venturi feed tank and in the salt makeup tank. These had not been alonized, and as disclosed by Figure III-3, they were severely corroded. The contrast between the appearance of these items and the vessel wall is dramatic evidence of the effectiveness of the alonizing treatment. The standpipe at the bottom of Figure III-3 was in the salt makeup tank. The narrow-tip end was fabricated from 1/2-in.-dia heavy wall tubing. This part was inserted into the exit line at the bottom of the tank so that the standpipe rested on the shoulder where the tubing was welded on. The opening for the exiting liquid is obscured by the 4-in. pipe cap. The tubing section corroded completely through and the standpipe was lying on its side when found. Pits so large they completely penetrate the tubing may be seen near the bottom end.

The standpipe with the 6-in. pipe cap was in the venturi feed tank. This too is severely corroded. The pitting does not seem quite as severe as on the other standpipe, but it is clear that unalonized metal will not survive for long. The exposure time of these pieces was approximately 700 hr to salt at 700°C to 730°C.

In addition to these standpipes it was necessary, in order to avoid program delay, to employ unalonized gate valves for flow control. In all cases these were installed in 1-in.-dia lines carrying a continuous salt phase. Figure III-4 shows the valve seat sections from two of these valves after 300 hours' exposure. The upper segment was cut from the valve controlling flow to the regeneration column. The lower segment was from the valve in the venturi feed line. The latter failed completely to restrict flow near the start of run C-14, and this forced termination of the run.

The salt flow entered the valve on the top side. The gate moved from right to left on opening. The shoulder of metal in the valve seat against which the gate sealed is intact in the upper picture, but is virtually

FIGURE III-3. Unalloyed 304SS Standpipes Suffer Severe Pitting Attack

destroyed in the lower picture. From 1/16 in. to 1/8 in. of metal has corroded away. All three gate valves were replaced before run C-14 could be resumed.

FIGURE III-4. Unalloyed Gate Valves Sectioned to Disclose Corrosion of Valve Seats

In view of the condition of the gate valve removed from the venturi feed line, the remainder of this line was a prime suspect for detection of corrosion effects. An elbow section downstream of the spoolpiece containing the valve was sectioned for examination. Severe corrosion or corrosion-erosion effects were evident. The extent of pitting and undercutting was most severe at the elbow as opposed to the straight sections. Figure III-5 shows this pipe segment. The top side of the pipe is to the left of the picture. Severe pitting and undercutting of the alonizing is evident in the elbow in both top and bottom segments. Though not clear in the picture the bottom sides of the straight segments may be more severely corroded than the top sides. This suggests that particles settling on the bottom side may have caused galvanic effects. This section was severely overheated ($\sim 1000^{\circ}\text{C}$) briefly during one run. Sections of pipe that had not been overheated showed some isolated pitting. The corrosion appeared to be worse in areas with increased turbulence.

The flow rate in the venturi feed line was ~ 1 gal/min = 0.37 ft/sec. This leads to a calculated Reynolds number of about 3000, which indicates that turbulent flow prevailed.

The venturi feed line was frequently exposed to temperatures in the range 740° to 780°C . For the most part this was due to limitations of the power and control circuitry (so much power was applied that the simple on-off proportioning band control system could not prevent over-shoot). This was eventually corrected by modifications to the circuit. Some overheating was deliberate and was done in an effort to resolve plugging problems and to eliminate cold spots.

On one occasion the heating element over the control thermocouple failed. As the pipe section under the heater cooled, the thermocouple called for more heat and all the other heaters came on and tended to stay on. The over-temperature condition was detected by the operators when signals from auxilliary thermocouples gave high readings at the digital datalogger. The control set point was turned to lower temperature, but when this did not suffice to reduce the over-temperature readings (reported to be near 1000°C), the heaters on the line were shut down.

FIGURE III-5. Elbow Section from the Venturi Feed Line

This severe over-temperature condition was short lived--lasting perhaps 30 to 40 min--but it caused severe damage. Even the outside of the line shows the effects. It is darkened and discolored due to oxidative attack.

By comparison, sections cut from the 1-in. line connecting the extraction column to the salt makeup tank (the makeup tank drain) show no corrosion. Faint blemishes indicative of pitting are present, but it would require a metallographic examination to decide whether these are, in fact, pits.

The makeup tank drain line has been subjected to modest over-temperature effects, but nothing like that which the venturi feed line experienced. The latter sees a salt, which is usually a bit higher in sulfide ion content than that in the makeup tank drain, but it appears most probable that the severe corrosion in the venturi feed line is the result of overheating.

Both of these lines have suffered overstressing during heatup to melt frozen salt inside the pipe. This occurs on startup and is due to heating at a rate that produces a liquid segment trapped between plugs of still-solid salt. Continued heating expands the liquid, and in one case caused rupture of a segment of the venturi feed line.

The segment of the makeup tank drain examined for corrosion-erosion effects (and which had the same length of service as the severely corroded section from the venturi feed line) showed stretch cracks in the alonizing caused by this expansion. Despite this apparent breaching of the alonizing layer, there was no corrosion; however, the cracks may not have completely penetrated the alonizing. The induced stress evidently had no effect upon the corrosion rate.

Figure III-6 is a view looking into and through a grayloc hub on the inlet end of the 1.5-in.-dia line which connects the standpipe in the coarse de-entrainer to the 4-in. gas-salt return line. Bright reflective material inside the pipe is a metallic deposit of unknown composition (probably derived from the pack-alonizing treatment). This pipe shows minor pitting along the bottom side, which was contacted by the recycle salt flow. The pipe was in service for the entire program. Its total hours at 700°C were 740. Of this time, its exposure to flowing salt corresponds roughly to the total time of venturi operation--i.e., 94 hours.

FIGURE III-6. View Looking Into the Inlet End of a 1.5-in. Jumper from the Coarse De-Entrainer to the 4-in. Return Flow Line

It is doubtful that this line ever runs full unless salt backs up due to the presence of a partial plug at the exit end. The salt simply spills over the weir (standpipe) and trickles down the standpipe. The total head to the location of the elbow is about 22 inches.

Figure III-7 is a photo of the jumper in the 2.5-in. line, which connects the straight section of the 2.5-in. venturi exhaust line to the coarse de-entrainer. This line carries a salt-in-gas dispersion. The view shown is of the inlet end. Figure III-8 is a view looking into the outlet end of the same pipe. The exposure to the entrained salt corresponds to the time of venturi scrubber operation--i.e., 94 hours.

In Figure III-7 the viewer is looking into a 90° elbow. In Figure III-8, the curvature is less--i.e., a 45° elbow. The 90° elbow is more severely pitted than is the 45° elbow, and it is likely that pitting is primarily due to corrosion-erosion by the dispersion, which is flowing at a velocity of 133 ft/sec.

In both figures the weld beads, where the flange was welded to the pipe, show pitting attack. This is much more severe on the inlet side.

The straight segments of the venturi exhaust line have not been dismantled for inspection. None of the 4-in. recycle salt and gas return line has been inspected. Of major process vessels, only the extraction column has not been examined.

In segments of the PDU which have been inspected, only a few examples of corrosion have been detected. In general, the alonizing treatment has provided the protection anticipated from prior experience and early corrosion screening tests. Some pitting was observed, which makes use of this material over extended periods impractical unless the temperature is reduced.

EVALUATION OF TEST COUPONS

Two corrosion coupons of Haynes-25 alloy were placed in the coarse de-entrainer before it was closed on 8/5/77. These were removed, cleaned, reweighed and measured, with results collected in Table III-1.

FIGURE III-7. Jumper from the 2.5-in. Venturi Exhaust to the Coarse De-Entrainer (inlet side)

FIGURE III-8. Outlet Side of 2.5-in. Jumper

TABLE III-1. Data on Corrosion Coupons Exposed in the Coarse De-entrainer--Haynes-25 Alloy

Parameter Measured	Coupon #1		Coupon #2	
	Before	After	Before	After
Weight, g	52.0032	47.4475	54.0642	48.8946
Length, in.	1.258	1.246	1.293	1.278
Width, in.	1.267	1.256	1.264	1.256
Thickness, in.	0.247	0.235	0.246	0.227
Hole dia, in.	0.381	0.388	0.375	0.380
Location	On Baffle Plate		On Vessel Wall	
Penetration	81.8 mils/year		89.6 mils/year	

Specimen #1 was mounted on a baffle plate on which the gas salt dispersion was supposed to impinge, but due to incorrect positioning of the plate, this did not occur. Specimen #2 was mounted on the wall. Both specimens were above the liquid level in the vessel, which functioned as a simple knock-out drum.

With the exception of one small pit, there was not the extensive pitting attack that occurs with unalloyed 304 SS or, for that matter, with alloyed 304 SS. There was, however, extensive and severe generalized corrosion, with the metal surface just washing away. Examination under low-power magnification discloses much surface roughening and removal of metal. Calculation of the penetration yields the values shown in Table III-1.

IV. EFFECT OF IMPURITY ELEMENTS

In shakedown runs of the PDU, serious difficulty was encountered as a result of contamination of the molten salt by impurity elements. Iron was the principal impurity, but some Cr, Ni, Mn, Al and Si were also observed. These were not uniformly distributed in the salt phase. They tended to separate in a black, viscous, high-melting phase separate from the bulk of the salt. They thus had an effect on process operation out of proportion to their concentration.

In early runs, impurities caused plugging of valves and the venturi orifice. In later runs solid deposits caused plugging in a number of places, including the regenerator bubble caps and downcomers, the salt cooler, the venturi orifice, and several salt transfer lines. The problem appeared to be more severe where the temperature was lower--i.e., in the salt cooler and regenerator.

THE BEHAVIOR OF IRON

Atomics International (AI) work⁽⁴⁾ on the solubility of iron in the molten alkali carbonate eutectic shows that the solubility is a function of the sulfide ion concentration. In sulfide-free melts, iron solubility was only 0.04 w/o at 500°C and 0.36 w/o at 640°C. It can be estimated from AI data that upon conversion of 10% of the mixed alkali carbonates to M_2S , iron solubility at 500°C would increase to 0.5 w/o. It would reach 2 w/o after 24% conversion to M_2S .

Atomics International also found that precipitates which were filtered from melts undergoing regeneration contained iron and sulfur but did not yield x-ray diffraction patterns typical of FeS or FeS_2 , but were suggestive of a more complex formula $MFeS_2$ ($M = Li, Na, K$). Figure IV-1 is a phase diagram of the system FeS- Na_2S .⁽⁵⁾ This, published subsequent to the AI work, discloses the existence of compounds ($5Na_2S \cdot 2FeS$ and $3Na_2S \cdot 4FeS$), which would account for many of the AI observations. These are high-melting and would likely have precipitated under all of the conditions studied.

FIGURE IV-1. Phase Diagram of the System Na_2S - FeS

In the first few shakedown runs of the PDU, serious difficulty was experienced in starting and in maintaining salt flow to the venturi scrubber. Upon subsequent disassembly of the venturi feed line (to ascertain the reason for flow stoppage) it was found the line contained salt which had solidified in separate phases. Figure IV-2 is a photo of salt frozen within the seal ring of a grayloc hub assembly. The black material was on the bottom side of the line.

The spool piece containing the bellows-sealed needle valve that controlled salt flow to the venturi orifice was filled with frozen salt. This was black on the upstream side of the valve and white on the downstream side. It appeared that the deposit obstructing but not totally blocking flow to the venturi orifice (which was also plugged) was acting like a filter. The black salt upstream of the valve contained 8.36 w/o iron and 8.35 w/o sulfur. Only 1.76 w/o of the black salt was insoluble in 4 M HCl , after a few minutes boiling, and this residue was 95% C. The white salt downstream of the valve contained 0.61 w/o sulfur and only a trace of iron. The fraction insoluble in

FIGURE IV-2. Cross Section of Frozen Salt in Grayloc Seal Ring
from the Venturi Feed Line, 2X

HCl comprised only 0.13 w/o of the total and was carbon-free. The compound $3M_2S \cdot 4FeS$ (cf. Figure IV-1) contains a 1:1 weight ratio of Fe:S, so the above iron and sulfur assays correspond to the composition of this compound. It seems probable that sulfide ions precipitate iron from molten (Li, Na, K)₂CO₃ salts as a compound of composition $3M_2S \cdot 4FeS$. With S⁻² ion in slight excess, precipitation of iron appears nearly quantitative.

This compound, as it precipitates, would tend to collect particulate matter such as carbon (char) and inorganic constituents of coal/coke ash. Figure IV-3 is an x-ray fluorescence spectrum of a general area scan of the black salt upstream of the valve taken with the Scanning Electron Microscope. Nickel, chromium, aluminum and silicon are associated with the iron and sulfur. On the other hand, Figure IV-4, which is the spectrum of the white salt, shows only aluminum and silicon in addition to the alkali metals. Aluminum and silicon probably exhibit appreciable solubility as aluminates and silicates.

In these first runs, the salt was picking up tramp material including residues from the alonizing treatment. This accounts for part of the aluminum detected. Black flakes of a metallic origin were numerous. These tended to lodge in constrictions and act as a filter for collection of additional solids. The black flakes were derived from the gas preheater and from a section of mild steel pipe between the gasifier and gas preheater. These solids combined with viscous, high-melting material such as $3M_2S \cdot 4FeS$ to seriously impede flow at small orifices and to precipitate at cold spots to cause difficulty in operation.

ADDITION OF CaCO₃ to (Li, Na, K)₂CO₃

The rapid buildup of black material described above led, initially, to the deduction that the ternary alkali carbonate eutectic, containing S⁻² ions, must be much more corrosive than salt mixtures high in CaCO₃ (~20 mole%) such as were used in early batch tests. In those tests, no corrosion product elements or black material were ever detected in the molten salt despite operation at much higher temperatures.

FIGURE IV-3. X-ray Fluorescence Spectrum of Black Salt Phase Upstream of the Nupro Valve

FIGURE IV-4. X-ray Fluorescence Spectrum of White Salt Downstream of the Nupro Valve

There is, of course, good reason to expect that CaCO_3 would act as a corrosion inhibitor in this system. When added to the ternary alkali carbonate mixture, CaCO_3 has been shown to react with S^{-2} ions more aggressively than do the alkali carbonates.⁽¹⁾ The formation of CaS results in suppression of the S^{-2} ion activity. Since it is the S^{-2} ion which is mainly responsible for corrosion in this system, CaCO_3 may act to inhibit corrosion.

CaCO_3 was added to the salt at a concentration of ~ 20 mole% starting with run C-6 and continuing until termination of the program. No evidence was obtained that it functioned effectively as a corrosion inhibitor. Corrosion was generally limited to parts which had not been alonized, or to parts where erosion played a significant role.

Due to the instability of FeCO_3 , which decomposes irreversibly with oxidation by CO_2 to Fe_3O_4 ,⁽⁶⁾ it might be expected that CaCO_3 would react with FeS to form stable CaS , e.g.,:

Using data from the JANNAF tables⁽⁷⁾ for the free energy of formation of CaS , CaO , CO_2 , and CO and data from Rosenquist⁽⁸⁾ for the free energy of formation of FeS and for the incremental free energy of formation of CaCO_3 , equilibrium constants for reaction (IV-1) have been calculated (cf. Table IV-1).

Defining the equilibrium constant in mole fraction units:

$$K = \frac{x_{\text{CaS}} \cdot x^{1/3}_{\text{Fe}_3\text{O}_4} \cdot x^{2/3}_{\text{CO}_2} \cdot x^{1/3}_{\text{CO}}}{x_{\text{FeS}} \cdot x_{\text{CaCO}_3}} \quad (\text{IV-2})$$

Rearranging,

$$\frac{x_{\text{FeS}}}{x_{\text{Fe}_3\text{O}_4}^{1/3}} = \frac{1}{K} \cdot \frac{x_{\text{CaS}}}{x_{\text{CaCO}_3}} \cdot x_{\text{CO}}^{1/3} \cdot x_{\text{CO}_2}^{2/3} \quad (\text{IV-3})$$

If FeS and Fe₃O₄ have limited solubility in the salt, their activities will be unity, and the ratio $x_{\text{FeS}}/x_{\text{Fe}_3\text{O}_4}^{1/3} = 1.0$. By assigning reasonable values to the quantities on the right side of equation (IV-3) the ratio $x_{\text{FeS}}/x_{\text{Fe}_3\text{O}_4}^{1/3}$ can be evaluated as a (f) of temperature. For the temperatures employed in the extraction section (700°C) and regeneration section (600°C) it turns out the ratio is very close to 1.0. At higher temperatures it is <<1.0 and at lower temperatures it is slightly greater than 1.0 and <10. Thus, when the ratio >1.0, iron tends to be present as FeS. When it is <1.0, Fe₃O₄ is favored.

If the ratio is equal to 1.0, equation (IV-3) becomes:

$$\frac{x_{\text{CaS}}}{x_{\text{CaCO}_3}} = \frac{K}{x_{\text{CO}}^{1/3} \cdot x_{\text{CO}_2}^{2/3}} \quad (\text{IV-4})$$

The ratio $x_{\text{CaS}}/x_{\text{CaCO}_3}$, evaluated from equation IV-4, has been plotted (Figure IV-5) versus reciprocal absolute temperature. The scale at right gives the w/o sulfur.

TABLE IV-1. Equilibrium Constants
for Reaction of CaCO₃
With FeS

<u>Temp, °K</u>	<u>K</u>
800	0.0032
1000	0.09
1200	558

FIGURE IV-5. Stability Boundary for CaS in Systems Containing Iron

This curve essentially defines a boundary of CaS stability in carbonate systems containing iron. At all sulfur concentrations below these curves, CaS is the sulfur-bearing species of greatest stability. At sulfur concentrations above the curves iron combines with sulfur until conversion to FeS is complete. The consequences of FeS formation with possible solvation to form compounds such as $3M_2S \cdot 4FeS$ are serious. This high-melting compound would tend to plate on cold spots. Figures IV-6 and IV-7 illustrate this.

Figure IV-6 shows the flange and the bottom side of the top tray in the regeneration column. A thick salt deposit has built up on the wall of the column at the flange area. The downcomer shows a deposit of salt and was plugged (two of the four downcomers in the column were plugged). Figure IV-7 shows the top side of the tray just below the top tray. Again a thick deposit of salt is visible on the wall near the flange area. A thermocouple near this flange indicated the temperature here (with no salt flow) was near 500°C at most. This is only 50°C below the temperature which it was hoped could be attained during regeneration. The revelation of these pictures thus came as a shock.

It is clearly very difficult to maintain temperature uniformity throughout all parts of a complex apparatus such as a bubble-cap tray column. This was recognized from the start. What was not recognized was that the salt would contain components that would prove extremely troublesome in operation of the column. Clearly, provision should have been made in the design of the salt cooler and regenerator to accommodate these salt components.

BEHAVIOR OF OTHER IMPURITIES

Nickel, chromium and manganese have been detected at low concentrations in the salt phase, but only in association with the black materials. Nickel is undoubtedly present as its sulfide.

It is of interest to examine a polished surface of a salt deposit taken from the downstream side of the salt recycle line--a 1.5-in.-dia line which connects the standpipe in the coarse de-entrainer to the 4-in. gas/salt return line. This line plugged during run C-16, and this sample is representative of the obstructing material.

FIGURE IV-6. View Showing the Lower Side of the Top Tray in the Regenerator Column

FIGURE IV-7. View Showing the Top Side of the Tray
Below that Shown in Figure IV-6

The sample shows black and white areas. The white areas yield x-ray fluorescence spectra typical of the pure salt components, with only traces of aluminum, silicon and sulfur as impurities. The nearly complete absence of sulfur in the white areas is noteworthy.

Figure IV-8 is an electron photomicrograph at 500X of a black area. The black object at the lower left is carbon and gives no signal. Superimposed on this are some small, highly reflective fragments identified as X#2. This material gives the x-ray fluorescence spectrum shown in Figure IV-9. It appears to be a mixture of potassium and iron sulfide and might be $3K_2S \cdot 4FeS$.

FIGURE IV-8. Electron Photomicrograph of Black Area, 500X

FIGURE IV-9. Reflective Features, X#2

The grey feature at the extreme left identified as X#3 yields the x-ray fluorescence spectrum shown in Figure IV-10. This appears to be the mixed carbonates and is unusually high in calcium. The darker grey area identified as X#4 gives the x-ray fluorescence spectrum of Figure IV-11. This shows the sodium and potassium carbonates. It may also contain Li_2CO_3 , which cannot be detected. The signals for sodium and potassium are relatively weak, so an undetected diluent is probably present. The absence of calcium here and its increased concentration in the lighter grey phase, X#3, indicates CaCO_3 precipitates from its solution in the alkali carbonates as the melt cools.

The fluffy-appearing feature, X#5, gives the x-ray fluorescence spectrum in Figure IV-12. This is high in chromium, and the chromium does not appear to be present as its sulfide.

FIGURE IV-10. Light Grey Feature, X#3

FIGURE IV-11. Dark Grey Feature, X#4

FIGURE IV-12. Feature Containing Chromium, X#5

Figure IV-13 is a general area scan at 100X of the features illustrated in Figure IV-8. This puts the relative concentrations of the elements in proper perspective. There clearly isn't much chromium present. Nickel and manganese are barely detected. Iron is the principal impurity element present.

It must be stressed that the segregation of materials evident from the photomicrograph and the x-ray fluorescence analyses is due to freezing and crystallization processes. The distribution of these elements would be much different (more uniform) in the molten state.

ORGANIC IMPURITIES (TARS AND OILS)

When the gasifier was operated on coal, tars and oils were carried over into the venturi scrubber and dispersed with the molten salt. At 700°C the nonvolatile tars would track with the coalescing salt phase. These would tend

FIGURE IV-13. General Area Scan

to float on the molten salt, spill over the standpipe, and return to the venturi feed tank. Feed to the venturi is out the bottom of the tank, and it would seem that the nonvolatile tars would not escape. They would gradually pyrolyze to carbon plus volatiles and disappear.

At times the coarse de-entrainer would be drained completely. At such times nonvolatile tars could flow through the salt cooler and regeneration column. Wax-like benzene and/or acetone-soluble materials have been isolated from the regeneration column. These have comprised a very small percentage of the salt; however, if these waxes associate with black solids and other particles, they could have adverse effects on column operation out of proportion to their concentration.

A portion of the tars are sufficiently volatile to make it through the entire extraction section. A product gas sample taken just downstream of the packed-bed de-entrainer was removed through a condenser that was flushed with

a co-currently flowing stream of water. The cooled gas was passed through two aqueous scrubbers and was metered before being routed to the secondary burner. Large gas samples on the order of 250ℓ to 500ℓ were collected.

During run C-11 the benzene-soluble tar content of the product gas ranged from 229 mg/M³ to 355 mg/M³. This fraction of the tars and oils would appear to be of no concern to turbine operators.

V. RUNS C-6 AND C-7

SUMMARY, RUN C-6

Run C-6 was the first made with CaCO_3 present in the salt (~20 mole%). CaCO_3 was added in an effort to reduce the apparent corrosivity of the salt. Part of the salt was discarded to permit addition of salt containing CaCO_3 .

In run C-6 the venturi scrubber was operated for approximately 3.5 hr, after which time salt flow could not be maintained. The venturi was later found to be plugged with black iron-bearing solids at the orifice. The extraction column operated under flow for about 1/2 to 3/4 of an hour and with static pools of salt for the remaining period. The regeneration column operated for 15 min to exhaust its feed supply, which could not be replenished with the venturi being inoperative.

The extraction section produced good overall sulfur recovery. The sulfur content of the product gas was in the range of 122 to 128 ppm sulfur.

PERFORMANCE OF THE EXTRACTION AND REGENERATION SECTIONS, RUN C-6

For a brief period from 05:45 to 09:25 (2/14/78) salt was flowing to the venturi orifice at a somewhat irregular and perhaps sporadic rate. From 05:00 to 05:30 salt flowed to the extraction column at a rate of about 130 ml/min. The flow was increased to 3.6 l/min, when the valve was opened wider. When this increase was detected, the valve was hurriedly closed. The column operated with static pools of salt on the trays until 09:10, when flow was resumed. Flow to the extractor was valved off again at 09:30.

Figure V-1 shows the results of analysis of gas samples. G-1 samples taken in the gasifier outlet line beginning at 03:00 (not shown) were showing a rapid increase in total sulfur content (to 801 ppm at 04:07). The gasifier was refueled shortly thereafter and the sulfur content of the inlet gas dropped to 267 ppm and then again began to climb.

FIGURE V-1. Performance of the Scrubber During Run C-6

Diamond-shaped points mark the V-1 samples taken at the coarse de-entrainer. These samples permit evaluation of the venturi performance (cf. Table V-1). The venturi improved steadily despite evidence that salt flow was

TABLE V-1. Extraction Section Performance
During Run C-6

Venturi Scrubber			
<u>Time</u>	<u>Inlet Gas, ppm S</u>	<u>V-1 Gas, ppm S</u>	<u>%S Removed</u>
05:45	315	248	21.3
06:45	367	238	35.1
09:25	460	204	55.7
10:55	500	203	59.4
Extraction Column (Including Venturi)			
<u>Time</u>	<u>Inlet Gas, ppm S</u>	<u>Lower Tray, ppm S</u>	<u>%S Removed</u>
06:05	332	110	66.9
07:10	386	110	71.5
		<u>Upper Tray, ppm S</u>	
10:25	490	92	81.2
		<u>Product Gas, ppm S</u>	
07:21	390	122	68.7
11:12	510	128	74.9

erratic. Improvement may have been caused by a gradual reduction in gas water content as the fuel bed was dried out.

A further reduction in sulfur content of the gas was achieved as it passed through the extraction column. Samples taken above the lower tray were measured at 110 ppm and a single sample taken above the top tray measured 92 ppm.

G-3 samples are taken in a 3-in. line between the packed-bed de-entrainer and the secondary burner. The two samples obtained measured 122 ppm and 128 ppm. These values are inconsistent with values at A-1 and A-2, and probably reflect the fact that salt carried into the packed-bed de-entrainer is higher in sulfur than salt on the trays of the column below. This probably would not be the case at steady-state operating conditions.

It was the intention to circulate the salt inventory for a few hours to build up a reasonable sulfur content before starting the regeneration column, but the plugged venturi upset these plans. When it was determined that no further flow to the venturi was possible, the regeneration column was operated for the period necessary to exhaust the supply of salt in the coarse de-entrainer. This was about 15 minutes. Meaningful analytical data was not obtained in this short time period.

CHRONOLOGICAL DESCRIPTION OF RUN C-6

This was the first run attempted using 20 mole% CaCO_3 in the salt. CaCO_3 was added in hopes of suppressing what appeared to be serious corrosion effects (cf. sections III and IV for details).

Prior to the start of this run the samplers on the extraction and regeneration columns were modified as described in Part I, Section V (cf. Figures V-2 and V-3). The bellows-sealed valves that controlled flow to the venturi and to the extraction and regeneration columns were removed. These were replaced with suitably modified gate valves. No time was taken to have these alonized prior to their installation, and corrosion forced their replacement during run C-14.

The salt was drained from both the venturi feed tank and the salt makeup tank. The standpipe was removed to permit the salt makeup tank to drain completely. This was easy to accomplish because access through the small lock hopper allows removal. The standpipe in the venturi feed tank cannot be reached without taking off the tank lid, which is a major task, so a heel was left in this tank. Fresh salt of the composition shown in Table V-2 was added to the salt makeup tank (~110 lb). It is never possible to completely empty

TABLE V-2. Salt Composition, Run C-6

<u>Component</u>	<u>Mole%</u>	<u>Wt%</u>
Li_2CO_3	35.2	27.3
Na_2CO_3	25.5	26.5
K_2CO_3	20.2	27.5
CaCO_3	19.1	18.8

the system. Salt is held up in the extraction and regeneration columns, the salt cooler, and as a heel in the coarse de-entrainer and venturi feed tanks. This can amount to 20 to 25 l.

Run C-6 was started at 08:00 on 2/13/78. Heatup of trace heating required 7 to 8 hr because of the severely cold weather which prevailed at the time. Difficulty was encountered in starting the secondary burner and this delayed start of the gasifier until nearly 16:00. It wasn't until 03:30 (2/14/78) that gas was first routed to the molten salt scrubber. The sudden increase in pressure within the gasifier resulted in a high leak rate at a seal on the lock hopper and a CO alarm forced re-routing of gas via the bypass line.

Correcting the problem required removal of clamps and a seal plate on top of the lock hopper, so it was decided to proceed with refueling. An additional 800 lb of coke was added to permit an extended run without interruption.

At 04:50 gas was again routed to the venturi scrubber. At 05:10 the valve to the venturi was opened, but salt flow was not attained until 05:45. Salt flow of a somewhat variable or even sporadic nature was maintained to the venturi until about 09:25, when the orifice plugged and flow could not be restarted.

Flow to the extraction column was initiated at 05:00. By 05:30 only 3 or 4 liters had flowed to the column, so the valve was opened wider. Within the next 7 min about 25 additional liters flowed to the column and the valve was closed again. The valve was opened briefly at 09:10 and closed at 09:30. These operational sequences and gas flow routings are illustrated at the bottom of Figure V-1.

Attempts were made to start the regeneration column at 10:08 even though it was clear that only very brief operation would be possible unless flow to the venturi could be established. The coarse de-entrainer contained 14 to 15 in. of salt at this time. Immediate flow response was obtained and operation continued for 20 to 30 min., at which time the feed supply was exhausted.

Post-run examination of the venturi feed line indicated there were sufficient black solids washed from the columns and from various tank heels to cause plugging of the venturi orifice. This occurred despite addition of 110 lb of fresh salt. The presence of CaCO_3 caused no problems.

RUN C-7 SUMMARY

Run C-7, also with 20 mole% CaCO_3 in the salt, was made following modification of the venturi to allow introducing CO_2 purge gas directly into the inlet orifice. The gate in the valve that admits salt to the venturi was also slotted on the downstream side so that the CO_2 purge around the valve stem would clear salt out of the line. This worked very well, and no plugging of the venturi orifice occurred during this run. Continued plugging of the venturi orifice in later runs, however, showed this was not an adequate solution to the problem.

In run C-7 the venturi scrubber was operated for about 4-1/2 hours. The extraction column also operated during this period, but with salt flowing in three short periods of 30 min., 10 min., and 15 minutes. The remainder of the time, the trays contained a static pool of salt.

The extraction section produced good sulfur recovery, with the product gas ranging in total sulfur from 41 to 203 ppm.

The regeneration column was not operated. Salt flow to this column could not be initiated, due to failure of a trace heater in a line feeding the column.

The run was terminated when the gas preheater failed. This caused cold gas to enter the scrubber resulting in soot deposition. This, in turn, caused a deposit to build in the 2.5-in. venturi exhaust line and resulted in pressure drop that prevented salt circulation.

PERFORMANCE OF THE EXTRACTION AND REGENERATION SECTIONS, RUN C-7

Gas flow was routed to the venturi scrubber at 14:40 (2/27/78). Flow was established to the venturi scrubber at 14:50. The valve was cycled between open and closed positions occasionally, and the action of the CO_2 purge that

cleared the line between the valve and the orifice was noted. Except for these brief lapses, flow to the venturi was maintained from 14:50 to 18:55.

As shown in Figure V-2, the flow of salt to the extraction column was in a series of brief spurts. Flow was first initiated at 14:00, was off at 14:33, back on at 15:10, et cetera. Overall performance of the extraction section was good despite the variable flow. The smooth curve defined by the G-1 and G-2 samples represents the inlet gas sulfur content. The dashed curve defined by diamonds represents the venturi outlet gas composition at the coarse de-entrainer. The reduced sulfur at the coarse de-entrainer is due to the action of the venturi extraction stage. The efficiency of the venturi decays with time as the salt sulfur content increases.

The extraction column effects a further reduction in sulfur content of the gas. Not enough time was available during this short run to obtain sufficient data to fully characterize the column performance, but the gas samples all indicate gas of good quality was being produced.

The regeneration column was not operated because a trace heater on the line coming out of the coarse de-entrainer and connecting to the salt cooler had failed. It was not possible to establish flow to the regeneration column.

It was necessary to terminate the run when the gas pre-heater failed. Cool gas entering the venturi scrubber caused soot deposition, loading the salt with carbon to the point where circulation of the salt could not be sustained.

CHRONOLOGICAL DESCRIPTION OF RUN C-7

Run C-7 was initiated following modifications to the venturi scrubber that consisted of drilling a 1/8-in. hole into the 1-in.-long x 1/4-in. venturi salt inlet port, so as to intersect this port at about the midpoint. This hole was used to introduce a CO₂ purge designed to keep the inlet port open and to prevent plugging of the orifice.

This modification, together with provision of a slot in the downstream side of the gate in the gate valve in the venturi feed line, seemed to be effective in maintaining flow to the venturi. Purge CO₂ would escape

FIGURE V-2. Performance of the Extraction Section, Run C-7

through the slot to keep the line between the valve and the venturi orifice free of salt so that solids would have no place to settle out. No plugging problems were experienced during run C-7; however, as will be seen later, additional modification of the venturi inlet orifice was necessary.

These modifications to the venturi salt inlet orifice provided an opportunity to inspect the alumina liner. This was found to contain a few cracks, which appeared to be minor, but no corrosion or erosion was evident. It was decided to take the opportunity to replace the liner, which was removed only with considerable difficulty, and a new liner was installed.

The run was initiated at 02:00 with start of heatup. With this early start the gasifier was started about 11:00, and at 14:07 salt flow to the extraction column was initiated. At 14:33 the column was valved off, and during this 26-min period 18 ℓ of salt flowed to the column for an average flow rate of 692 ml/min.

The venturi feed valve was opened at 14:50 with immediate flow response. The valve was closed and opened two or three times during the next hour, and each time the CO₂ purge cleared the line and immediate salt flow response at the venturi was noted on re-opening the valve.

Intermittent addition of salt to the extraction column was continued to fill the venturi feed tank and the coarse de-entrainer. By 15:43 salt had overflowed the standpipe in the coarse de-entrainer and operation in recycle mode began--i.e., with salt returning to the venturi feed tank via the 4-in. gas-salt return flow line.

At 17:00 salt flow to the extraction column was valved off to prevent overfilling the venturi feed tank. At this point it was necessary to get the regeneration column operating to have a place to put salt flowing to the extraction column and on to the venturi feed tank. Difficulty was being experienced here in that it was not possible to establish salt flow to the regeneration column.

Another problem had appeared at 16:00 when the data logger began indicating an over-temperature in the 2.5-in. venturi exhaust section just above the venturi. Investigation disclosed that the gas preheater was not heating and the trace heaters on the line were staying on in an effort to heat the cold entering gas. This caused an excessive pipe wall temperature in some areas and low temperatures in others.

Unfortunately, the molten salt catalyzes the Boudouard reaction,^(a) but at the low temperatures which prevailed the position of the equilibrium favored carbon deposition (with loss of CO from the fuel gas). Local soot accumulation in the climbing film of salt on the venturi exhaust line formed a thick sludge that produced a condition resembling flooding, wherein excessive salt is present. This resulted in excessive pressure drop, with pressure drop increasing to the point where no further circulation of salt was possible, and salt flow was valved off.

The problem with the regeneration column was traced to a failed trace heater in the line leading out of the coarse de-entrainer and connecting to the salt cooler. Repairing this would entail several hours' delay; however, when it was found that the gas preheater could not be repaired, the decision was reached to terminate the run.

Inspection of the gas preheater disclosed open circuits on all heating elements. When the heating elements were removed, severe damage was evident. It appeared the unit had been near the end of its useful life for some time. The heating element sheath material (321 SS) showed generalized corrosion and carbonizing. The metal was flaking away and was extremely brittle and fragile. The elements were obviously contributing significantly to the burden of iron and other elements found in salt samples and presumed to be arising from corrosion.

It appeared that seven or eight of the heating elements had failed catastrophically. The over-temperature protection thermocouple is clamped to one of the elements. If this element should fail and cool, the over-temperature protection is lost. This may have been the reason for failure of so many elements.

The internals involved were replaced by the original supplier and the unit was back in service after a delay of about six weeks. The failed trace heater below the coarse de-entrainer was also repaired.

(a) $2 \text{ CO} \rightleftharpoons \text{CO}_2 + \text{C}$.

VI. RUN C-8

SUMMARY

Run C-8 was conducted in two segments because a forced shutdown due to a plugged venturi orifice was reversed when the orifice was cleared in time to restart the gasifier. This run disclosed that the purge gas inlet to the venturi orifice, installed after run C-6, does not suffice to prevent plugging of the venturi orifice. During this run the orifice plugged at points upstream and downstream of the point where the purge inlet intersects the venturi orifice. After run C-8 the venturi orifice was reamed out to reduce the potential for plugging, and a port was installed opposite the orifice to allow rodding when the orifice did plug (cf. Run C-9).

The regeneration column overflowed and plugged the H_2S exhaust line, prohibiting further operation of the column. The operating data indicated that the column either contained plugged risers or had been incorrectly fabricated. Run C-9 was made to assess this possibility. The siphon leg at the bottom of the regenerator may have frozen, thus aggravating the overflow problem.

Good sulfur recovery was obtained during the brief period of operation of the extraction section. No data was obtained from operation of the regenerator.

PERFORMANCE OF THE EXTRACTION AND REGENERATION SECTIONS, RUN C-8

Figure VI-1 illustrates the sequence of events during the run and gives the results of gas analyses for H_2S and COS (reported here as $COS + H_2S$). Due to difficulties in maintaining salt flow at the venturi orifice, the run occurs in two segments. The gasifier and scrubber were actually shut down for a time between segments.

On 4/11/78 the scrubber operated from 13:15 to 16:45 under fuel gas flow, but salt flow to the venturi was only on for about 1-3/4 hr of this period. As shown in Figure VI-1, the regeneration and extraction columns received intermittent salt feed during this period. Gas phase analyses, though few in

FIGURE VI-1. Performance of the Extraction Section, Run C-8

number show the extraction section performed well. The samples taken in the extraction column all indicate sulfur recoveries in the 93% to 90% range. Sulfur recoveries at the venturi outlet ranged from 71% to 91%.

A few samples were analyzed within the regenerator, but not until after salt flow had ceased and the steam flow was off. The results have only qualitative significance.

The venturi salt feed was valved off to prime the trays in the extraction column, and salt flow could not be restarted. Salt flow was regained the next morning, so the run was restarted. In this portion of the run the feed to the extraction column was started first, and was followed by start of feed to the regenerator and finally to the venturi scrubber. For a brief period all systems were operating, but at 17:45 salt suddenly overflowed the regeneration column, forcing shutdown of this unit. The venturi scrubber was operated until 20:40, at which time it plugged and the plant was shut down.

Figure VI-1 shows that the extraction section performed well during this period. By starting the feed to the extraction column first the column contained pools of fairly clean salt on the trays. Unfortunately, salt samples were not taken, but calculations indicate that the salt contained less than 0.25% sulfur. Inspection of Table VI-1 shows sulfur recovery was very high. In the extraction column H_2S levels were of the order of 11 to 12 ppm, with COS at 9 to 10 ppm.

The regeneration column was evidently flooding from the start, and in the light of observations made during run C-9, it is clear that proper operation of the column was not possible. All sample ports were giving problems and the technicians were unable to obtain samples for analysis.

CHRONOLOGICAL DESCRIPTION, RUN C-8

Run C-8 was initiated at 24:00 on 4/11/78. The gasifier was fueled at 08:00, and at 13:15 gas was routed to the scrubber; after a few minutes' delay, salt flow to the venturi was achieved at 13:55. Salt flow was maintained until 14:23 to fill the coarse de-entrainer. Salt flow to the venturi was resumed at 14:30, when it was assumed that salt flow to the regenerator had been achieved. The regenerator was actually receiving salt flow,

TABLE VI-1. Performance of the Extraction Section
During Run C-8 on 4/12/78

Venturi Scrubber (Only)					
Time	Inlet Gas, ppm S	Venturi Outlet Gas			% Sulfur Recovered
		COS, ppm	H ₂ S, ppm	S, ppm	
17:13	375	22	22	44	88
18:05	450	42	45	87	81
18:34	550	39	28	67	88
19:23	610	208	112	320	48
20:22	720	77	103	180	75

Venturi Scrubber & Extraction Column						
Time	Inlet Gas, ppm S	Sample Point	COS, ppm	H ₂ S, ppm	S, ppm	% Sulfur Recovered
17:32	380	A-2	9	12	21	94
17:46	420	G-3	18	23	41	90
18:22	490	A-1	10	12	22	96
19:35	610	A-2	10	12	22	96
19:47	640	A-1	9	11	20	97
19:57	650	A-0	75	12	87	87
20:34	710	A-2	9	16	25	96
20:48	710	A-1	9	19	28	96

but with intermittent deliberate stoppages to ensure the trays were priming from 15:20 to about 16:20. The extraction column was receiving a small flow (perhaps an intermittent flow) of salt from 15:35 to 16:20.

At about 15:40 the venturi feed valve was closed and gas flow bypassed for a few seconds to allow the extraction column trays to prime. No further salt flow to the venturi could be obtained after this, and after several hours the decision was reached to shut down.

The following morning a steam lance was directed through the CO₂ purge recently installed into the venturi orifice, which in this instance was plugged upstream of the purge inlet point. Within an hour the obstruction

was cleared and it was decided to continue the run if the gasifier would restart on its residual heat. Restart was achieved, and by 14:30 (4/12/78) another 800 lb of coke was added.

At 17:07 salt flow to the venturi was valved on with immediate flow response. Meanwhile, salt flow to the extraction column had been initiated in a series of pulses to fill the venturi feed tank. Salt flow to the regeneration column, also in pulses, had been initiated at 16:47. Thus, at 17:07 all systems were in simultaneous operation.

Problems with the regenerator were immediately evident. The ΔP at trays 6 and 7 was erratic and too high. Suddenly, at 17:45 salt began leaking from a flange in the H_2S exhaust line above the regeneration column and it was obvious the column was flooding. In fact, it was overflowing.

The salt that reached the H_2S exhaust line froze and plugged this line, which is heated only to 150° to $200^{\circ}C$ to prevent steam condensation. This prohibited further operation of the regeneration column.

The venturi scrubber was operated until about 20:40, when the orifice again plugged. The plug this time was downstream of the CO_2 purge entry point. CO_2 pressure merely forced salt back up the venturi feed line, but did not free the obstruction. The combination of difficulties led to a decision to shut down about midnight.

VII. RUNS C-9 AND C-10

SUMMARY, RUN C-9

Salt overflow problems at the regeneration column during runs C-5 and C-8 led to the conclusion that the column was incorrectly fabricated or was plugged. Run C-9 was made expressly for the purpose of determining the condition of the regeneration column. Salt feed to the extraction column and venturi scrubber was solely for the purpose of filling the coarse de-entrainer, which is the feed reservoir for the regenerator. Salt feed to the venturi and extraction columns was suspended while the regeneration column was operated so that level measurements in the coarse de-entrainer could be made precisely to yield an accurate measure of average (and total) flow to the regeneration column. This procedure reduced the data obtained from the extraction section. Product gas contained <200 ppm sulfur, with recoveries in the range of 70 to 95%.

It was found that the regeneration column was plugged either at tray 6 or 7. The column was thoroughly cleaned with HNO_3 , water and steam, and was disassembled at the end of the run. The center segment containing trays 4, 5, 6 and 7 was removed. Tray 7 was visible and appeared to be clear, so the column segment was cut to expose tray 6. The risers on this tray were found to be completely plugged. Most of the obstructing material was derived from the pack-alonizing treatment, but a part may have been derived from insoluble process impurities. These would have to be insoluble in 1:1 HNO_3 (aq).

Run C-9 confirmed that the regeneration column could not be operated. Salt could flow through the column only under conditions of minimum (or no) gas flow. With design steam- CO_2 rates, salt entering the column would inevitably be forced out the H_2S exhaust line, as occurred during runs C-5 and C-8.

A port was installed on the venturi to allow mechanical cleaning of the venturi orifice. This proved to be effective and was used a number of times in this and following runs.

OPERATING DATA, RUN C-9

During operation of the regeneration column the ΔP sensor across trays 6 and 7 was observed to cycle between 6 in. and 10 in. of water at low inlet gas flow and to peg out at inlet gas flows of over 0.8 SCFM CO_2 . It appeared that gas flowing up the column was trapped below plugged risers on one of these trays and developed pressure sufficient to drive downflowing salt back up the downcomer. This relieved the pressure for an instant, and the salt resealed to allow the pressure to build again.

This was demonstrated three times by carefully metering salt from the coarse de-entrainer through the column while varying the gas flow rate. As the gas flow was increased, the ΔP gauge pegged out at 10 in. H_2O and remained pegged. With this much pressure, gas would flow continuously up the downcomer (because it cannot go up the risers) and salt was prevented from flowing down. With continued addition of salt the column would overflow, as happened in runs C-5 and C-8. The only way salt can make it through the column is with low or no gas flow. By deliberate flow manipulation it was possible to build an accumulation of salt above the tray containing the plugged risers, and to then dump it down the column into the salt makeup tank. This, of course, is not a practical operating mode. It was clearly necessary to effect repairs before continuing operations.

Modifications to the venturi described in section C (below) proved to be effective. The orifice continued to plug, but when it did so it could easily be re-opened with the poker.

CHRONOLOGICAL DESCRIPTION OF RUN C-9

Run C-8 was terminated when substantial quantities of salt overflowed the regeneration column. This filled the H_2S exhaust line, penetrating all the way to the burner block in the secondary burner. The H_2S exhaust line (over 30 ft in length) is normally not heated above 200°C , and there was no convenient way to melt the concrete-like solid salt from this pipe. Mechanical or chemical means would be laborious and time consuming. It was cheaper to fabricate a new line from 304 SS. The burner block in the secondary burner also had to be replaced.

It was evident the column had overflowed when salt leaked from a poorly made flange in the H_2S exhaust line. Salt feed was immediately valved off and steam- CO_2 flow turned down (possibly off). This last action was an operating error, for salt backed into the steam- CO_2 inlet line and filled the steam- CO_2 preheater--and even got into portions of the 1-in.-dia steam line between the superheater and the steam- CO_2 preheater. As much as 1.5 to 2 gal of salt was lost to this section.

The steam- CO_2 preheater is a 2-ft-long x 8-in.-dia stainless steel pall-ring-packed heat exchanger. It was approximately half filled with salt, which had to be leached out with nitric acid. The section of 1.5-in. line between the preheater and the column (which was filled with salt) had to be replaced, and parts of the steam line to the preheater had to be rebuilt. To prevent a recurrence of this problem, a trap that could hold up to 3 gal of salt was installed in the H_2S exhaust line, and a check valve was inserted in the line between the preheater and the regeneration column.

Erratic operation of the venturi scrubber caused by plugging of the 1/4-in.-dia x 1-in.-long salt inlet orifice continued, despite provision for purge CO_2 introduction near the middle of the orifice that was made prior to run C-6. The salt inlet orifice introduced the salt into the venturi scrubber just below the shoulder that supports the ceramic liner. The orifice was located at the bottom of the 1-in.-dia salt inlet line. It would plug with solids that settled out near the orifice inlet. The CO_2 purge would not remove the plug. To reduce the probability of plugging, the orifice was reamed so that it was 1/4 in. in dia on the inlet side (for flow control) and 1/2 in. in dia on the outlet side. An access port was provided immediately opposite the orifice so that a poker could be inserted to remove obstructions. With these preparations complete, run C-9 was initiated on 4/26/78.

Figure VII-1 is a graphical representation of run C-9. The gas routing, venturi valve positions, and fuel or salt additions are shown at the bottom of the figure. Upward-pointing arrows indicate salt flow to the venturi is on. The figure shows salt flow to the venturi rarely remained on for more than

FIGURE VII-1. Run C-9 Graphical Summary

20 min. at a time (just long enough to fill the coarse de-entrainer). This was equally true of the extraction column, which received only short spurts of salt.

The middle portion of Figure VII-1 shows tank level fluctuations in the salt makeup tank and in the coarse de-entrainer. The filling sequences for the coarse de-entrainer can be observed to coincide with opening of the venturi feed valve.

The upper portion of the figure shows gas phase analytical data. This would normally indicate the performance of the extraction section with respect to sulfur extraction. In this case, the extraction section was operated for such brief periods (between operations of the regeneration column) that the analytical technicians rarely had time to take meaningful samples.

The analytical technicians were instructed to measure inlet and outlet gas samples (e.g., G-1 and G-3). These show that overall sulfur recovery in the extraction section was quite good. The first G-3 sample was taken just after the venturi operated briefly from 16:00 to 16:16, and showed only 24 ppm sulfur (11 ppm COS, 13 ppm H₂S) for an indicated recovery of 96%. The next two product gas samples taken while the venturi was off, and with static pools of salt on the trays of the extraction column effectively the only factor operating, gave values of 133 ppm and 187 ppm sulfur. The venturi and extraction column then received salt while the coarse de-entrainer filled, and the next G-3 sample was back down to 71 ppm sulfur. After refueling the gasifier, gas was routed through the scrubber for over 2.5 hr with no salt flow. The G-3 sample at 23:46, containing 247 ppm sulfur, reflects the buildup of sulfur in the static salt pools in the extraction column. A final pulse of salt introduced at about 01:30 (4/28/78) again causes improved extraction, as shown by the G-3 sample at 01:40 at 210 ppm. The sample may have been taken too soon to reflect the full effect of this last salt addition. It is clear the G-3 samples accurately reflect operational variables.

System heatup was started at 15:00 (4/26/78). Portions of the venturi feed line failed to heat, and the affected trace heaters were replaced. At 24:00 the gasifier was started. By 06:10 (4/27/78) gas flow was routed to the

scrubber, and at 07:50 attempts to start salt flow to the venturi failed and it was found that another trace heater on the venturi feed line had failed. This was replaced and, using great care, the line was re-heated--but the same heater failed again. Heaters on either side of the failed heater were functioning, so additional insulation was added, and at 16:00 salt flow to the venturi was finally achieved.

As soon as salt flow to the venturi was established the valve feeding salt to the extraction column was opened. After about ten minutes it was clear that the top tray of the extraction column had not primed. Gas flow was bypassed for a few seconds to allow sufficient accumulation of salt to prime the tray. This required that the salt flow to the venturi be shut off. When the venturi feed valve was re-opened salt flow was not achieved. The cap was removed from the access port and the venturi orifice was rodded out. At 17:15 full salt flow was obtained. The venturi was operated until about 17:40, when it was shut down. At this point the coarse de-entrainer was full. It was desired to operate the regenerator by carefully monitoring average flow rate to the column through frequent level measurements in the coarse de-entrainer. This is only meaningful if no salt is entering from the venturi.

Operation of the regeneration column continued from 17:40 until about 18:45. During this time the gauges measuring pressure drop across the trays behaved erratically. The pressure drop across trays 6 and 7 was abnormally high and was cycling between approximately 6 and 10 in. H_2O . It was concluded that the risers on either tray 6 or 7 were plugged. Gas flowing up the column was trapped below a tray on which the risers were plugged. When a sufficiently high pressure was obtained the gas would blow the liquid up the downcomer to relieve the pressure momentarily. The liquid would reseal and the pressure would start building again. At higher gas flow rates the gas pressure below the tray was high enough to keep the liquid blown out of the downcomer and continually held on the next-higher tray. In effect, no salt could flow down the column. This is the reason severe overflows of salt occurred during runs C-5 and C-8.

At about 19:24 the venturi was restarted to fill the coarse de-entrainer with salt so that the regeneration column could be operated at various gas

flow rates. The salt feed was started to the regeneration column at 20:50 and was shut off after ten minutes. The siphon tube that takes the salt from the regeneration column had plugged. When this siphon was cleared the venturi was restarted (at 23:20) to refill the coarse de-entrainer. At 23:45 an attempt was made to restart the regeneration column. Salt flow did not start when the feed valve was opened. At 01:09 (4/28/78) salt flow to the regeneration column was obtained, and the column was operated until 01:16. This operation of the regeneration column confirmed that the pressure drop across trays 6 and 7 was abnormally high. The venturi was operated again from 01:23 to 01:44. During this time the venturi was operated with insufficient gas flow to maintain a climbing film in the venturi exhaust line, and salt was lost to the emergency salt reservoir.

Seventy-eight pounds of fresh salt was mixed and added to the salt in the upper tank. This addition was completed at 03:30. After allowing the fresh salt to be heated to operating temperature, the extraction column feed valve was opened at 05:00. It was discovered that heating elements had failed on the feed valve to the extraction column and flow could not be established. This effectively shut down salt flow and it was decided to terminate this run and proceed with repairs to the regeneration column.

When equipment had cooled the regeneration column was thoroughly flushed with water and nitric acid. The center segment of the column was removed, which exposed tray 7 (the topmost tray in this segment). The risers appeared clean on this tray. The column was then sectioned on a lathe so as to expose tray 6, and here the risers were found completely plugged with material (Al_2O_3) that appeared to have derived from the pack-alonizing process of corrosion-proofing.

The top and bottom segments of the regeneration column were joined to yield a column containing four trays. This is believed sufficient to permit salt regeneration.

Material from the plugged risers on tray 6 was examined with the scanning electron microscope. The x-ray fluorescence spectrum shows aluminum as the principal constituent (Figure VII-2). The material is presumed to be Al_2O_3 derived from the alonizing treatment.

FIGURE VII-2. X-ray Fluorescence Spectrum of Material from Plugged Risers

The plugged section of the column trapped substantial quantities of insoluble material, much of which washed out during the vigorous washing with HNO_3 , water and steam. Large black flakes were found one of which measured 1/4 in. x 3/8 in. and had a thickness of a few mils. The x-ray fluorescence spectra of the top and bottom sides of this flake (Figures VII-3 and VII-4) clearly reveal its origin as a flake from the sheath material on the gas pre-heater. Such material would be especially prone to lodge and obstruct small openings.

FIGURE VII-3. Top Surface of Large Black Flake
Washed from the Regenerator

FIGURE VII-4. Bottom Surface of Flake

SUMMARY, RUN C-10

Run C-10 was started at midnight on May 22, 1978. When the scrubbing system was heated to operating temperature and the gasifier was started it was discovered that a heating element on the salt makeup tank drain line had failed. The start of salt flow was delayed several hours while this element was replaced and the line was brought back up to operating temperature. When salt flow was started, the venturi feed tank was filled in preparation to start the venturi scrubber. As this was attempted it was discovered that the heating elements were not working over a 2-ft section of the venturi feed line. Inspection revealed that the 1-in. pipe that comprised the venturi feed line had ruptured, releasing a moderate salt leak that shorted out the heating element in that area. It was decided to terminate the run and replace the venturi feed line.

The 1-in.-dia schedule 40 alonized 304SS pipe had expanded and split open as a result of heating to melt salt in the line. When heating is non-uniform a molten zone can become trapped between plugs of still-frozen salt. Continued heating causes the liquid to expand, producing high stresses on the pipe wall. Dimensional measurements showed both the venturi feed line and the salt makeup tank drain line had expanded sections. The venturi feed line had been cycled through the salt melt temperature about a dozen times before it failed.

To reduce the stress on these lines, variable transformers were obtained and placed in the circuit to reduce the applied voltage on the trace heating units. In addition, the circuit on the venturi feed line was divided into two circuits. It was divided in such a way that heaters opposite one another (e.g., as split half segments) were on different circuits. Thus, in event of a heater failure the heater on the opposite side of the pipe would pick up the load and shutdown would not be required. With these modifications it was possible to heat the line slowly and uniformly. No further problems were encountered with this line during the 6 runs which followed. The reduction in voltage dramatically increased the dependability of heaters used on the 1-in. salt transfer lines.

VIII. RUN C-11

SUMMARY

From an operating standpoint, run C-11 was the most successful run made. All equipment was operated over fairly extended periods of time. Simultaneous operation of all systems was achieved during one period of nearly eight hours, and for another period of over three hours' duration. A total of 3700 lb of coal and coke were gasified. During this run, 20 hr of venturi operation were logged; the maximum continuous operating time was nearly 8 hours. The extraction column operated with salt flow for 13 hr, with a maximum continuous operation of nearly 8 hours. The regenerator operated for a total of 13.4 hr, with a maximum continuous operation of over 8 hours.

While continuous operation was achieved over fairly long periods, it was not possible to maintain steady salt flow rates to the extraction column and regenerator. In addition, the flow rate to these units was much higher than desired (approximately 6X the design basis). The salt flow rate far exceeded the capacity of the salt cooler, making it impossible to adequately cool the salt for regeneration. As in most other runs, the scrubber system was started up with only the H_2S present in the raw fuel gas from the gasifier. It was planned to increase the H_2S concentration by addition of H_2S cylinder gas after all units were operating smoothly. This H_2S gas addition was about to start when the forced shutdown occurred. Because of the high temperature in the regenerator and the modest H_2S content in the fuel gas, the H_2S concentration in the strip gas remained fairly low, reaching a maximum of 2.3% on a dry basis. The ability to adequately regenerate the salt also suffered somewhat; it was, however, possible to show a significant reduction in salt sulfur loading due to operation of the regenerator. Early in the run, sulfur removal through the scrubber system was quite good. After the salt became loaded with sulfur the cleaning efficiency became somewhat less, as would be expected. Sulfur removal and regenerator performance were roughly as predicted by theoretical calculations.

Alkali metal concentration was measured in the product gas and found to be approximately 13.6 mg/M^3 . This is about 10 times the allowable concentration for turbine applications.

The run consisted of four major operating periods, with some debugging, troubleshooting and maintenance occurring between each of these. Each of the first three operating periods was ended when it became necessary to shut down and refuel the gasifier. The fourth operating period (and the run) ended when several furnace elements on the salt cooler burned out and salt within the unit froze. Spare elements were on hand and could have been installed; however, when they were unpacked it was found that they had been damaged in shipment, eliminating any possibility of resuming operation within a reasonable length of time.

After the run it was apparent that it would not be possible to control salt flow at the design basis value of $\sim 500 \text{ ml/min}$ with the gate valves that had been installed. The small opening required to restrict flow down to this low rate was prone to plugging with solids entrained in the salt, so that probably no valve would have been entirely satisfactory. Calculations showed that the plant should give reasonably good performance at higher flow rates, provided that better cooling of the salt in the regenerator could be achieved. For runs following C-11 it was planned to increase the cooling air rate to the salt cooler and to cool the top tray of the regeneration column in order to reduce the salt temperature in the regenerator. Unfortunately, in subsequent runs it was never possible to operate the system long enough to evaluate the effectiveness of these measures.

It was found during the run that by injecting liquid water on top of the coal bed in the gasifier the fuel gas could be humidified sufficiently to suppress carbon deposition in the scrubber system. This reduced the extraction efficiency. At higher operating temperatures carbon deposition should not be a problem. Water injection should not be required above $\sim 750^\circ\text{C}$. At temperatures much below 700°C , suppression of carbon deposition may be difficult or impossible.

GAS CLEANING PERFORMANCE

Run C-11 consisted of four main operating periods separated by coal feeding, maintenance, and several attempted starts. During each of these periods significant data was obtained on performance of the scrubber system; data on performance of the regenerator was obtained during two of these periods. The system operated about as expected; however, undesirably high liquid flow to the regenerator resulted in excessive temperature in that unit, which precluded efficient regeneration. As a result, sulfur removal efficiency was reduced and the salt carried higher sulfur content than desired. The water injected to reduce carbon deposition also had an adverse effect upon H_2S removal efficiency.

VENTURI SCRUBBER/EXTRACTION COLUMN PERFORMANCE

A summary of fuel gas sulfur analyses is shown graphically in Figures VIII-1, VIII-2 and VIII-3. Also shown is the operating history of the venturi, extractor, and regenerator with respect to salt feed status.

During the first operating period (12:00 to 16:30 on 6/5/77) the scrubber inlet gas ranged downward from 700 ppm ($H_2S + COS$ - Mole basis). Gas samples taken early in the period (at 12:50 and 13:50) indicated an average 92% sulfur removal with only the venturi operating. After 13:50 the gas chromatograph malfunctioned and no data was obtained for nearly two hours. The samples taken after the G.C. operation was restored reflect the effect of the static pools of salt on the trays of the extraction column. The results look a little low, and it is possible that the columns in the gas chromatograph have not conditioned properly.

At startup the venturi feed tank was full and there was some salt on the trays of the extraction column. Fuel gas was directed through the scrubber at 10:00, but it was 12:20 before salt flow to the venturi was established. During this interval the salt in the system would extract most of the sulfur in the entering gas. This would raise the sulfur content of the salt circulating in the recycle loop and that in the column to an overall average of 0.67 w/o sulfur (from 0.14 w/o sulfur). Salt of this composition would be

FIGURE VIII-1. Extraction Section Performance: First and Second Operating Periods

**FIGURE VIII-2. Extraction Section Performance:
Third Operating Period**

FIGURE VIII-3. Performance of the Extraction Section:
Fourth Operating Period

in equilibrium with gas containing 39 ppm H₂S (basis 6% H₂O and 5% CO₂). This is in good agreement with analyses of the V-1 and G-3 samples at 12:50 and 13:22, which contained 43 ppm H₂S and 34 ppm H₂S, respectively.

At 16:00, calculation shows the sulfur content of the salt will have increased to 1.13% sulfur and the equilibrium gas would contain 71 ppm H_2S . The A-1 and A-2 samples at 15:35 and 15:54 assayed at 26 and 21 ppm H_2S are definitely too low, but the A-0 sample at 16:15 and analyzed at 75 ppm H_2S is probably correct.

Toward the end of the first operating period the gasifier was approaching burnout, as indicated by an analysis at 22:06 showing 24.3% CO_2 , 20.8% CO , 9.7% H_2 , and 44.2% N_2 . As the gasifier burns out, the concentration of sulfur compounds drops sharply. These factors make computation of equilibrium gas compositions too uncertain to be of value.

With just the venturi scrubber operating, and with relatively clean salt, sulfur recovery of 90+% was achieved. As will be shown, however, the dry gas produced was prone to soot deposition, and with humidification to prevent this, such high recoveries in one extraction stage will not be attained.

From 19:20 to 21:40 attempts to continue operating were complicated by increased pressure drop across the venturi. Soot deposited in the venturi exhaust line had built up to the point where satisfactory salt flow could not be maintained. The soot was burned out with air and the gasifier was fitted with a water injection line so that water could be injected directly on top of the bed. This provided a convenient method of humidifying the scrubber feed gas and was successful in controlling soot deposition. During the balance of the run, water was injected at rates of 100 to 350 ml/min, which is equivalent to 6 to 22 mole% added water in scrubber feed gas. This increase from the normal 5 to 10 mole% water content resulted in reduced gas cleaning efficiency, as is predicted by the thermodynamics of the H_2S extraction reaction. It also diluted the inlet fuel gas.

The second operating period lasted from 13:30 to 16:00 on 6/6/77. The single inlet gas sample contained 248 ppm sulfur, but the gasifier had just been refueled and the sulfur content probably increased rapidly thereafter. Analyses at 14:34 and 14:44 indicate about 55% sulfur removal through the venturi. Unfortunately, no salt samples were taken during this operating

period, and the added 195 lb of salt (which was not sulfur-free) makes a performance check with theory impossible.

Pressure drop across the regeneration column had been too high to start the column. This finally cleared at about 18:00 and it was decided to refuel the gasifier before continuing. The third operating period lasted from 20:00 on 6/6/78 to 05:30 on 6/7/78, and is illustrated in Figure VIII-2. The feed gas was not analyzed until 05:10, and it contained 360 ppm. Based on experience with this fuel and with the gasifier, it is probable the feed gas sulfur content varied as shown by the upper dashed curve.

Venturi salt flow was started at 20:23, but continued only sporadically until 22:33, after which it operated continuously until 05:20 on 6/7/78. The extraction column ran essentially continuously from 21:39 on 6/6/78 to 05:20 on 6/7/78. The regenerator ran continuously from 21:00 on 6/6/78 to 05:20 on 6/7/78. Samples taken before 22:30 show sulfur concentrations of 590 ppm to 820 ppm at the absorber and venturi outlet. These high values probably resulted from the high feed gas water content resulting from initial drying of the 800 lb coal feed batch. At a sufficiently high water concentration sulfur will be stripped from the salt. Once all systems were operating continuously, the gas cleaning efficiency began to increase. Near the end of the period, the venturi outlet concentration was reduced to 160 ppm and the extraction column and product gas concentrations were reduced to 59 ppm and 98 ppm, respectively. The major factor responsible for the continual increase in sulfur removal efficiency was the gradual reduction in salt sulfur content effected by operation of the regenerator. The gas phase water content remained high (~ 25 mole%) throughout the period, and may have been as high as $\sim 50\%$ early in the period. The modest decrease in gas phase water content after the first few hours of operation was approximately offset by an increase in CO_2 concentration from 6 mole% (dry basis) at 21:00 to 11.8 mole% at 2:48 and to 12.7 mole% at 4:35. The relatively high CO_2 concentration late in the run is believed to have resulted from channeling and/or cold spots in the gasifier due to injection of water directly on top of the coal bed.

The gas cleaning efficiency during this period was fairly low; however, this was caused by known factors (i.e., high water content, partially spent

salt, and low inlet sulfur concentration). Once regenerator operations began, steadily improving gas cleaning efficiency was observed, clearly demonstrating successful regeneration of the absorptive capacity of the salt.

During the fourth operating period (10:00 to 21:00 on 6/7/78) the venturi was operated with salt flow for nearly 6 hr, and the absorber and regenerator for 4-1/2 hr each (cf Figure VIII-3). Operation during most of this period was sporadic, and these problems complicated sampling and analysis--thus limiting the analytical data. Near the end of the period all systems were in operation for approximately three hours. The gas sulfur content was reduced from 260 ppm at the inlet to an average 124 ppm at the venturi outlet and 66 ppm at the absorber. This is similar to the results obtained near the end of the third operating period, and represents very satisfactory sulfur removal performance.

REGENERATOR PERFORMANCE

The regenerator operated continuously for over 8 hr during the third operating period and provided the first test of the shortened (4-tray) configuration. The regeneration column itself operated with no problems; however, problems with flow control at valves caused salt to be supplied at a much higher flow rate and temperature than the unit was designed for. This had two major effects on regenerator performance. The maximum H_2S concentration in the regenerator off gas was equilibrium-limited to a relatively low value (0.6 mole% wet basis, 2.2 mole% dry). The high liquid flow rate coupled with this low regenerator product gas sulfur content resulted in a relatively small change in salt sulfur content, in a single pass through the regenerator. Therefore, the gas and liquid concentrations profile in the regenerator was relatively flat.

A summary of the regenerator gas analyses and operating conditions during the third operating period is given in Table VIII-1. The outlet gas averaged 1.5% H_2S (dry basis), with a maximum and minimum of 2.21% and 0.75%, respectively. Strip gas flow was gradually increased from 4.8 SCFM early in the period to 7.6 SCFM near the end.

TABLE VIII-1. Run C-11 Third Operating Period, Regenerator
Operating Data 6/6/78 and 6/7/78

Time	Sample (b) Point	H ₂ S, %	Wall (c) Temp., °C	Sampler (d) Temp., °C	Eq. S, (e) Wt. %	Steam, SCFM	CO, SCFM	Notes
21:10	S-8	10 ppm				Off	0.4	COS-100 ppm
22:18	S-8	795 ppm				1.6	1.3	
22:40	S-8	1173 ppm	600	640	0.07	1.6	1.3	COS-98 ppm
22:47	S-8	1.39	605	636	0.37	3.5	1.3	Rapid Temp. Drop
23:21	S-5	1.70	610	637	0.48	3.5	1.3	Rapid Temp. Increase
23:42	S-8	1.19	620	653	0.39	3.5	1.3	Low Flow
23:57	S-7	1.88	604	635	0.49	3.5	1.3	Temp. Dropping
00:11	S-5	2.21	597	610	0.51	3.5	1.3	
00:24	S-8	1.58	595	647	0.37	3.5	1.3	
00:33	S-5	1.54	605	655	0.41	3.5	1.3	Temp. Increasing
00:55	S-8	1.43	605	669	0.38	3.5	1.3	
1:41	S-5	1.73	625	665	0.55	5.1	1.3	
1:56	S-8	1.58	625	671	0.50	5.1	1.3	
2:10	S-7	2.12	620	660	0.68	5.1	2.0	
2:26	S-5	1.52	620	658	0.50	5.1	2.0	
4:21	S-8	0.97	605	622	0.29	5.1	2.5	Temp. Dropping
5:00	S-5	0.75	620	671	0.28	5.1	2.5	
5:13	S-7	1.11	610	678	0.35	5.1	2.5	

(a) All gas analysis on dry basis.

(b) S-8 is above the top tray, S-5 is below the top tray, and S-7 is in the off-gas line.

(c) Temperature of column wall above top tray.

(d) Temperature near center of column.

(e) Equilibrium salt sulfur loading at wall temperature (calculated).

An approximate integration of the H_2S flow rate from the regenerator indicates that roughly 1 lb of sulfur was removed from the salt during the third operating period. With about 440 lb of salt in the system, this would result in a decrease in sulfur content of 0.23 w/o. Absorption of sulfur from the fuel gas amounted to approximately 0.4 lb, which reduces the predicted decrease in salt sulfur loading to 0.14 wt%. From considerations discussed below, it appears that actual sulfur removal may have been appreciably greater--perhaps as much as twice as great.

Although real-time salt sulfur loading analysis are not available, it is possible to at least approximately track the salt sulfur content by calculating the salt composition that should be in equilibrium with the measured gas phase composition. The equilibrium salt sulfur loading is calculated from

$$S \text{ (wt\%)} = \frac{0.32 \text{ } [CaCO_3] \times 100\%}{1 + \frac{[H_2O] [CO_2]}{K [H_2S]}} , \quad (VII-1)$$

where $[CaCO_3]$ is the weight fraction $CaCO_3$ in the clean salt, $[H_2O]$, $[CO_2]$, and $[H_2S]$ are the mole fraction of water, CO_2 and H_2S respectively in the gas, and K is the measured equilibrium constant for the reaction of H_2S with $CaCO_3$. Unfortunately the accuracy of this calculation is not high. There is some uncertainty in every variable term in the equation, and in particular the values for $[H_2O]$ and K are often suspect. The constant K is dependent on temperature, and it was typically found that temperature could vary substantially as a function of both time and position in the column. Although this calculation is approximate, it is valuable for making rough comparisons and for evaluating trends.

It was found that salt sulfur concentrations calculated using the regenerator wall temperature were in fair agreement with measured values and with values calculated using the fuel gas analyses. Concentrations calculated

using the temperature measured at the center of the column were much too high. It is expected that the center temperature corresponds to the gas temperature, whereas the wall temperature corresponds more closely to the liquid temperature.

The calculated salt loadings in the regenerator are also shown in Table VIII-1 for the third operating period. These results are shown graphically in Figure VIII-4 together with similar data based on venturi exhaust, extraction column, and product gas analyses. Also shown are the measured salt loadings from salt samples taken during the run. The data for the third operating period show a continual decline of salt sulfur loading with time; however, the exact magnitude of the decline is somewhat uncertain. It appears to be somewhere between 0.1 wt% and 0.6 wt%, with a "best guess" of ~ 0.3 wt%. The general range appears to be somewhat higher than expected, based on the H_2S production rate in the regenerator. In order to evaluate the possibility of loss of sulfur to other chemical species in the regenerator, a number of equilibria were examined. It was found that in the absence of significant amounts of hydrogen and carbon monoxide, CO_2 and steam are sufficiently strong oxidizing agents to oxidize a significant fraction of the H_2S to elemental sulfur and to SO_2 , and that a significant amount of elemental sulfur could be produced by dissociation of H_2S . The reactions involved are:

FIGURE VIII-4. Calculated Salt Sulfur Loading as a Function of Time of Regenerator Operation

The equilibrium constants for these reactions have been calculated from thermodynamic data⁽⁸⁾ to allow evaluation of the partial pressures of S_2 and SO_2 to be expected (cf Table VIII-2). The ratio of S_2 to S (as H_2S) and of S (as SO_2) to S (as H_2S) has also been calculated.

The reaction

was also taken into account. At 1000°K, $K_p = 2.2 \times 10^{-2}$ atm., $p_{COS} = 5.7 \times 10^{-5}$ atm., and the calculated equilibrium ratio of sulfur (in COS) to

TABLE VIII-2. Side Reactions in the Regenerator

Reactions	Temp., °K	Kp, atm	P_{S_2} , atm	S_2		P_{SO_2} , atm	S (as SO_2)	
				S (as H_2S)	S (as H_2S)		S (as H_2S)	S (as H_2S)
VIII-2	900	2.1×10^{-3}	1×10^{-5}	3.3×10^{-3}	3.3×10^{-3}	--	--	--
VIII-2	1000	6.5×10^{-3}	1×10^{-4}	3.3×10^{-2}	3.3×10^{-2}	--	--	--
VIII-3	1000	4.5×10^{-3}	1.3×10^{-4}	4.4×10^{-2}	4.4×10^{-2}	--	--	--
VIII-4	1000	2.9×10^{-8}	--	--	--	2.9×10^{-3}	0.65	0.65
VIII-5	900	5.5×10^{-9}	--	--	--	2.5×10^{-4}	0.042	0.042
VIII-5	1000	5.8×10^{-8}	--	--	--	2.7×10^{-3}	0.45	0.45

(a) $P_{CO_2} = 0.3$
 $P_{CO} = 0.001$
 $P_{H_2} = 0.004$
 $P_{H_2O} = 0.689$
 $P_{H_2S} = 0.006$

sulfur (in H_2S) is 0.01. It was found that COS was typically measured at 2% to 12% of H_2S .

After considering these thermodynamic equilibrium calculations, it is apparent that at the operating temperature of the regenerator (870°K to 960°K) a significant fraction of the total sulfur stripped from the salt could be as compounds other than H_2S . However, the amount cannot be accurately predicted. Unfortunately, these equilibria were examined after the test runs were completed, so no attempt was made to measure SO_2 and elemental sulfur concentrations in the strip gas. Production of SO_2 from H_2S and either H_2O or CO_2 yields a total of three moles of ($H_2 + CO$) per mole of SO_2 . If all of the $H_2 + CO$ found in the gas were produced in this way it would indicate that the SO_2 concentration was on the order of 1/4 to 1/3 of the H_2S . This is well within the range of the thermodynamic predictions. If the H_2 and CO result from production of elemental sulfur, one mole is produced for each mole of sulfur produced. If all of the H_2 and CO were produced in this manner, it would indicate that the elemental sulfur produced is nearly equal to the H_2S ; this is clearly outside the range of

the thermodynamic predictions. The H_2 and CO could also be produced by reaction of steam and CO_2 with carbon, which may be present in the salt. This obviously results in no conversion of H_2S . Production of COS from H_2S and CO_2 results in no production of H_2 or CO, the COS was typically measured at 2% to 12% of the H_2S concentration when steam was being fed to the regenerator. Thus, it is entirely possible that the total sulfur stripped from the salt is 30% to 40% greater than that calculated from the H_2S flow rate. A 30% increase in sulfur stripping rate increases the calculated total sulfur stripped to 1.3 lb, equivalent to a decrease in average salt sulfur loading of 0.3 wt%, which is in better agreement with the measured and calculated salt loadings. It should be noted that at the design basis operating conditions, SO_2 and elemental sulfur production would be much less significant.

The regenerator performance during the fourth operating period was similar to that observed during the third period. Gas analyses and operating conditions are summarized in Table VIII-3. The H_2S content of the product strip gas varied between 0.7% and 2.4% (dry basis). The regenerator was operated for approximately 1/2 hr between 10:00 and 11:00; no significant data was obtained. Salt flow was again established at 13:40 and continued for 80 minutes. Gas samples between 14:06 and 14:59 showed 0.7% to 0.9% H_2S , corresponding to a calculated salt sulfur loading of 0.25% to 0.37%. These numbers agree well with those calculated for the last part of the third operating period. At 15:00, salt feed to the regenerator was stopped because the column drain line had plugged. Salt flow was restarted at 17:00 and continued for three hours. By 17:58 the H_2S concentration had increased to 1.13% and was beginning to show the effects of increased salt sulfur loading. The H_2S concentration reached a peak of 2.4% at 18:56 and remained fairly constant until salt flow was interrupted at about 20:00.

In both the third and fourth operating periods, the gas samples taken from the regenerator product gas line were significantly higher than those taken directly above the trays. It is believed that this is the result of

TABLE VIII-3. Run C-11, Fourth Operating Period Regenerator
Operating Data

Time	Sample Point	H ₂ S% Temp., °C	Wall Temp., °C	Center Temp., °C	Eq. S Wt%	Steam, SCFM	CO ₂ , SCFM	H ₂ , %	Notes
14:08	S-8	0.9	634	680	0.37	4.2	1.6	0.3	
14:29	S-5	0.7	623	645	0.25	4.2	1.6		
14:44	S-8	0.8	619	649	0.27	4.2	1.6		
14:59	S-5	0.86	617	635	0.28	4.2	1.6	0.13	CO - 0.03%
17:58	S-8	1.13	625	668	0.42	4.2	1.6	1.5	CO - 32%
18:35	S-8	1.59	610	647	0.43	5.4	1.6	1.2	CO - 11%
18:56	S-7	2.40	615	645	0.67	5.4	1.6	1.8	CO - 0.02%
19:16	S-8	1.82	600	616	0.43	5.4	1.6	2.4	Low Flow
19:33	S-7	1.98	590	608	0.40	5.4	1.6	1.5	Low Flow
19:46	S-8	2.13	605	656	0.53	5.4	1.6	2.3	Rapid Temp. Increase
20:00	S-7	2.20	620	655	0.66	5.4	1.6	1.5	
20:13	S-8	1.19	605	634	0.31	5.4	1.6	1.5	Lost Salt Flow ~10 to 15 min prior to sample
20:55	S-8	0.36	610	630	0.10	5.4	1.6	0.85	No Salt Flow Since 20:00

lower temperatures in the upper part of the 3-ft de-entrainment section above the top tray. Once salt flow was established the external heaters on this section (and the rest of the column) were switched off in order to reduce the regenerator operating temperature. Salt entrained in the gas or salt running down the wall below the salt inlet port (at the top of the de-entrainment section) could be cooled sufficiently to transfer additional H₂S to the gas. Calculations show that a temperature of ~590°C will bring the calculated equilibrium salt composition based on the product gas analysis into agreement with those calculated using the tray gas analyses.

Comparison of the calculated salt sulfur loadings with the measured values shows fair agreement with the makeup tank samples, but rather poor agreement with the coarse de-entrainer samples. The fact that the coarse

de-entrainer samples are lower in sulfur content than the makeup tank samples clearly indicates that at least one of these is not representative of the salt actually flowing through the system. A material balance calculation shows that at an average salt flow rate of 3 ℓ /min the sulfur content of the salt flowing from the regenerator should be ~ 0.02 wt% lower than the inlet. This can be compared with a 0.12% and 0.15 wt% increase indicated by the salt samples.

In summary, the performance of the regenerator during run C-11 was at least roughly as predicted under the operating conditions experienced. The period of operation was not of sufficient duration, nor was the operating data of sufficient accuracy to provide verification of the models used in designing the system. Because of difficulty in controlling liquid flow rate, the actual operating conditions achieved were considerably different from those for which the system was designed.

RUN C-11, CHRONOLOGY

A summary of the major modifications to the plant made prior to this run is as follows:

1. A 1-in. gate valve has been installed to control salt flow to the venturi, regeneration column, and extraction column.
2. The venturi orifice has been reamed out and a poker port installed to allow manual cleaning of the orifice.
3. The middle section of the regenerator column has been removed, leaving only four trays. The de-entrainment packing above the top tray has also been removed.
4. The venturi feed line and extraction column feed line heaters are powered at substantially reduced voltage, using variable transformers.
5. A check valve has been installed in the regenerator gas feed line to prevent salt from backing up into the gas preheater in the event of a drain line plug.

6. A trap has been installed in the regenerator off-gas line to prevent carryover of liquid salt in the event that the column floods.
7. Standpipes have been installed in the venturi feed tank and salt makeup tank to allow zones for heavy-particle settling.
8. Sample port heaters and salt traps have been installed to reduce the problem of frozen salt plugging sample lines.

The system was started up with the salt remaining from the previous run (C-10). Heatup of the system began at 00:30 on 6/5/78; shutdown of the system began at 02:00 on 6/8/78. A chronological description of the run follows.

6/7/78

- 00:30 Start up furnaces on piping and equipment.
- 03:23 Equipment heating normally.
- 03:40 Start up sample port heaters.
- 03:55 Start air flow to salt cooler; repair thermocouple on extraction column.
- 04:10 Start secondary burner.
- 05:30 Add 50 lb pre-ignited charcoal to gasifier.
- 05:40-06:45 Add 800 lb coke to gasifier.
- 08:20 Start steam flow to gasifier air feed.
- 10:00 Route gas flow to molten salt scrubber section.
- 12:00-16:30 First operating period.
- 12:10 Start salt flow to venturi (ΔP gauges indicate flooding). Flow adjusted to obtain stable operation.
- 12:30 Stable operation of venturi continued until 16:20.
- 12:30-13:41 Trying to start salt flow to regenerator. Feed line not completely melted.
- 13:41-13:51 A small amount of flow to the regenerator.

15:20-15:40 A small amount of flow to regenerator.

16:20 Shut off flow to venturi because of difficulty in establishing flow to the regenerator.

16:20-1:55 (6/6) Attempts are being made to start the regeneration column. The feed line to the regenerator apparently has a cold spot. Furnace temperatures are increased. At 01:10 on 6/6/78 the plug broke loose and flow was established to the regenerator. The salt immediately froze when it hit the drain line (also due to a cold spot). This forced a suspension in salt feed until the cold spot could be heated enough to melt the salt.

19:03-19:08 Flow established to extraction column (13 & total flow). Feed shut off until regenerator flow could be established.

21:30 Pressure drop through the venturi exhaust line is increasing (no salt flow) - control temperature is increased and CO₂ added to the feed gas to reduce carbon deposition in the line.

6/7/78

01:55 Pressure drop across the venturi exhaust line has increased to the point that operation of the scrubber system is not possible. Gas flow is suspended and attempts initiated to clear the line.

01:55-13:00 The venturi exhaust line was cleared. Initially, steam and CO₂ were injected through the line; when this appeared to be acting only slowly air was added, which proved to be very effective in clearing the line.

It was concluded that the best way to control carbon deposition would be to inject steam into the scrubber feed gas and to increase the scrubber operating temperature. The existing boiler did not have sufficient capacity to provide the steam required, so it was decided to simply inject liquid water on top of the hot coal bed in the gasifier.

The extraction side set point temperature was increased to 715⁰ to 725⁰C and water was injected at 1.5 to 5.5 GPH for the balance of the run. Once these changes were made, no further problems with carbon deposition were encountered.

Also during this period 400 lb of coke and 200 lb of coal were fed to the gasifier, and 195 lb of salt were added to the salt makeup tank. This salt was salvaged from an overflow tank used in a previous run and was partially loaded with sulfur.

13:00-16:00 Second operating period.

13:30 Open venturi feed valve — immediate flow.

13:42 Shut off venturi salt flow to make sure exhaust line is clear.

13:50 Start salt flow to the extraction column.

13:51 Restart venturi salt flow.

13:58 Shut off venturi salt flow and shut off gas flow briefly to prime absorber trays.

14:15 Restart venturi salt flow; continued to 16:00.

13:50-15:30 Five brief periods of salt flow to absorber, total flow 7 $\frac{1}{2}$.

16:00 Regenerator column pressure is higher than expected — may have a partially plugged off gas line. Shut down gas flow temporarily to check this out and to add coal to the gasifier.

19:30 Completed addition of 800 lb coal.

20:00-05:30 Third operating period.

20:23 Start salt flow to venturi.

20:45 Start salt flow to regenerator (CO₂ flow only).

21:10 Turned off venturi flow for a few minutes to clear exhaust line.

21:32-21:38 Attempting to restart venturi.

21:45 Venturi salt flow restarted.

21:48 Start steam flow to the regenerator @ 1.6 SFCM.

21:55 Stop and restart venturi salt and gas to prime the extraction column.

22:28 Stop and restart venturi salt and gas feed to prime the extraction column. All systems are now operating.

22:43 Increase regenerator steam feed to 3.5 SCFM; CO₂ to 1.3 SCFM.

00:48-00:53 Extractor feed off briefly because of flow imbalance.

01:01 Increase regenerator steam flow to 5.1 SCFM.

02:04 Increase regenerator CO₂ flow to 2.04 SCFM.

03:24 Increase regenerator CO₂ flow to 2.5 SCFM.

05:20 Shut down all salt flows to charge gasifier.

05:29 Bypass gas flow and valve off gasifier.

06:30 Complete addition of 1000 lb coal.

06:30-09:30 Attempts to establish pilot flame and light main burner in the secondary burner failed. Finally touched it off with a propane torch directed through the spark plug opening. The resulting deflagration almost blew the storm cap off the burner stack. A repeat of this procedure is not recommended.

10:00-21:00 Fourth operating period (see also section III).

10:00 Open regenerator salt feed valve — immediate flow.

10:08 Start steam flow to regenerator @ 1.8 SCFM.

10:13 Start venturi salt flow.

10:15 Start salt flow to the extraction column.

10:20 Due to preoccupation with the secondary burner problem, the fact that gas preheater had tripped out went unnoticed (this resulted from low gas flow). Once gas flow was increased to the normal rate the heater quickly cooled off so that cold gas was being fed to the scrubber.

10:25 Venturi orifice plugged; all salt flows shut off.

11:25 Venturi orifice rodded out.

11:35 Resume salt flow to venturi.

11:38 Opened regenerator feed valve; no flow.

11:50 Lost salt flow to venturi (plugged orifice).

12:50 Rodded out venturi orifice.

13:20 Restart venturi salt flow.

13:30 Restart extraction column salt flow.

13:47 Start steam flow to regenerator @ 1.8 SCFM; CO₂ @ 1.3 SCFM.

13:56 Increase regenerator steam feed to 4.2 SCFM; CO₂ to 1.6 SCFM.

15:00 Pressure drop across regenerator has increased to ~3 psig; salt and steam flow shut off. Problem is found to be a buildup of excess liquid due to a frozen regenerator drain line.

15:07 Venturi salt flow valved off.

16:29 Plug in regenerator drain line melts; column drains.

16:40 Start venturi salt flow; start salt flow to the extraction column.

16:53 Start regenerator salt flow.

16:59 Extraction column valved off to reduce salt in venturi circuit.

17:15 Start steam flow to regenerator @ 1.8 SCFM; CO₂ to 1.3 SCFM.

17:19 Salt flow to the extraction column.

17:35 Increase regenerator steam to 4.2 SCFM; CO₂ to 1.6 SCFM.

18:30 Increase regenerator steam flow to 5.4 SCFM.

20:00 Flow to the regenerator was lost. Apparently the salt cooler froze because of a reduction in cooling air temperature that had been made to increase the salt cooling efficiency.

20:09 Shut off salt flow to extraction column.

20:35 Shut off salt flow to venturi and bypass gas in order to recharge gasifier.

22:30 Completed addition of 1000 lb coke to gasifier. Again had difficulties in starting the secondary burner.

6/8/78

01:15 Start venturi.

01:25 Salt flow to regenerator cannot be established; critical heaters on the salt cooler have failed. Replacements on hand were found to have been damaged in shipment and were not useable. Shut off venturi salt flow and gas flow.

02:00 Begin shutdown of system.

IX. RUN C-12

SUMMARY

Run C-12 was initiated on 6/25/78. The scrubber was started at 13:30 on 6/26/78 and shut down at 22:30, when flooding in the extraction column plugged all of the samplers and ΔP sensor lines. These were cleaned and repaired the following day. Since flooding was partly due to overfilling of the venturi feed tank it was decided to jettison some of this salt, but a portion of the jettisoned salt flowed into the gas preheater. An additional 12 hr was required to repair this damage.

The run was resumed at 09:00 on 6/28/78 and continued until 20:00, when the salt cooler plugged. Though efforts continued until the following morning to restore flow through this unit, these efforts were unsuccessful and run C-12 was terminated.

During the second part of run C-12, H_2S cylinder gas was added. Very heavy water injection to suppress carbon formation was also employed, with moisture running $\sim 45\%$ (avg). Despite the moist gas, H_2S recoveries of 89% were observed. The 4-tray regeneration column was effective in maintaining low sulfur content in the regenerated salt.

During this run the venturi operated about 14.5 hours. Salt flow to the extraction and regeneration columns was maintained for 5.5 hours and 9.5 hr, respectively. About 3700 lb of coke and coal were gasified.

PERFORMANCE OF THE EXTRACTION AND REGENERATION SECTIONS

During startup of run C-12, the gasifier was fueled at 03:00 (6/26/78) with 800 lb of coke. Startup of the scrubber was delayed until 13:30 when the siphon that drains the regeneration column to the salt makeup tank finally opened to allow flow through the column.

Figure IX-1 shows the gas flow routing and the operational status of the venturi scrubber, extraction column, and regeneration column over the time period from 13:00 to 22:30. Gas was routed to the scrubber at 13:30. Salt flow to the venturi scrubber was obtained at 13:38 and to the regenerator at

FIGURE IX-1. Run C-12, Performance of the Extraction and Regeneration Section, 6/26/78

13:48. Operation was continued for about an hour, and a test was made to determine whether salt flow to the extraction column could be achieved. This was positive, and all salt flows were valved off to permit refueling of the gasifier.

A charge of 851 lb coke + 164 lb of coal was added, and at 16:25 gas was again routed to the scrubber. Salt flow to the venturi was established without difficulty. The regenerator was operated with a salt flow estimated from heat balance data at 1.4 & /min (avg). The cooled salt reached a minimum of 620°C and was near 640°C much of the time. As was pointed out in Section VIII, however, temperatures above the top tray and between this tray and the regenerator product gas sampler (S-7) were usually about 20° to 30°C

cooler, and caused transfer of additional sulfur to the gas phase. The regeneration reaction is highly temperature-dependent--a decrease from 620⁰ to 600⁰C would increase the H₂S concentration in the regenerator product gas from 0.54% to 1.0%.

The upper portion of Figure IX-1 displays gas phase analyses obtained during this part of run C-12. Gas was routed to the scrubber at 13:30. Sulfur content of this gas was 427ppm (G-1). The analytical technicians were having difficulties and obtained only one other analysis--i.e., above the top tray in the extraction column (A-2) at 20 ppm sulfur. Salt phase assays and salt volumes at the start of the run indicate the salt was relatively clean, e.g.,:

- Coarse De-entr. - 14.5 l (67 lb) @ 0.24% S.
- Makeup Tank - 35 l (162 lb) @ 0.22% S.
- Vent. Feed Tank - 27.5 l (148 lb) @ 0.93% S.

Salt on the trays of the extraction column at startup is of unknown sulfur content, but if it is the same as that in the makeup tank it would be in equilibrium with a gas phase with 12 ppm H₂S. The single A-2 sample assayed 10 ppm H₂S (and 10 ppm COS) in agreement with this calculation.

After refueling, the inlet gas sulfur content dropped sharply and began a slow climb back toward the earlier level. Between 16:45 and 19:45, sulfur recoveries across the venturi scrubber were good, ranging from 45% to 68%. Additional recovery in the extraction column is illustrated by the lower dashed curve. The A-2 and G-3 samples ranged from 55 to 65 ppm total sulfur, indicating an overall recovery of 80%, which is very good when it is noted that the feed gas was at 275 ppm sulfur.

Difficulties with slight flooding of the venturi scrubber and a buildup of pressure drop in the venturi exhaust line led to a decision to start water injection to the gasifier and to increase temperatures in the extraction section to 715⁰C. Since H₂S recovery is directly proportional to the mole fraction of H₂O (or CO₂) in the gas phase, the effect was noted immediately. The overall recovery across the extraction section was reduced from 80% to 47% and the total sulfur in the product gas ranged from 150 ppm to

170 ppm. This was a three-fold increase over the concentration which prevailed prior to H₂O injection.

Results of analyses within the regeneration column are collected in Table IX-1. The data are too limited to plot after the manner shown in Figure VIII-2 (Run C-11). From salt sample analyses taken at the start and end of this operating period and from gas analyses, a material balance calculation shows the regeneration column removed 0.95 lb of sulfur. The H₂S analyses shown in Table IX-1 are on a dry basis. From the volumetric flow (of CO₂) and estimating an average of 1% H₂S in the regenerator product gas (dry basis) it appears 0.64 lb of sulfur was removed. If, as suggested in the preceeding section, some sulfur removal as SO₂ or S₂ occurs, this discrepancy can be accounted for. It is clear, however, that the 4-tray regeneration column functioned effectively during this operating period.

Shutdown of the scrubber was forced by accumulating troubles with plugged sample ports in both the extraction and regeneration columns. There was

TABLE IX-1. Performance of the Regeneration Column
(13:00 - 22:00, 6/26/78)

<u>Sample Point^(a)</u>	<u>Time Sampled</u>	<u>H₂S, %</u>	<u>Other Gases, %</u>
S-5	17:36	0.88	
S-3	18:19	1.05	
S-5	18:56	0.92	H ₂ = 4.6
S-7	19:13	1.10	H ₂ = 0.85 COS = 0.016
S-8	19:28	0.93	H ₂ = 1.27
S-3	20:06	0.95	H ₂ = 0.45

(a) Numbering from the bottom upward, S-3 is above the bottom tray, S-5 is above the third tray, S-8 is above the fourth (top) tray, and S-7 is in the regenerator product gas line.

concern about carbon buildup in the salt, and plans were made to remove part of the salt and replace it with fresh salt.

The samplers were cleaned and made ready during the interval from 22:30 (6/26/78) to 11:00 (6/27/78). At 08:00, 900 lb of coke and 100 lb of coal had been charged to the gasifier.

Flooding of the venturi had occurred during the first operating period, and 26 lb (5.6 ℓ) of salt was lost to the lower pot. This was due to a heater outage at the base of the standpipe in the venturi feed tank, which prevented salt from overflowing via the standpipe. Salt accumulated above the level of the standpipe and generated additional head and increased flow.

Unfortunately, the lower pot furnace had tripped its breaker, cooled, and when the trickle of salt entered as a result of flooding, it froze and eventually formed a plug that obstructed further entry of salt to the lower pot. This condition was unknown to operators, who decided to improve salt quality by jettisoning salt to the lower pot and subsequently adding an equivalent quantity of fresh salt. The salt was jettisoned by opening the venturi feed valve. In the absence of gas flow, the salt should drain to the lower pot. Instead, substantial portions of it entered the 3-in. line to the gas preheater. This unit was off, and the presence of salt was sensed by the control thermocouple positioned at the outlet of the gas preheater. Salt flow was valved off in time to prevent damage to heating elements in this unit. The task of removing this misplaced salt delayed start of the second operating period until 09:00 (6/28/78).

Figure IX-2 shows the operating sequence during the second operating period. Gas flow was routed to the scrubber at 09:20 and was followed immediately by initiation of salt flow to the venturi scrubber and both columns. At 10:20 it was necessary to shut down when the gas preheater tripped out and cooled to 550 $^{\circ}$ C. Flow was resumed at 10:30 with restart of the venturi and regenerator. A brief pulse of salt flowed to the extractor at 11:15.

FIGURE IX-2. Run C-12, Performance of the Scrubber, 6/28/78

Flow to the venturi was lost at 11:45. The orifice was rodded (twice) and flow was successfully resumed at 14:15. Flow to the venturi was lost at 15:10 due to exhaustion of feed, but was resumed at 15:45 after feed to the extraction column allowed replenishment.

Flow control to the extraction column proved very difficult, and this column was operated by essentially dumping in quantities of salt at intervals by opening and closing the feed valve. The column thus received spurts of salt at flows far exceeding the design basis.

Throughout this operating period the gasifier was operated with a high rate of water injection. This reduced the coal gasification rate and caused a certain amount of channeling in the gasifier, so that the CO_2 content of the gas was higher than normal. A few values are shown together with the averaged water content.

The gas analyses from the venturi outlet and the extraction column were measured "as is," but the G-1, G-2 and G-3 samplers were equipped with condensers to remove moisture, and the results plotted in Figure X-2 have been corrected to the moist (or "as is") basis. So much moisture reduces the sulfur content of the inlet gas to an average of about 150 ppm sulfur. With 45% H_2O and 12% to 14% CO_2 in the gas, equilibrium calculations indicate a gas phase H_2S content exceeding the feed concentration would be obtained.

The gasifier had been refueled at 08:00, and water injection did not start until it began producing good gas again. The first few samples at the venturi outlet, in the extraction column, and the clean product gas all exhibited low H_2S concentrations.

After water injection started, the venturi outlet samples indicated zero or negative extraction (until H_2S cylinder gas addition began). Some H_2S extraction occurred in the extraction column, which means that the salt on the trays (entering from the makeup tank) was lower in sulfur than the salt in the coarse de-entrainer. (Salt samples confirm this.) After a few hours' operation this will be the case only if salt regeneration is occurring. With no regeneration the coarse de-entrainer and salt makeup tank sulfur content will converge.

At 16:14 H_2S cylinder gas addition was begun. With corrections due to moisture, the clean product gas remained below 190 ppm throughout this period. Using the sulfur content of the makeup salt at 16:50, equilibrium calculations show the gas should contain 189 ppm H_2S ($\text{H}_2\text{O} = 45\%$, $\text{CO}_2 = 13\%$). Overall sulfur recoveries averaged 89%. During the period of operation with H_2S cylinder gas addition, difficulty was encountered in holding the flow of H_2S at the prescribed levels, and there were brief intervals when the H_2S flow was much higher than normal. In addition, no entry appears to have been made in the log at the time when the H_2S cylinder gas was valved off. This probably occurred near the time indicated on Figure IX-2. These uncertainties make calculation of a material balance of little value.

The performance of the regenerator is indicated by data in Table IX-2. This operating period started with relatively clean salt. (After addition of fresh salt, the makeup tank assayed only 0.10% sulfur. This may have been a bad sample, due to poor mixing. A better value calculated from the assay at the end of the first operating period would be 0.35% sulfur).

The salt makeup tank was sampled at 17:00 and again at 22:00, with results of 0.22% and 0.18% sulfur. This continuous decline in sulfur content shows the regenerator was operating effectively.

In Table IX-2 the next-to-last column shows the calculated equilibrium salt concentration corresponding to the gas analyses. These numbers vary up and down erratically and reflect the variations in liquid flow. An exception may be those numbers at the very start. There seems to be a lag in steam entry from the point of flow measurement to the column.

At 13:58 a good spurt of salt entered the column, but salt flow didn't really stabilize until 15:36, then the flow was fairly constant until 17:43, then it tailed off to a low flow. From 18:00 on, flow of salt was on the order of 100 to 150 ml/min. At such low flow, even though most of the sulfur was being removed, a high H_2S concentration could not be produced. Flow finally stopped completely and the run was terminated.

In the interval from 15:36 to 17:43 salt phase sulfur concentrations calculated from the gas analyses correspond closely to analyses of salt

TABLE IX-2. Regenerator Performance: Second Operating Period Run C-12

Sample Point	Sample Time	H ₂ S, %	Calc. Equiv. Salt S%	CO ₂ Flow, SCFM	Steam Flow, SCFM	Temp., °C (Top)	Temp., °C (Bottom)	Remarks
S-3	10:14	0.009	0.0029	1.9	4.2	610	610	
S-1	10:27	0.027	0.011	1.9	4.2	624	595	
S-8	10:43	0.018	0.0062	1.9	4.2	614	600	
S-3	11:07	0.010	0.0037	1.9	4.2	618	---	
S-3	13:58	0.60	0.244	1.9	4.2	629	625	• Spurt of salt flow
S-8	14:22	0.021	0.009	1.9	4.2	628	625	
S-7	14:41	0.108	0.044	1.9	4.2	627	---	
S-3	15:05	0.107	0.036	1.9	4.2	613	630	
S-8	15:36	0.77	0.280	1.9	4.2	621	600	• Good steady salt flow
S-7	16:37	1.01	0.220	1.9	5.4	590	560	• Good steady salt flow
S-3	17:17	0.99	0.194	1.9	5.4	590	560	• Good steady salt flow
S-8	17:30	1.26	0.238	1.9	5.4	580	---	• Good steady salt flow
S-7	17:43	1.23	0.220	1.9	5.4	576	---	• Good steady salt flow
S-3	18:08	0.37	0.066	1.9	5.4	574	550	• Reduced salt flow
S-8	18:22	0.62	0.110	1.9	5.4	574	550	• Reduced salt flow
S-7	18:52	0.48	0.088	1.9	5.4	576	---	• Reduced salt flow
S-3	19:08	0.75	0.144	1.9	5.4	580	---	• Reduced salt flow
S-8	19:33	0.40	0.072	1.9	5.4	575	---	• Reduced salt flow
S-7	21:05	0.39	0.154	1.9	off	631	---	• Reduced salt flow
S-3	21:18	0.20	0.079	1.9	off	630	550	• Column temperatures being increased in hopes of increasing flow rate
S-8	21:43	0.19	0.089	1.9	off	643	---	
S-7	21:55	0.23	0.107	1.9	off	---	---	
S-1	22:07	0.21	0.108	1.9	off	650	---	
S-3	22:27	0.13	0.067	1.9	off	650	---	
S-8	23:06	0.092	0.047	1.9	off	650	---	

samples. The average of the calculated values is 0.23% sulfur. The coarse de-entrainer salt, which is the feed to the regenerator, measured 0.26% at the start and had increased to 0.48% sulfur at 17:20. As the flow through the regenerator slowed, and with feed to the extraction column off after 17:15, the salt kept circulating in the recycle loop as a result of the venturi action. The sulfur content of the salt in the loop continued to build because no clean (regenerated) salt was entering the venturi feed tank. The increasing sulfur content of salt entering the regenerator was not detected in regenerator product gas because the salt flow rate was so low. Operators should have reduced the steam and CO₂ rates accordingly.

From 21:00 on, steam flow was valved off. The CO₂ flow remained on and will pull some moisture from the lines into the column for some time after steam is valved off.

CHRONOLOGICAL OPERATION

Prior to the start of run C-12, the leaking slide valve on the gasifier lock hopper was cleaned and repacked. The lower pot furnace was rewired and now operates at 67% of its normal power. This is adequate to bring it to and to maintain normal operating temperatures. Faulty heaters on the salt cooler and at the outlet of the coarse de-entrainer were replaced.

6/25/78

10:15 Trace heaters set to 150°C.

10:55 Trace heaters at 250° to 350°C; thermocouples 45, 47 and 49 found to be faulty. Adjust cable stay on the salt cooler exhaust stack.

6/26/78

01:00 Start secondary burner.

03:00 Complete addition of 800 lb coke.

07:15-08:00 Take salt samples in all tanks.

08:05-10:30 Get regeneration column ready to operate.

09:00-12:00 Bypass gas. Secondary burner malfunctioning. Clean, repair, and re-ignite.

13:30 Start fuel gas to scrubber.

13:38 Start salt flow to venturi.

13:47 Start salt flow to regenerator.

14:35 Stop all salt flow; bypass.

16:15 Complete addition of 851 lb coke + 154 lb of coal.

16:25 Resume fuel gas flow to scrubber.

16:40 Resume salt feeds.

20:05 Start water injection to gasifier and increase temperatures to 715⁰C.

20:55-21:30 Stop salt flows.

22:30 Bypass gas flow.

At this point salt has foam floating on it, which makes tank readings uncertain. The venturi feed tank was overfilled, backing salt into the extraction column and flooding and plugging all sample ports and ΔP sensors.

6/27/78

12:00 Clean and repair sample ports.

15:50 Attempt to jettison salt to lower pot. Salt backs into gas preheater.

15:50-24:00 Remove errant salt; repair 3-in. jumper. Clear G-2 sampler and H₂S cylinder gas inlet port.

6/28/78

02:00 Add 75 lb of fresh salt.

08:00 Add 800 lb coke.

09:00 Route fuel gas to scrubber and start salt flow to all units.

09:44 Start steam to regenerator.

11:27 Extraction column flooding; stop salt flow.

11:45 Lost salt flow to venturi; shut down all salt flows and bypass gas.

11:45-13:30 Rod out venturi; resume gas flow.

13:38-14:13 Venturi plugged again; rod out and resume flow.

14:13-20:30 Continue operating. At 20:30 the salt cooler froze and plugged.
All salt flows valved off.

6/29/78

24:00-08:00 Salt was slowly drained through the salt cooler and regenerator to the salt makeup tank, but no reasonable flow rate could be achieved. This led to a decision to shut down and acid-flush the salt cooler in preparation for the following run.

X. RUN C-13

SUMMARY

Run C-13 was initiated at 20:00, 7/16/78, with startup of the trace heating. The gasifier was started at 06:00, 7/17/78. All systems were operating from about 15:50 to 19:00, when it was necessary to shut down and refuel the gasifier. The regeneration column was plugged at this time.

From 19:00 (7/17/78) to about 16:00 (7/18/78) the scrubber was down and all efforts were focused upon getting the regenerator operating. By 16:00 (7/18/78) these efforts succeeded and all systems were again operated for about 1 to 1.5 hours. Intermittent plugging of the regenerator and a high pressure drop across a polishing filter forced a decision to terminate run C-13.

The extraction section and regeneration column performed well during the brief period of operation on 7/17/78. Product gas composition (G-3) ranged from 169 ppm to 275 ppm. Feed gas sulfur concentrations were low (with no spike gas addition) so the scrubber extracted comparatively little sulfur. During a brief period of operation, the regeneration column produced a regenerant product gas of up to 17,000 ppm sulfur—a feed gas/regenerant gas sulfur ratio of about 70. Regeneration was at the comparatively high temperature of 630° to 640°C, where efficiency is low.

The isokinetic particle sampler was operated on the product gas side in tests of a polishing filter. The inlet gas sampler was plugged and inoperable. The product gas was found to contain a particle burden of 37 mg/M³ (.017 gr/SCF) with 90% < 4μ M diameter. Of this, 21% was alkali metals (Li, Na and K) derived from entrained salt.

PERFORMANCE OF THE EXTRACTION AND REGENERATION SECTIONS

Figure X-1 illustrates the performance of the extraction section. The curve defined by solid and open circles (G-1 and G-2) yields the inlet gas total sulfur content. The gasifier was refueled at 06:00 and the sulfur content of the gas should have been increasing. This trend was arrested and

FIGURE X-1. Performance of the Extraction Section, Run C-13

slightly reversed when water injection was initiated after 13:00. Gas routing and operational periods of the venturi and the extraction and regeneration columns are shown in the lower part of the figure.

The A-0 sampler below the lower tray became inoperable when the siphon drain at the bottom of the extraction column plugged. The column filled to the level of the gas inlet line--a 4-in.-dia line that connects to the top of the venturi feed tank. Salt trickled along the bottom of this line to the venturi feed tank so the column remained operable, but the salt flooded the A-0 sampler.

Final product gas samples (G-3) range from 150 ppm to 223 ppm sulfur. A-1 samples taken above the bottom tray in the extraction column (illustrated with a slashed dot) range from 126 ppm to 186 ppm sulfur.

The A-2 samples taken above the top tray in the column are all too high. It is not certain why this is so. Instrument error is ruled out because standards analyze correctly and all the other samples appear reasonable. The result indicates that the salt on the top tray is inordinately high in sulfur.

It is possible for this to happen if a sludge of iron-bearing sulfur compounds was to feed to this tray and hold up on the tray until the sulfur goes into solution. The stage was set for this event when the polishing filter blinded with soot. This pressurized the equipment upstream of the filter. Thus, when the valve to the extraction column was opened, salt and gas was blown back into the salt makeup tank. The gas lifted the bell-shaped stand-pipe out of the exit line and toppled it over (it was later found lying on its side in the bottom of the tank). Later, when salt flow to the extraction column was established, the sludge that was trapped in the bottom of the tank entered the process.

The trays in the extraction column have a holdup volume of 3 liters, which is probably ample to accommodate the volume of sludge trapped in the salt makeup tank. The overflow to the downcomer would skim good-quality salt off the top and feed it to the lower tray. It would take a while for the sludge to work its way through the process. The high sulfur content in the sludge trapped on the tray would cause the abnormally high sulfur in the A-2 gas samples.

Additional evidence for the existence of an iron-bearing, high-sulfur sludge in the salt makeup tank comes from salt phase assays at the end of run C-12 and at the start of run C-13. Samples taken from the salt makeup tank give the result shown in Table X-1. The salt was simply cooled and frozen and re-melted between times when it was sampled. This resulted in precipitation of most of the iron and part of the sulfur.

It is regrettable that the operation was not extended beyond 19:30 hours. It might have been possible to show a return to normalcy in A-2 sample assays as this material moved out.

Part of the sludge must have moved out and reached the salt cooler and regeneration column. The valve at the exit of the salt cooler gave a lot of trouble in this run, and the regeneration column plugged and remained so for 24 hours.

The regeneration column did operate for a brief period from about 16:50 to 19:00 before it plugged. Recalling that sampler S-1 is above the bottom tray, S-3 is above the 3rd tray, S-8 is above the top tray, and S-7 is in the off-gas line, the results of assays of samples taken from these points are collected in Table X-2.

The first three samples S-3, S-1 and S-7 taken on or before 18:41 are the only ones obtained with salt flowing and with steam-CO₂ flow. The salt sulfur content calculated from equilibrium considerations and corresponding to these gas samples was 0.35 w/o, 0.46 w/o and 0.60 w/o, respectively. This is about in the range anticipated (using a temperature of 640°C) in view of the salt assay at the end of run C-12 (0.42 w/o sulfur).

TABLE X-1. Salt Assays at the End of Run C-12
and at the Start of Run C-13

Point	Sample		S, %	Fe, %	Li, %	Na, %	K, %	Ca, %
	Time	Date						
Makeup Tank	22:45	6/28	0.42	0.50	5.15	10.5	15.7	7.61
Makeup Tank	10:00	7/17	0.20	0.013	5.82	12.7	16.8	6.67

TABLE X-2. Performance of the Regenerator(a)

Sample	Time	COS, %	H ₂ S, %	S, %	CO ₂ , %	H ₂ , %	Other, %
S-3	17:31	0.02	0.6	0.62	97	--	--
S-1	17:44	0.02	0.8	0.82	99	--	--
S-8	18:29	sampler plugged					
S-7	18:41	0.014	1.69	1.70	95.2	0.21	--
S-3	18:55	0.11	1.36	1.47	75.4	0.15	--
S-1	19:09	0.012	1.19	1.20	99	0.11	--
S-7	19:23	--	0.92	0.92	35.4	5.11	--
S-3	19:37	--	0.89	0.89	37.7	1.96	--
S-1	19:50	--	1.2	1.2	98.5	0.32	--
S-7	20:03	--	0.22	0.22	34.5	5.7	N -44.4 CO-12.2
S-1	20:38	--	0.23	0.23	100.1	--	--

(a) Note: All gas analyses are dry basis.

The S-3 sampler was almost plugged at 18:55 and the low CO₂ assay makes the results questionable. The S-1 sample at 19:09 should be good and the sulfur assays reflect the continued stripping of static pools of salt on the trays. The S-7 and S-3 samples at 19:23, 19:37 and 20:03 reflect the effect of dilution by producer gas that enters the column when the coarse de-entrainer and salt cooler are drained of salt. The S-1 sample at 19:50 is apparently good. By 20:38 steam flow was off and only a slight trickle of CO₂ was maintained. This S-1 sample reflects the effect of the absence of steam.

The column appeared to be plugging, so the trace heaters were increased in temperature to attempt to induce a more even flow. Heating was continued to about 16:00 hr on 7/18/78. At about 15:00 hr air temperatures at the salt cooler exhaust indicated salt flow to the regeneration column had been achieved. The column was operated with intermittent plugging at the flow

control valve for about an hour. No analytical data could be obtained during this period due to plugged samplers, so no performance data could be obtained.

These problems, together with increasing pressure drop across the polishing filter prompted a decision to shut down. All salt was drained to the lower pot in preparation for thorough flushing before the next run.

PARTICLE COLLECTION

Isokinetic sampling probes for particle collection were installed in the inlet and outlet lines near the G-2 and G-3 gas samplers. During the period from about 17:00 to 18:30 (7/17/78) the product gas was sampled using an Anderson-2000 impinger heated to $\sim 350^{\circ}\text{C}$ and the Joy Manufacturing Company's Emission Parameter Analyzer. A 3l-CF gas sample was drawn through this apparatus under isokinetic conditions. Only the product gas was sampled. The process upset in the preceeding run had backed salt into the inlet gas sampling probe, rendering it unusable.

Data obtained with the Anderson-2000 impinger are collected in Table X-3. Plates 1 and 2 contained no visible deposits. Plate 3 had a deposit which appeared to be mostly soot, but gave an x-ray absorption spectrum. Plate 4 showed a deposit with much soot, but the electron photomicrographs reveal discrete particles in the 3- to 4- μM range. Plates 5 and 6 show progressively less of the soot, which has disappeared completely on Plates 7 and 8.

Figures X-2 to X-7 show the x-ray fluorescence spectra of the deposits on plates 3 through 8. Zinc is present in all cases, and becomes the principal impurity on plates 7 and 8. Zinc is an accidental contaminant in the coke recently procured from the Bunker Hill Company, a large Pb-Zn mining and refining company. Appreciable iron is present on plates 3, 4 and 5 and is not detected on plates 7 and 8. Silicon is strongly evident on plates 3, 4, 5 and 6 but is virtually absent on plates 7 and 8.

The calculated effective cutoff diameter (ECD) is compared with size measured by the electron microscope (Table X-3). Agreement is good except for the smallest sizes, where the electron microscope gives the more accurate value.

TABLE X-3. Particle Size Distribution by Isokinetic Sampling,
Run C-13, 7/17/78

<u>Plate</u>	<u>Tare, g</u>	<u>Gross, g</u>	<u>Net, mg</u>	<u>%</u>	<u>Cum. %</u>	<u>ECD μM</u>	<u>Particle Dia, μM</u>
1	20.4430	20.4458	2.8 ^(c)	--	--	14.0	--
2	20.9224	20.9252	2.8 ^(c)	--	--	9.0	--
3	21.3979	21.4010	3.1	9.5	100	6.0	--
4	21.9053	21.9087	3.4	10.4	90.3	4.0	3-4
5	11.5520	11.5553	3.3	10.0	79.9	2.5	3
6	11.7146	11.7185	3.9	11.9	69.9	1.4	1-2
7	11.3105	11.3172	6.7	20.4	58.0	0.8	0.3-0.5
8	21.0289	21.0391	10.2	31.2	37.6	0.5	0.1-0.2
Backup Filter	0.6620	0.6641	<u>2.1</u>	6.4	6.4	0.5	--
Total			32.7				

(a) Effective Cutoff Diameter.

(b) Particle diameter as measured from electron photomicrographs.

(c) Not included in total weight. No visible deposit. Low-power microscope reveals only randomly distributed soot particles.

Total Particles = 1.05 mg/CF = 37 mg/M³ = .016 g/CF.

The total particle burden in the product gas stream is calculated from these data to be 37 mg/M³. The deposits were rinsed from the plates, made to volume, and analyzed for salt components with the results shown in Table X-4. The total of alkali metals plus Ca comes to 21% of the total of material collected by the Anderson-2000 impinger and backup filter. This mix of alkali metals and Ca totals 7.9 mg/M³. Of the particles collected, 90% were below 4 μM in diameter.

FIGURE X-2. X-ray Fluorescence Spectrum of the Deposit on Plate No. 3

FIGURE X-3. X-ray Fluorescence Spectrum of the Deposit on Plate No. 4

FIGURE X-4. Deposit on Plate No. 5

FIGURE X-5. Deposit on Plate No. 6

FIGURE X-6. Deposit on Plate No. 7

FIGURE X-7. Deposit on Plate No. 8

TABLE X-4. Analysis of Deposits on the Plates of the Anderson-2000 Impinger and the Filter

Plate	Weight Deposit, mg	Li		Na		K		Ca	
		%	mg	%	mg	%	mg	%	mg
5	3.3	0.097	0.0032	7.2	0.24	1.92	0.06	5.8	0.19
6	3.9	0.37	0.0144	6.5	0.25	4.5	0.17	0.77	0.03
7	6.7	0.19	0.0127	4.1	0.28	8.4	0.56	0.48	0.03
8	10.2	0.16	0.0163	5.5	0.56	11.6	1.18	0.47	0.05
Filter	2.1	0.65	0.0137	88.8	1.86	18.2	0.38	3.2	0.07
% in Deposit		0.23		12.2		9.0		1.4	
Avg. % in Salt		5.14		10.4		15.3		7.4	
(makeup salt)									

At the end of the run, the polishing filter was removed and examined. Figure X-8 shows electron photomicrographs of the inlet and outlet sides of the fibrous filter media. The fibers range from 3 to 10 μM in diameter. The trapped particles appear to average 5-6 μM in dia, but with many larger and smaller particles. A segment of the filter was removed and acid-leached, and the leach solution was analyzed, with results reported in Table X-5. The middle columns in this table compare the amounts trapped by the filter with amounts passed and collected by the Anderson-2000 impinger. This comparison permits calculation of the removal efficiency for the elements. Clearly, where removal of alkali metals is important, a polishing filter can be of value.

During run C-11, an aqueous scrub of the product gas was conducted. The results are compared with a similar test performed during earlier batch operation of the PDU. This comparison is shown in Table X-6.

FIGURE X-8. Electron Photomicrographs of the Outlet and Inlet (lower) Sides of the Polishing Filter

TABLE X-5. Assay of Filter Segment

Element	Particles Removed, mg/SCF	Particles Passing Filter, mg/SCF	Percent Removed
Li	0.0042	0.0019	68.4
Na	0.025	0.103	19.5
K	0.12	0.075	61.5
Ca	0.0085	0.012	41.5
Zn	0.52	--	--

TABLE X-6. Analysis of Aqueous Scrub Solutions Used for Detection of Alkalies and Tars in Cleaned Product Gas

Element	Concentration		Calc. Equiv. Vapor Pressure, atm
	mg/M ³	g-atoms/M ³	
Li ^(a)	0.69	9.9×10^{-5}	2×10^{-6}
Na ^(a)	16.60	72.2×10^{-5}	1.6×10^{-5}
K ^(a)	8.92	22.8×10^{-5}	5×10^{-6}
Ca ^(a)	10.9	27.3×10^{-5}	--
Li ^(b)	0.44	6.3×10^{-5}	1.4×10^{-6}
Na ^(b)	32.9	143×10^{-5}	3.2×10^{-5}
K ^(b)	5.6	14.3×10^{-5}	3.2×10^{-6}

(a) Run temperature = 700°C - Run C-11, Gasification of Coal.

(b) Run temperature = 750°C - Run 3, Gasification of Coke.

These data can be utilized to estimate the vapor pressure of the alkali metal-bearing species coming through to the product gas scrub solution. The mole-fraction ratio of the elements/gas is calculated and related to partial pressure. The order of magnitude of the results is in agreement with measurements by United Technologies Corporation on $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ systems-- i.e., pressures of the order of 10^{-6} atm.⁽⁹⁾ United Technologies

proposed that hydrolysis to volatile hydroxides would account for the observed vapor pressure. This does not appear to be the case here, for LiOH formation is more favorable than NaOH or KOH formation, yet lithium exhibits the lowest vapor pressure. Alkali metal transport as the hydroxide thus seems improbable.

If the alkalies and calcium were being carried over by a simple process of entrainment, they would be present in the scrub solutions and on the plates of the Anderson-2000 impactor, or on the surface of the polishing filter in amounts proportional to their atom fractions in the salt--i.e.,: Li, 11.06; Na, 8.0; K, 6.36; and Ca, 3.0. Clearly, this is not the case. When the elements are compared on the basis of atom fractions (Table X-6) it is sodium which is high, with lithium low. Calcium is also higher than it should be. This effect may be due to variations in the activity coefficients of these ions in the molten salt. A more detailed study of volatilization from such melts will be required to permit a full understanding of this behavior.

Experimental difficulties prevented further measurements of particle behavior; however, data taken earlier in batch operation of the PDU at somewhat higher temperatures can be compared with data of Table X-3. Thus, Table X-7 shows data for a run at 750°C with the gasifier operating on coke. In this case the packed-bed de-entrainer contained only 1-in.-dia balls, and the product gas had a particle burden of 160.7 mg/M³.

Table X-8 shows data for a run at > 800°C, again with coke being gasified, and with a wire screen demister in place. This produced an improved product gas with a particle burden of 56.1 mg/M³. This is not quite as good as the result obtained with the fibrous polishing filter.

In no case have results approached the level of 1.0 mg/M³, which has been indicated to be the goal of turbine operators.⁽¹⁰⁾ The results have been favorable enough, however, to suggest that a more vigorous effort to assess polishing filters may be productive.

TABLE X-7. Particle Behavior During Operation of the PDU at 750°C(a)

Plate	Net Wt., mg	%	ECD, μM	Conc. in Gas, mg/M
1	4.8	1.5	17.6	2.4
2	4.2	1.3	11.2	2.1
3	32.7	10.1	7.5	16.1
4	49.8	15.3	5.3	24.6
5	40.5	12.5	3.5	20.0
6	38.1	11.7	1.7	18.8
7	28.9	8.9	1.0	14.2
8	31.4	9.7	0.7	15.5
Filter	94.8	29.2	0.15 est	46.8

Total 323.3 mg 160.7

Gas Vol. Sampled = 71.48 SCF = 2.024 M³

Inlet Gas Filter wt Gain--228.9 mg

Vol. Inlet Gas Sampled--0.908 M³

Inlet Gas Particle Burden--252 mg/M³

(a) Operation during batch mode configuration.

TABLE X-8. Particle Behavior During Operation of the PDU at >800°C(a)

Plate	Net Wt., mg	%	ECD, μM	Conc. in Gas, mg/M
1	1.5	5.0	20.1	2.8
2	1.3	4.3	10.5	2.4
3	1.6	5.3	7.0	3.0
4	1.9	6.3	5.0	3.5
5	2.6	8.6	3.1	4.8
6	2.9	9.6	1.6	5.4
7	3.0	10.0	1.0	5.6
8	4.7	15.6	0.6	8.8
Filter	10.6	35.2	0.15 est	19.7

Total 30.1 mg 56.1

Gas Vol. Sampled = 18.95 SCF = 0.537 M³

Inlet Gas Filter wt Gain--17.9 mg

Vol. Inlet Gas Sampled--0.106 M³

Inlet Gas Particle Burden--169 mg/M³

(a) Operation during batch mode configuration and with a wire screen demister above the packing in the de-entrainer.

CHRONOLOGICAL DESCRIPTION OF RUN C-13

Run C-13 was made to obtain additional data after H_2S cylinder gas was added with all systems operating. All systems were operated, but so much difficulty was experienced with flooding in the regeneration column that H_2S gas flow was not initiated.^(a) A polishing filter had been fabricated and installed above the packing in the packed-bed de-entrainer, and provision was made for operation of the isokinetic particle samplers and associated impingers during the run.

In preparation for this run, the salt cooler, which had plugged and caused termination of run C-12, was heated under CO_2 pressure until the pressure relieved, indicating a flow passage was established. The unit was then cooled under continuous gas flow and flushed with HNO_3 and water until clean.

The secondary burner, which had malfunctioned repeatedly (pilot flame failure) during run C-12, was disassembled and cleaned. A new high-voltage transformer for the spark igniter was installed.

The polishing filter media was a ceramic felt with fibers 3 to 10 μM in diameter. This was supported on a cylinder of 1/4-in.-mesh stainless steel screen 7 in. in dia x 12 in. long welded to a 16-in.-dia section of sheet SS with a 7-in.-dia. center hole. The opposite end of the cylinder was closed by welding it to a 7-in.-dia, SS circle. When the ceramic felt was in place it was secured by an overlay of ~ 20 mesh SS screen, wired in place. This filter had an area of 1.83 ft², and filtered a total gas flow of 45,000 SCF during the run.

Figure X-1 illustrates only a part of the operational history of this run. The time scale extends from 10:00 of 7/17/78 to 21:00; however, the trace heating was turned on at 20:10, 7/16/78. The interval between this time and 6:00, 7/17/78, when the gasifier was started, was occupied with the work

(a) H_2S gas addition, by increasing the sulfur ion activity causes additional corrosion. If iron is present, FeS can precipitate or form high-melting $xM_2S \cdot yFeS$ compounds of limited solubility. These cause problems in operation of the regeneration column.

of bringing the heaters to temperature, checking and repairing thermocouples, starting the secondary burner, and charging fuel (coke) to the gasifier.

Gas flow was routed to the scrubber at 12:00, but the gas preheater temperature was low, as were the temperatures in the salt cooler, so start of salt flow to the venturi was delayed. The low gas temperature resulted in production of soot, which partially blinded the polishing filter. It was necessary to increase the extraction side temperatures to 730°C and to start water injection to the top of the bed in the gasifier to clear the filter.

Salt flow to the venturi was finally established about 15:50 after taking time to rod out the orifice. Flow was maintained until 19:17 (except for a brief interruption to prime the trays in the extraction column). Shutdown at 19:17 was for gasifier refueling.

Efforts to initiate flow to the extraction column began as early as 13:00, but the first indication of flow came at 14:30. By 15:00 tank level readings indicated that 6.5 l of salt had flowed to the extraction column (avg. flow 217 ml/min). From 15:00 to 15:17 the flow increased to 765 ml/min.

At 15:16, flow to the regenerator was initiated. This was indicated by the sudden increase in air temperature at the exit of the salt cooler.

There was an interruption of flow at 16:04 as the siphon plugged, but flow was re-established about 17:00. Operations of the regeneration column continued until about 18:40, when flow was valved off when it appeared the column had plugged. The temperature of the regenerator was increased to 700°C in an effect to free the obstructions.

Meanwhile, the venturi and the extraction column were valved off (19:00) and time was taken to refuel the gasifier with 805 lb of coal. Attempts to restart the regenerator continued. A trickle of salt may have flowed at 03:00 (7/18/78) but it went unnoticed at the time. At about 15:00 on 7/18/78, flow to the regenerator was established. Flow to the extractors was obtained at 13:00. After rodding out, flow to the venturi was established at 14:25.

Flow to the regenerator was very erratic. It appeared to be plugging and restarting. Temperatures were much too high for effective regeneration, but it was necessary to maintain high temperatures to induce flow.

Pressure drops across the extraction section were increasing and it was surmised that the polishing filter was beginning to blind. This factor, together with all the problems with salt flow, led to a decision to shut down while a trickle of flow could be maintained. Efforts were then directed toward draining all salt to the lower catch tank in preparation for exhaustive aqueous flushing of the entire plant. Salt drainage was completed during the interval from 17:00 to 19:30 (7/18/77).

XI. RUN C-14

SUMMARY

Run C-14 was started on 8/7/78 but was shut down as a result of a serious salt spill that occurred when the venturi feed valve failed to restrict salt flow. All salt flow control valves were replaced and the run was resumed on 8/14/78.

Operation from 09:00 on 8/14/78 to 02:00 the next day occurred in two periods of about 6 hr each. Hydrogen sulfide cylinder gas was used to increase the sulfur loading. The extraction section operated with only minor difficulties in salt flow control to the extraction column and with little plugging of the venturi orifice. The regenerator flooded severely on two occasions. The first time, the siphon drain froze (or plugged), causing the column to over-fill. It is not certain what caused flooding the second time; however, flow control with the newly installed valves proved very difficult and the salt feed rate may have been too high.

With clean salt H_2S recovery was very high (exceeding 97%) during the early part of the run and remained high during the second part. Difficulty in analysis of inlet gas samples resulted in some uncertainty regarding extraction performance early in 8/15/78. The regenerator was starting to produce H_2S at 1.8% - 1.9% (dry basis) when it flooded. The run was terminated to permit replacement of a cracked line between the salt makeup tank and the extraction column feed valve.

PERFORMANCE OF THE EXTRACTION AND REGENERATION SECTIONS

At the end of run C-13 all salts were drained from the system, which was cooled and cleaned as thoroughly as possible with aqueous HNO_3 , water, and steam. Run C-14 was initiated on 8/7/78 using clean salt. The venturi feed tank was filled by opening the valve to the extraction column. About 24 to 26 liters of salt was introduced (~ 165 lb). Flow to the venturi failed to start, and it appeared there was a plug of salt in the venturi feed line. The orifice was clear. The venturi feed line was pressurized by inserting a pipe

into the orifice via the clean-out port. Using 80 lb of air the plug was broken loose, but when the pressurizing line was removed salt spewed out of the clean-out port and the venturi feed valve would not seal off the flow. The contents of the venturi feed tank drained completely, with 2/3 spewing out onto the concrete slab. Fortunately, no injuries to personnel resulted. The run was suspended and the valves were replaced. Examination disclosed the seat in the venturi feed valve had corroded away (cf. Figure III-4). It appeared that sludge had settled in the valve seat and allowed a seal despite extensive corrosion. The aqueous HNO_3 flush had dissolved the sludge, or most of it, and a seal was no longer possible.

Run C-14 was resumed on 8/14/78 after replacing all salt control valves. Figure XI-1 illustrates the operating sequence from 08:00 (8/14/78) to 02:00 (8/15/78). Troubles were immediately encountered with operation of the new valves. Though they were the same make and model previously used, they seemed more difficult to operate at low flows.

The regenerator flooded immediately after startup. The siphon drain froze, and with high inlet salt flow the column over-filled, plugging the sample ports and ΔP sensor lines and overflowing a small amount of salt into the product gas line. The venturi was continued in operation with H_2S cylinder gas addition to produce a reasonable sulfur loading while work to restore the regenerator to operability went on.

During the period from 15:05 to 21:05, while gas flow was off, about 20% of salt in the venturi feed tank leaked through the venturi feed valve to the lower pot. The latter was initially provided for just this eventuality.

From 09:05, when gas was first routed to the scrubber, to 15:05 the extraction column and venturi scrubber were operated. Starting with clean salt and with fuel gas to which cylinder H_2S was added, recovery was in the range of 97% to 98% across the venturi.

Preoccupation with the problem of restoring regenerator operation upset the sampling routine and salt samples were not taken as required. Integration of the areas under the curve which is defined by open circles (i.e., the inlet gas compositions) gives the added sulfur from which the salt composition can be calculated. From these numbers the concentration of H_2S in the gas at

FIGURE XI-1. Performance of the Extraction Section During Run C-14

the venturi outlet can be calculated. The result is shown as the dashed curve in Figure XI-1. In the operating period from 09:05 to 15:05, the venturi outlet assays scatter about this curve but are of the correct order of magnitude.

When operation resumed at 21:05 the salt feed to the extraction column was started first. The makeup tank contained 42.5 l, of which 27.5 l was clean salt and 15 l was salt which had drained from the regenerator and which is estimated to have contained 0.48% sulfur. This 42.5 l of relatively clean salt was fed to the extraction column over the period 21:05 to 22:00. It mixed with 9 l of salt in the column and 11 l of salt in the coarse de-entrainer. If mixing was complete (very doubtful) the average sulfur content of the salt would be 0.89%, and this would be in equilibrium with gas containing 54 ppm H_2S . The venturi outlet sample at 21:41 contained 173 ppm, which is less than that computed for the salt at the end of the first period of operation and is reasonable.

The clean product gas sample should be lower in sulfur than the venturi exhaust sample, and the G-3 sample at 21:58 contained 20 ppm S + 77 ppm COS. The G-3 sample at 22:23 contained 129 ppm H_2S + 19 ppm COS, which is a more usual H_2S /COS ratio.

At 21:57, H_2S cylinder gas was introduced at a flow calculated to yield 3000 ppm H_2S . Uncertainty in analytical data makes precise evaluation of the inlet sulfur difficult beyond 22:00. The curve has been drawn to correspond with additions during the first period because the rotometer settings were the same; however, the analytical data over the period 23:00 to 02:00 indicate the presumed inlet sulfur is lower.

Samples of regenerator product gas and their analyses are shown in Table XI-1. Here, too, the regenerator does not yield gas sulfur concentrations as high as would be expected at this inlet sulfur content. The calculated equilibrium sulfur content of the salt is about 1/3 of that estimated by accrual of inlet sulfur levels. It appears that either the inlet sulfur is lower than shown in Figure XI-1, or some other factor is operating to sequester sulfur irreversibly. Data presented in Run C-15 will disclose

TABLE XI-1. Run C-14, Regenerator Performance 21:00 to 02:00

Sample Point	Sample Time	H ₂ S, %	Temp., °C (Top)	Temp., °C (Bottom)	CO ₂ , SCFM	Steam, SCFM	Eq. wt% S
S-8	22:32	0.49	651		1.9	4.2	0.274
S-7	22:58	0.20	650		1.9	4.2	0.114
S-7	23:16	0.099	650		1.9	4.2	0.057
S-7	23:57	1.68	652	640	1.9	4.2	0.855
S-7	00:11	1.18	-		1.9	4.2	0.627
S-7	00:32	1.90	652		1.9	4.2	0.949
S-7	00:47	1.80	653	650	1.9	4.2	0.917

additional data to further define what has occurred. It appears, however, that high iron concentrations in the salt are causing irreversible absorption of sulfur in the salt.

Operation was continued until 02:00 of 8/15/78, when the regenerator again flooded severely. After this occurred approximately 8 hr were spent cleaning the sample ports and product gas line. When this was completed, the regenerator was checked out using the reservoir of salt in the coarse de-entrainer. It appeared to be working properly, so preparations were made to start the rest of the system. When the valve to the extraction column was opened no flow resulted and a failed heater on the line was located. This was removed and it was discovered that the 1-in. line was bulged slightly and had developed a small salt leak that had destroyed the heater. To remove and repair this line would require shutting down the furnace on the salt makeup tank to allow the salt to freeze. Because of the time required for repairs, it was decided to terminate the run.

RUN C-14 CHRONOLOGY

6/7/78

20:00 Start trace heaters.

8/14/78

02:35 - 03:30 Charge gasifier, 800 lb coke.

07:30 Repair extr'n. col. sample port heaters.

09:05 Start gas to scrubber.

09:20 Start salt feed to extraction column.

09:56 Start venturi scrubber.

10:30 Venturi orifice plugged. Rod out and restart at 10:50.

N.B. By 10:30 approximately 44 ℓ (205 lb) of salt has been fed to the extraction column and venturi feed tank. At this time the coarse de-entrainer was filled.

11:15 Introduce H_2S cylinder gas at 5.8 ℓ /m (calculated to yield ~ 3000 ppm in inlet gas).

11:32 Start salt flow to the regeneration column (CO_2 flow at 1.9 SCFM, but no steam flow).

11:47 Stop regenerator salt feed. Siphon drain is plugged. When thawed, 15 ℓ of salt drained to the salt makeup tank.

12:28 May have lost salt flow to venturi. Inlet gas temperature very low ($\sim 510^\circ C$).

13:14 Bypass gas, shut off H_2S cyl. gas, and rod venturi orifice.

13:32 Restart. Salt flow is erratic.

14:05 Shut off H_2S cylinder gas.

15:07 Shut off salt flows and bypass gas.

17:00 - 18:45 Charge 1000 lb of coke to the gasifier.

20:40 Regenerator checks out satisfactorily.

21:05 Route fuel gas to scrubber.

21:10 Start salt flow to the extraction column.

21:28 Start salt to regenerator – off at 21:34.

21:28 Start salt to the venturi. Flow continued to 24:00. Between 24:00 and 00:52 salt flow was reduced for unknown reasons.

21:57 Start H₂S cylinder gas at 5.8 l/m.

22:45 - 01:53 Flow through both the extraction and regeneration columns approximately in balance, though frequent valve adjustment is necessary at both feed points.

00:52 Venturi salt valved off to prime absorber trays.

01:13 Restart salt to the venturi.

01:33 Regeneration column is severely flooded. All sample ports and the exhaust line are plugged.

02:00 Shut down all salt feeds and bypassed gas.

02:30 - 13:30 Cleared salt from the regenerator exhaust line and have partly cleared sample ports.

14:54 - 15:42 Trying to establish salt flow to the extraction column.

15:50 - 16:61 Salt and gas flow to the regenerator show no problems.

16:40 - 18:30 Located burned out heater on extraction column feed line.

19:30 Extraction column feed line found to be cracked and leaking salt (very low rate, but sufficient to damage trace heater). To repair, it is necessary to replace the line, and the salt in the makeup tank must be cooled and solidified. This is time-consuming, and the decision was made to terminate run C-14.

XII. RUN C-15

SUMMARY

Run C-15 began on 8/20/78 and continued for nearly 4 days. A number of operating problems were encountered that reduced the total time the venturi operated with salt flow down to 12 hours. During all but 4 hr of this time the salt flow to the venturi was intermittent or at a very low rate. The extraction column and regenerator operated with salt flowing for 8.8 hr and 12 hr, respectively.

The run was terminated because of severe plugging of the regeneration column. The salt cooler and the extraction column feed valve also plugged, but were subsequently cleared. Plugging problems were traced to high levels of iron, sulfur, and/or coke dust in the salt.

The H_2S content of the feed gas was increased to 0.5% to 0.7% (vol). This resulted in very high salt phase sulfur loadings. The sulfur removal efficiency of the scrubber systems remained above 95%, which was substantially higher than expected. It appears that the high iron substantially altered the H_2S extraction and salt regeneration chemistry as described in Section IV so that the results obtained are not representative of those expected from the process when operated relatively free of iron.

Run C-15 was essentially a continuation of run C-14. Between runs, the absorber feed line was repaired and a larger drain line installed on the regenerator. The larger regenerator drain line eliminated the plugging problems that had caused several process upsets in run C-14 and several other runs. The new valves installed for run C-14 continued to cause problems. They were difficult to adjust and set reproducibly and then failed to provide a tight shutoff, which led to large salt losses from leakage.

PERFORMANCE OF THE EXTRACTION AND REGENERATION SECTIONS

The trace heaters were started at 20:00 on 8/20/78, and shutdown was initiated nearly four days later (on 8/24/78). Because of a number of operating problems, the scrubber system was operated for only a part of this

time. The venturi scrubber was operated with salt flow for approximately 12 hr, the extraction column 8.8 hr, and the regenerator 12 hours. During a significant fraction of this time the operation was sporadic and uncertain.

Nearly all of the operating time was logged during two separate operating periods. See Figure XII-1 and XII-2 for a summary of component operation. During the first operating period, problems were encountered with the venturi scrubber. The pressure drop was higher than normal, which reduced the amount of head available for salt flow. At times the back pressure became greater than the salt pressure, which caused gas to be blown through the venturi orifice and feed line to the venturi feed tank. This was first thought to be due to problems with carbon deposition. The usual measures were taken to mitigate this problem, but these were totally ineffective. After concluding that soot deposition was not causing the flow restriction, other potential problems were assessed. It was finally necessary to disassemble the venturi exhaust line to locate the obstruction. The ceramic venturi liner had fragmented and several pieces had been transported up the venturi off gas line and had lodged in an elbow near the entrance to the coarse de-entrainer. After removing the obstruction and reassembling the line, preparations were made to restart the scrubber system.

During the second operating period all systems were operated simultaneously and continuously for approximately eight hours. After the first four hours, plugging problems began to develop. The extraction column feed valve plugged, causing liquid to build up in the makeup tank. This stopped salt flow to the venturi feed tank, which soon ran dry, interrupting salt flow to the venturi. After numerous attempts to clear the extraction column feed valve the plug finally broke loose. After the salt supply to the venturi feed tank was replenished, salt flow to the venturi was reestablished but was sporadic and at a low rate. Partial operation of the venturi continued for the next three hours (23:00 on 8/22/78 to 02:00 8/23/78). During this period the pressure drop across the regenerator trays began increasing markedly. By 03:48 on 8/23/78 it appeared that the column was almost totally plugged; all gas and salt flows were shut off. The regenerator off-gas line was removed, which allowed inspections of the off-gas line and regenerator top tray. The exhaust

FIGURE XII-1. Scrubber Performance, 8/21-22/79

FIGURE XII-2. Scrubber Performance, 8/22-23/79

line was clear and the liquid level on the top tray normal. This led to the conclusion that the bubble caps and/or risers must be plugged (which was subsequently verified when the column was dismantled). During the period when the regenerator pressure drop was increasing, the salt cooler also began to plug. Near the end of this period salt flow was measured at 103 ml/min with the valve set at a position which normally gave several l/min.

In an effort to clear the restriction in the regeneration column, air was blown through it. This produced a vigorous exothermic reaction and billows of dark smoke but had little effect upon the flow restriction. However, blowing air through the salt cooler did eliminate the plug in that unit.

From the available data it is not possible to absolutely pin down the cause of the plugging experienced during this run. However, it is almost certain that the plugging resulted from some combination of three factors: high iron loading, high sulfur loadings, and high particulate loading from coke dust carryover. In this regard, a number of key pieces of information should be pointed out. H_2S cylinder gas was added to the scrubber feed gas for seven hours during this second operating period. Sulfur loading was relatively high--particularly in the last part of the period, when the severe plugging problems began to appear. Salt samples taken at the end of the period showed 6.1% (wt) sulfur in the venturi feed tank, 4.8% in the makeup tank and 6.9% on the top tray of the regenerator. These samples were also high in iron, with 1.8%, 1.7%, and 4.7% in the venturi feed tank, makeup tank, and regenerator top tray, respectively. The much higher iron concentrations on the regenerator top tray indicate that iron-bearing precipitates had settled out in the cooler parts of the system. Samples of deposits from the venturi exhaust line and regenerator off-gas line also showed very high iron and sulfur contents. When the venturi exhaust line was disassembled to remove the fragments of ceramic, it was noticed that a hard deposit $\sim 1/4$ in. thick was present on the pipe wall in the area of the flange. A sample of this material assayed 9.4% iron and 14.4% sulfur. The calcium content of this sample was also higher than expected. This sample came from a vertical section of a line

that had been operating at $\sim 720^{\circ}\text{C}$ with hot gas flowing inside at a high velocity. The fact that the material did not drain when the gas flow was stopped indicates that it was solid or semi-solid at the operating temperature. Another deposit, this time from the regenerator exhaust line, contained 13.2% iron and 14.2% sulfur. This deposit was a mushy semi-solid when removed from the line. After blowing air through the regenerator another sample of salt was taken from the top tray. The iron and sulfur contents had increased to 11.1% and 8.8%, respectively, from 6.9% and 4.7% found prior to the air oxidation. It is believed that this substantial increase resulted from resuspension of solid deposits from the tray. Resuspension may have been caused by the high temperature ($\sim 800^{\circ}\text{C}$) or by the oxidizing atmosphere present. It is possible that an abnormally large quantity of coke dust was carried over into the scrubber feed gas and subsequently deposited in the salt. Once in the salt, it could have contributed substantially to the plugging problem. By the end of run C-11 the original coke supply for the gasifier was nearly exhausted. Additional coke was obtained and used in runs C-12 through C-16. This coke was of rather poor quality and contained a large percentage of fines. It does appear that plugging problems were more severe in runs where this coke was used. The presence of carbonaceous material in the regenerator is confirmed by a gas sample taken while air was being blown through the columns. The sample contained 5.5% CO_2 , 16.3% O_2 and 78.2% N_2 . It has been suggested that precipitation of iron sulfide in the cooler regions could act to agglomerate and settle other particulates, which might greatly increase plugging problems.

After the equipment had cooled, the regenerator was removed and cut open. Two of the four downcomers were completely plugged, and many of the bubble caps were totally plugged. All of the bubble caps were at least partially blocked with solids. The inside of the risers was coated with solid deposits typically $\sim 1/2$ in. thick. A thick salt deposit had built up on the pipe wall at the flange located in the center of the column. (See also Section IV for additional discussion and photographs of the columns--e.g., Figures IV-6 and IV-7.)

In summary then, it is concluded that the regeneration column was made inoperable by deposits of solid materials that precipitated from the salt.

The deposits contain iron, sulfur, and carbon, and their appearance is closely related to high levels of iron, sulfur, and/or coke dust in the salt.

The sulfur removal performance of the molten salt scrubber system was exceptionally good during run C-15. An examination of the data however, reveals that a high concentration of iron in the salt substantially altered the chemistry of the H_2S absorption and regeneration reactions, resulting in better than expected absorption and in poor regeneration. The performance results are of somewhat limited usefulness, since they are substantially different from the results expected when the process is operated free of iron contamination.

Data on gas cleaning and regeneration performance were obtained during two operating periods. However, data during the first operating period is fairly limited. Gas analyses and operating data are summarized in Figure XII-1 and XII-2. Hydrogen sulfide cylinder gas was added during both operating periods. Sulfur removal efficiency was typically very good when H_2S gas was being added. Between 21:10 and 22:40 on 8/21/78, the fuel gas sulfur content was reduced from 7200 ppm (average) at the inlet to less than 270 ppm. Similar performance was observed in the second operating period; between 19:10 on 8/22/78 and 02:10 on 8/23/78 the sulfur content was reduced from an average 6800 ppm at the inlet to less than 260 ppm. Comparison of measured gas phase H_2S concentration with calculated equilibrium values shows that the measured concentrations are much lower than expected. For example, absorber and product gas samples taken during the second operating period averaged 150 ppm H_2S with a maximum concentration of 244 ppm. These H_2S concentrations correspond to a calculated equilibrium salt phase sulfur loading of 1.1% and 1.6%, respectively. These concentrations are much lower than the measured salt loadings of 4.8% and 6.1% on samples taken at the makeup and venturi feed tanks at the end of the operating period. A material balance calculation indicates that the average salt sulfur loading in the system should have increased steadily from 0.7% when the H_2S cylinder gas was turned on, to 5.4% when it was turned off. A portion of the difference between the calculated and measured sulfur loadings can be accounted for by

assuming all iron is present as FeS. Subtracting out the sulfur assumed to be present as FeS leaves a balance of 3.8% in the makeup tank sample and 5.1% in the venturi feed tank sample, which indicates the sulfur is still substantially higher than the calculated equilibrium loading. It is possible that compounds of iron, sulfur and alkali metals may form (See section IV). If such compounds are formed they could further reduce the effective sulfide ion concentration in the salt. This would result in the type of behavior observed--i.e., the equilibrium salt sulfur loading for a particular H_2S concentration would be greater than that for the salt mixture with no iron present. In any event, it appears that the high iron concentration in the salt during this run affected the chemistry of the H_2S removal process to the extent that the measured sulfur removal efficiencies bear little resemblance to those that could be expected once the problem of iron contamination is eliminated. The effect on the regenerator performance was similar. Reduction of the effective sulfide ion concentration greatly reduced the equilibrium H_2S concentration for a given salt sulfur loading. This obviously has a detrimental effect upon regenerator performance, since the rate of sulfur removal in the regenerator is directly proportional to the gas phase sulfur concentration. The regenerator gas analyses and operating data are summarized in Table XII-1. A number of times during this run the salt level in the course de-entrainer and salt cooler ran low. When this happened, fuel gas could leak into the top of the column and be carried out with the regenerator product gas. While this did not cause any operating problems, it did cause errors in the regenerator product gas analysis. Samples which may have been diluted in this way are noted in the table.

RUN C-15 CHRONOLOGY

8/20/78

20:00 Start heatup of system.

8/21/78

00:30 Most heaters up to $600^{\circ}C$ -- secondary burner started.

00:45 Sample port heaters started.

TABLE XII-1. Run C-15--Regenerator Operating Data

Time	Sample Point	Gas Analysis (Dry Basis)			Stripping Gas Feed		Center Temp., °C	Wall Temp., °C	Comments
		H ₂ S, %	COS, %	H ₂ , %	CO ₂ Rate, SCFM	Steam Rate, SCFM			
8/21/78									
15:42	S-8	1185 (ppm)	77.8 (ppm)		0.5	1.8	609	604	Salt flow off for ~30 min
17:55	S-7	238 ppm	135 ppm		--	--	620	606	No salt flow for 2-1/2 hr
19:04	S-7	0.6		1.5	--	--	637	606	
19:20	S-7	0.6		0.24	0.5	1.8	642	605	
19:58	S-7	0.65	0.01	0.75	0.5	1.8	645	605	
20:27	S-7	0.96		--	1.0	1.8	644	606	Diluted with 30% producer gas
20:47	S-7	1.42	.014	0.35	1.0	1.8	644	606	
21:10	S-7	1.92	.013	--	1.0	1.8	642	609	Diluted with 40% producer gas
21:35	Gas bypassing through salt cooler						643	594	
8/22/78									
19:46	S-7	0.98		0.09	0.5	4.1	635	602	
19:59	S-7	0.73	--	--	0.5	4.1	635	602	Little or no salt flow
20:16	S-7	0.34	--	--	0.5	4.1	635	605	Little or no salt flow
20:45	S-7	0.77	--	--	0.5	4.1	636	620	Diluted with 20% producer gas
21:47	S-7	1.1	0.01	0.18	0.5	4.1	636	631	
22:08	S-7	1.1	--	0.24	0.5	4.1	625	631	
22:23	S-7	4.1	0.02	4.6	0.5	4.1	621	631	
22:39	S-7	4.4	0.01	8.6	0.5	4.1	618	631	
23:36	S-7	1.8	0.011	0.17	1.0	4.1	609	609	Salt flow to regenerator lost 23:20
00:05	S-7	1.8	0.011	0.16	1.0	4.1	607	603	No salt flow
00:21	S-7	1.6		0.92	1.0	4.1	608	604	No salt flow
00:36	S-7	1.9		3.9	0.5	4.1	605	604	Salt flowing possible dilution with ~10% producer gas
00:53	S-7	1.9		2.2	0.5	4.1	605	604	Dilution with ~20% producer gas
02:16	S-7	1.75	0.014	0.31	0.5	4.1	624	604	
02:37	S-7	2.13	0.014	0.53	0.5	4.1	626	604	
02:55	S-7	2.42	0.019	1.12	0.5	4.1	625	604	
03:14	S-7	2.75	0.021	0.91	0.5	4.1	626	604	
03:42	S-7	1.63	0.116	1.79	0.5		619	609	Steam feed off at 03:38

02:30 Finished loading 50 lb charcoal and 800 lb coke into gasifier.

03:00 Sample port heaters not working.

05:00 Sample port heater on extraction column repaired.

09:15 Sample port heaters on regenerator repaired. Secondary burner went out. Burner block dismantled and cleaned--working O.K. now. Waiting for regenerator drain line to thaw before starting salt flow.

09:50 Regenerator drain line thawed. Take initial tank readings and prepare for startup.

09:55 Valve gas to scrubber system.

10:15 Cannot get salt flow to venturi. Some portions of feed line not completely up to temperature yet--bypass gas.

11:17 Valve gas through scrubber system.

11:24 Start salt flow to venturi.

11:28 Shut off salt flow to venturi. High venturi pressure drop with no salt flow. Start injection water to gasifier. Will transfer more salt to venturi feed tank.

11:47 - 11:57 Salt flow to extractor (transferring salt from makeup tank to venturi feed tank).

11:57 - 12:08 Salt flow to venturi.

12:08 Increase gasifier injection water to 275 ml/min.

13:10 Start venturi salt flow -- good flow for a few minutes then lost flow -- 5 & total flow.

13:50 Increase temperature on extractor and venturi system to 730°C.

13:52 - 15:40 Venturi flow stopped and started several times. Flow cannot be maintained for more than a few minutes. It appears there is a partial blockage of the venturi exhaust line. This causes a large back pressure at the venturi which results in gas being blown back into the venturi feed line. Once this starts the liquid head decreases and flow ceases.

14:19 - 15:12 Cautiously working salt through regenerator by opening feed valve for 30 to 60 sec at a time. Steam on at 1.8 SCFM, CO₂ at 0.5 SCFM. Regenerator appears to be working properly.

15:45 Shut off venturi salt flow and bypass gas.

16:00 - 18:00 Add coke to gasifier.

18:50 Gas flow to scrubber system.

19:03 Cleared regenerator feed valve. Got positive indications of flow.

19:08 Start steam flow to regenerator, 1.8 SCFM CO₂ at 0.5 SCFM.

19:09 - 19:52 Open and clear extraction column feed valve. Little or no salt flow.

19:10 - 22:36 Sporadic salt flow to venturi. Having continued problems with loss of salt flow to venturi caused by high back pressure. Shut down briefly at 23:15 to check salt level in venturi feed tank. While flow was bypassed the entire contents of the venturi feed tank leaked out (into the lower salt tank). The remaining salt in the system was not enough to operate, so 150 lb of fresh salt was added.

19:08 - 21:00 Pressure drop measurements indicate regenerator is operating properly. Pressure drop across the middle two trays may be a little higher than normal.

19:14 Salt flow briefly to regenerator.

19:48 Increase steam flow to regenerator to 4.15 SCFM.

19:50 - 22:31 Continuous salt flow to regenerator; flow rate appears to be fairly low (~180 ml/min average).

19:52 - 22:31 Salt flow to the extraction column; high rate for first few minutes, then feed tank is empty. After this, feed is equal to salt flowing out of regenerator.

20:26 Increase regenerator CO₂ feed to 1.0 SCFM.

21:06 - 22:36 Pressure drop across regenerator top tray has increased to about 2x the normal drop. Total column ΔP also is somewhat higher than normal.

22:36 Shut off all salt flow bypass gas. Low on salt, will add 150 lb, 8/22/78 as indicated above.

02:05 Valve fuel gas through scrubber system. Pressure drop across venturi is 3.4 psi versus ~0.5 psi normally. It appears that increasing the operating temperature and the fuel gas water content are not helping as they have in previous runs. The plug appears to be getting worse. Will try salt flow one more time.

03:03 - 03:21 Salt flow to extractor (7 l total).

03:04 -03:41 Opened regenerator feed valve several times - no flow.

03:18 Start salt flow to venturi. Back pressure is too high, cannot maintain full gas flow.

03:21 Closed extractor feed valve. Did not stop flow - 23 l of salt leaked past valve in next 20 min.

03:32 Gas flowing back through venturi feed line.

03:45 Extraction column and venturi feed valves are not completely stopping salt flow when closed. An additional 110 lb of salt has been lost to the lower catch tank.

03:45 - 12:00 Checked venturi exhaust line for cold spots or other evidence of problems--could not find any. Tried blowing steam through line - no help. Then tried blowing air through line - still no help. Finally decided to start dismantling the line to locate the plug.

06:07 Venturi feed valve not stopping flow; have lost another 110 lb of salt to lower catch tank.

12:00 - 16:00 A flange at the top of the venturi exhaust line was opened, and it was found that the plug was in an elbow section of pipe connected to

the coarse de-entrainer. This pipe was removed and cleaned out. It was found that the ceramic liner in the venturi had fractured and pieces were carried up the venturi exhaust line, where they lodged in an elbow.

16:00 - 17:40 Charge coke to gasifier and get ready to restart scrubber system. Add 112 lb fresh salt.

17:40 Start gas flow through scrubber system. Venturi ΔP is back to normal.

18:22 Water injection to gasifier turned on at 180 ml/min.

18:23 Steam to regenerator at 4.1 SCFM CO_2 at 0.5 SCFM.

18:30 - 18:37 Running salt through regenerator in brief spurts.

18:37 - 22:30 Salt flow to the regenerator.

18:40 - 22:39 Salt flow to the extraction column.

18:53 Start salt flow to venturi.

19:05 Start H_2S spike gas at 7 l/min.

21:20 Pressure drop on regenerator bottom tray has increased; drop across middle two trays also looks a bit high.

22:17 Salt flow to venturi appears to be dropping.

22:20 Pressure drop on all trays of regenerator are increasing. Total column ΔP is about 2 to 3 times normal.

22:30 Salt flow to venturi appears to have stopped.

22:54 - 23:05 Extraction column feed has plugged - trying to clean valve. Coarse de-entrainer empties, allowing fuel gas to bypass into regenerator exhaust line.

8/23/78

23:00 - 2:00 Low sporadic flow to venturi.

23:05 - 01:13 Salt flow lost to regenerator.

00:30 - 03:48 Salt flow established to regenerator. Pressure is high; column appears to be plugging up.

01:13 Extraction column feed valve shut off.

02:10 Shut off H_2S cylinder.

02:25 - 04:30 Have lost salt flow to the venturi.

03:48 Regenerator salt flow off. Column appears to be plugged.

04:30 Bypass gas and rod out venturi orifice.

05:25 Restart venturi gas and salt flow.

05:30 - 05:50 Salt flow briefly to regenerator.

05:40 Have lost salt flow to venturi.

05:46 Close venturi feed valve and bypass.

06:00 Remove regenerator exhaust line to investigate reason for high pressure drop. Exhaust line is clear and top tray has proper salt level. It is concluded that internals of the column are plugging. A liquid salt sample taken from the top tray analyzed 4.7 wt% iron and 6.9 wt% sulfur; a semi-solid material removed from the exhaust line directly above the tray contained 13.2 wt% iron and 14.2 wt% sulfur (analyzed at a later date).

14:00 It was decided to try blowing air through the regenerator in an effort to burn the plug out.

15:20 - 17:06 Air blowing through the regenerator causes an immediate exothermic reaction; air flow must be kept low to avoid severely overheating the column. Smoke pours out the top of the column. Gas analysis shows high CO_2 content, indicating that we are burning carbonaceous material.

17:50 Check out regenerator with gas flow but no salt flow. Pressure drop has been reduced, but still appears higher than normal.

8/24/78

18:00 - 01:30 Tried to get salt flow through regenerator; found that the salt cooler was plugged. After turning up heater set point and checking for

cold spots it was decided to try blowing air backwards through the salt cooler. This successfully removed the plug.

01:43 Start salt flow to regenerator. Approximately 3 l of salt flow before the feed line froze up. It was later found that in removing the off-gas line a crack about 1/2 in. wide had been made in the insulation on the regenerator feed line. When the insulation was repaired the line quickly thawed and the coarse de-entrainer and salt cooler were completely drained in a few minutes.

01:45 - 2:22 Pressure drop measurements show that the regenerator trays are still plugged.

13:00 Insulation repaired on regenerator salt feed line.

14:00 Coarse de-entrainer and salt cooler drain.

18:00 Start shutdown of system.

XIII. RUN C-16

SUMMARY

Run C-16 was initiated at 20:00 on 9/10/78 and continued for four days. Serious plugging problems, caused partly by heater failures, resulted in limited operation with salt flow. Gas cleaning performance of the extraction section was difficult to evaluate because the short operating intervals did not allow adequate sampling and analysis. In the few cases where samples were taken and analyzed, gas cleaning performance was excellent.

The packed regeneration column did not operate for a time sufficient to generate data that would indicate proper operation. Only a single sample point was available, on the product gas line, and the highest H_2S concentration observed was only 0.3%. During much of the run samples taken here were invalidated as a result of air in-leakage.

Operation was seriously hampered when the salt return flow line plugged near the start of the run. (It may never have been open.) This caused the coarse de-entrainer to over-fill and eliminated the recycle flow of salt to the venturi feed tank. The decision was made to operate without recycle flow--i.e., the venturi would take whatever flow came through the extraction and regeneration columns. This reduced the normal flow at the venturi, which attains a maximum in recycle mode of ~ 3 l/min. Without recycle, flow was sporadic and on the order of 1 to 1.5 l/min. at most.

Total sulfur level in the salt leveled out at 2 to 2.5%. Iron levels ranged from 0.5% to 1.0% on 9/11/78, to 1.75% on 9/12/78, from 0.5% to 3.0% on 9/13/78, and from 0.5% to 1.0% on 9/14/78. On the whole, the sulfur level rarely was high enough to favor extraction by iron over that by $CaCO_3$, but some high-melting iron-containing compounds were surely present and contributed to operating difficulties.

PERFORMANCE OF THE EXTRACTION AND REGENERATION SECTION

The severe plugging problems encountered in run C-15 led to the conclusion that a more open type of contactor was needed to replace the 6-in.-dia bubble-cap tray column used for salt regeneration. In order to stay within

time and funding restraints, the only option was to cut the trays out of the bubble-cap tray column and convert it to a packed column. This was done, and a 6-in.-dia column with a 48-in.-deep packing of 5/8-in.-dia x 5/8-in.-long hollow cylinders (1/4-in.-dia center hole) was installed.

Pressure drop across this column could be measured and a gas sample could be taken in the product gas exhaust line. No internal sampling was practical.

Figure XIII-1 illustrates the very limited operating performance obtained. At the bottom of the figure the venturi, extraction column, and regeneration column salt feed sequences are shown. On 9/11/78, the brief operation of the venturi and of the extraction column caused the coarse de-entrainer to over-fill and salt flows were valved off. Salt flow to the regenerator at about 15:00 simply resulted in an excessive pressure drop across the column. Investigation disclosed 11 in. of salt above the packing. The column temperature was increased, and at 18:12 the column drained.

The regenerator now appeared ready to operate, so at 20:00 feed to the extraction column was initiated, but the venturi would not start. Salt to the extractor was valved off and the venturi orifice rodded out. At 20:45 a start was again tried and both the venturi and extraction column salt flows were achieved, but no salt would flow to the regenerator. With the coarse de-entrainer already overfull, immediate shutdown was required.

From 22:00 (9/11/78) until 09:00, efforts to get salt flow to the regenerator were pursued, and between 09:00 and 10:20 (9/12/78) the coarse de-entrainer finally drained through this column. A single gas sample analysis at 0.3% H_2S was obtained. At 10:20 the siphon at the bottom of the regenerator froze and salt backed up in the column. As the pressure drop mounted, salt flow and steam flow were valved off. The CO_2 was reduced and salt promptly flowed into the steam- CO_2 inlet line and froze. This was not cleared until 08:00 on 9/13/78.

Flow of salt was started to the extraction column and venturi at 09:50 to 10:03, but the regenerator siphon was plugged with frozen salt due to a faulty heater and shutdown was required when the coarse de-entrainer again over-filled. At about 12:00 it was discovered that a faulty control thermocouple

FIGURE XIII-1. Extraction Section Performance

was causing the salt makeup tank to overheat. Salt temperature had reached 860°C when the problem was recognized and steps were taken to correct it.

From 14:00 to 14:40 (9/13/78) salt flowed to the regenerator, emptying the coarse de-entrainer. Immediately, gas was noted backing through the salt cooler and coarse de-entrainer, and the H₂S exhaust line was found to be plugged just above the regeneration column. The column had evidently flooded. All salt was now in the makeup tank.

At 15:30 it was noted that the lower catch tank could be pressurized with CO₂, which meant it was not open to the venturi exhaust line. Any flooding of the venturi would result in salt backing into the gas preheater.

By 16:50 the regenerator product gas (H₂S exhaust) line was cleared of salt and the valve to the extraction column was opened, but the venturi feed line was plugged with frozen salt. This was cleared by blowing high-pressure air back through the venturi orifice. Attempts to start again were not successful when no flow could be induced at the extraction column feed valve. By working this valve, flow in a trickle could be obtained, but again the venturi feed line plugged and had to be blown out. Finally, at 21:15 salt flow to the venturi was achieved and salt levels in the coarse de-entrainer were sufficient to start the regenerator, but the heater on the siphon had failed again and had to be repaired.

At 00:45 and 00:52 flow to the extraction column and venturi was started, but no salt flow to the regenerator could be obtained (9/14/78). The gasifier was refueled, fresh salt was added, and during coke addition the conveyor chain parted and limited fuel addition to only 600 pounds. This was repaired on the following day shift, but the gasifier was depressurized while this work went on. When repairs were complete, 1000 lb of coke was added and salt flow to all units was achieved. At about 18:00 the extraction column feed valve plugged and could not be reopened. With all salt trapped in the makeup tank behind this valve, the decision to terminate the run was made.

As was the case in run C-15, it is believed that precipitation of iron salts and coke dust combined to cause serious plugging problems. At the end

of the run, the 3-in. line at the exit of the gas preheater was opened. This was partially filled with a loose sludge of particulate material, including large flakes (1/4 in. x 3/8 in.) of black, strongly magnetic material. These are believed to derive from scale falling off the inside of mild steel pipe between the gasifier and the gas preheater. Iron introduced into the salt is difficult to remove. It reacts under certain conditions to form FeS , which combines with alkali sulfides. Under process conditions these are partly in solution and partly in precipitate or sludge form.

Deposits have built up on pipe walls, which are very high in iron content--some as high as 13%. These appear to be relatively high-melting. Nothing is known about the solubility of these deposits in the molten salt, but in view of the rapidity with which iron builds up in freshly added salt, it may be that with low overall sulfur the material goes into solution to form CaS . At high sulfur (>2%) it may reform and tend to deposit again.

XIV. ADVANCED PROCESS CONCEPTS

Operating problems with this PDU have to a considerable extent been caused by equipment upstream of the PDU. The gas preheater and upstream piping caused excessive introduction of iron in small flakes, which partly dissolved in the salt. The PNL gasifier caused problems. It could not be operated for more than 12 hr at a stretch without refueling. Refueling required shutdown of the PDU for a 1- to 2-hr period and made steady-state operation difficult to attain.

Even with these problems, it is probable that operation would have been considerably improved had it been possible to operate at higher temperatures. Operation at 750⁰ to 800⁰C would have eliminated the need for water injection to the gasifier to reduce soot deposition which, due to molten salt catalysis of the reverse Boudouard reaction, places a lower temperature limit (near 730⁰C) on the applicability of this process.

LOW-PRESSURE GASIFIERS

For gasifiers which operate at near atmospheric pressure and at temperatures in the range 800⁰ to 900⁰C, considerable process simplification becomes possible due to the exponential dependence of the reaction constant on temperature. At these temperatures it has been shown that a single extraction stage is sufficient to yield sulfur recoveries adequate for compliance with EPA standards.⁽¹⁾ With regeneration at 550⁰C, 6% to 8% H₂S (prior to steam condensation) in the product gas from the regenerator would be expected. Using sensible heat from the inlet fuel gas for salt reheat would require about 0.7% of the energy in the coal being gasified.

A process flow diagram that discloses the simplicity of this process is shown in Figure XIV-1. Feed gas is scrubbed in a venturi scrubber, the salt is de-entrained, and the product gas flows through a polishing filter. The salt is regenerated with steam + CO₂ in a unit that also contains provision for salt cooling to 550⁰C at the entering stage. As the salt flows to

FIGURE XIV-1. Low-Pressure Process Flow Diagram

additional regeneration stages, the exothermic regeneration reaction would be allowed to reheat the salt a few degrees.

Salt leaving the regenerator flows to the venturi feed and salt makeup tank, from which a bleed of ~10% of the circulating salt flow is continuously withdrawn while makeup or reprocessed bleed salt is continuously added. Salt leaving this vessel will be reheated by the entering feed gas.

Though a detailed analysis of this flowsheet has not been made, preliminary calculations indicate it is feasible. It differs from the flowsheet used in early batch mode operation in that continuous regeneration is provided.

HIGH-PRESSURE GASIFIERS

The extraction reaction is pressure-sensitive and the concentration of H_2S in the cleaned product gas is directly proportional to pressure. This means additional extraction stages will be required to achieve the sulfur recovery required for compliance with EPA regulations.

At high pressures all vessels and piping must meet pressure vessel coding requirements, and this means the molten salt process will require cold wall construction techniques. Except for small-diameter lines, alonized steel for vessels and pipe cannot be utilized. All large pipe and equipment will require use of ceramic linings.

For this reason it would appear desirable to feed the salt to a ceramic-lined column containing a stacked ceramic packing configuration designed to yield 4 to 5 extraction stages. This can be operated frozen-wall with the sensible heat in the gas supplying heat requirements.

Figure XIV-2 shows a flow diagram for a possible process. Salt flows counter to entering fuel gas in the extractor. It is valved alternately into tanks 1 and 2. While 2 is filling, tank 1 will empty, feeding the regenerator. Salt leaving the regenerator will flow through filters to tanks 1a and 2a, which will be alternately valved off and pressurized with N_2 to return the filtered and regenerated salt to the extraction column. Molten salt flow control is admittedly difficult, but here a definite ΔP can be established from point to point to drive the salt as desired.

FIGURE XIV-2. High-Pressure Gas Cleaning Process

XV. CONCLUSIONS

Operation of the PDU has shown that extraction of sulfur compounds from low-BTU fuel gases with molten carbonate salts occurs readily. Extraction proceeds in accordance with thermodynamic theory and as predicted from earlier laboratory data. The venturi scrubber is an efficient device for particle agglomeration and removal assisted by the packed-bed de-entrainer. The regeneration section failed to meet the design criteria, but operation exceeded theoretical expectations. On the whole, the chemistry of the process has been fully confirmed.

The extraction section performed about as designed, and produced gas that would meet sulfur control criteria. With a crude polishing filter, gas with 37 mg/M^3 (0.016 grain/SCF) particle burden was produced. The regeneration section operated under limitations not anticipated at the design stage. It operated with 4 instead of the 8 stages planned for because of damage sustained during the pack-alonizing process for corrosion protection. It also had to be operated at higher salt flow rates and at higher temperatures than those for which it was designed. This resulted in poor performance, but performance which exceeded that predicted from theory when the high flows and temperatures are taken into account. There is no reason to expect that regeneration would not meet design criteria if column temperatures and salt flow could be properly adjusted.

Numerous problems arose in operation of the PDU, some of which will require additional research to resolve. Salt flow measurement and control was a problem for which no real solution was found in this study, but this was partly due to the difficulty being experienced in maintaining salt quality. Serious iron contamination occurred at the onset of the program. This had far more serious consequences than expected. The iron formed compounds containing S and probably alkali sulfides (e.g. $3 \text{ Na}_2\text{S} \cdot 4 \text{ FeS}$) which melt near 700°C --the temperature at which the extraction section operated. These would tend to precipitate when the salt was cooled for regeneration, carrying all other particles present down also. Serious plugging of small flow passages resulted.

Ironically, post-run analyses and detailed examination of the PDU has pinpointed the source of iron to be external to the PDU. The iron was derived from corrosion-induced spalling of calrod sheath material in the gas preheater just upstream of the venturi scrubber. The amount of iron in the salt at a given time was a function of the condition of the calrod elements in this heater. When the heating elements were replaced after run C-7, low iron levels prevailed in the salt in runs C-8 through C-12 or -13. High iron again appeared in the salt in runs C-14, -15 and -16, rendering the PDU virtually inoperable in Run C-16. Post-run examination has disclosed the presence of large amounts of material high in iron derived from the calrod heaters in the line leading from the heater to the venturi scrubber. The unit is evidently near the point of failure again. Had this source of iron contamination been pinpointed early on, a simple screen might have made a world of difference! Unfortunately, with a PDU fabricated of 314 SS and exposed to sulfide ion and to molten salts at high temperatures, corrosion is too obvious an answer. As it turned out, corrosion of the PDU internals was minimal and would account for only small amounts of the total iron contamination.

Means to meter low salt flow was needed. The siphon-type flowmeters tested for metering average flow failed to function reliably, if at all. Salt flow rates had to be estimated from measurements of fluctuations in tank levels. Flow measurement is a difficult problem at the PDU-scale when flows below 1 l/min are to be sensed and measured.

Valves for flow control posed a problem. Needle valves, such as the bellows-sealed Nupro valves with which the PDU was equipped at the start, can give fine adjustment of flow but proved unsuitable for use with salt carrying separable solids. Such valves plugged easily and irreversibly, causing process shutdowns. They might be useable if placed just downstream of a solids catch pot or coarse filter. Various designs of such devices were developed but never adopted. Instead, a switch to full-opening gate valves was made.

These did not plug irreversibly. They could be opened to the full pipe diameter to flush accumulated solids along and then pinched down to control flow. They required frequent resetting, however, and flow regulation was poor.

The valves were not properly positioned. They were centered in horizontal pipe runs, and when closed at the end of a run did not allow the pipe to drain. When the pipe was reheated it was possible to obtain a pipe segment filled with liquid trapped between plugs of still-frozen salt. Continued heating expanded the liquid, and in two instances caused pipe rupture.

Trace heater failures frequently delayed or caused suspension of a run. For the most part these were failures of small heaters on 1-in.-dia pipe. Large heaters rarely failed. These problems were largely solved by the end of the program by use of variable transformers to reduce applied voltage and temperature of the heating elements.

Finally, many of the problems encountered would have been alleviated had the operating temperature been raised to 750⁰ or 800⁰C. This was feared to be too high for use with alonized steel, and corrosion might indeed have become a problem. The gas preheater would have suffered worse corrosion, and a different approach to gas preheat might have been taken. A higher operating temperature would eliminate problems of soot deposition. This would eliminate the need for humidification of the fuel gas. These factors would combine to yield much higher extraction efficiency.

At higher temperatures, no precipitation of iron compounds would occur. The salt would exhibit higher fluidity, which would reduce plugging at the venturi orifice or other flow constriction. Higher extraction side temperatures would allow higher regeneration side temperatures, with improved reliability of regenerator operation.

As to the latter, a contactor of more open design would have been a better choice. Very early in the design stage a plastic model of a column comprised of a stacked cascade of shallow liquid pools overflowing weirs was tested. This would have been difficult to plug, but would have required preliminary experimentation to yeild assured success in design, and this did not appear warranted at the time.

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