

CHAPTER VII: SUMMARY AND SUGGESTIONS FOR FUTURE WORK

7.1 Summary

The present study revealed several points of value for summary:

- A systematic approach toward the evaluation of the behavior of single-metal sorbents for removing hydrogen sulfide (H_2S) from hot coal-derived fuel gases is developed based on thermodynamic considerations. This new method of comparative analysis singled out manganese oxide as a prime candidate sorbent capable of being utilized under a wide temperature range to reduce H_2S concentrations in the fuel gas to less than 150 ppmv (parts per million by volume).
- A novel pelletization process is developed for the manufacture of manganese-based spherical pellets which have the desired physical and chemical characteristics required during the long-term cyclic sulfidation and regeneration in a high-temperature desulfurization operation.
- Single sulfidation (loading) tests via thermogravimetric (TGA) analysis at temperatures ranging from 700 to 1000 °C showed that FORM4-A pellets ($MnCO_3$ + alundum + bentonite) exhibits the best combination of sulfur capacity and reaction kinetics; FORM1-A pellets (Mn ore + alundum + dextrin) exhibits the best combination of strength, sulfur capacity, and reaction kinetics. Both formulations, however, are deemed to be successful in reducing the H_2S concentration in the coal-derived fuel gas to less than 150 ppmv.
- Although the pellets may be loaded at temperatures below 800 °C, regeneration with air or oxygen-deficient air must be conducted above 900 °C to avoid sulfate formation; under these conditions the regeneration reaction is essentially complete in 10 to 15 minutes.
- Repeated cycling of the leading pellet formulation (FORM4-A), up to five consecutive cycles, revealed that the capacity of these pellets for sulfur pickup from fuel gases and the kinetics of reduction, sulfidation, and regeneration improve with recycling. This unique phenomenon is attributed to the formation of radial micro-cracks which reduced the diffusion distance required for transport of sulfur into the pellet and oxygen out of the pellet. These cracks did not have a significant effect upon pellet strength which continued to be no less than 5 lbs/mm of diameter.
- Fixed-bed tests using FORM4-A pellets and a simulated Tampella-U gas (with 3% H_2S) for sulfidation and air for regeneration (both at 900 °C) indicated improvement in capacity and kinetics with the sulfur loading capacity ranging from 21.1% to 23.1% by weight of the original bed, which corresponds to > 90%

of bed utilization. These results are consistent with the above results obtained from TGA sulfidation and regeneration tests on individual pellets.

- Rate equations (time-fractional conversion) were derived for diffusion through gas film control, diffusion through product layer control, and surface reaction control. The shrinking-unreacted core model was found to approximate very closely the kinetic behavior of manganese-based pellets during both the sulfidation and the regeneration reactions. Analysis of TGA experimental data determined that beyond about 35% reaction, when the product layer becomes sufficiently thick, the sulfidation reaction rate is controlled primarily by countercurrent diffusion of sulfur and oxygen through the porous layer of manganese sulfide (MnS) formed.

- A re-assessment of the equilibrium states of reactions involving solid MnO, MnS, Mn₃O₄, and MnSO₄ is presented based on the results obtained and a recent study by Turkdogan.

7.2 Suggestions for Future Work

Leach solutions from bench-scale in-situ mining tests of core samples from manganese deposits in the Emily District of Minnesota are currently being produced by the Twin Cities Research Center of the U. S. Bureau of Mines. These solutions are made by leaching the manganese contained in the cores with acidic solution saturated with sulfur dioxide. A typical composition of such solution is as reported in Table 7.1

Table 7.1 Typical Composition of In-Situ Mined Manganese Leach Solution from Mn deposits in the Emily District of Minnesota

Mn (g/l)	Fe (g/l)	K (ppm)	Al (ppm)	Ca (ppm)
28.075	2.3775	675	357.5	267.5
Si (ppm)	Na (ppm)	Mg (ppm)	Ba (ppm)	
85.0	80.00	67.5	4.00	

To ensure the economic viability of this innovative and environmentally sound mining method, the resulting solution must be treated with focus on the development of a useful and more valuable product from the in situ-leached manganese product than would be possible if it were simply utilized as a manganese steel additive. The possibility of manganese being employed as a sulfur sorbent in coal-gasification cleanup processes is the potential market which should be explored. The present study on the manganese-sulfur-oxygen (Mn-S-O) system indicated that a Mn-based sorbent pellet has considerable potential application in the area of desulfurization of coal-derived fuel gases at high temperature. In addition, the comparative experimental investigations concluded that a MnCO₃-based sorbent pellet offers the best combination of reaction kinetics and sulfur loading capacity. For these reasons, the treatment of

the leach solution mentioned above should aim at the production of manganese in the form of carbonate.

The author was initially involved in a study to effect a separation of manganese from the other constituents in solution, primarily iron. The removal of iron is particularly required since it forms low melting point systems which may cause the pellets to lose their reactivity. Studies on the recovery of manganese from these solutions have been conducted and involved oxidation and selective precipitation of iron followed by precipitation of manganese in the form of manganese carbonate.

Considerable success in obtaining a pure manganese product in accordance with the above procedure (see Figure 7.1) has been reported by the Salt Lake Research Center (SLRC) of the U. S. Bureau of Mines. The manganese carbonate resulting from this procedure will very likely be an excellent feed material for sulfur sorbent pellets since they will, upon calcination and loss of carbon dioxide, have potential for a high degree of porosity and resulting high surface area. As mentioned above, a somewhat similar manganese carbonate material which is commercially available was found to be a critical component in the manufacturing of regenerable manganese-based sorbent pellets for the desulfurization of coal-derived fuel gases at high temperature. The desulfurization process constitutes a crucial sub-system in the Integral Gasification Combined Cycle (IGCC), an emerging innovative method of power generation.

A typical assay of product filter cake resulting from studies conducted by the SLRC is shown in Table 7.2.

Table 7.2 Assays (in Percent unless Otherwise Noted) of Manganese Carbonate Filter Cake Product.

Species	Conc.	Species	Conc.	Species	Conc.
Mn	40	V	<0.01	Na	0.2
CO ₂	47	Sr	0.016	K	0.2
As	0.0002	Co	0.0004	Ca	0.16
Sb	<0.002	Ni	<0.001	Mo	<0.01
Cr	<0.0006	Pb	<0.0034	Hg	<0.13ppm

If cyclic testing during loading (sulfur pickup from fuel gases) and regeneration (oxidation to produce a gas of high sulfur dioxide content) demonstrate that pellets made from in-situ mined Minnesota manganese yields a superior sorbent, then the potential exists to produce a high value-added product having a sale price ranging 2 to 3 dollars per pound compared with prices of cents per pound for manganese in competition with manganese ore as additives to steel.

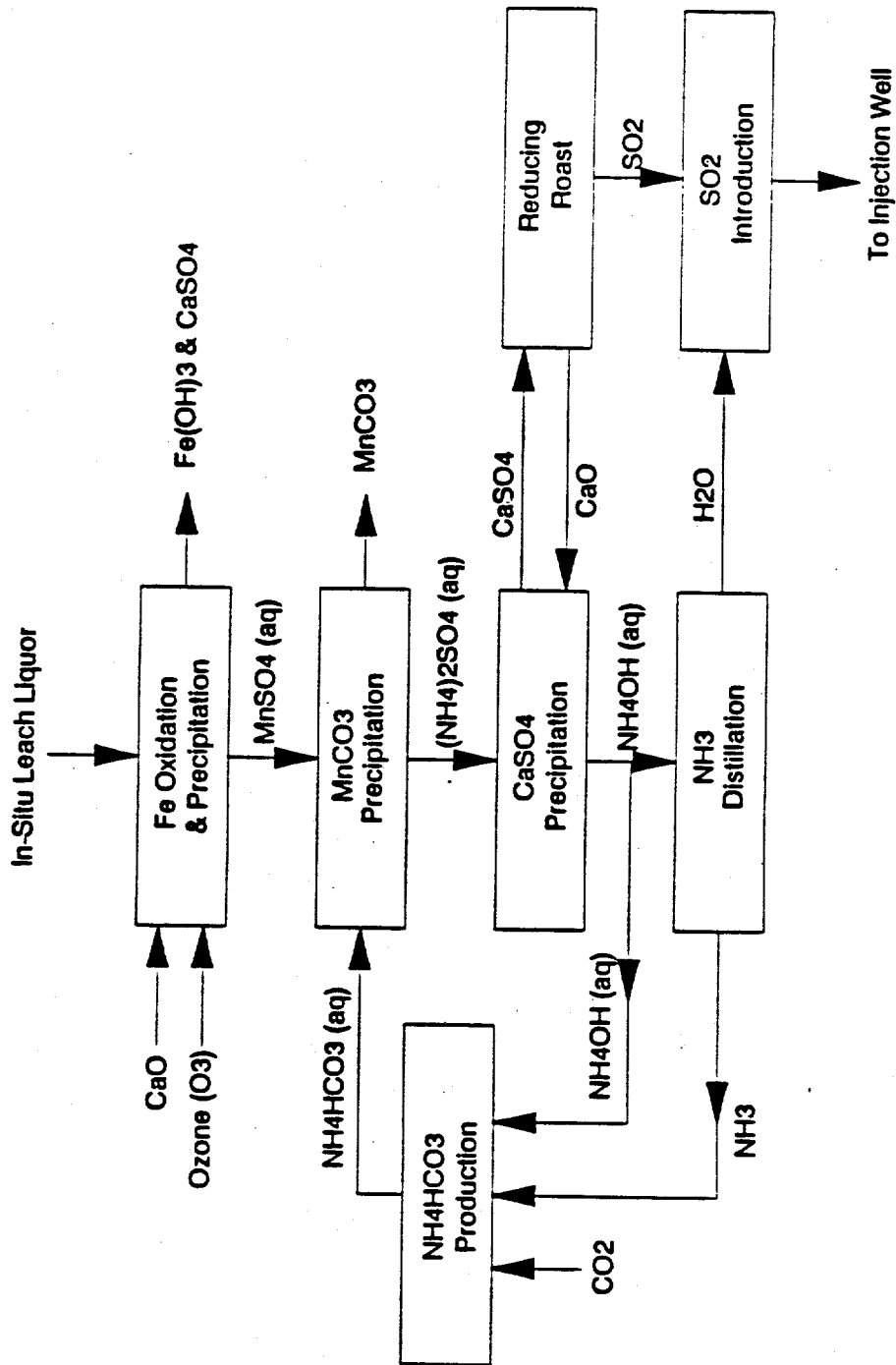


Figure 7.1 Schematic diagram of the Salt Lake City Research Center MnCO₃ recovery process.