

SOLID SUPPORTED MOLTEN SALT HOT GAS CLEANUP
FOR CARBONATE FUEL CELL POWER PLANTS.

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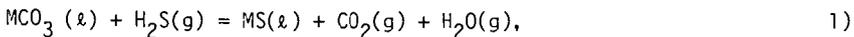
INTRODUCTION

A regenerable sorbent for removing sulfur from hot fuel gas was developed at Battelle, Pacific Northwest Laboratories by supporting molten carbonates in porous ceramic pellets. Recent development work has shown the sorbent to be a promising candidate to meet the stringent cleanup requirements for coal gasification molten carbonate fuel cell power plants while allowing elemental sulfur recovery and maintaining high power production efficiency. Solid supported molten salt (SSMS) differs from other methods of hot gas cleanup in that 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. At the clean end of an SSMS absorber the concentrations of reaction product sulfides and chlorides in the sorbent approach zero and the concentration of contaminants in the cleaned gas can also approach zero. The approach is limited only by the size of the bed, mass transfer efficiency and the degree of regeneration.

This paper begins by presenting the background and the overall approach and scope of the recent developmental effort. More detail is then given on equilibrium measurements, mass transfer performance and modeling of the H₂S absorption and regeneration steps. The paper closes with a discussion of process flowsheet development and preliminary economics.

BACKGROUND

The reversible reaction of H₂S with molten carbonates has been under study at Battelle Northwest since 1974⁽¹⁾.



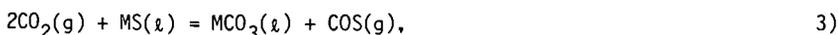
Where "M" represents Li₂, Na₂, K₂ or Ca.

A process was first developed based on continuous, countercurrent gas liquid contacting (2). Absorption of H₂S and particulates, deentrainment and regeneration of the carbonate were demonstrated in a process development unit (PDU) operating with gas from an air blown, fixed-bed coal 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 CO₂ were used to recover H₂S. Use of the hot, corrosive molten salt in a countercurrent contactor led to severe equipment problems, and operation was never sustained for more than a few hours at a time.

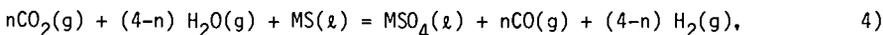
The SSMS concept was developed as a practical means for handling the corrosive molten carbonates (3). Several ceramics were investigated as potential supports. Lithium aluminate was chosen for chemical stability and for ease of fabrication of strong, porous pellets. Use in a cyclically-operated fixed-bed allowed the advantages of a gas-liquid equilibrium system to be exploited through breakthrough behavior rather than countercurrent contacting. 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% H₂S and produced regeneration gases containing up to 50% H₂S on a dry basis. The tests showed that COS was generated during absorption breakthrough and regeneration in amounts consistent with equilibrium by the gas phase reaction:



which could not be distinguished from the direct regeneration reaction:



The same study identified redox reactions involving H₂ and CO which may involve several oxidation states of sulfur such as poly sulfides or sulfites but can be characterized by:



Where n = 0, 1, 2, 3 or 4. It was found that H₂ or CO had to be included in the regeneration feed gas to avoid leaving traces of oxidized sulfur in the bed that would be reduced during the subsequent absorption contaminating the product gas before breakthrough.

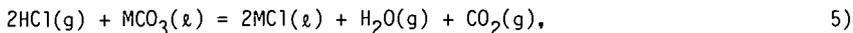
DEVELOPMENT FOR PRESSURIZED FUEL CELLS

The molten carbonate fuel cell application addressed by the recent study requires: 1) operation at elevated pressure which has a detrimental effect on the absorption equilibrium, Equation 1; 2) design for removal to less than 1 ppm through multiple cycles; 3) removal of COS and HCl as well as H₂S; and 4) design for an air-blown gasifier making the H₂ and CO needed to avoid oxidation, Equation 4, available only in streams diluted with nitrogen.

Laboratory equilibrium experiments to optimize salt composition, bench scale experiments to establish mass transfer performance and modeling efforts were directed primarily toward the first two requirements. Results will be discussed in more detail later in the paper.

The third requirement was addressed by including COS and HCl in feed gases and by a few experiments directed solely at HCl behavior. The method used for effluent COS (4) analysis had a detection limit of 1 to 10 ppm depending upon experimental conditions. Removal from 1000 to less than 10 ppm was demonstrated in most cases but in several cases COS was detected in absorber effluent at more than 1 ppm when H₂S levels were lower. Because of the high detection limits, results are not conclusive but COS removal may be slower than H₂S under some conditions.

Hydrogen chloride removal occurs by chloride formation:



which has an equilibrium shifted well to the right under hot cleanup conditions. Equilibrium tests confirmed the thermodynamics and removal from 200 to less than 1 ppm was demonstrated in several tests. Because of the high equilibrium conversion by Equation 5, no regeneration tests during representative sulfur cycles achieved high enough HCl concentrations for practice chloride removal. A separate method for HCl regeneration appears necessary. The behaviors of chlorides and COS in the SSMS system both require additional study.

The fourth fuel cell application requirement was addressed by using nitrogen diluted feed gas such as would be available in an air-blown gasification plant. Thermodynamic calculations (4) based on published data (5, 6, 7) indicated 5 to 10% CO + H₂ is required to avoid oxidation (Equation 4) during regeneration. About 10% was used throughout and found to be adequate. Because the exact level used does affect process efficiency, a direct study of Equation 4 would eventually be necessary for commercial design.

EQUILIBRIUM MEASUREMENTS

The sulfide/carbonate equilibrium was measured in various mixtures of molten Li, Na, K and Ca carbonates to select an optimum composition for use in the MCFC application.

APPARATUS AND METHODS: A pressure-capable experimental apparatus was designed and constructed for use in both equilibrium and subsequent bench-scale mass transfer tests. Gases (metered into the system under cylinder pressure) and water (pumped into a steam generator by a high pressure feed pump) were used to generate simulated coal gas of the desired composition. Accuracy of metering the fuel gas, contaminant and steam streams is estimated to have been $\pm 5\%$ or less of each component. A section of Incoloy 800H pipe served as a pressure vessel (rated for 250 psig at 1600°F) and was heated by ceramic fiber heaters. An alumina thimble suspended inside the pipe contained free liquid or solid supported molten carbonate. Smaller tubes sealed through the top flange provided a thermowell and access to the thimble through its loose fitting lid. A small nitrogen purge into the pipe assured that system gases remained inside the alumina. Heat traced, teflon lined tubes conducted effluent gas to stainless steel scrubbers where circulating sodium hydroxide solutions condensed steam and absorbed contaminants for analysis. The solutions were monitored for sulfide by specific ion potentiometry giving an effective detection limit of 0.5 ppmv for H₂S. A letdown valve after the scrubbers provided pressure control. Gas samples were taken downstream of the valve and analyzed by gas chromatography. Using the known composition of the fuel gas as a standard, changes in the CO/H₂ ratio and the CO + H₂ balance were measured. Because of drift in the CO response factor the CO/H₂ ratios and CO + H₂ balance are only considered accurate to $\pm 10\%$.

Equilibrium measurements were performed by melting the desired salt composition in the thimble, loading it with H₂S, purging simulated fuel gas

through the molten liquid and measuring the effluent gas composition as a function of the sulfide content determined by material balance. Purge gas without H_2S or with slightly more than the expected effluent level was used to check approach to equilibrium from below or above. Equilibrium constants were calculated assuming ideal gas and liquid solutions.

RESULTS: Screening experiments for sulfide capacity were completed with four different salt mixtures (Table 1) at atmospheric pressure. Salt mix #1 is the composition used by Moore et. al. (8) and Stegen (3) as unsupported and supported sorbents respectively at atmospheric pressure. 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. 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.

TABLE 1. Carbonate Mixtures Screened for Sulfide Capacity, mole %

<u>Salt Mix</u>	<u>Li₂CO₃</u>	<u>Na₂CO₃</u>	<u>K₂CO₃</u>	<u>CaCO₃</u>
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

Figure 1 shows that calcium content can be used to correlate the results of this work with the calcium-free results of Moore. Moore's data with calcium showed a low temperature dependence relative to pure component thermodynamics. Although pure component solid thermodynamic data (5) would indicate a stronger effect of calcium, the high estimated melting point for CaS (2725K, 9) relative to CaCO₃ (1500K, 10) apparently leads to lower relative stability in the liquid phase. Projecting data from (5) into the subcooled liquid range, assuming entropies of fusion at reported (5, 9, 10) melting points for Li₂S, CaCO₃ and CaS of 5, 6 and 6 cal/degree/mole and assuming constant liquid heat capacities of 22, 33 and 16 cal/degree/mole respectively, allows the calculation of pure component equilibrium constants for Reaction 1. These are compared with the full range of experimental data from this work in Figure 2. The lower constants found for mixed carbonates probably reflect the stability of the inter-alkali carbonate eutectics. Although Figure 2 would indicate a lower activity for calcium than potassium, the correlation of Figure 1 apparently shows that calcium sulfide is relatively more stable in the carbonate matrix than the alkali metal sulfides. Precipitation of solid calcium sulfide cannot be eliminated as a possibility but was judged unlikely at the low sulfur concentrations (less than 3 mole%) used in the screening studies.

BENCH SCALE MASS TRANSFER EXPERIMENTS

Mass transfer data on the absorption/regeneration cycle were obtained by experiments with packed beds of solid supported sorbent. Methods and an overview of results are presented here. Results are discussed in more detail in connection with the mass transfer model.

METHODS: Porous, lithium aluminate ceramic pellets (1.4 to 2.8 mm size range) were fabricated by methods developed in previous work (3). The pellets were loaded close to saturation with molten salt (0.36 to 0.42g of salt per bulk cc of sorbent). In the apparatus already described a ceramic thimble of 4.6 or 9.1 cm² cross section served as an absorber. The smaller thimble was filled with a 25 cm bed of pellets. The larger thimble was operated at both 25 and 50 cm depths. Sorbent was supported on dense alumina beads (1/16 in. diameter) and, at the 50 cm depth, topped with a layer of the same beads to provide gas distribution.

For each absorption experiment the bed was brought to temperature and pressure under a nitrogen atmosphere, a simulated coal gas flow started, contaminant gas added and effluent concentration monitored as a function of time by methods described earlier under "Equilibrium Measurements." For regenerations, temperature was adjusted (generally 100°C cooler) and a CO₂-H₂O rich fuel gas fed in the opposite direction.

RESULTS: Sorbents with two different salt compositions were tested in the smaller absorber. The first, Li_{0.96}K_{0.54}Ca_{0.3}CO₃, selected from the equilibrium results, demonstrated poor mass transfer (broad breakthrough curves). A low-calcium composition, Li_{1.1}K_{0.7}Ca_{0.1}CO₃, showed better mass transfer performance and was used for all tests in the larger absorber. It was postulated that the high-calcium salt precipitated solid calcium sulfide which interfered with both absorption and regeneration.

After thorough regeneration, both salt compositions removed H₂S to less than 1 ppm with the length of time before breakthrough ("breakthrough time") limited by equilibrium and mass transfer effects. Incomplete regeneration further shortened breakthrough time and/or added a background level of H₂S before breakthrough. Projecting breakthrough curves to one half the inlet H₂S* concentration checked with "equilibrium times" for saturation of the bed with feed gas calculated from results of the equilibrium measurements. Similar treatment of low-calcium results allowed the estimation of thermodynamic constants, Table 2, for the carbonate/sulfide equilibrium which are consistent with Figure 1 and with mass transfer results over the range studied.

TABLE 2. Thermodynamic Constants for Reaction 1 (900 to 1100°K, 1 to 15 atm)

Salt	Li _{0.96} K _{0.54} Ca _{0.3} CO ₃	Li _{1.1} K _{0.7} Ca _{0.1} CO ₃
Heat of Reaction	26K cal/mole	27K cal/mole
Entropy of Reaction	26.8 cal/mole-K	26.4 cal/mole-K

Varying space velocity and gas composition changed the breakthrough and equilibrium times but the general shape of the breakthrough curves remained the same. A total of 16 absorption and regeneration experiments were completed with the same half or full load of sorbent in the larger absorber. Space velocities from 300 to 2300 per hour, absorption temperatures of 750 and 800°C, pressures of 100 and 180 psig and several levels of steam-carbon

* actually, 1/2 inlet H₂S + COS minus equilibrium COS for that concentration.

dioxide back pressure were tested. A complete presentation and discussion of laboratory and bench scale results obtained in this study has been reported elsewhere (4).

MASS TRANSFER MODEL

Having shown the significant effect of mass transfer resistance on breakthrough time for SSMS cleanup under the desired conditions, a quantitative treatment was developed as a basis for design and optimization. It was found that simple two-film mass transfer theory used with the equilibrium expressions presented earlier gave a good representation of both absorption and regeneration behavior. The mass transfer equation:

$$N = k_g a(y - y_i) = k_p a(x_i - x), \quad (6)$$

must be solved in an unsteady state material balance framework:

$$\epsilon dy/dt + \rho_b dx/dt + G dy/dh = 0 \quad (7)$$

In these expressions: N = interphase molar flux per unit volume, k_g and k_p = gas and pellet mass transfer coefficients, a = surface area per unit volume, y and x = gas and liquid mole fractions with the subscript "i" representing interface concentrations (assumed at equilibrium), ϵ = void fraction, t = time, ρ_b = molar density of liquid (salt) in the bulk pellets, G = superficial molar velocity of gas and h = distance through the bed.

Rigorous analytical solutions of Equation 7 are possible (11) but restricted to linear equilibrium and simple boundary conditions. For the non-linear equilibrium that results from a preceding absorption or regeneration, a model was developed using finite elements of time and distance (4). Preliminary calculations showed that the $\epsilon dy/dt$ term was relatively small and that particle phase transfer should control. The void volume term was eliminated from Equation 7 and although $k_p a$ was retained in Equation 6 it was assigned an arbitrarily high value so that the values of the combined term " $k_p a$ " used to fit the data were in effect overall particle-phase mass transfer coefficients.

Figures 3 and 4 show calculated and typical experimental results for a low-calcium absorption and regeneration respectively. Dead volume in the experimental system caused a delay and reduction of the regeneration peak. The data are plotted on an adjusted time scale to show that the regeneration decay slope is matched by the model. A value of 2×10^{-5} g-moles/cm³/sec fitted the low-calcium absorption data at 750°C and was adjusted for a linear decrease in diffusivity with absolute temperature to fit the regeneration data at 650°C. The model does not reflect the pre-breakthrough background H₂S during absorptions or a break in decay slope observed during extended regenerations. Both phenomena were highly temperature sensitive and may be the effect of a trace side reaction such as oxidation (Equation 4).

Slow mass transfer in the SSMS pellets studied probably results from a low surface to volume ratio. Loading more porous pellets to a lower degree of saturation with molten salt could lead to a significant improvement.

PROCESS DESIGN

Cyclic regeneration for sulfur recovery and the need to include contaminant-free reducing gas in the regeneration feed to avoid oxidation of sulfur to sulfate suggest several flowsheet options. The source of regeneration gas, choice of sulfur recovery process, disposition of the tail gas from sulfur recovery, operating temperature and pressure and the use of temperature and/or pressure cycling for regeneration all must be determined. This section reviews flowsheet development and preliminary estimates of efficiency and economics with reference to a study performed by Stone and Webster Engineering Corporation (SWEC) and suggests additional options outside the scope of that study.

FLWSHEET DEVELOPMENT: Seven flowsheet options were evaluated by SWEC. Six used temperature cycling to effect regeneration while the seventh used only increased CO_2 and steam content. A blend of anode feed and exhaust gas made up the regeneration feed. The reader is referred to our final report (4) for a complete description of the options. Because experimental data were obtained for essentially isothermal operation during absorption and regeneration, SWEC added separate heating and cooling cycles requiring two beds in addition to those in the absorption or regeneration positions. It is likely that the cooling and heating periods can be incorporated into the regeneration cycle eliminating the extra beds.

SWEC used commercially available sulfur recovery technology which dilutes the sulfur-bearing regeneration product stream with the air required to oxidize H_2S to elemental sulfur. As a result, the energy value of the CO , H_2 and CH_4 in that stream could only be recovered by incineration to raise steam. Use of advanced sulfur recovery technology (12) that removes and recovers CO_2 and sulfur without adding air could allow recycle of sulfur recovery tail gas to the MCFC which would recover the energy value at higher efficiency.

The difficulties involved in heating and cooling large beds of sorbent could be avoided by using a pressure cycle to obtain the necessary driving force for regeneration. After absorption at the fuel cell feed pressure regeneration could be performed with CO_2 (from a CO_2 recovery unit) and steam, both of which could easily be supplied at high pressure. Adding a relatively small amount of cooled and compressed fuel cell feed gas would supply the necessary CO and H_2 . Stone and Webster's flowsheet used a swing from 4.4% CO_2 and 14.4% steam to 32.9% CO_2 and 27.3% steam plus a 126°F temperature swing to effect regeneration while suffering a pressure reduction from 150 to 110 psia. Increasing regeneration gas steam and CO_2 contents to about 39% each and pressure to 215 psia would more than compensate for the loss of the equilibrium advantage from the temperature swing. This option could reduce capital cost by eliminating the inter-bed coolers as well as reducing the number of beds. It could also increase process efficiency by eliminating the dilution and thermal losses associated with the temperature cycle.

EFFICIENCY: The primary reason for considering hot gas cleanup is increased power generation efficiency. The net power production efficiency calculated by SWEC for an integrated coal gasification/molten carbonate fuel cell power plant with SSMS hot gas cleanup was 45.6% or 7478 Btu/kWh (4). This figure compares well with conventional technology and with 7300 to 7700 Btu/kWh

calculated by Westinghouse (13) for air blown gasification with other developmental hot gas cleanup systems. Further improvement is likely upon optimization of the coal gasification-SSMS-MCFC system.

CAPITAL AND OPERATING COSTS: Capital and operating costs were calculated by SWEC for an integrated coal gasification/MCFC power plant with SSMS hot gas cleanup (4). The commercial plant burning 1000 tons/day of coal and producing 135.9 MW net power had an estimated investment of 216 million dollars. Operating costs were estimated for the power recovery, absorption/regeneration, sulfur recovery and incineration sections at 11.8 million dollars per year or about one cent per kilowatt-hour.

The overall investment figure was developed for comparison with other cost estimates. The Westinghouse hot gas cleanup study (13) reported total costs based on other developmental cleanup systems representing 169 to 188 million dollars when adjusted to the same time and scale. SWEC performed detailed cost analysis only for sections of the plant directly affected by the SSMS system. A more complete process optimization/cost study is in progress. The most significant result of the SWEC study is that the absorption/regeneration section accounts for 34% of the power plant cost. With process and/or sorbent optimization, a reduction in cost of the SSMS system by 50% appears possible which would make the estimated cost of coal gasification/MCFC power plants using SSMS cleanup competitive with the published estimates for other hot gas cleanup systems.

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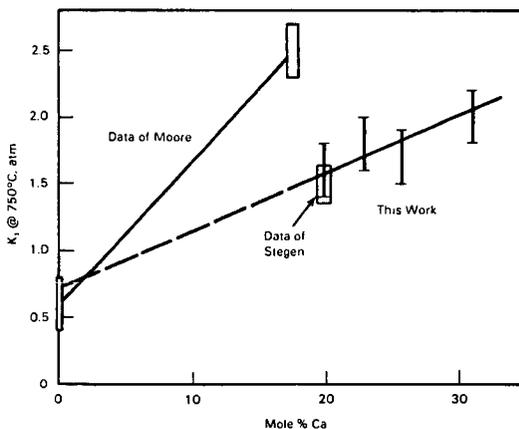


Figure 1. Correlation of Carbonate/Sulfide Equilibrium with Calcium Content.

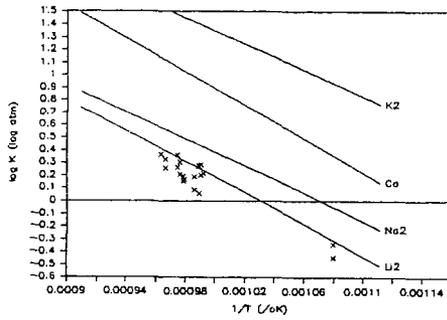


Figure 2. Estimated Pure Liquid Carbonate/Sulfide Equilibria and Data for Mixed Liquids.

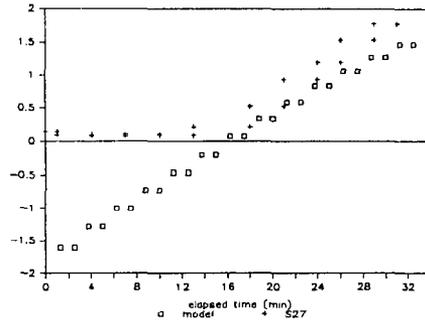


Figure 3. Absorption S27 and Model.

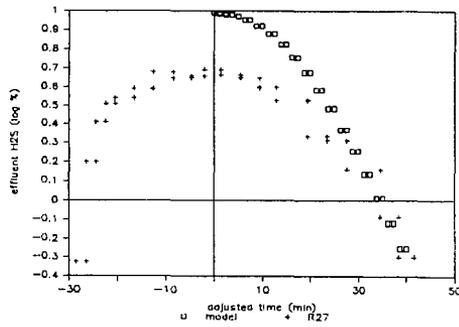


Figure 4. Regeneration R27 and Model.