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HOT GAS CLEANUP USING SOLID SUPPORTED MOLTEN SALT FOR INTEGRATED COAL GASIFICATION/MOLTEN CARBONATE FUEL CELL POWER PLANTS

Topical Report for the Period October 1982-December 1983

By
S. E. Lyke
L. J. Sealock, Jr.
G. L. Roberts

December 1983

Work Performed Under Contract No.: DE-AC21-82MC19077

For
U. S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Battelle
Pacific Northwest Laboratories
Richland, Washington

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ABSTRACT

Battelle, Pacific Northwest Laboratories is developing a solid supported molten salt (SSMS) hot gas cleanup process for integrated coal gasification/ molten carbonate fuel cell (MCFC) power plants. Exploratory and demonstration experiments have been completed to select a salt composition and evaluate its potential for simultaneous hydrogen sulfide (H_2S) and hydrogen chloride (HCl) removal under the conditions projected for the MCFC plants. Results to date indicate that equilibrium capacity and removal efficiencies may be adequate for one step H_2S and HCl removal. Regeneration produced a lower H_2S concentration than expected, but one from which sulfur could be recovered. Bench scale experiments will be designed to confirm laboratory results, check carbonyl sulfide removal, refine dual cycle (sulfide-chloride) regeneration techniques and obtain data for engineering/economic evaluation and scale-up.

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EXECUTIVE SUMMARY

Battelle, Pacific Northwest Laboratories is developing a solid supported molten salt (SSMS) hot gas cleanup process for integrated coal gasification/molten carbonate fuel cell (MCFC) power plants. Hot gas cleanup is needed to allow maximum thermal efficiency without interference from hydrogen chloride (HCl) and sulfur-containing contaminants while generating electricity from coal at the low heat rates possible with MCFC's. The process must reduce 200 parts per million by volume (ppmv) HCl and 6000 ppmv sulfur compounds to less than 1 ppmv. It should operate at or above the MCFC temperature (1200°F) and pressure (5-15 atmospheres, atm) and in the presence of sufficient steam and/or carbon dioxide to prevent carbon deposition from carbon monoxide. A regeneration gas is to be produced from which elemental sulfur can be economically recovered.

Development work to date has included equipment design and construction, equilibrium measurements, sorbent fabrication and successful completion of demonstration experiments. An experimental system capable of pressures to 15 atm was constructed which includes steam generation, feed gas metering, a sorbent containment vessel that can operate up to 1500°F and an off-gas analytical system that can measure HCl and hydrogen sulfide (H_2S) from less than 1 ppmv to the highest concentrations encountered. Equilibrium measurements were performed with unsupported molten salt mixtures and a preferred composition selected. Solid supported sorbent was fabricated using the selected composition. Demonstration experiments were performed from which preliminary kinetic information was derived. The SSMS sorbent would be expected to add alkali to the coal gas primarily in the form of lithium and potassium hydroxides. This addition was not studied because the alkali levels should not exceed vapor pressures which were considered unlikely to interfere with fuel cell performance.

The selected salt composition, $Li_{.86}K_{.54}Ca_{.3}CO_3$, excludes sodium (used in earlier SSMS work) but includes calcium for high retention of sulfide. Its similarity to the lithium-potassium carbonate fuel cell electrolyte should assure compatibility and removal with a single sorbent of all contaminants that would react with the electrolyte. Equilibrium capacity measurements indicated that up to 150 standard cubic feet of simulated coal gas in the specified and coke free composition range at 1400°F and 10 atm could be treated per pound of the selected salt composition per absorption cycle. Equilibrium HCl removal capacities were shown to be 50 to 100 times greater. Demonstration experiments with solid supported sorbent at 1350°F and 7.8 atm showed that each contaminant could be removed to less than 1 ppmv with the other present in the sorbent and that multiple H_2S removal/regeneration cycles could be performed before chloride regeneration. In the demonstration experiments, absorption kinetics allowed H_2S removal to less than 1 ppmv for the first 12 percent of equilibrium capacity at the low gas velocity used. Higher capacity utilization is expected due to improved mass transfer at higher velocities. One sulfur recovery regeneration test produced 2% H_2S from which elemental sulfur could be recovered but higher concentrations are expected upon more extensive testing.

Technical feasibility has been demonstrated using simulated gasifier streams under expected conditions for simultaneous HCl and H_2S removal to less than 1 ppmv from fuel cell feed gas and the necessary data have been obtained to continue into bench scale development. Similar results are expected for carbonyl sulfide (COS) removal based on previous work. Economic feasibility of SSMS cleanup for a given MCFC application will depend upon results of the next year of development which is expected to include: 1) Bench scale experiments to optimize absorption kinetics, check COS removal and facilitate scale-up, 2) refinement of dual cycle (sulfide-chloride) regeneration techniques and 3) engineering/economic analysis for a conceptual design of a commercial-scale absorption process.

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INTRODUCTION

Integration of coal gasification with molten carbonate fuel cells (MCFC) offers the opportunity to generate electrical power at high thermal efficiency from an economically attractive resource. Contaminants, including H_2S, COS and HCl, must be removed to avoid accumulation in the molten carbonate fuel cell electrolyte and resultant performance losses. For maximum efficiency and minimum complexity, the cleanup process should be performed at fuel cell pressure and at temperatures between those of the gasifier and fuel cell. Cleanup with a molten carbonate absorbent could be performed under the desired conditions and should provide a high degree of assurance that all contaminants reactive to the molten carbonate electrolyte would be removed. Prior to the current development effort, Battelle Northwest's Solid Supported Molten Salt (SSMS) process had been shown capable of removing 99+% of the H_2S from a hot coal-gas and producing an H_2S-rich regeneration product but had not been tested at pressure or with HCl. The Department of Energy's Morgantown Energy Technology Center contracted with Battelle to develop a regenerable hot gas cleanup process for the coal gasification/MCFC application. The process is to remove H_2S, COS and HCl to less than 1 ppm at 1200 to 1500°F and up to 200 psig and produce a regeneration gas from which sulfur can be recovered. A hot gas cleanup system including the SSMS process and particulate removal should remove all contaminants unacceptable to the MCFC system.

Other hot gas cleanup systems are under study for integrated coal gasification/MCFC power plants. The SSMS system being developed by Battelle differs in that HCl and sulfur compounds can be removed with a single sorbent, resulting in less complexity. In addition, the reaction products dissolve in the molten carbonate matrix resulting in a theoretically unlimited extent of contaminant removal. If only a solid reaction product is formed, removal cannot proceed below the level at which the contaminant in the cleaned gas is in equilibrium with that solid. In the SSMS process, the reaction product sulfides and chlorides dissolve so that at the clean end of the bed, where their concentration in the sorbent approaches zero, the concentration of contaminants in the cleaned gas can also approach zero. The approach is limited only by the size of the bed and the related mass transfer efficiency.

The reversible reaction of H_2S with molten carbonates has been under study at Battelle Northwest since 1974 (Moore et al. 1974):

$$MCO_3(\ell) + H_2S(g) \leftrightarrow MS(\ell) + CO_2(g) + H_2O(g), \qquad (1)$$

where "M" represents Li_2, Na_2, K_2 or Ca.

A process was first developed based on continuous, countercurrent gas liquid contacting (Moore et al. 1979). Absorption of H_2S and particulates, de-entrainment and regeneration of the carbonate were demonstrated in a process development unit (PDU) operating with gas from a fixed-bed gasifier. A venturi scrubber provided the first sulfur absorption stage and also circulated the molten salt between bubble-cap absorption and stripping columns. In the latter, steam and CO_2 were used to recover H_2S. Circulation of the hot, corrosive molten salt led to severe equipment problems, and operation was never sustained for more than a few hours at a time.

The solid supported molten salt (SSMS) concept was developed as a practical means for handling the corrosive molten carbonates (Stegen 1982). Several ceramics were investigated as potential supports. Lithium aluminate was chosen for chemical stability and for ease of fabrication of strong, porous pellets. Although the pellets could be fluidized, use in a cyclically-operated fixed-bed avoided possible agglomeration problems and still allowed the advantages of a gas-liquid equilibrium system to be exploited. Operation was relatively trouble-free with bench-scale absorption cycles of up to 7 hours duration. Laboratory and bench-scale testing demonstrated up to 99.5% sulfur removal (adequate for the combined cycle application under study) from a feed gas containing 1% H_2S and produced regeneration gases containing up to 50% H_2S on a dry basis. The tests also showed that COS was removed to well below the effluent H_2S concentration. This was apparently due either to catalysis by the molten carbonate of the sulfur analog of the shift reaction:

$$COS(g) + H_2O(g) \rightarrow H_2S(g) + CO_2(g), \qquad (1A)$$

and subsequent absorption of H_2S or direct absorption:

$$COS(g) + MCO_3(\ell) \rightarrow MS\ (\ell) + 2CO_2(g). \qquad (1B)$$

Specific goals of the current development program are to select and characterize a fuel cell-compatible salt composition to give maximum sulfur loading under CO_2 and H_2O back pressures, demonstrate removal of HCl as well as H_2S/COS, develop a regeneration scheme to allow continued removal of these contaminants to less than one part per million (1 ppmv) while producing an H_2S-rich stream for sulfur recovery, and obtain necessary data for evaluation and scale-up of the process. The program includes six major tasks:

Task 1. Project Plan and Design of Experiments

Task 2. Exploratory and Supporting Studies

Task 3. Design of Bench-Scale Development Reactor and Associated Equipment

Task 4. Ordering of Equipment and Construction of Reactor and Associated Equipment (as required)

Task 5. Bench-Scale H_2S, COS and HCl Absorption Regeneration Tests

Task 6. Engineering and Economic Assessment of the Process.

This report covers results obtained in completing the first two tasks and is organized according to the subtasks of Task 2. Sections are devoted to the experimental apparatus and analytical methods, liquid phase absorption equilibrium measurements, preparation of the solid supported sorbent and solid supported sorbent tests. The last section presents process concepts consistent with the results of the exploratory phase of process development. A model developed to predict metal chloride vapor transport in a SSMS packed bed is presented in the appendix.

EXPERIMENTAL APPARATUS AND ANALYTICAL METHODS

Figure 1 is a simplified diagram of the experimental system designed and constructed for use in this program. Gases, (metered into the system under cylinder pressure) and water (pumped into a steam generator by a high pressure feed pump) can be used to generate simulated coal gas of any desired composition. A section of Incoloy 800H pipe serves as a pressure vessel (rated for 250 psig at 1600°F) and is heated by ceramic fiber heaters. A 1 in. ID alumina thimble suspended inside the pipe can contain free liquid or solid supported molten carbonate. Smaller tubes sealed through the top flange provide a thermowell and access to the thimble through its loose fitting lid. A small nitrogen purge into the pipe assures that system gases remain inside the alumina. Heat traced, teflon lined tubes conduct effluent gas to stainless steel scrubbers where circulating solutions can condense steam and absorb contaminants for analysis. A letdown valve after the scrubbers provides pressure control.

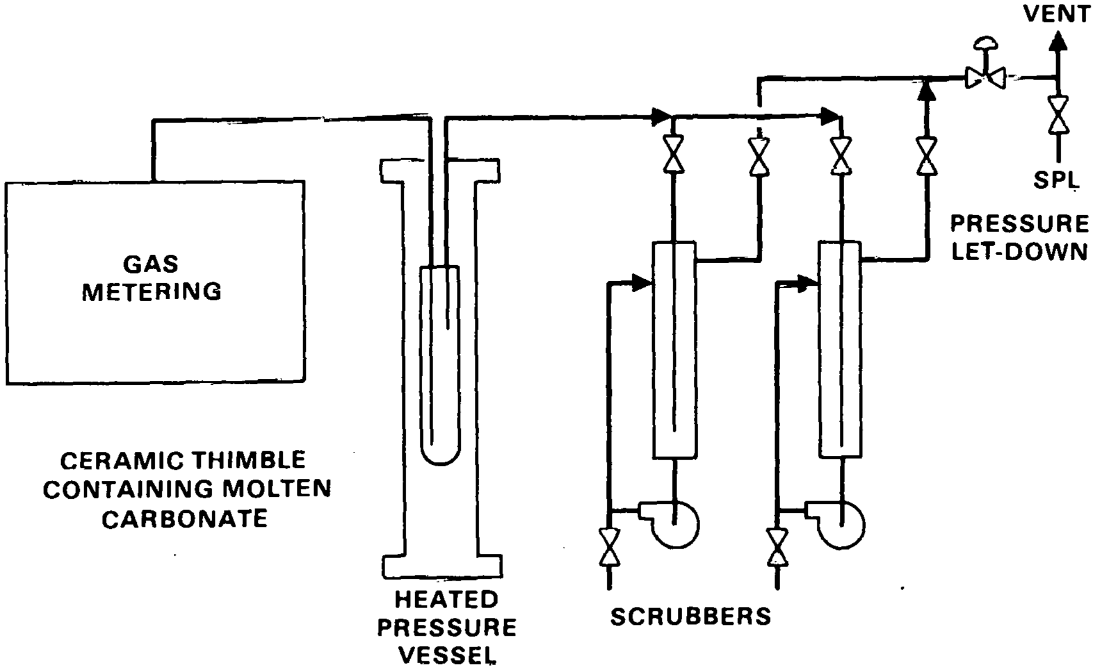

FIGURE 1. Pressure-Capable Sorption Test Apparatus

Figure 2 shows the feed system, the heated pressure vessel with shielding removed and the shielded scrubbers. Figure 3 is a view of the scrubbers and circulating pumps.

During early experiments the circulating, 4 to 8 wt% NaOH scrub solutions were periodically sampled with tared bottles containing a known quantity of anti-oxidant (Na_2EDTA) solution. The samples were analyzed with Orion Model 94 silver sulfide specific ion and Model 90 silver/silver chloride reference electrodes. Calibration standards containing similar amounts of NaOH and EDTA were prepared daily from a Na_2S stock solution standardized by potentiometric titration with $Pb(ClO_4)_2$. Later, a continuous bleed from the scrubbers was passed by the electrodes in an air-free loop and returned by the high pressure circulation pumps. Detection limits for sulfide were shown to be less than 0.05 ppm by weight. An H_2S concentration of 0.5 ppmv would thus be detected in a 1 liter per minute gas flow after 19 minutes.

Samples from the scrubbers were analyzed for chloride by three methods. Initially, Orion Model 96 halide specific ion electrodes were used after neutralizing the sample with HNO_3 to eliminate hydroxide interference and adding $Ni(NO_3)_2$ to eliminate sulfide interference when present. In the second method, samples were titrated with $AgNO_3$. Silver ion concentration was followed potentiometrically with the silver sulfide electrodes and the effect of silver chloride precipitation was determined by graphical analysis. In the third method, to obtain the precision and sensitivity required for the demonstration experiments, deionized water was used in the scrubbers precluding simultaneous H_2S determination but allowing a Dionex System 12 ion chromatograph to be used for chloride analysis. The Dionex chromatograph has a detection limit of 0.015 ppm by weight for chloride in water.

During the next year of development it will be desirable to analyze for H_2S, HCl and COS simultaneously. The strong $NaOH/Na_2CO_3$ matrix required to absorb sulfide in the presence of CO_2 would make ion chromatography for chloride difficult but would allow simultaneous determination of HCl and H_2S in the absorber effluent gas. Alternatively, the gas may be passed first through water then NaOH solution. The CO_2-saturated water would retain very little sulfide and virtually all of the chloride. Only low COS concentrations, in

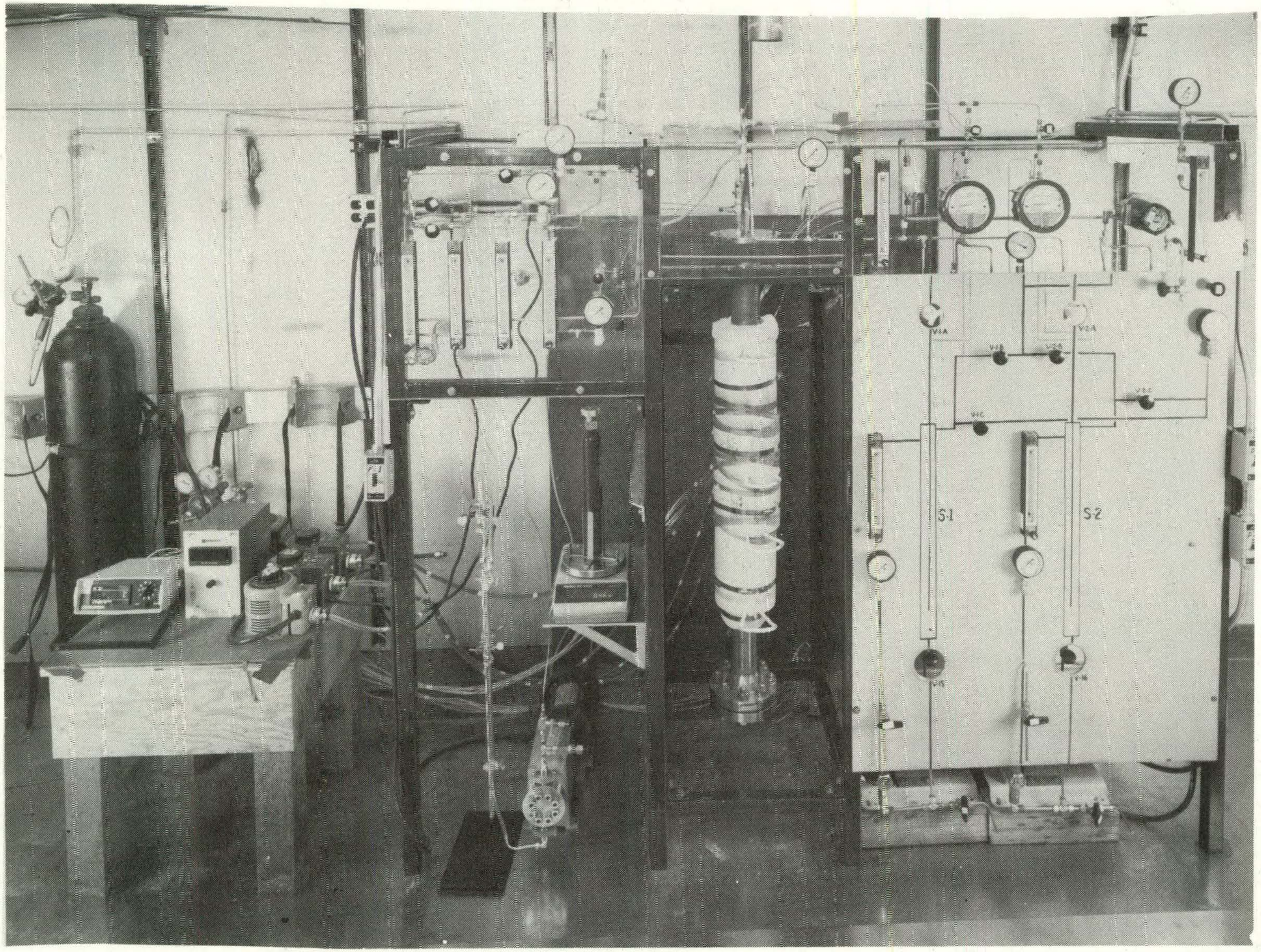

FIGURE 2. Apparatus During Assembly

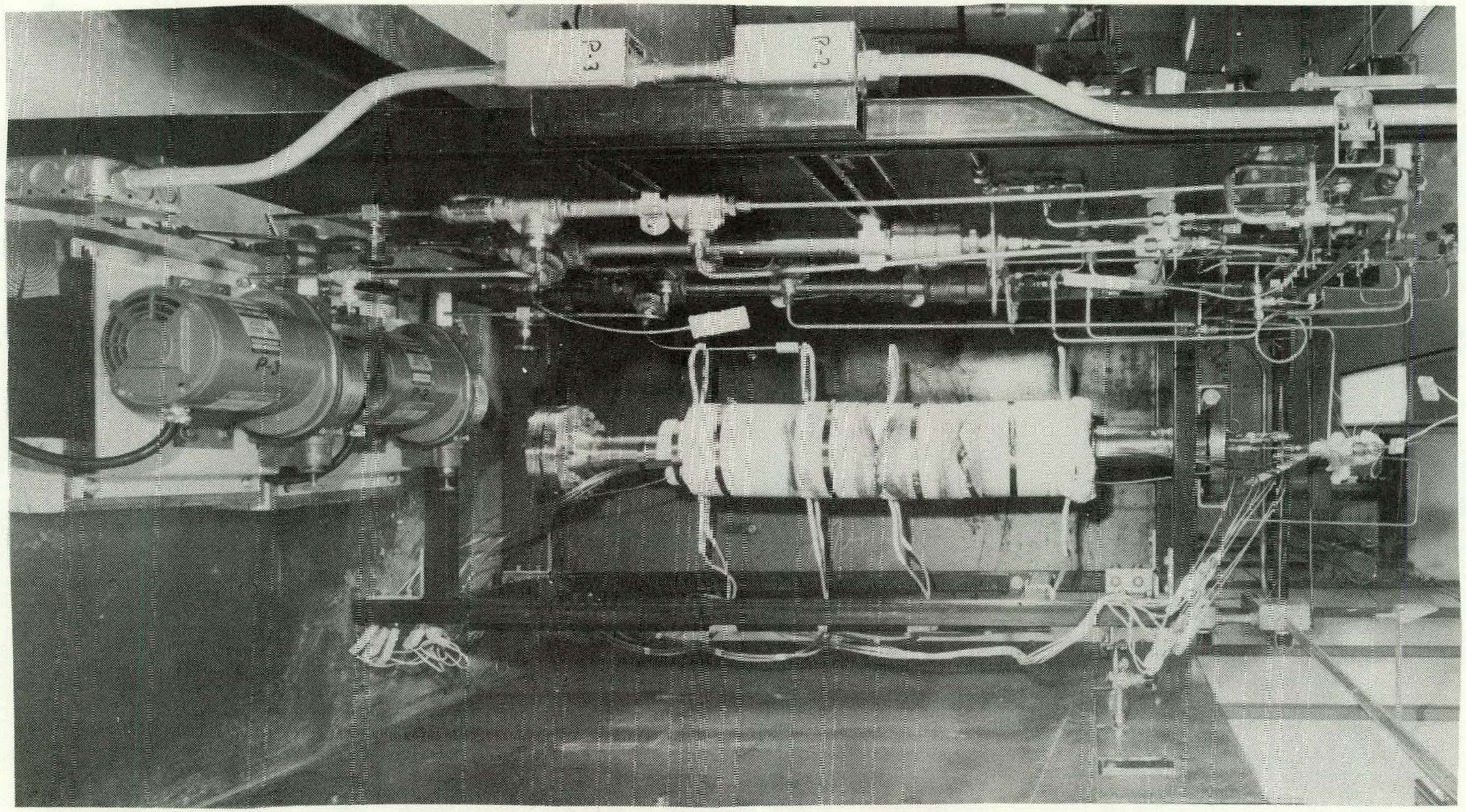

FIGURE 3. Side View of Apparatus

shift equilibrium with H_2S, are expected based on previous work (Stegen 1982). COS may not be completely removed by the NaOH scrub. Wet chemical methods can be used to detect any COS downstream of the let down valve.

ABSORPTION EQUILIBRIUM MEASUREMENTS

/The amount of contaminant that can be removed by a SSMS bed before regeneration is ultimately limited by equilibrium with the inlet gas. The sulfide/carbonate equilibrium is critical for sulfur removal performance while in the case of chloride, mass transfer limitations are likely to predominate. Results of extensive liquid phase measurements of the sulfide/carbonate equilibrium, salt composition selection and a check of the chloride/carbonate equilibrium are reported in this section.

METHODS

The following procedure was used in equilibrium measurements with unsupported molten salt. The desired molten carbonate mix was prepared by dry blending reagent grade powders and loaded into the tared ceramic thimble. The thimble was lowered into the open pressure vessel which was heated until a clear melt was obtained. The ceramic lid was fit on the thimble and the vessel closed. After leak testing, the vessel was purged with nitrogen until the effluent gas contained less than 1% oxygen and brought to operating pressure. Simulated fuel gas flow was started and the salt allowed to equilibrate with the H_2O and CO_2 in the gas. Contaminant gas (H_2S or HCl) was then metered into the salt at about 25% of the fuel gas flow and the amount added was checked by change in cylinder weight. After bulk addition, fuel gas feed continued and contaminant gas feed was stopped completely or continued at a low rate to check effluent concentration upon approach from below or above equilibrium with the loaded salt.

The equilibrated gas passed through one of the caustic scrubbers which were sampled periodically and analyzed for sulfide or chloride by specific ion potentiometry. Titrating the excess caustic in the samples provided a measure of CO_2 absorbed. After pressure let-down, the gas was sampled for determination of H_2, CO, CO_2, CH_4, N_2 and any O_2 by gas chromatography. After steady conditions were obtained (60 to 90 minutes), additional contaminant gas was loaded into the salt, or gas flows, temperature and/or pressure changed. After the last measurement with a given salt it was poured into a tared alumina crucible. The residual and poured salt weights were determined and a sample taken for analysis.

Data from the experiments were stored on magnetic disks and analyzed with a material balance algorithm using a desk-top computer. The algorithm used nitrogen flow, adjusted for added purge gas, as a tie to calculate CO and H_2 flows leaving the salt from the gas analysis. Total CO_2 and H_2O flows were calculated by material balance and their ratio by assuming the shift reaction reached equilibrium. Contaminant partial pressure was calculated using the scrubber sulfide or chloride analyses. Contaminant loading in the salt was determined from the flowmeter readings and material balance.

After most experiments, the analysis of the poured salt sample indicated less than the sulfur content determined by material balance. The difference could be explained by solid (presumably CaS) formation apparent in some cases, upon pouring the molten salt from the thimble. The sulfur-rich solid was concentrated in the residue. Because it would be impossible to obtain a sample representative of the entire residual and poured salt, considerable care was taken to confirm the methods upon which the material balance calculation was based. Checks of scrubber efficiency and the sulfur metering system were performed by wet chemical analytical methods. In some early experiments, loss of alkalinity resulted in poor scrubber efficiency. Although losses from that source could not explain the entire discrepancy between salt analyses and material balance, improved methods were developed to maintain scrubber efficiency. Good agreement was obtained in one case with a low melting salt which was not heavily loaded with sulfur. In the remaining cases, sulfide precipitation before or during the pouring process probably caused the poured sample to be unrepresentative. Sulfur content in the data reported here is based on material balance.

SULFIDE EQUILIBRIUM RESULTS

Screening experiments for sulfide capacity were completed with four different salt mixtures (Table 1) at atmospheric pressure. Table 2 summarizes the results.

TABLE 1. Carbonate Mixtures Screened for Sulfide Capacity

Salt Mix	Li_2CO_3	Na_2CO_3	K_2CO_3	$CaCO_3$
1	37.5	23.4	19.3	19.8
2	48.9	0	25.2	25.8
3	35.1	0	33.8	31.1
4	23.3	0	53.9	22.9

Salt mix #1 is the composition used by Moore et. al. (1976) and Stegen (1982) as unsupported and supported sorbents respectively at atmospheric pressure. Figure 4 shows that data of this work are in agreement with Moore's data at higher temperatures but that a sharper temperature dependence was found. The data of this work reflect 26 Kcal/mole which is typical of the pure carbonates for the reaction:

$$MCO_3 + H_2S \rightarrow MS + CO_2 + H_2O \qquad (1)$$

$M = Li_2, Na_2, K_2$ or Ca

$\Delta H = 34, 31, 26$ & 26 Kcal/mole @ 900°K.

Stegen's data were for solid supported salt at higher sulfide loadings and may not be completely comparable but correspond to $K = 1.8$ at reciprocal temperature 0.932×10^{-3} $°K^{-1}$.

Sodium in the mixed carbonate sorbent represents a possible source of contamination to a Li/K-eutectic fuel cell. The elimination of sodium was tested with salt mix #2. Equilibrium pressure of H_2S was measured at two levels of sulfide loading. Figure 5 shows the expected linear dependence on sulfide concentration. Higher calcium and lower lithium contents were tested with salt mix #3 and salt mix #4, respectively. Adjusting to 750°C and averaging gives $K_1 = 1.6$, 1.7, 2.0 and 1.8 all ± 0.2 atm for salt mix #1, #2, #3, and #4, respectively. It is apparent that the sulfide/carbonate equilibrium is relatively insensitive to the cation mix. Figure 6 shows that calcium content can be used to correlate the results of this work with the calcium-free results of Moore.

TABLE 2. Results of Screening Experiments

Exp. #	Salt Mix	Temp. °C	Salt $S^=$ Mole %	Exit Gas Stream			K_1^* atm	$^{**}R_{750}$
				H_2O %	CO_2 %	H_2S ppm		
9B	1	653	1.38	19.0	20.1	1140	0.46	0.0078
9C	1	653	1.38	15.4	16.4	975	0.36	0.0101
9D	1	653	1.37	15.4	16.4	956	0.36	0.0099
10B	1	748	1.36	16.8	14.4	224	1.47	0.0091
10C	1	749	1.36	18.4	10.4	167	1.56	0.0086
10D	1	749	1.36	18.4	10.4	182	1.43	0.0094
10E	1	751	1.36	18.8	9.8	153	1.63	0.0084
10F	1	751	1.43	18.8	9.8	130	2.03	0.0072
11B	2	741	1.34	21.3	11.9	220	1.55	0.0077
11C	2	741	1.34	21.3	11.9	280	1.21	0.0098
12E	2	765	2.84	25.7	14.2	444	2.33	0.0147
12F	2	762	2.84	25.7	10.8	433	1.82	0.0181
12G	2	762	2.84	25.7	10.8	374	2.11	0.0157
13B	3	753	1.07	24.3	11.8	133	2.30	0.0049
13C	3	753	1.07	24.3	11.8	166	1.85	0.0060
15B	4	738	1.32	21.2	10.4	156	1.88	0.0066
15C	4	738	1.31	21.2	10.4	256	1.14	0.0100
15D	4	737	1.30	22.2	10.8	164	1.92	0.0058
15E	4	737	1.30	22.2	10.8	198	1.59	0.0070
16B	4	735	2.83	21.5	10.6	404	1.64	0.0147
16C	4	735	2.83	21.5	10.6	477	1.39	0.0174

$$^*K_1 = \frac{[S^=]}{[CO_3^{\,=}]}\,\frac{P_{CO_2}\,P_{H_2O}}{P_{H_2S}}\text{, at temperature.}$$

$$^{**}R_{750} = \frac{P_{H_2S}}{P_{CO_2}\,P_{H_2O}}\text{, adjusted for } 750^0\text{C assuming } K \sim \exp\,(26{,}000/1.98//T).$$

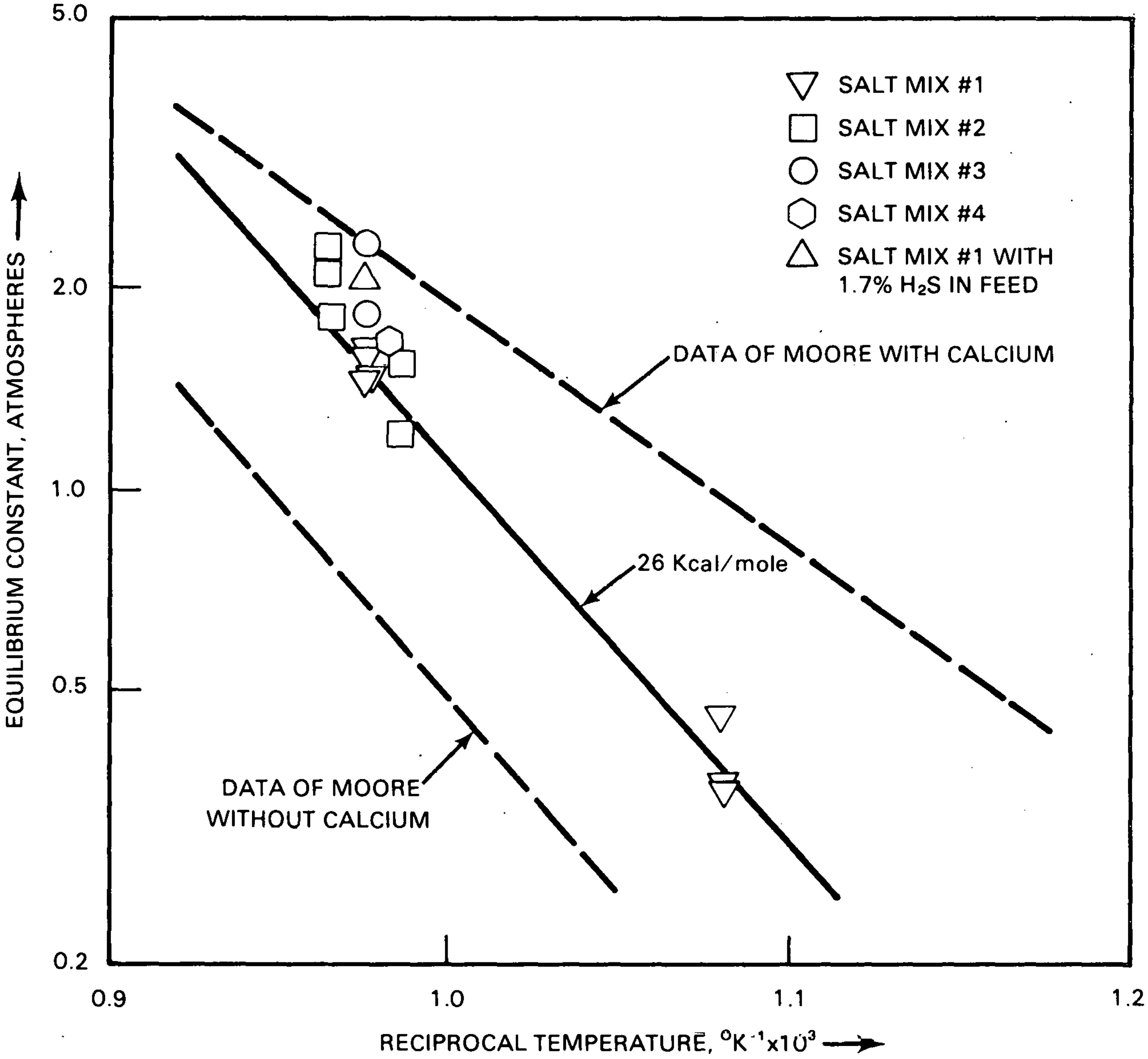

FIGURE 4. Carbonate-Sulfide Equilibrium

After the measurement at 1% $S^=$ mix #3 was loaded to 4% $S^=$. A flow stoppage prevented H_2S pressure measurement at that concentration and, upon pouring out the salt, a precipitate that analyzed high in sulfur (presumably CaS) was observed. Similar precipitation probably occurred to a lesser extent with mix #2 as indicated by the low sulfur concentration (1.2%) in the poured sample relative to the sulfur content calculated by material balance (2.8%). Precipitation of CaS can be represented by the reaction:

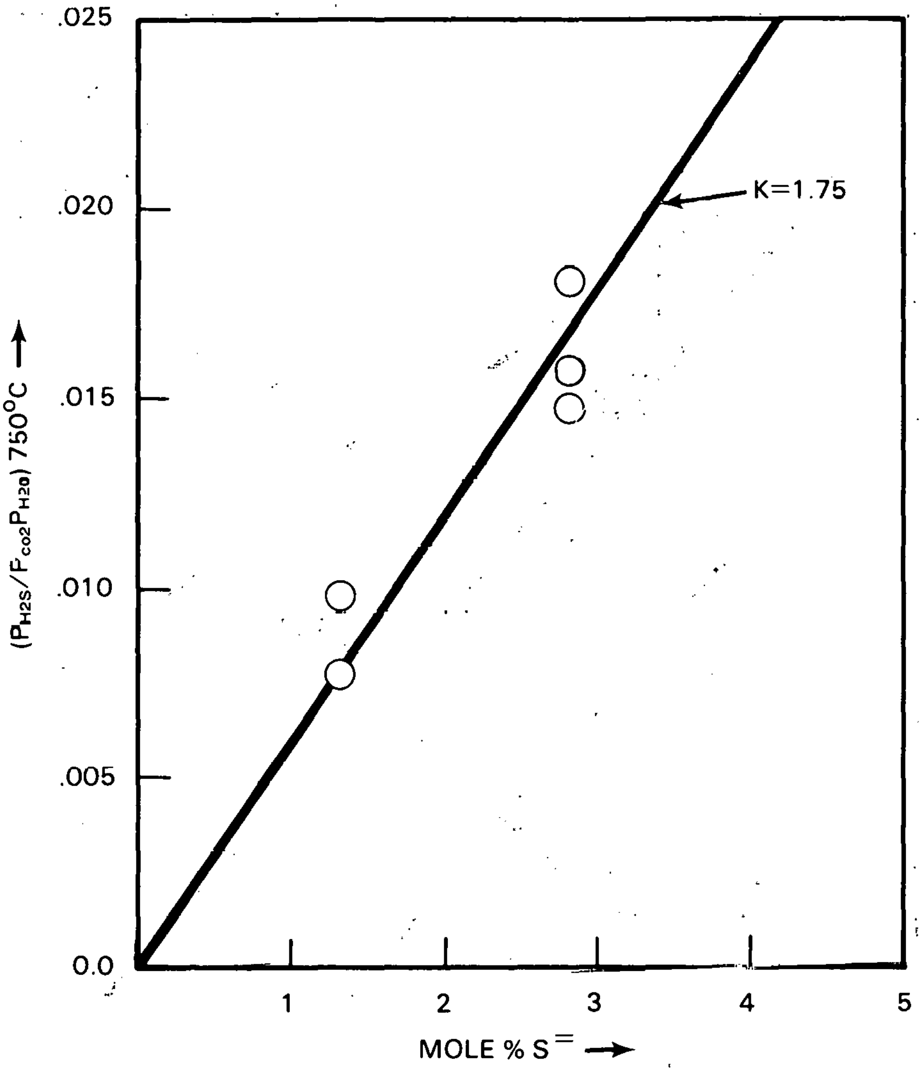

FIGURE 5. Gas Pressure Over Salt Mix #2

$$Ca^{++} + S^{=} \rightarrow CaS. \quad (2)$$

If we assume ideal behavior and consider the sample taken from salt mix #2 representative of the liquid phase, we calculate a solubility product of 2.9 x 10^{-3} based on mole fractions. If we further assume that changing the relative concentrations of the other cations has a negligible effect and that the same effective temperature was reached in pouring the other salts, we can calculate that CaS would precipitate at 1.5% from salt mix #1 and 1.0% from mix #3. Although the assumptions may not be accurate the results are consistent with

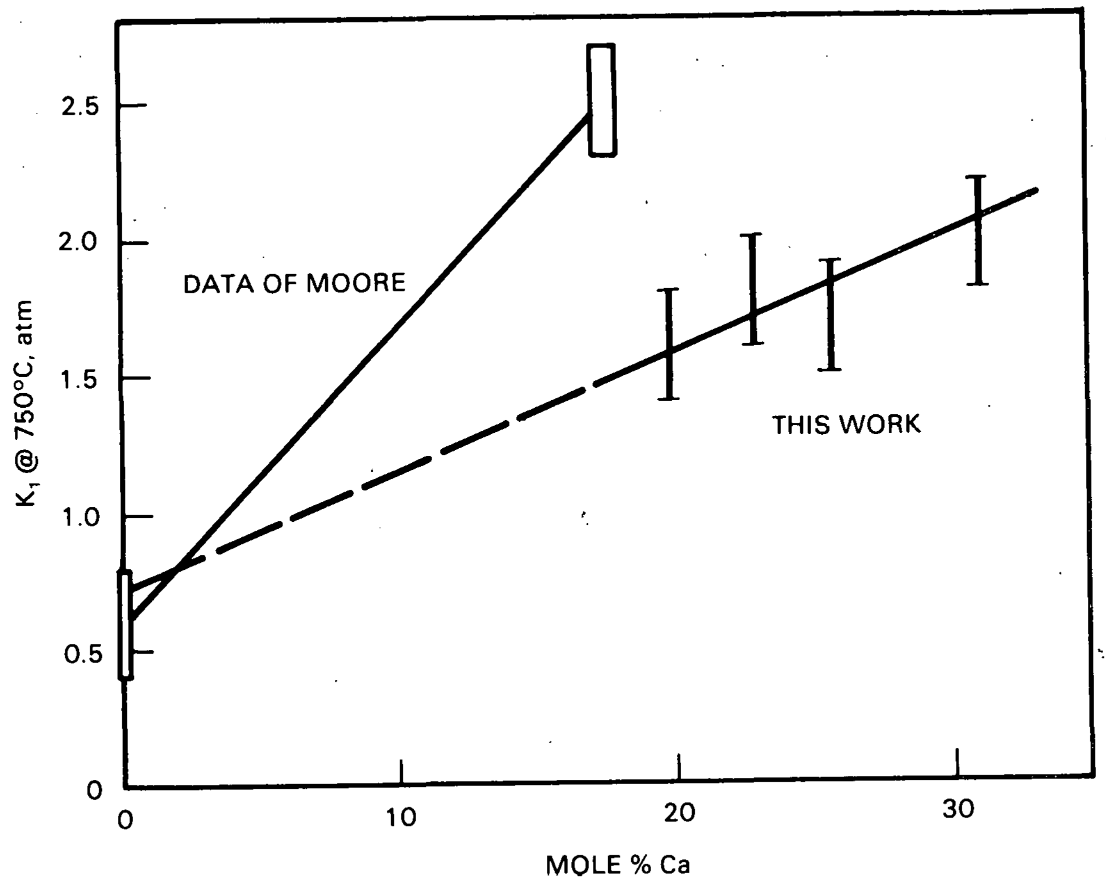

FIGURE 6. Correlation of Sulfide/Carbonate Equilibrium with Calcium Content

the good agreement between analyses and material balance after loading mix #1 to 1.4% and the heavy precipitation observed after loading mix #3 to 4%. The linearity of Figure 5 indicated that CaS did not precipitate to a significant extent at 750°C and 2.8% $S^=$ from salt mix #2.

SALT SELECTION

The sulfide equilibrium results showed that sodium could be eliminated from the cation mix without detrimental effect on sulfur capacity, that the ratio of lithium to potassium had little effect and confirmed the beneficial effect of calcium. Sodium was eliminated to preclude contamination of the Li/K fuel cell matrix by sodium hydroxide vapor. The only probable transport mechanism for calcium would be entrainment which was judged to be insignificant for the SSMS sorbent system relative to the improvement in sulfur capacity.

Calcium content is limited by its tendency to increase the freezing point of the molten salt mixture. The more stable of the two Li_2CO_3-K_2CO_3 eutectic compositions was chosen for the Li/K ratio. Calcium content was selected based on freezing point measurements that showed ternary eutectic behavior would allow up to 30% $CaCO_3$ in Li_2CO_3/K_2CO_3 melts before a significant increase in freezing point. The selected composition (Table 3) should freeze at about 550°C.

TABLE 3. Selected Salt Composition

	Wt%	Mole%
Li_2CO_3	32	43
K_2CO_3	38	27
$CaCO_3$	30	30

Because equilibrium sulfide loading depends almost linearly on H_2S (or H_2S + COS) concentration, the maximum volume of gas that can be treated per unit of salt is nearly independent of concentration in the expected range of 3000 to 5000 ppm H_2S. The expected equilibrium performance of the selected molten carbonate mixture is summarized in Figure 7 which is based on Figures 4 and 6. Gas capacity is sensitive to steam content and temperature. Representative air-blown gasifier product compositions were calculated, Table 4, based on a reducing gas to carbon ratio of 1.5 with nitrogen and steam contents selected to span the conditions specified in the contract. The figure shows the equilibrium limited gas cleanup capacity for the gas compositions of Table 4 assuming the shift reaction also reaches equilibrium. The maximum carbon deposition (coking) temperature is shown for each composition based on the Boudouard reaction and assuming no methanation occurs (methanation would increase the operable range). It would be desirable to perform cleanup with a minimum amount of steam at temperatures above the coking zone then add steam to avoid coking upon cooling to the fuel cell temperature.

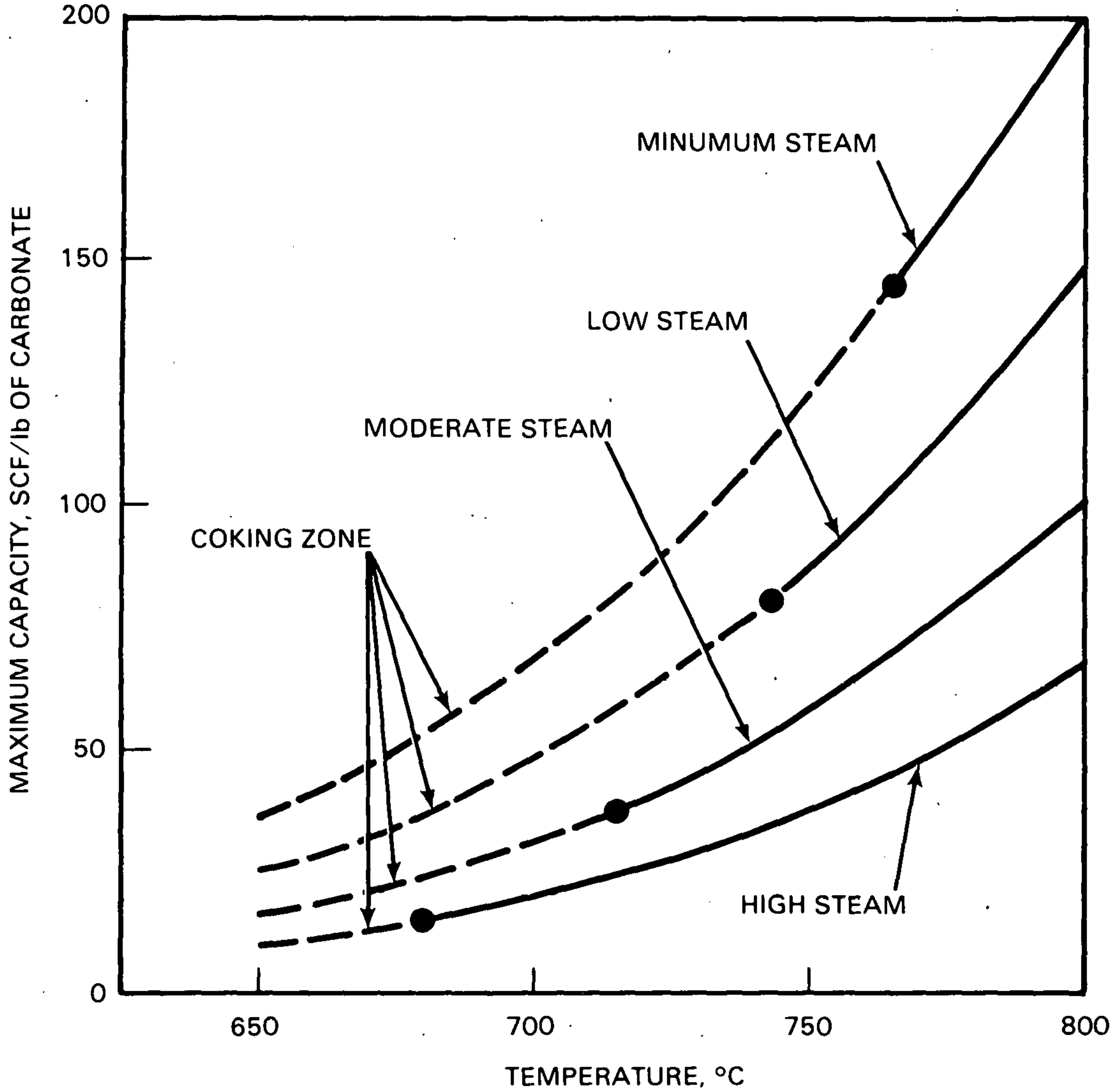

FIGURE 7. Steam and Temperature Effect on Sulfide Equilibrium Gas Cleanup Capacity of Selected Salt at 10 atm.

TABLE 4. Representative Air-Blown Gasifier Product Compositions, Volume %

	H_2	N_2	CO	CO_2	Steam	Air/C[(a)]	H_2O/C
Expected range	15-20	30-50	10-20	5-15	5-25	-	-
"Minimum steam"	19.2	50.2	16.4	7.3	6.9	2.7	0.47
Low steam	18.5	48.5	15.9	7.0	10.1	2.7	0.62
Moderate steam	17.5	45.8	15.0	6.7	15.0	2.7	0.88
High steam	16.1	42.2	13.8	6.1	21.8	2.7	1.27

(a) Assuming oxygen enters only as air and water.

CHLORIDE EQUILIBRIUM RESULTS

Thermodynamic data indicate that hydrogen chloride should react very favorably with molten carbonates building up high concentrations of chloride:

$$2HCl + M_2CO_3 \rightarrow 2MCl + H_2O + CO_2 \qquad (3)$$

Although chloride loading may be limited by mass transfer or volatility in practice, experiments were performed with the selected salt composition to confirm the thermodynamic predictions for reaction 3 and to check for interaction between HCl and H_2S absorption.

A mixture of carbonates and chlorides with the cation composition of the selected salt (43% Li_2, 27% K_2, 30% Ca) but with 12% of the anions replaced by chloride was melted. Equilibrium measurements were made at 690 and 740°C by stripping with simulated fuel gas and the equilibrium constant, K_3, calculated:

$$K_3 = \frac{[Cl^-]^2}{[CO_3^=]} \frac{P_{H_2O} P_{CO_2}}{P_{HCl}^2}.$$

Mole fractions $[Cl^-]$ and $[CO_3^=]$ were based on total number of anions. In a third experiment HCl was added to the simulated fuel gas until the replacement of carbonate by chloride reached 16% and K_3 was measured again.

In Figure 8, results are compared with thermodynamic predictions. The pure component Li and K lines were calculated for the subcooled liquid salts from the data of Barin and Knacke (1973). For the Ca line, the free energy of subcooled liquid $CaCO_3$ was calculated from the data for the solid assuming a melting point of 1200°C and estimating entropy of fusion and liquid heat capacity at 6 and 32 cal/mole-deg respectively by analogy with the other carbonates. The ideal solution line represents an average of free energies based on number of cations in the mixed salt. The results confirm the favorable equilibrium predicted from theory for Reaction 3.

In a fourth experiment, a simulated fuel gas spiked with 26% H_2S was bubbled into the same salt as a check on the H_2S absorption equilibrium in the presence of large quantities of chloride. An approximate value of 0.5 atm at

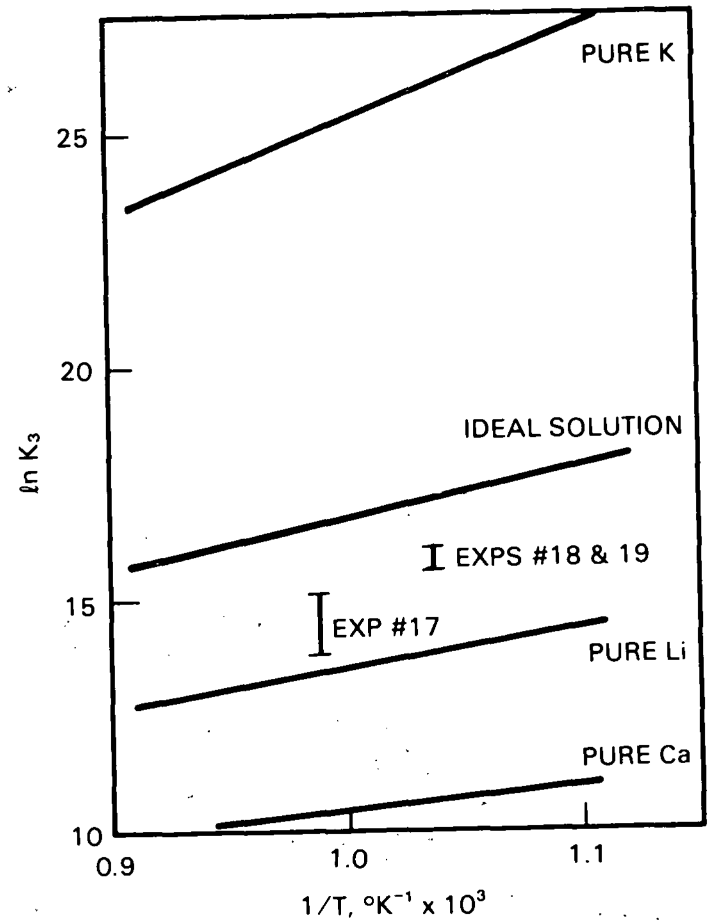

FIGURE 8. Chloride/Carbonate Equilibrium

690°C for K_1 was calculated from the averages of the increasing sulfide and effluent H_2S concentrations up to 0.6 mole% and 1300 ppm respectively. A value of 0.75 atm would be read from Figure 4 for that temperature. The agreement is good considering the high concentration of H_2S fed into the salt.

Equilibrium measurements showed that HCl reacts very favorably with molten carbonates and that the presence of chloride does not significantly displace the H_2S absorption equilibrium. The vapor pressure of absorbed metal chloride may be as significant as Reaction 3 in determining the saturation level of chloride in an SSMS bed. Metal vapor pressure can be calculated from pure component free energies (Barin and Knacke, 1973) by assuming ideal solution behavior. Figure 9 shows that very high levels of conversion to chloride are still possible under typical MCFC feed gas conditions. The appendix deals with the transport of alkali metal through the SSMS bed as chloride vapor.

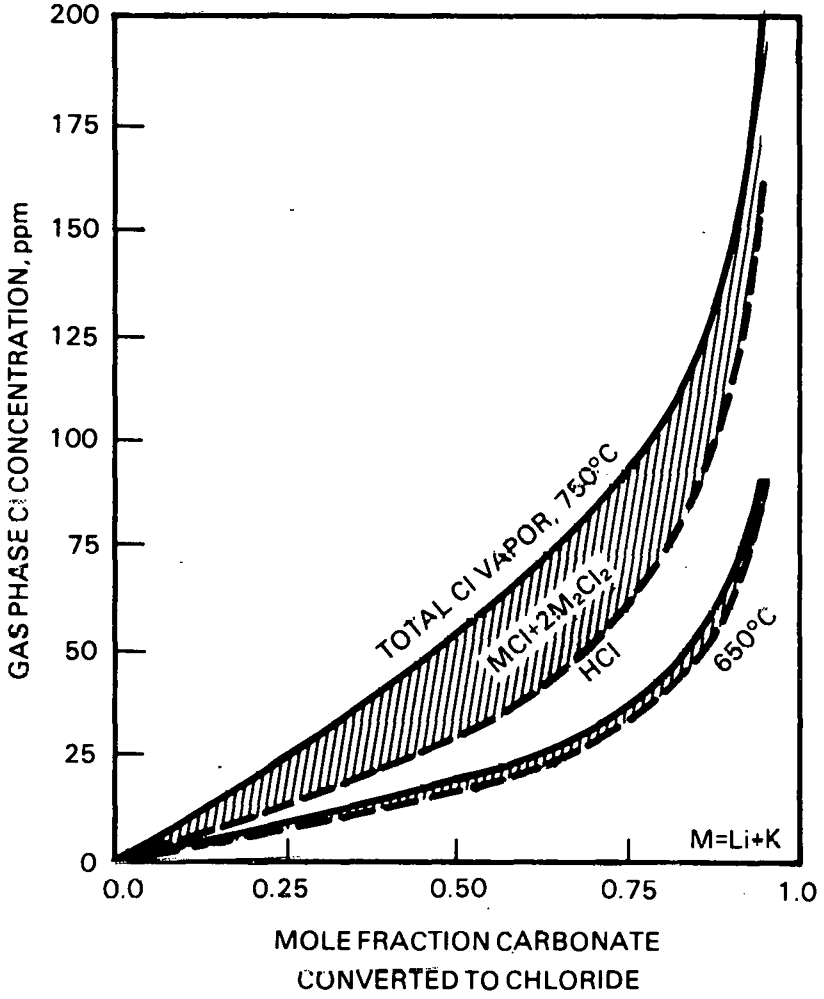

FIGURE 9. Equilibrium Vapor Composition Over $Li_{.86}K_{.54}Ca_{.3}CO_3/Cl_2$ in 10% Steam, 10% CO_2 at 10 atm Total Pressure

PREPARATION OF SOLID SUPPORTED SORBENT

The SSMS sorbent used in initial testing with the selected salt composition was prepared by techniques similar to those developed by Stegen (1982). Porous lithium aluminate ceramic beads were fabricated and then loaded with the mixed carbonates.

FABRICATION OF CERAMIC SUPPORT

Lithium aluminate is produced by the reaction of lithium carbonate or hydroxide with alumina:

$$Li_2CO_3 + Al_2O_3 \rightarrow Li_2O \cdot Al_2O_3 \pm CO_2 \qquad (4)$$

$$2LiOH + Al_2O_3 \rightarrow Li_2O \cdot Al_2O_3 + H_2O \qquad (5)$$

Stegen (1982), reported that Reaction 4 produced a more porous product than Reaction 5. The 1.4 to 2.8 mm (-7 + 14 U.S. Sieve Series) beads required for initial testing were produced by tumbling agglomeration of mixed Li_2CO_3/Al_2O_3 powder followed by firing to effect reaction. Pellets of any size could be produced commercially by the same technique or larger pellets could be produced by cold pressing and firing.

Lithium carbonate and aluminum oxide powders (J. T. Baker Reagent Grade) were mixed in the molar ratio 1.03 to 1 and ball milled for at least twelve hours. Shorter milling periods resulted in finished ceramic with poor strength. The intimately mixed powders were rolled into beads in a tumbling agglomerator with a fine water mist used to cause cohesion. Batches of raw beads were sieved into +7, -7 + 14 and -14 U.S. Sieve Series fractions. Undersized beads were returned directly to the agglomerator and over sized beads were dried, ground and returned. It was found that simply breaking up oversized beads resulted in finished ceramic with low porosity. The raw beads were oven dried and then fired from 500 to 800°C over at least four hours and held at 800°C for at least 12 hours. The finished beads showed the stoichiometric weight loss for Reaction 4 and had a bulk density of 0.75 ± 0.03 g/cc over three separate batches.

LOADING SUPPORT WITH MOLTEN SALT

The fabricated lithium aluminate ceramic support beads were loaded with the selected carbonate mixture ($Li_{.86}K_{.54}Ca_{.3}CO_3$) by pouring the molten salt into a preheated beaker of beads with stirring. Stegen (1982) had found that larger pellets could be soaked and drained but that -7 mesh beads did not drain well.

Beads were loaded in four batches with 0.56 ± 0.08 g of salt per gram. Batches loaded with 0.64 g/g showed signs of saturation. The salt was completely absorbed by the beads resulting in no volume change so that the finished SSMS sorbent after removing fines (about 5%) had a bulk density of 1.56 x 0.75 = 1.17 g/cc. The sorbent contained 0.36 g carbonate per gram or 0.42 g/cc. These data are summarized in Table 5.

TABLE 5. Solid Supported Sorbent

	$Li_2O \cdot Al_2O_3$ Support	Finished Sorbent
Size range, mm	1.4-2.8	1.4-2.8
Bulk density, g/cc	0.75	1.17
$Li_{.86}K_{.54}Ca_{.3}CO_3$, g/cc	-	0.42

SOLID SUPPORTED SORBENT TESTS

Initial tests with solid supported sorbent were directed toward establishing the technical feasibility of removing H_2S and HCl to less than 1 ppm from pressurized fuel gas with a single packed bed and of producing an H_2S-rich regeneration gas from which sulfur can be recovered. Experimental methods, absorption and regeneration results are presented followed by a discussion of process concepts consistent with results to date.

METHODS

Solid supported sorbent was loaded into an alumina thimble similar to that used in the absorption equilibrium experiments and suspended in the same test apparatus. Because simultaneous feed and analysis of H_2S and HCl was not yet possible with the apparatus, conditions approaching simultaneous removal were approached by removing the contaminants sequentially with and without intervening regeneration.

The SSMS sorbent, described under "Preparation of Solid Supported Sorbent," was loaded into the 1 in. ID thimble around a 3/16 in. OD feed tube and a 1/4 in. OD thermowell which extended into a 1 1/2 in. deep layer of bare lithium aluminate support beads in the bottom of the thimble. The 10 in. deep sorbent layer required 125 cc of salt-loaded beads representing 51.9 g of salt. A 1 1/2 in. layer of bare beads was loaded on top of the sorbent layer. A 1/4 in. OD outlet/regeneration tube and the 3/16 in. feed tube passed through 8 in. of heated pipe above the thimble to allow preheat of entering gases. The bare ceramic beads provided additional heat transfer surface while distributing the gas flow entering the sorbent layer.

The following general procedure was followed in the sorbent tests: The sorbent was brought to temperature as determined by three thermocouples in the thermowell and the system pressurized with nitrogen. A flow of simulated coal gas without contaminant was established and the bed allowed to equilibrate with the CO_2 and H_2O content of the gas. During the equilibration period, contaminant gas was metered into the contaminant feed line to fill it. The contaminant feed time began when enough had been metered to reach the tee where it joined the simulated coal gas flow. Gases leaving the sorbent bed passed to the scrubbers which absorbed effluent HCl and H_2S for analysis as described under "Experimental Apparatus and Analytical Methods." For regeneration runs, reverse flow of a CO_2 and H_2O-rich coal gas was used without contaminant and timing begun as soon as flow was established.

Initially, the bed was left under a nitrogen blanket between runs and the feed and off-gas lines were manually interchanged at their connections through the top flange of the pressure vessel to effect regeneration. Later, a four-way valve was added so that flow could be reversed at pressure and a small back-purge of nitrogen maintained to prevent forward diffusion of metal chloride vapor between runs.

SULFIDE ABSORPTION RESULTS

After a shakedown run at atmospheric pressure (S1) and extended regeneration to reduce and remove sulfate present from impurities in the SSMS component materials, two H_2S removal runs (S3 and S5) were performed at 100 psig with an intervening thorough regeneration. Both runs demonstrated removal to less than 1 ppm with a regenerated sorbent. They both immediately followed HCl removal runs assuring that the HCl absorption reaction or chloride volatility did not interfere with H_2S removal. Another H_2S removal run (S6) followed a partial regeneration to check its effectiveness and to load the bed with sulfur for an HCl removal test.

Table 6 summarizes all four sulfide absorption runs. Run S1 showed a steadily increasing sulfide concentration (see Figure 10) in the effluent gas even before starting H_2S feed. A check of the materials used to fabricate the sorbent showed that most of the reagent grade chemicals had sulfate specifications of <0.01% but the Li_2CO_3 specification was <0.2% sulfate by weight. The finished sorbent could have contained up to 1100 ppm sulfate by weight from that source. That sulfate could generate H_2S, by the reaction:

$$2H_2 + 2CO + SO_4^{=} \rightarrow H_2S + H_2O + CO_2 + CO_3^{=} \quad (6)$$

TABLE 6. Solid Supported Sulfide Absorption Runs

Run #	S1	S3	S5	S6
Feed Gas, mole%				
H_2S	0.4	0.4	0.4	0.4
H_2	15.6	19.5	20.3	20.1
N_2	40.0	48.5	50.7	50.1
CO	9.9	11.3	11.8	11.7
CO_2	9.9	5.7	6.0	5.9
H_2O	25.2	14.6	10.8	11.9
Space velocity,(a) hr^{-1}	460	483	459	464
Pressure, psig	0	100	100	100
Temperature, °C	645	720	737	738
Calculated capacity, min	171	154	342	340
H_2S feed time, min	47.5	60.5	107	42
Projected 50% breakthrough, min	75±20	130±20	300±100	-
Time to 1 ppm, min	-	20	40	(b)
Initial outlet H_2S, ppm	6	<0.7	<0.4	4

(a) Volumes of feed gas at 70°F and 1atm per hour per volume of bed.
(b) Apparent breakthrough start at 40 min.

in sufficient quantity to account for the apparent early breakthrough observed in the run. Sulfate was eliminated by an extended purge with reducing gas (20% H_2, 10% CO, 10% CO_2) before the next absorption tests.

Breakthrough behavior for pressurized, simulated coal gas containing 4000 ppm H_2S at different steam contents and temperatures was measured in Runs S3 and S5. Figure 11 shows the results of Run S3 and Figure 12 the results of S5 compared with the lower portion of the S3 curve.

Table 6 lists the calculated capacity for each run, based on equilibrium data reported under "Sulfide Equilibrium Results," as minutes of gas feed to saturate the bed at run conditions. Figure 12 shows that the breakthrough time is proportional to expected capacity. Projecting the curves from Figures 11 and 12 to half the feed concentrations results in times that agree with the calculated capacities within the accuracy of projection. Both runs showed

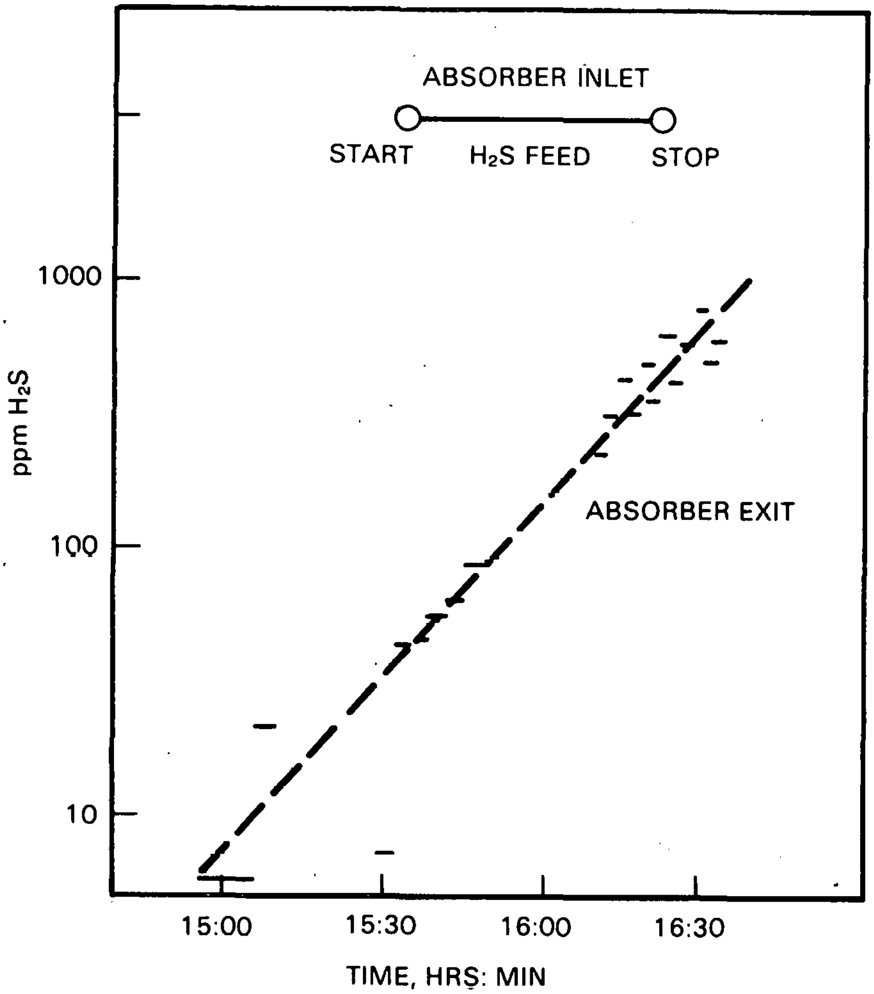

FIGURE 10. H_2S Concentrations During Run S1

removal to <1 ppm H_2S for the first 12% of calculated capacity. The results of Run S6 will be discussed with respect to regeneration later in this report but Figure 13 shows that breakthrough apparently started at about the same fraction of calculated capacity.

The results of S3 and S5 can be used to project the performance of a larger bed. Calculated capacity is inversely proportional to space velocity (see Table 6 for definition). Capacity utilization is limited by the shape of the breakthrough curve which is determined by the mass transfer efficiency achieved in a bed of a given geometry. If the breakthrough curve is fully developed, the time from start of breakthrough to saturation should be independent of

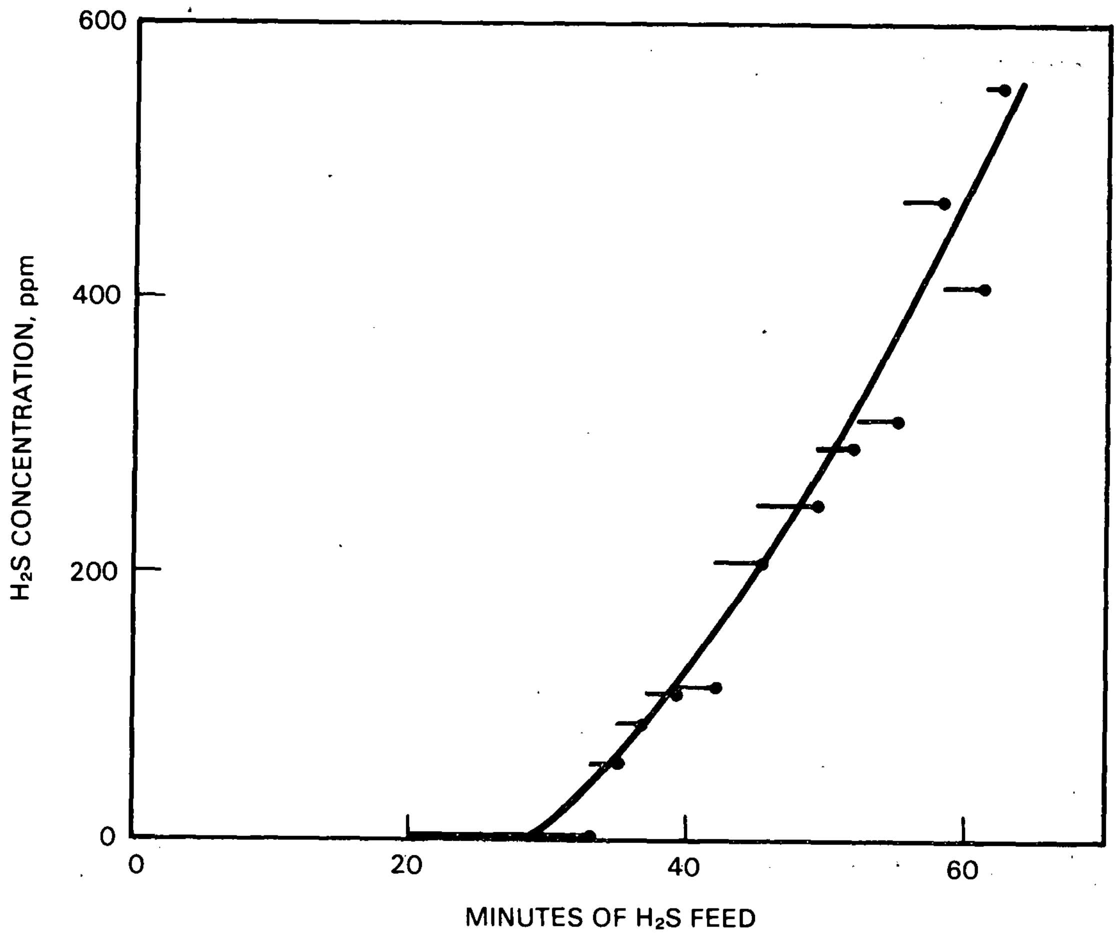

FIGURE 11. Effluent H_2S During Run S3

space velocity under constant mass transfer and feed conditions. For example, increasing bed height 50% while holding all other conditions constant would decrease space velocity by 33% and increase calculated capacity 50%. Breakthrough to 1 ppm would then be expected at (50 + 12)/1.5 or about 40% of calculated capacity using a space velocity of about 300 hr^{-1}. If the breakthrough curve is not fully developed, a somewhat smaller improvement in capacity utilization would be expected.

Improved mass transfer performance would increase the usable space velocity (reduce equipment size) at a given degree of capacity utilization. Sorbent phase mass transfer resistance becomes less significant with decreasing space velocity while gas phase mass transfer improves with increasing superficial velocity. Relatively low velocities were used in the initial tests in order to assure that removal to 1 ppm could be demonstrated in the laboratory scale bed.

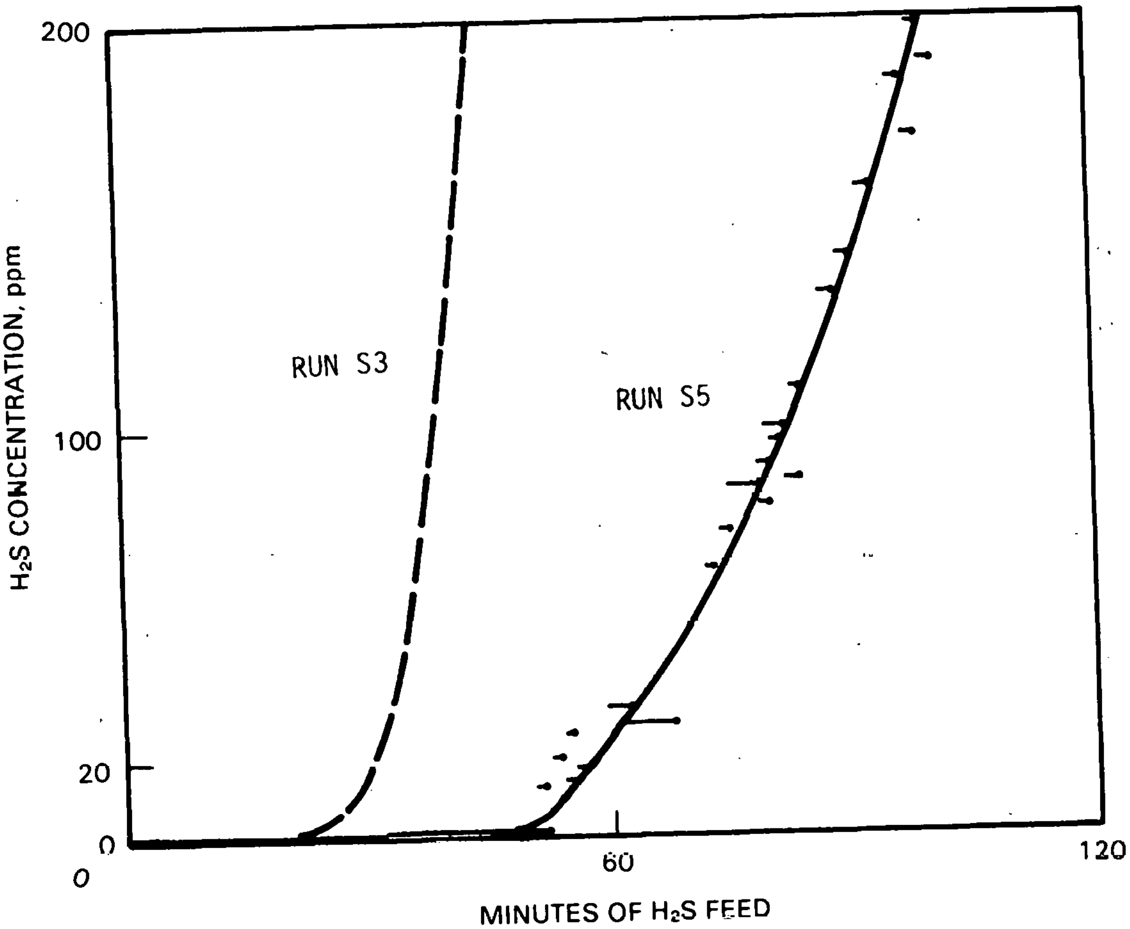

FIGURE 12. Effluent H_2S During Run S5

Higher superficial velocities may be found to improve mass transfer performance. If so, superficial velocity could be increased independently from space velocity by increasing the aspect ratio (length/diameter) of a scaled up bed.

CHLORIDE ABSORPTION RESULTS

As in the case of sulfide removal, the first chloride run (S2) identified a problem with initial contamination of the bed. After alleviation of that problem, two runs were performed that demonstrated removal to less than 1 ppm. The first (S4) was performed with the bed freshly regenerated and the second (S7) immediately after a sulfur removal run. Only low temperature sulfide regenerations were performed between S4 and S7 demonstrating that at least three sulfur cycles can be completed without a separate chloride regeneration.

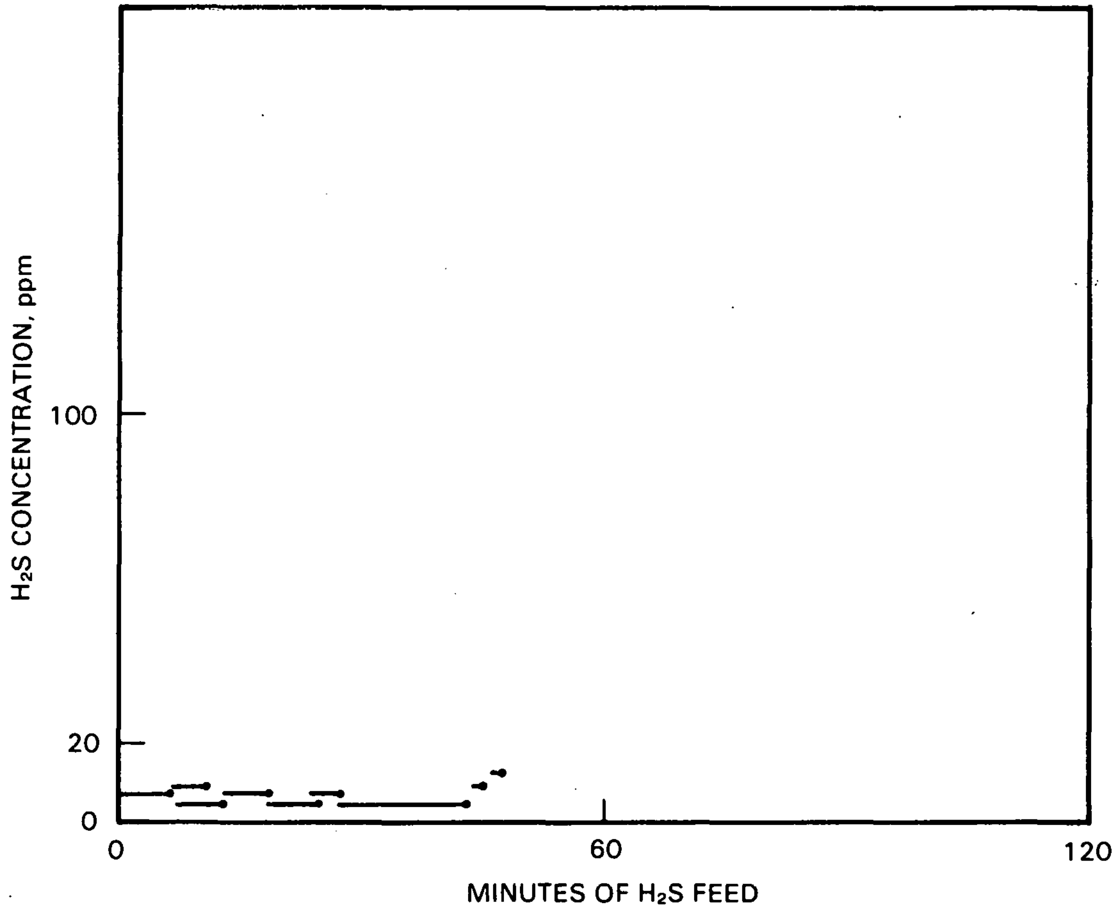

FIGURE 13. Effluent H_2S During Run S6

Table 7 summarizes all three chloride absorption runs. Chloride was detected in the outlet gas both before and after starting HCl feed in Run S2. Uncertainty in the specific ion potentiometric method used for chloride left some doubt about its presence but later, intermediate tests with analysis by ion chromatography confirmed 10 ppm HCl in the outlet gas produced while purging clean gas through the bed. The maximum chloride specification in the chemicals used to fabricate the bed, 0.005% by weight, could only have represented enough HCl to account for its detection before the first run if it was concentrated at the bed outlet. It was concluded that the volatile alkali chlorides (LiCl, Li_2Cl_2, K_2Cl_2) were diffusing slowly through the bed during the long periods between runs and condensing on the cooler walls of the outlet tubes and/or concentrating in the cooler beads near the outlet. Equipment

TABLE 7. Solid Supported Chloride Absorption Runs

Run #	S2	S4	S7
Feed Gas, mole%			
HCl	0.1	0.02	0.02
H_2	19.5	20.3	20.1
N_2	48.6	50.7	50.2
CO	11.3	11.8	11.7
CO_2	5.7	6.0	5.9
H_2O	14.8	11.2	12.1
Space Velocity, hr^{-1}	481	458	463
Pressure, psig	100	100	100
Temperature, °C	729	735	751
HCl feed time, min	30	58	34
Outlet HCl, ppm	10±8	<0.5	<0.5 (0.1-0.3)

changes to allow a constant, small back purge of nitrogen between runs alleviated the problem and HCl in the outlet gas during forward purge checks dropped below detection limits.

As Table 7 reports, HCl was not detected in the outlet gas during Run S4 and may have been just measurable in Run S7. As indicated by Figure 9, before reaching saturation with the 200 ppm HCl feed the bed could be almost completely converted to chloride which would require 2000 hrs of operation. Because the capacity of the SSMS bed for HCl is much greater than for H_2S, HCl removal is very efficient under conditions selected for H_2S removal.

Run S7 represented a relatively severe test of HCl removal in that no specific regeneration for chloride was effected between Runs S4 and S7, and Runs S5 and S6 included about three hours of forward feed. The sulfur regeneration after Run S5 was performed at a reduced temperature, 655°C, increasing effluent H_2S concentration but, as can be seen from Figure 9, decreasing effluent HCl concentration. We would not expect chloride loaded at 735°C to be efficiently regenerated at 655°C. The continued high HCl removal efficiency demonstrated in Run S7 after more than four hours of forward feed at temperatures above 730°C supports process concepts based on combining short sulfur regeneration cycles with a long HCl regeneration cycle.

REGENERATION RESULTS

After Runs S1 and S3 the lab scale SSMS bed was regenerated for further sulfur removal using a reverse flow of 13% CO_2, 13% CO and 23% H_2 at 650°C and atmospheric pressure. After Run S5 a sulfur recovery regeneration test (Run R5) was performed which, as explained in the previous section, was also sufficient to allow further HCl removal. No separate chloride regeneration was performed. Chloride regeneration options are discussed in the next section.

In R5 a reverse flow of 20% CO_2, 25% H_2O, 5% CO and 9% H_2 was used at 655°C, and 100 psig for about the same period of time as the preceding sulfur absorption (S5) but at 25% of the S5 feed rate. The reduced temperature and increased CO_2 and H_2O contents acted through the equilibrium relationship for sulfide absorption (Reaction 1) to cause a five-fold increase in outlet H_2S concentration (Figure 14) over the 4000 ppm feed concentration of S5. The regeneration gas contained CO and H_2 to avoid oxidation of absorbed sulfide by the reaction:

$$2CO_2 + 2H_2O + S^= \rightarrow 2CO + 2H_2 + SO_4^= \qquad (7)$$

Regeneration of sulfide by the reverse of Reaction 1 should have resulted in no change in the H_2 + CO content of the regeneration gas. The regeneration product gas was in fact depleted in H_2 + CO indicating the presence of sulfate. Some of the absorbed sulfur may have been oxidized to sulfate by reduction of carbonate to oxide plus CO during the nitrogen back purge over the weekend that intervened between S5 and R5. Regeneration of sulfate by Reaction 6 would have been limited by the depletion of reducing gas. If only Reaction 1 was involved and in the absence of mass transfer limitations, the reduced temperature and increased CO_2 and H_2O contents used would have been expected to produce a 15 fold increase in H_2S concentration over the 4000 ppm S5 feed rather than the observed 5 fold increase.

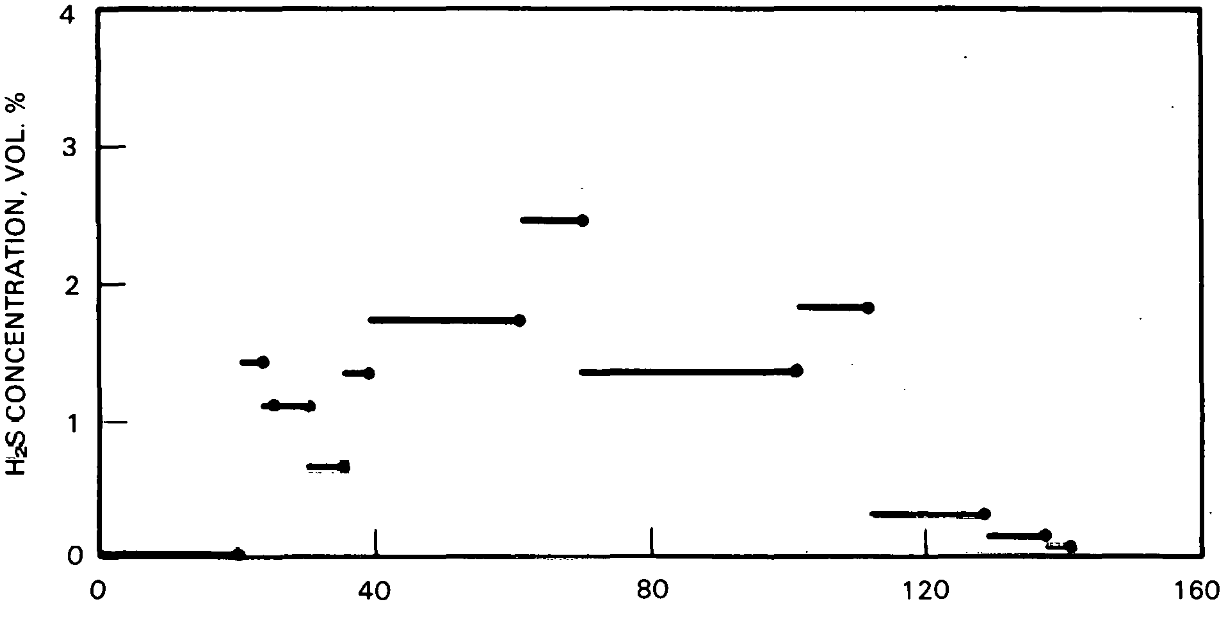

FIGURE 14. Effluent H_2S During R5

Although less than the expected H_2S concentration was produced, feeding 25% of the gas volume of S5 recovered 75% of the sulfur fed in that run. Run S6 (Figure 13) showed that most of the bed capacity was restored and that the equilibrium H_2S concentration was reduced from 4000 ppm to about 4 ppm or by three orders of magnitude. A 33% increase in regeneration gas volume over that used in R5 should have completed regeneration and restored removal efficiency to less than 1 ppm. The 2% H_2S gas produced in R5 would be adequate for sulfur recovery by the recycle Selectox (Clause-type) or the Stretford process (Chute, 1982). Elimination of oxidation problems should improve regeneration efficiency increasing the product H_2S concentration.

PROCESS CONCEPTS

The detailed configuration of a SSMS hot gas cleanup system in an integrated coal gasification/MCFC power plant will depend upon relative absorption and regeneration rates for sulfide and chloride to be established during Tasks 3 through 5. This section discusses some of the options for integrating the SSMS system with the MCFC plant.

In a commercial plant, the SSMS cleanup system could consist of several beds in series and/or parallel arrangement. For simplicity a single bed will be drawn in each of the absorption, sulfide regeneration and chloride regeneration modes. Depending upon relative rates, fewer or more beds could be in either of the regeneration modes at any time than in the absorption mode.

Figure 15 shows a coal gasification/MCFC power plant using an SSMS/Recycle Selectox cleanup and sulfur recovery system. The sulfur regeneration cycle uses a clean fuel gas with added steam and CO_2. Cleaned feed gas could be used with a source of relatively pure CO_2 (solid line) or with cathode exhaust gas as the CO_2 source (dashed line). In a large scale plant, CO_2 recovery might be included (dashed boxes) for sale as a byproduct making a source of pure CO_2 readily available. The Selectox off-gas still contains H_2 and CO values which could be recovered by combining the off-gas with gasifier product (solid lines) or by combusting it in an auxiliary burner for expansion reheat (dotted lines). Depending upon the regeneration gas source and relative volume and upon the selection of air or oxygen for H_2S oxidation, the auxiliary burner option might be selected to avoid dilution of anode feed with the recycled gas.

A third option for both sulfide regeneration gas source and off-gas disposition is shown in Figure 16. A portion of the anode exhaust gas stream might be routed through the regenerating bed and sulfur recovery process. Residual sulfur could be removed as sulfate in a separate SSMS (or other carbonate-containing) guard bed after combustion of the anode exhaust gas. The guard bed would provide cathode feed protection and would produce a small enough quantity of sulfate product that it might be combined with ash/slag from the gasifier for disposal.

Chloride regeneration is expected to be performed in a much longer cycle than sulfide regeneration. Some chloride removal would be provided by the reverse of Reaction 3 in the auxiliary burner or guard bed sulfide regeneration cycle options. In either case, chloride would slowly accumulate in the SSMS beds reducing their sulfide capacity and eventually breaking through if not regenerated. Figure 15 shows chloride removal as HCl by routing cathode exhaust gas through the chloride-regenerating bed (solid lines) or as metal chlorides

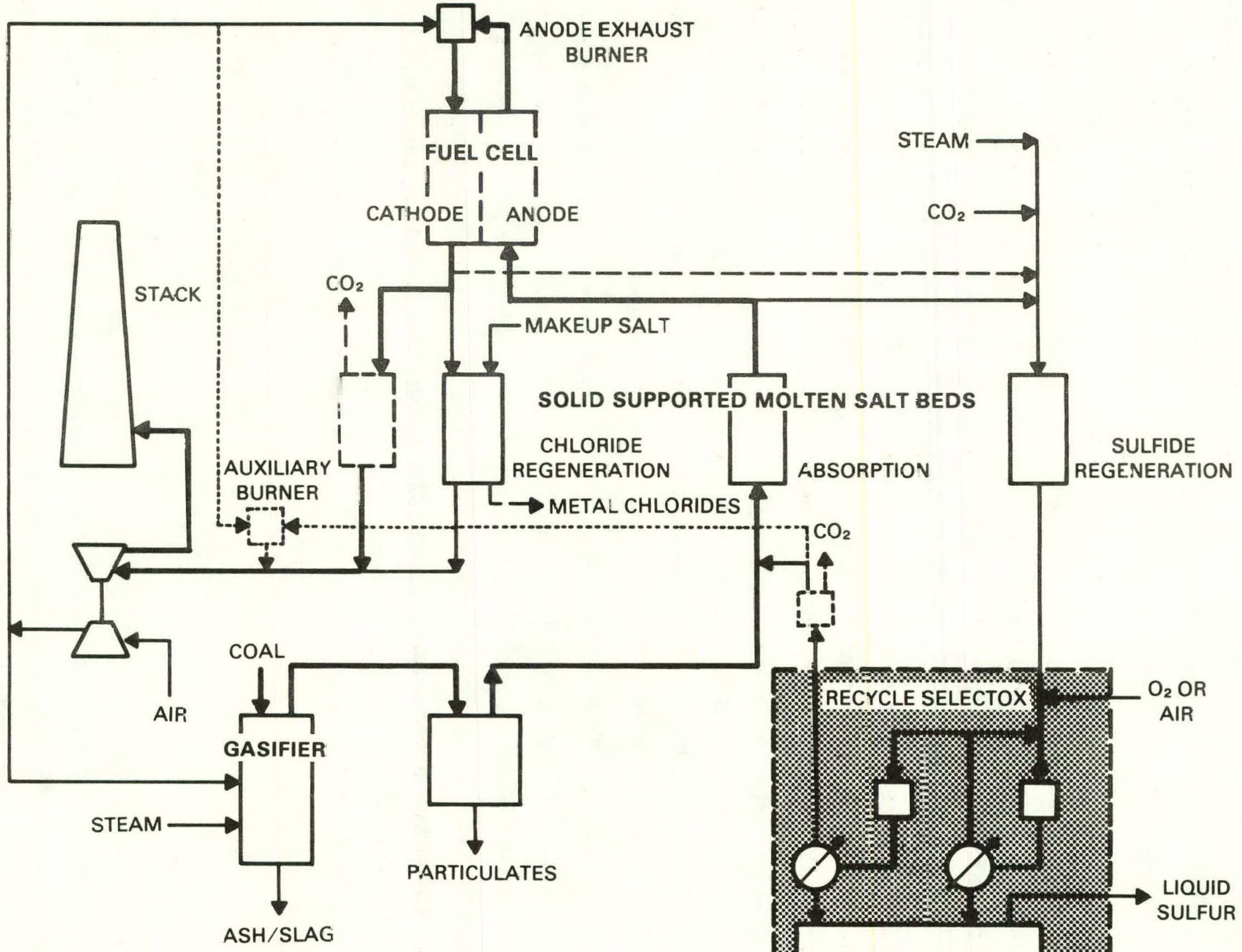

FIGURE 15. SSMS/Recycle Selectox System Integration

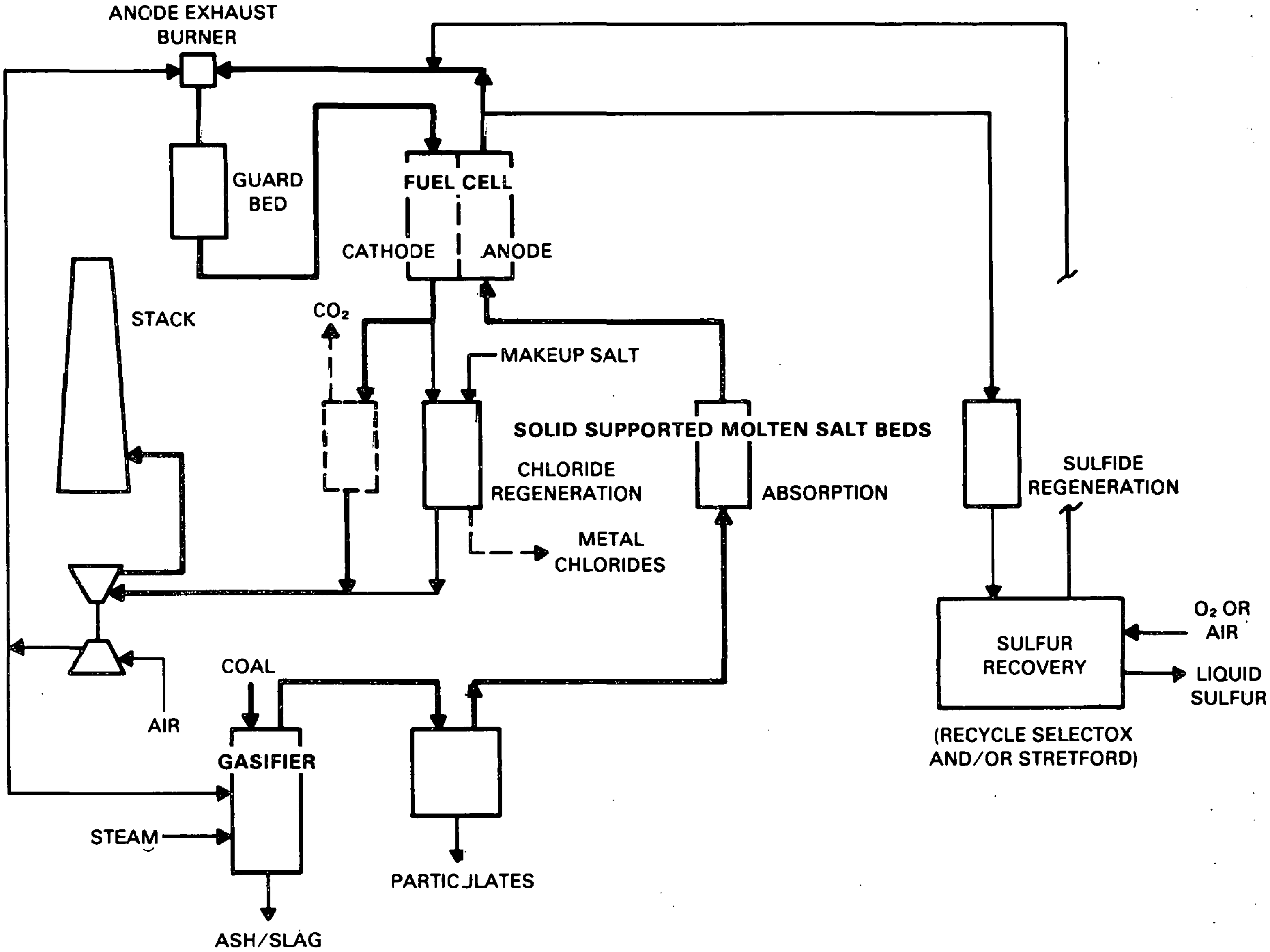

FIGURE 16. SSMS, Guard Bed Option

during periodic bed maintenance (dashed arrow). The HCl option would expose the expansion turbines to chloride concentrations somewhat below those found in the raw gasifier product.

FY 1983 ACCOMPLISHMENTS

- Design, construction and successful operation of an apparatus to generate simulated fuel or regeneration gases, contact them with liquid or solid-supported molten salt at temperatures and pressures up to 1500°F and 200 psig and measure HCl and H_2S in the effluent gas.
- Definition of "coke free" operating regions in the specified range of fuel gas compositions by computerized multicomponent equilibrium calculations.
- Measurement of freezing points for Li, Na, K, Ca/CO_3 compositions of interest.
- Measurement of $CO_3^=/S^=$ equilibrium relationships and temperature dependence for salt and gas compositions of interest.
- Selection and characterization of a fuel cell compatible salt composition which can reach up to 10 wt% sulfur at 10 atm and 750°C in the specified and coke-free range of gas compositions.
- Demonstration of the very favorable HCl removal reaction and absorption of H_2S with a chloride-loaded salt of the selected composition.
- Development of a mathematical model for metal chloride volatility in a packed bed.
- Fabrication of porous aluminate support pellets and loading with 60% by weight of the selected salt composition.
- Demonstration/preliminary-kinetic experiments in which H_2S was reduced from 4000 to <1 ppm and HCl from 200 <1 ppm with regenerated, solid-supported sorbent at 100 psig and 750°C using simulated coal gas.

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PUBLICATIONS

Papers were presented at two technical meetings during 1983. "Equilibrium Measurements for the Absorption of H_2S, COS and HCl by Alkali Metal Carbonates" was presented before the Fourth International Symposium on Molten Salts, May 13, 1983 in San Francisco. "Development of a Hot Gas Cleanup System for Integrated Coal Gasification/Molten Carbonate Fuel Cell Power Plants" was presented to the Third Annual Contractors Meeting on Contaminate Control in Hot Coal Derived Gas Streams, May 24, 1983 in Washington, Pennsylvania.

CONCLUSIONS AND RECOMMENDATIONS

Based on results of exploratory studies and demonstration experiments, the solid supported molten salt process is likely to provide effective and economical hot gas cleanup of hydrogen chloride and sulfur compounds for integrated coal gasification/molten carbonate fuel cell power plants.

The molten salt composition $Li_{.86}K_{.54}Ca_{.3}CO_3$ was selected for compatibility with the fuel cell electrolyte, maximum sulfide retention and minimum freezing point. Equilibrium measurements indicated that up to 150 SCF of feed gas in the specified and coke-free composition range at 1400°F and 10 atm could be treated per pound of the selected salt before saturation with sulfide. Equilibrium HCl removal capacities were shown to be 50 to 100 times greater.

Demonstration experiments with solid supported salt at 7.8 atm and 1350°F showed that either H_2S or HCl could be removed to less than 1 ppmv with the other present and that at least three H_2S, absorption/regeneration cycles could be performed before chloride regeneration.

The demonstration experiments showed breakthrough behavior consistent with the equilibrium measurements. At the low velocities used, absorption kinetics allowed H_2S removal to less than 1 ppmv for the first 12% of the saturation sulfur capacity. Higher capacity utilization is expected at higher velocities.

One sulfur recovery regeneration test performed at 7.8 atm and 1210°F (three days after the preceding absorption) produced a 2% H_2S gas from which elemental sulfur could be recovered. H_2S concentrations are expected to increase when immediate regeneration, lower temperatures and/or higher steam/CO_2 contents are used. Higher concentrations were demonstrated in previous studies at atmospheric pressure (Stegen, 1982).

Simultaneous removal of HCl and H_2S to less than 1 ppmv and production of an H_2S-rich regeneration gas has been shown to be technically feasible for the general application of the solid supported molten salt process to integrated coal gasification/MCFC power plants. Economic feasibility in specific applications will be determined from the results of further development. Based on results of the exploratory studies and demonstration tests, the next year of development is planned to include:

- *Bench scale experiments to optimize absorption kinetics and facilitate scale-up.* To establish the effects of velocity, pellet size and bed geometry, experiments should include higher velocities in the current bed as well as construction and testing of a higher-capacity bed.
- *Refinement of dual cycle (sulfide-chloride) regeneration techniques.* Because of the complexity of experiments to establish simultaneous absorption behavior, they should be supplemented by mathematical modeling.
- *Engineering/economic analysis for a conceptual design of a commercial-scale absorber system.* To provide an independent assessment, process economic studies by a qualified architect engineering firm should be included under a subcontract as well as detailed design of a unit to process low Btu or medium Btu gas from a gasifier burning 150 pounds/hour of coal.

A preliminary analysis of options for integrating the SSMS process with coal gasification/MCFC power plants led to the conclusion that including a cathode feed gas SO_x guard bed could simplify the elemental sulfur recovery loop. An SSMS or other, nonregenerable, carbonate-containing bed should be highly effective. Because sulfur is much more stable in the fuel cell matrix under the oxidizing conditions of the cathode than under the reducing conditions of the anode, such a bed might be desirable independent of the method of anode feed gas cleanup. Battelle Northwest recommends that Morgantown Energy Technology Center consider the SSMS process in developing a cathode feed gas guard bed for MCFC power plants.

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APPENDIX

CHLORIDE VOLATILITY MODEL

Hydrogen chloride is expected to react very readily with molten carbonates to form the respective chloride:

$$2HCl + M_xCO_3 \rightarrow xM^{2/x+} + 2Cl^- + H_2O + CO_2 \qquad (1)$$

where $M_x = Li_2$, Na_2, K_2 or Ca. This reaction should remove hydrogen chloride from the gas early in the bed. The metal chlorides are in turn volatile and will be carried further into the bed as vapor:

$$M^{2/x+} + 2/xCl^- \rightarrow MCl_{2/x} \qquad (2)$$

The vapor will in turn be absorbed by the chloride-free carbonate further in the bed, but eventually metal chloride vapor (and HCl) would break through at the outlet. It is expected that chloride breakthrough would take considerably longer than a sulfur absorption cycle but redistribution of metal in the bed is of concern. Both breakthrough behavior and redistribution can be estimated with an equilibrium stage model.

Figure A.1 illustrates the packed bed and the flows entering and leaving stage "i". A chloride balance on stage "i" gives:

$$\frac{G}{P}\left(P_{HCl,\,i-1} + P_{MCl,\,i-1} - P_{HCl,\,i} - P_{MCl,\,i}\right) = \frac{d}{dt}\left(\frac{x}{2-x} M_i \Delta h\right) \qquad (3)$$

where: G = gas flow, moles/hr; P = total pressure, atm; P_{HCl} = partial pressure of HCl, atm; P_{MCl} = partial pressure of metal chloride, atm; t = time, hours; x = mole fraction chloride, moles/mole of chloride plus carbonate; M_i = metal density, moles Li + K + 2Ca/bed volume; and h = fraction of bed volume in stage "i".

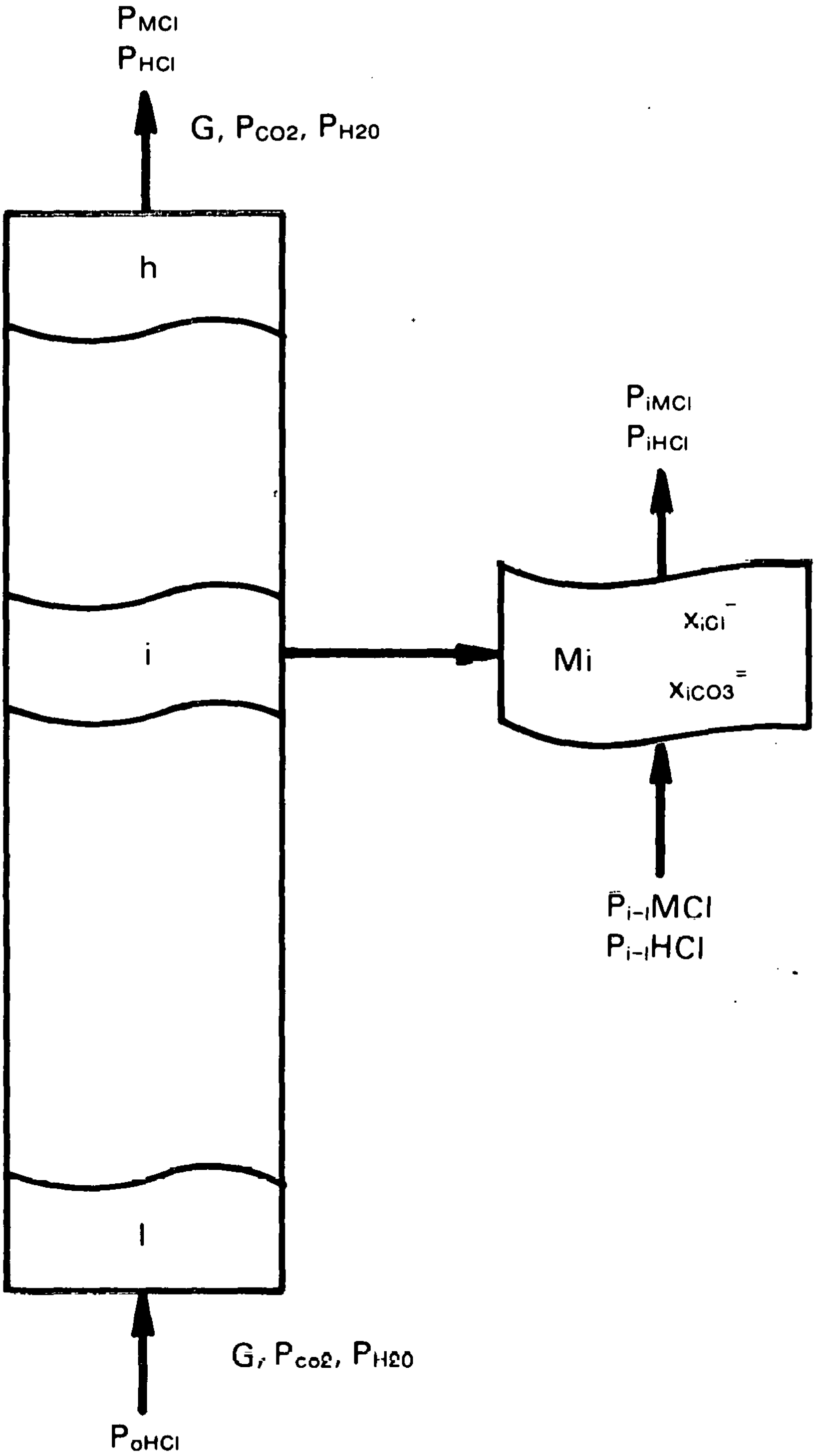

FIGURE 17. Packed Bed Equilibrium Stage

A metal balance gives:

$$\frac{G}{P}(P_{MCl,\ i-1} - P_{MCl,\ i}) = \frac{d}{dt}(Mi\Delta h) \qquad (4)$$

From the equilibrium expression for reaction (1):

$$P_{HCl} = \frac{x}{(1-x)^{1/2}} P\left(\frac{yH_2O\ yCO_2}{K_1}\right)^{1/2} \qquad (5)$$

where "y"'s represent mole fractions in the gas and K_1 is the equilibrium constant based on mole fractions. From Reaction 2 we can derive:

$$P_{MCl} = K_2 x \qquad (6)$$

where K_2 is the equilibrium constant for reaction 2 averaged over the mole fraction of the metals. An algorithm has been developed to solve Equations 3 through 6 by calculating $(P_{HCl} + P_{MCl})_h$ at increments in x using Newton-Raphson convergence on time at each of any number (1/h) of equilibrium stages.

Chloride volatility would be most severe for pure lithium carbonate sorbent at high temperature, high HCl concentrations and atmospheric pressure. The algorithm was applied using $K_1 = 3.78 \times 10^5$ and $K_2 = 1.417 \times 10^{-3}$, calculated from the JANAF tables for Li_2CO_3 and LiCl at 1100°K, $P_{HCl} = 0.003$ atm, P = 1 atm and $y_{CO_2}\ y_{H_2O} = 0.04$. A value of 0.075 hours was used for M/G which would give 75% saturation of the bed with sulfide in a 3.5 hour cycle at atmospheric pressure or in a 25 minute cycle at 10 atm pressure. Calculations have been performed for 4, 10 and 20 equilibrium stages. The bed would be designed for 10 to 20 equilibrium stages. Results are presented in Figures A.2 through A.8.

The variations of total chloride (MCl+HCl) vapor concentration with location in the bed are shown in the first three figures. For 10 and 20 equilibrium stages chloride vapor concentrations of 1 ppm would reach less than halfway through the bed in an hour, more than twice the duration of an absorption cycle. For the four stage case, Figure A.5 shows that the bed exit would

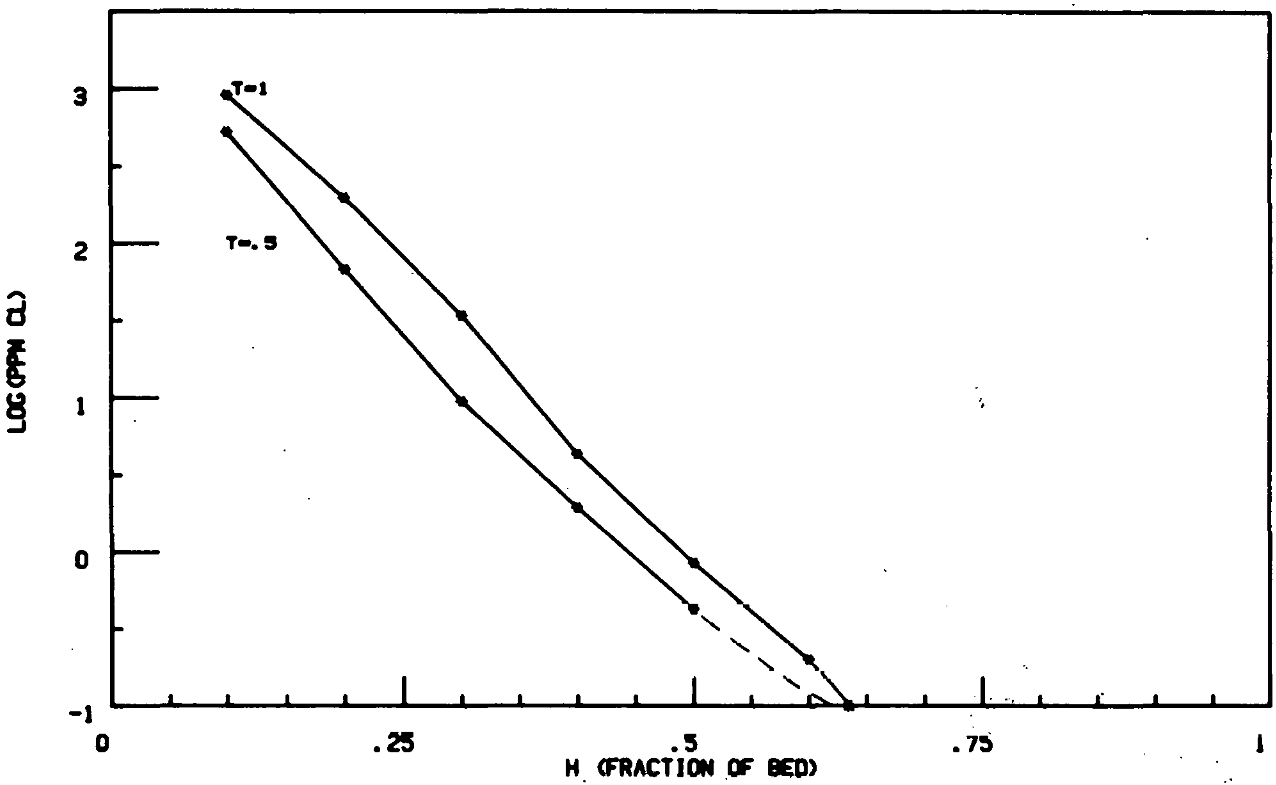

FIGURE 18. Chloride Vapor Profile in 20 Stage Bed at 1/2 and 1 Hour

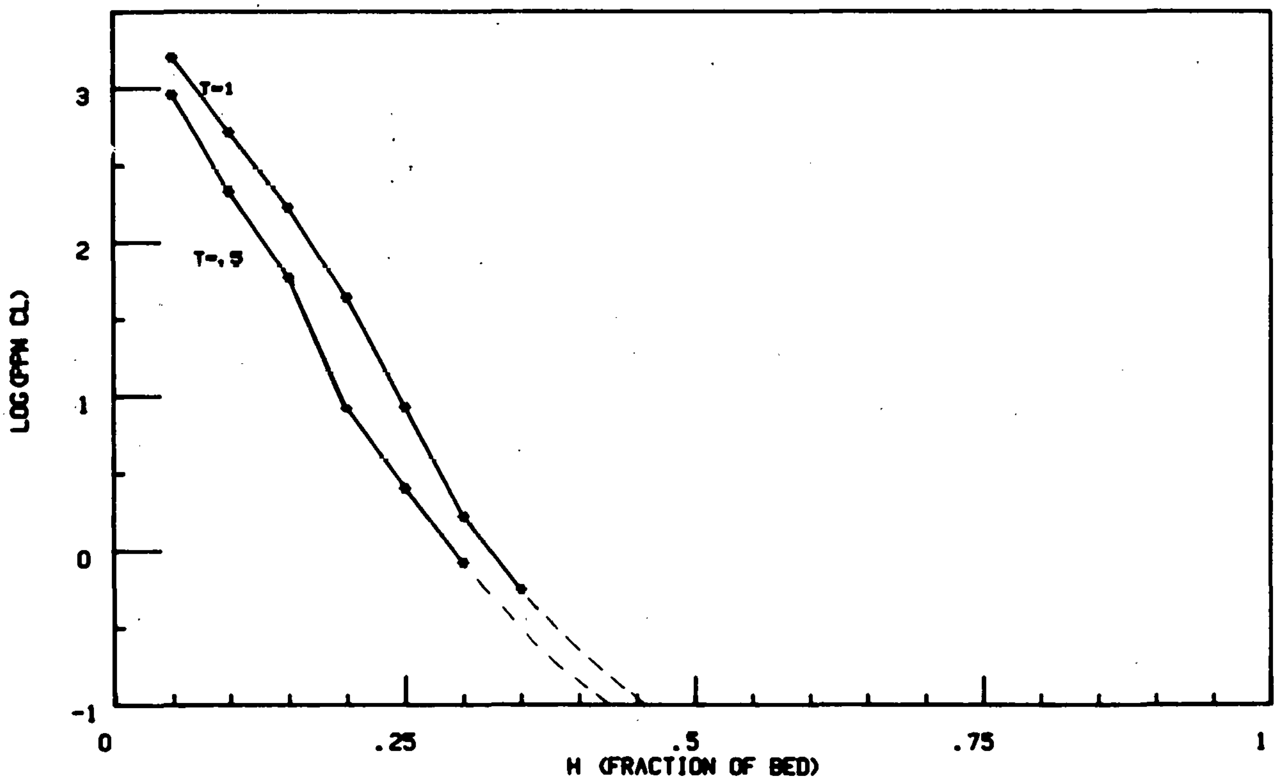

FIGURE 19. Chloride Vapor Profile in 10 Stage Bed at 1/2 and 1 Hour

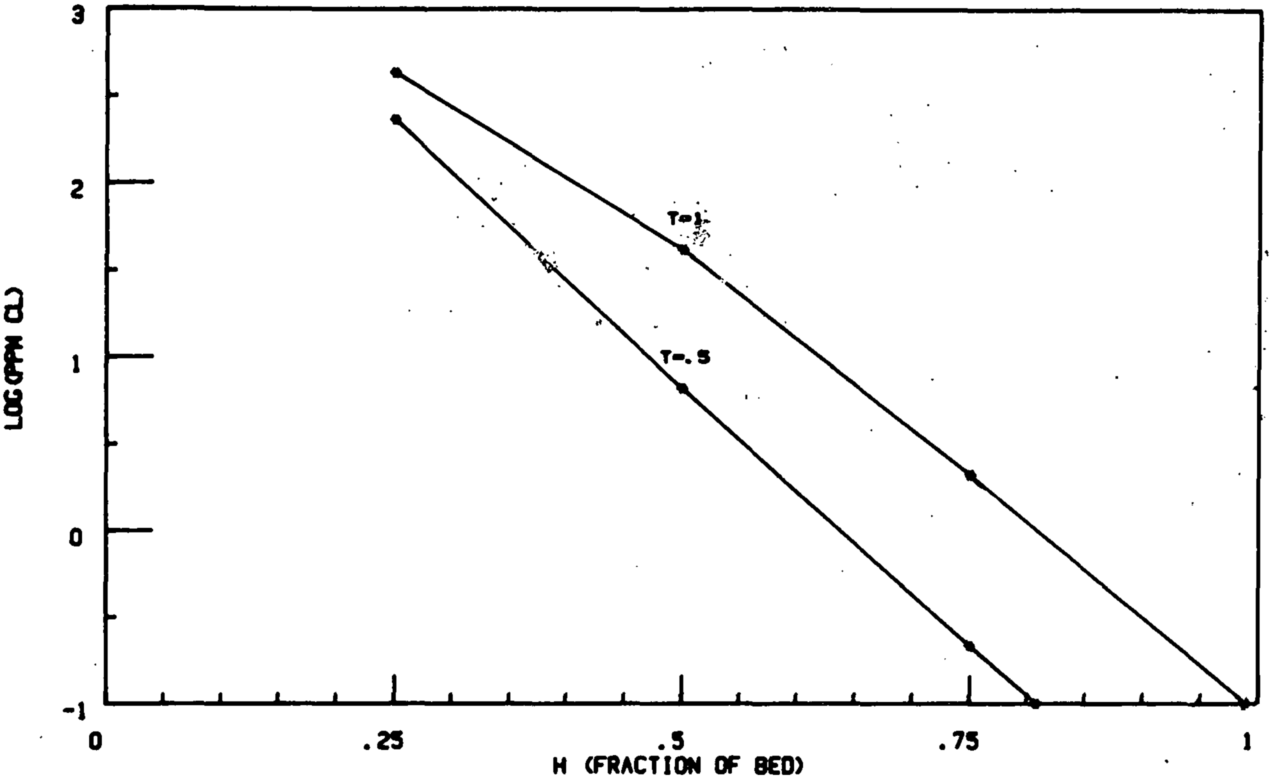

FIGURE 20. Chloride Vapor Profile in 4 Stage Bed at 1/2 and 1 Hour

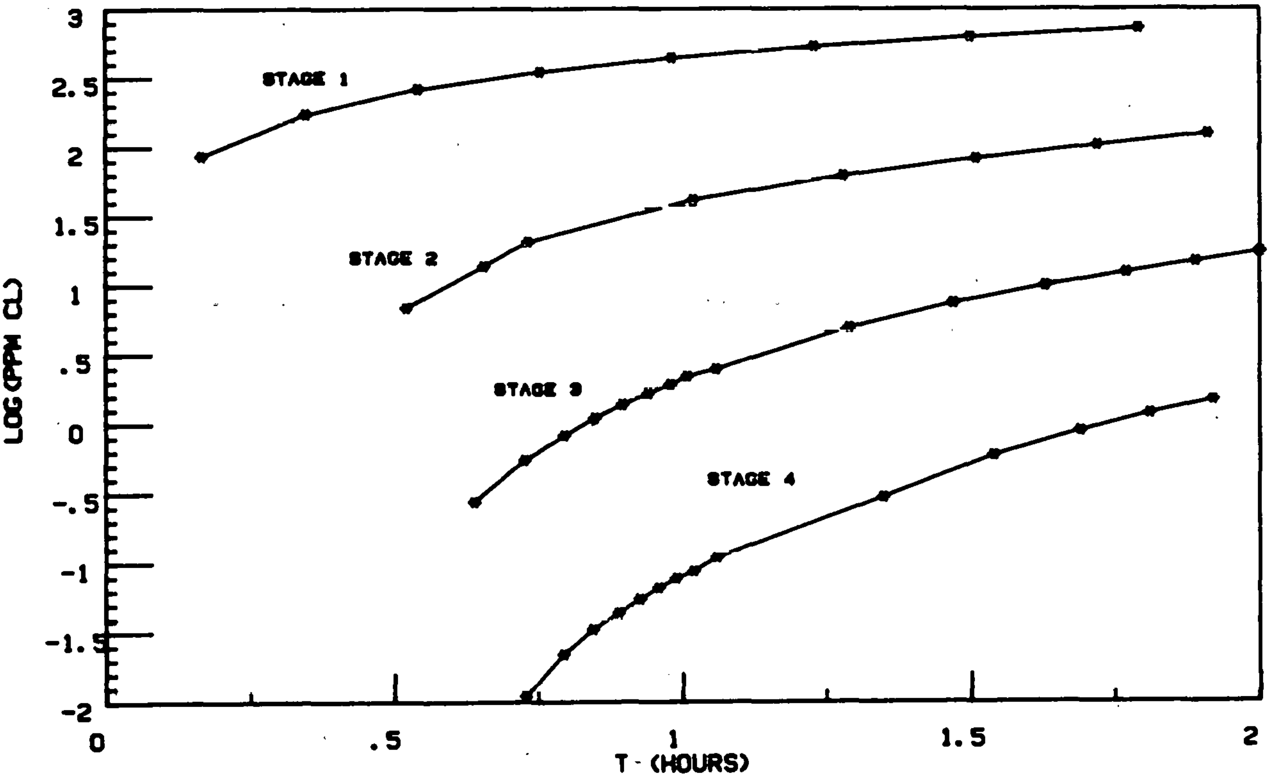

FIGURE 21. Chloride Vapor in 4 Stage Bed Through 2 Hours

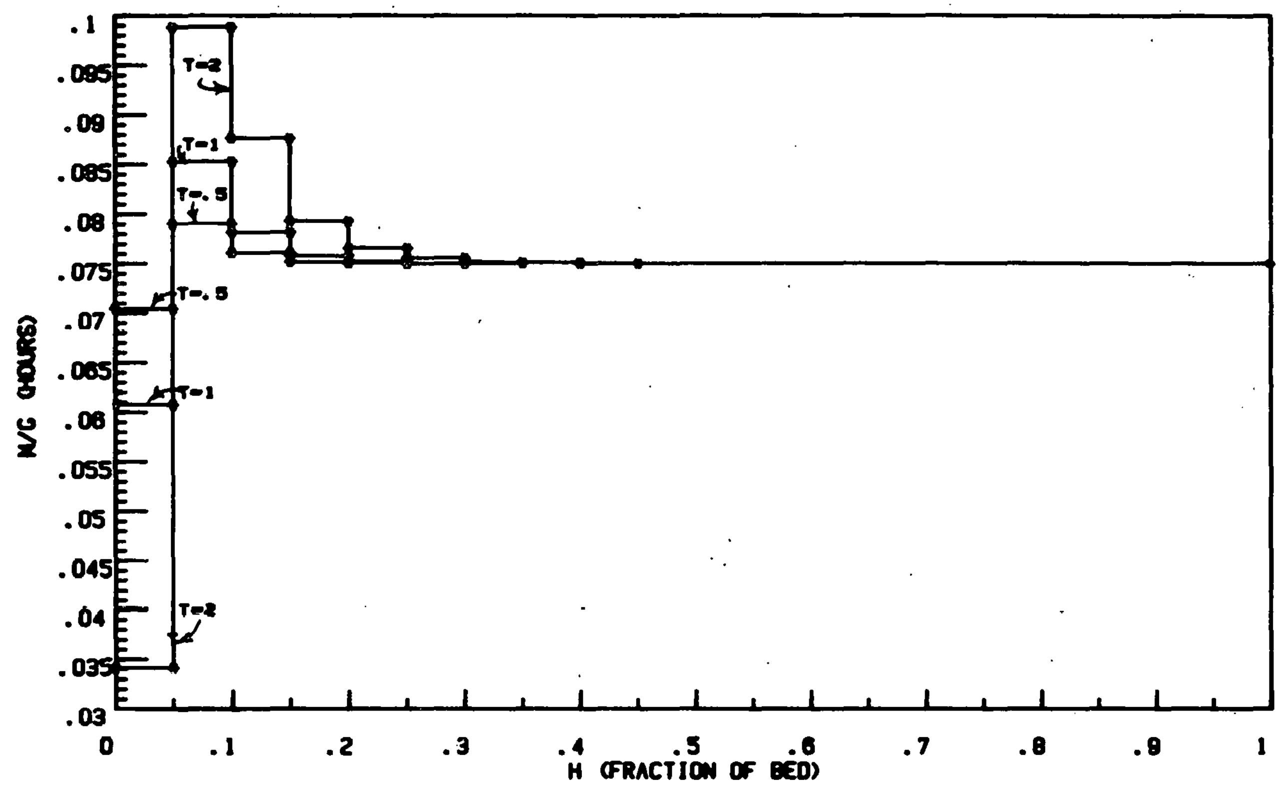

FIGURE 22 Metal Distribution in 20 Stage Bed 1/2 and 1 Hour

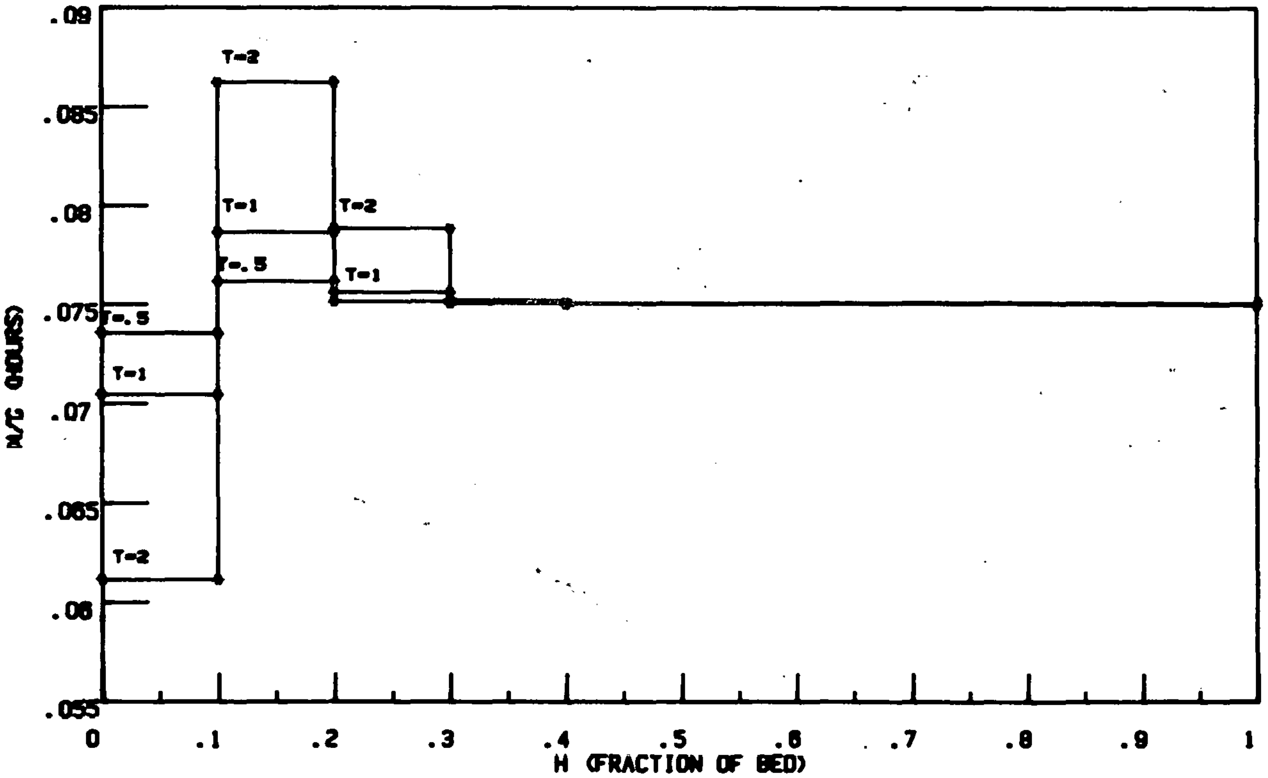

FIGURE 23 Metal Distribution in 10 Stage Bed 1/2 and 1 Hour

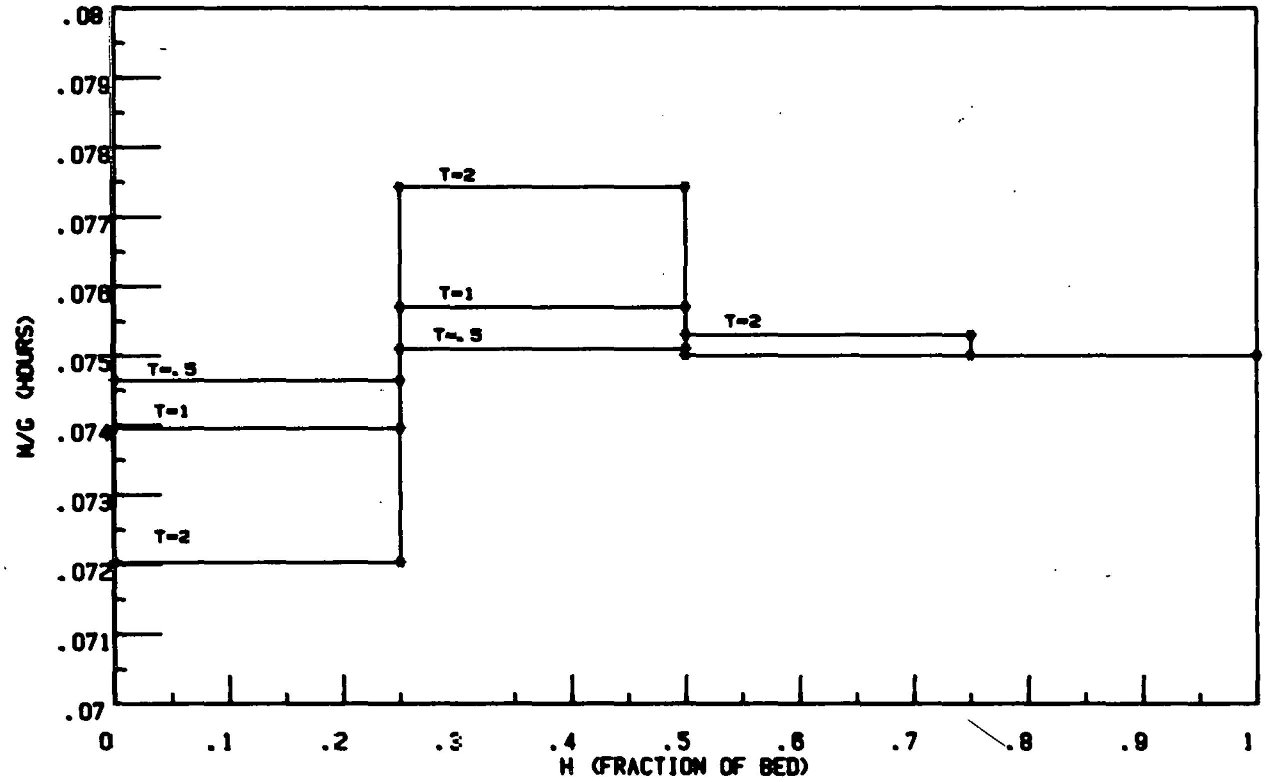

FIGURE 24 Metal Distribution in 4 Stage Bed 1/2 and 1 Hour

reach 1 ppm chloride in 2 hours. Variation of M/G from its initial value of 0.075 hours indicates the distribution of metal. Figures A.6 through A.8 show that redistribution would involve only the early portion of the bed for efficient mass transfer (10 to 20 stages) or only small fractions of the metal for mass transfer-limited design (4 to 10 stages).

The model presented here is crude but should provide a fairly reliable picture of bed performance. Making conservative assumptions, the model shows that chloride volatility would not present a serious problem even at atmospheric pressure. Metal chloride vapor concentrations are inversely proportional to pressure making their effect on breakthrough behavior even less at higher pressures. For a more pertinent case, the same calculation gives the following results:

- Salt Composition: 1/3 Li_2CO_3, 1/3 K_2CO_3, 1/3 $CaCO_3$(a)
- Temperature: 1100°K Pressure: 10 atm
- HCl Absorption Equilibrium Constant: 4.5×10^6
- Metal Chloride Henry's Law Constant: 5.5×10^{-4} atm
- Inlet HCl Concentration: 500 ppm
- Inlet H_2S Concentration: 3000 ppm
- Inlet Gas: 10% CO_2, 15% H_2O
- Length of H_2S Cycle: 1 hour

• Number of Equilibrium Stages:	10	20
• % Bed Penetration of 1 ppm Chloride Vapor in 10 hours	35	25
• Maximum % Metal Redistribution in 10 hours:	3.5	10

The results indicate that under projected operating conditions, chloride could be handled for well beyond 10 H_2S absorption cycles with no regeneration. In fact under the projected H_2S regeneration conditions of 900°K, 10 atm, 40% CO_2 and 40% H_2O the HCl concentration would approach 500 ppm while metal chloride vapor pressure would drop by a factor of 100. Thus a substantial amount of chloride would be removed in the H_2S cycle. If the height of an equilibrium

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(a) $CaCl_2$ vapor pressure assumed negligible, {{/ΔG for solid $CaCO_3/CaCl_2$ reaction used in average for HCl absorption equilibrium.

stage is determined from sulfur breakthrough analysis, the behavior of chlorides can be predicted with some confidence. A refined model could then be used to help identify optimal regeneration cycles for sulfide and chloride.

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