

## SYNGAS DESULFURIZATION OVER METAL ZEOLITES

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Metal oxides supported on zeolites have been demonstrated as effective regenerable desulfurization agents for high temperature removal of hydrogen sulfide from fossil fuels. Desulfurization occurs by sulfide formation with Fe or Zn on the surface of the zeolite lattice with the hydrogen sulfide of the fuel gas. Regeneration by air oxidation of the supported metal sulfide displaces the sulfur as sulfur oxides. Both sulfidation and oxidation show efficient kinetics within a temperature range of 500-600C, which is above the range of physical adsorption and below where metal vaporization or support instability prove limitations. Zinc faujasite Y is of particular interest because of demonstrated ability to reduce the sulfur concentration to several PPM in the temperature range 500 to 650 C.

### INTRODUCTION

The potential for increased efficiency of gas cleanup and improved economics provides the incentive for development of high temperature desulfurization of fossil fuels (coal gas or syngas). Numerous processes are available for low temperature desulfurization. However, advantages in processing, notably energy conservation and capital savings, make high temperature desulfurization attractive.

Attention is given here to the use of metal zeolites as regenerable desulfurization agents. Consideration is given to the merits of high temperature desulfurization, the rationale of agent selection and bench scale evaluations have been conducted of the desulfurization-regeneration performance of iron and zinc zeolites.

### THE MERITS OF HOT DESULFURIZATION

Two assessments that show the energy and capital cost advantages of high temperature desulfurization of several available coal gasification alternatives are summarized here:

One comparison (1) has been made for low and high temperature gas cleanup of a 1000 MW coal gasification combined cycle power plant for two possible gas turbine inlet temperatures (1070 C and 1320 C) for 4 gasification options: 1) air blown Lurgi (fixed bed), 2) oxygen blown Lurgi (fixed bed), 3) oxygen blown bituminous gasifier cleaner (slagging fixed bed) and 4) an air blown Foster Wheeler (entrained bed). The high temperature hot gas cleanup (HGC) used was the Morgantown Energy Technology Center (METC) iron oxide fixed bed desulfurization process. The low temperature gas cleanup (LGC) used was the Benefield process. The HGC alternative provided advantages in thermal efficiency, capital cost, electricity cost and purification system component costs. Savings of 34% in capital requirements and 30% in cost of electricity were obtained with HGC.

In a second assessment (2) 4 gasifier configurations were evaluated, 3 employing entrained flow, by Texaco, Shell-Koppers and by Foster Wheeler/Bituminous Coal Research (FW/BCR) and Institute of Gas Technology (IGT) fluid bed using 24 variations of air and gas blown gasification with 3 temperatures for desulfurization. Low temperature (150C) desulfurization was with a Selexol liquid scrubber. Intermediate temperature (540C) desulfurization was with the METC iron oxide fixed bed. High temperature (820C) desulfurization used a Conoco half-calcined dolomite in a fluidized bed. All processes met EPA emission standards. The medium and high temperature processes provided advantages in thermal efficiency, plant capital and overall electricity cost. The greatest advantage provided was reduced capital cost.

#### SELECTION OF DESULFURIZATION AGENTS -PRIOR WORK

The elements considered for desulfurization agents have been selected largely on an empirical basis from essentially every group of the periodic table. Westmoreland and Harrison (3) made a systematic examination of candidates for the hot desulfurization of low BTU coal gases. In their approach they made use of the free energy minimization method of Van Zeggeren and Story and selected 11 of 28 elements as potential candidates for fuel gas desulfurization within a temperature range of 400-1200C. These candidates were Fe, Zn, Mo, Mn, V, Ca, Sr, Ba, Co, Cu and W. Based on thermodynamic considerations they selected MnO, CuO,  $V_2O_3$  and ZnO for kinetic studies. A second systematic selection of sulfur removal agents based on thermodynamics has been made for fuel cell applications (4). Attainable equilibrium  $H_2S$  concentrations for coal gas at 650C was the selection criterion. Of 42 agents examined, 12 candidates Fe, Co, Cd, Mo, Pb, W, Zn, V, Mn, Ba, Sr and Cu were evaluated with Cu/CuO, ZnO, and  $V_2O_3$  examined experimentally.

A comprehensive review of hot gas (>430C) cleanup processes applicable to sulfur removal, as  $H_2S$  from coal gases was prepared by Onursal (5) in 1979. Comment on desulfurization work with an updating since 1979 is appropriate. First comments will be made of results obtained with the single component systems Fe, Cu and Zn:

Early work with iron oxides on the Appleby-Frodingham process (6,7) demonstrated excessive sorbent degradation and was abandoned. The MERC iron oxide/silica (fly ash) sorbent (8,9) achieved 200-800 ppm  $H_2S$  in coal gases in the temperature range 400-750C with regeneration at 950C in air or steam.

Zinc oxide has been widely used for removal of low concentrations of  $H_2S$  at low to mid temperatures but only as a nonregenerable system. Supported ZnO has been evaluated at Giner Inc. (10,11) and by Institute Francais Du Petrole (IFP) (12) and  $H_2S$  levels down to 1 ppm were obtained at bench scale. Evaluations of the IFP ZnO at METC (12) confirmed the low  $H_2S$  concentrations but indicated low sulfur loadings relative to unsupported ZnO.

Several studies have involved copper sorbents (13,14,15,16,17). Copper supported on silica (16) has been used to desulfurize  $H_2S/H_2$  mixtures over the temperature range 300-1000C with ultimate application intended for coke oven, producer, and water gases and hydrocarbon vapors. Studies have been conducted by Kennecott Copper Co. (13,17) for Lurgi fuel gases containing  $H_2$ , CO and 1-1.5%  $H_2S$  in the temperature range 480-510C. Sulfur removal efficiencies of 80% (to 1500 ppm  $H_2S$ ) were obtained. Sorbents were regenerated at 816C using solid-solid reaction with CuO but with limited success.

Most desulfurization studies have been conducted with mixed metal oxides. About the earliest significant study was made at Johns Hopkins University (14) for mixed oxides of Cu, Fe, U, Cr, Sn, Mn, V, Mo, Sb, Bi as binary and ternary combinations with various binders such as clay, pumice, alundum and lime. Regeneration of the sulfided sorbents was by air oxidation, but sustained performance was not obtained. Nachod (15) used mixed oxides of Cu, Zn and Pb supported on aluminosilicates to remove sulfur from petroleum distillates and gases with  $H_2S$  and organic sulfur compounds in the temperature range 90-550C. Regeneration was with air/steam at 370-540C, but the supports were lacking in stability.

Investigations at METC extending earlier work with Fe oxides (6-9) have shown that sulfur levels of 2-10 ppm in the temperature range 550-750C can be achieved for a zinc ferrite sorbent with simulated Lurgi fixed-bed gasifier off-gas. To date this zinc ferrite of METC has been advanced to the highest stage of development, pilot plant, of any sorbent.

However, investigations by Battelle, IGT, MIT, Giner, Research Triangle and Electrochem, largely under DOE funding, continue to evaluate promising alternatives for high temperature regenerable desulfurization of coal gases. Work at Battelle (18) has been conducted with molten carbonates supported on Ca-Li aluminate. Dual adsorbent beds with mixed oxides of ZnO,  $Fe_2O_3$ , CuO in

one bed and CoTiO<sub>3</sub> in a second bed have been evaluated at ICT (19). Work with oxides of Cu and Zn has been done at Giner (20) and work with oxides of Cu and Mn pursued at Electrochem (21). A number of mixed oxides of ZnO, CuO, TiO<sub>2</sub>, and MoO<sub>3</sub>, notably co-precipitated with alumina have been investigated at MIT (22). Additional studies with mixed oxides of ZnO/CuO/Fe<sub>2</sub>O<sub>3</sub>; ZnO/TiO<sub>2</sub>; CuO/Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and CuO/Al<sub>2</sub>O<sub>3</sub> have been conducted by the Research Triangle (23).

#### SELECTION OF ADSORBENT COMPONENTS

Iron and zinc were selected as the desulfurization agents for evaluation based on consideration of the results of prior work and the prospects for favorable sulfidation kinetics, low equilibrium sulfur concentration at high temperature and good oxidation regeneration kinetics. Most prior desulfurization work has been conducted and continues with co-precipitated metal oxides. In this study a zeolite support was chosen to provide a hydrothermally stable substrate favorable for maintenance of a highly dispersed desulfurization agent for many sulfidation/oxidation duty cycles. A synthetic mordenite (Zeolon 900) was initially evaluated but the availability of rare-earth stabilized faujasite Y zeolite (Linde SK 500) led to making it the support of choice.

#### EXPERIMENTAL PROCEDURES

The metals of interest Fe and Zn were ion exchanged with the zeolite pellets by equilibration at 25-60C with 3 Molar aq. solutions of nitrate salts of the metals. Ion exchanged zeolites were separated from the exchange solutions, dried at 150C and air calcined at 500C. The properties of the sorbents are given in Table 1.

The desulfurization performance tests were conducted in a stainless steel fixed bed reactor with 2-12 gr. of adsorbent (20-40 mesh). Corrosion resistant alloys must be used if the reactor is to have bare metal walls to avoid wall effects. The safest practice is to use a quartz liner in the reaction zone. Gas compositions consisted of dry and wet (10-20 Mol % H<sub>2</sub>O) H<sub>2</sub> with 200-8000 ppm H<sub>2</sub>S. Reaction conditions consisted of 1-2 atmos. gas pressure, a 450-650C temperature range and a space velocity range of 500-10000 hr<sup>-1</sup>. Tests were conducted to breakthrough concentrations of 20 ppm H<sub>2</sub>S. Sulfur concentration in the exit gas was determined with Kitagawa tubes and at intervals of 30-60 min. by absorption in CdSO<sub>4</sub> aq. solution and thiosulfate titration.

The sulfided adsorbents were regenerated with air or simulated fuel cell exhaust gas (11 Mol % O<sub>2</sub>) at 450-650C with periodic measurement of SO<sub>2</sub> in the exit gas by Kitagawa tube and absorption in aq. NaOH.

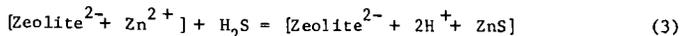
Post test adsorbents were characterized by sulfur analysis and for selected systems metal analysis, X-Ray diffraction analysis and BET surface area determinations.

#### REACTION MECHANISMS

The sulfidation reactions postulated for the supported metals as separate interstitial entities with H<sub>2</sub>S at temperature in the range 450-650C in a reducing atmosphere are assumed to be:



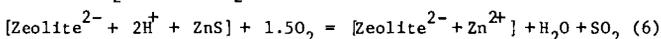
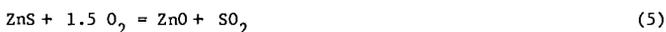
The mechanism proposed for the exchanged cations is that they are present predominantly as integral components of the zeolite lattice surface so that the sulfidation reaction can be visualized:



Limited thermal stability precludes sulfide stoichiometries with sulfur to metal ratios higher than indicated in reactions (1)-(3).

Reactions (1)-(2) would lead to significant inhibition of sulfidation by an appreciable water partial pressure. Since coal gases will contain 10-20 Mole % H<sub>2</sub>O depending upon whether the gas is air or O<sub>2</sub> blown this is an important consideration. While the water partial pressure of 10 Mole % might raise the H<sub>2</sub>S equilibrium concentration from 1-2 to 10 ppm at 650C there would be an advantage in minimizing the volatility of Zn.

The oxidation regeneration reactions for the sulfided metals are considered to be:



The expectation is that at the elevated temperature of oxidation most of the sulfur will be evolved as SO<sub>2</sub>/SO<sub>3</sub> with minimal sulfate formation if extended exposure to excess oxygen is avoided. The decomposition temperatures of the sulfates, if formed, are relatively high being 500-630C for FeSO<sub>4</sub> and 600-840C for ZnSO<sub>4</sub> (24).

#### DESULFURIZATION PERFORMANCE

In Table 2 a comparison is made for 4 adsorbents, Fe and Zn mordenite, a Zn impregnated alumina and a rare earth loaded Zn faujasite Y. After 5 sulfidation/regeneration duty cycles at 540C the Zn faujasite Y demonstrated a decided advantage in sulfur loading at breakthrough at 20 ppm with a H<sub>2</sub>S concentration less than 10 ppm prior to breakthrough combined with maintenance of a high BET area of 360 M<sup>2</sup>/Gr. Typical results with wet (15 Mole %) H<sub>2</sub> with 1000 ppm H<sub>2</sub>S at 500C over Zn faujasite Y (Fig. 1) show sustained performance for 4 duty cycles with less than 10 ppm H<sub>2</sub>S.

If the objective is to obtain a low sulfur concentration prior to breakthrough Zn zeolite is decidedly superior to Fe zeolite (Fig. 2). For this test with a sulfur concentration of 7900 ppm, typical of coal gas, for wet (10 Mole %) H<sub>2</sub> residual sulfur concentrations before breakthrough appreciably less than equilibrium H<sub>2</sub>S values are obtained for either Fe or Zn.

The role of the rare earths present on the SK 500 faujasite Y used as support for the Fe and Zn in the desulfurization process has not been determined but published results (25,26) indicate La has potential as a sulfidation adsorbent but would require a temperature above 650C for oxidation regeneration. The present study indicates the rare earths play a minor role in sulfidation but a major role in contributing to thermal stability. Zinc has been proposed (27) for improving the thermal stability of zeolites.

#### OXIDATION REGENERATION

Oxidation-regeneration at 650C of sulfided Fe and Zn faujasite Y adsorbents with simulated fuel cell exhaust gas (11 Mole % O<sub>2</sub>) is essentially complete within 60 minutes (Fig. 3). The extent of residual sulfur retention after regeneration is shown in Table 2.

To complete thermal decomposition of residual ZnSO<sub>4</sub> a temperature approaching 800C is necessary for a gas with less than about 15 Mole % O<sub>2</sub>. By using a N<sub>2</sub> purge between completion of the oxidation-regeneration cycle and the next fuel gas desulfurization cycle combined with utilization of the exothermic heat from the oxidation reaction permits completion of regeneration of the adsorbent at a temperature between 800C and 650C the temperature desired in the bed for the next desulfurization cycle.

The thermal stability of the Zn faujasite Y is promising in view of the high BET surface area observed for the regenerated adsorbent (Table 2). An

important consideration is that the Zn zeolite should not experience temperatures much above 650C in a reducing atmosphere to minimize losses by volatilization. In the interval between oxidation-regeneration and the next desulfurization cycle the adsorbent exposure to temperatures above 650C is in an oxidized state minimizing volatilization.

#### CONCLUSIONS

Bench scale evaluations have demonstrated the performance of metal zeolites for high temperature regenerable desulfurization of fossil fuels containing H<sub>2</sub>S. Metal zeolites, notably with zinc, provide regenerable sulfur removal capability and achieve low residual sulfur concentrations and a good potential for repetitive sulfidation/oxidation duty cycles. Zinc faujasite Y, in particular, provides a superior desulfurization agent with the active metal in a high state of dispersion on a hydrothermally stable support. Alternation of sulfidation and oxidation typical of desulfurization-regeneration duty cycles favors maintenance of the initial high state of dispersion for the active desulfurization agent, Fe or Zn, notably if the metal is retained in close proximity to the surface of the zeolite lattice.

Potential applications for these metal zeolite desulfurization agents consists of:

1) Providing sulfur removal for low to intermediate BTU coal gases for combined cycle power plants to minimize sulfur emissions and the protection of gas turbine or fuel cell power plants.

2) Protecting sulfur sensitive catalysts used for processing fossil fuels, notable coal syngas.

#### REFERENCES

1. Jones, C.H. and Donohue, J.M., Stone and Webster Eng. Corp., New York EPRI-AF-416, 151 (1977).
2. Robson, F.L. and Blecher, W.A., United Technologies Corp., Hartford, DOE/METC 12050-149 (1981).
3. Westmoreland, P.R. and Harrison, D.P., Environ. Sci. & Tech. 10, 659 (1976).
4. Jalan, V., Conf. Proceed. 1981 Int. Gas Res., Los Angeles, CA., 291 (1981).
5. Onursal, A.B., Hot Gas Cleanup Process, EPS-600-7-79-169, (1979).
6. Reeve, L., J. Inst. of Fuel, Vol. 319 (1958).
7. Bureau, A.C. and Olden, J.J.F., The Chemical Engineer, (1967).
8. Shultz, F.G. and Berber, J.S., J. Air Pollution Control Assoc., 20,93 (1970).
9. Oldaker E.C., etal, Removal of Hydrogen Sulfide from Hot Low BTU Gas with Iron Oxide-Fly Ash Sorbents, MERC/TPR-75-1, (1975).
10. Jalan, V., Brooks, C.S., Georgakis, C. and Desai, M., Metal Oxide Adsorbents for Hydrogen Sulfide Control, Second Annual Contractors Meeting on Contaminant Control in Hot Coal Gas, Proceedings, 350, NTIS, DOE/METC-82-47, (1982).
11. Jalan, V., Studies Involving High Temperature Desulfurization/Regeneration Reactions of Metal Oxides for Fuel Cell Development, Giner Inc. NTIS, DOE/METC/16021-1486 (1983).
12. Steinfield G. and Grindley, T., Development and Testing of Regenerable

- Hot Coal Gas Desulfurization Sorbents, 332, ref. 10.
13. Agarwal, J.C., Metal Oxide Hot Gas Desulfurization Process, AIChE Conf. Philadelphia, PA, (1980).
  14. Huff, W.J. and Logan, L., AGA Proceed., 18, 359 (1965).
  15. Nachod, F.C., U.S. Patent 2,442,982, (1948).
  16. Lewis, W.K., U.S. Patent 3,079,223, (1963).
  17. Meyer, J.P. and Edwards, M.S., ORNL Rept. TM-6072, (1978).
  18. Lyke, S.E. and Sealock, L.J. (Battelle Pacific NW Labs) Proceed. 3rd Annual Contaminant Control in Hot Coal Derived Gas Streams, Merkel, K.E., Ed., DOE/METC 84-6, NTIS DE84000216,173 (1983).
  19. Anderson, G.L., (IGT), Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Vol. 2, Chate, M.R., Markel, K.E., Jarr, L.A. and Bossart, S.J., Eds. Morgantown, W.VA, DOE/METC87/6079-DE87006496, 642 (1987).
  20. Jalan, V., Studies Involving High Temperature Desulfurization/Regeneration Reactions of Metal Oxides for Fuel Cells, (Giner Inc.) DOE Rpts. 31-109-39-5804, ANL-K-83-12 and NTIS DE3008714 and DE83008715 (1981).
  21. Jalan, V., 9th Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, METC, Morgantown, W.VA B4, (1989).
  22. Flytzani-Stephanopoulos, M., See ref. 19, 726 (1987).
  23. Harkins, S.M. and Gangwal, S.K., (Research Triangle), see ref. 19, 749 (1987).
  24. Mu, J. and Perlmutter, D.D., Ind. Eng. Chem. Process Des. & Dev., 20, 640 (1981).
  25. Wheelock, K.S. and Aldridge, C.L., U.S. Patent 3,974,256, (1976).
  26. Wheelock, K.S. and Say, R.S., U.S. Patent 4,002,720, (1977).
  27. Wilson, R.C., U.S. Patent 3,804,780, (1974).

Table 1. Sulfur Removal Capacity for Zinc Zeolites

Zeolite	Cation Exchange Capacity CEC MEQ/Gr.	Metal Loading Equiv. to CEC Wt. %	Theoretical Sulfur Loading as ZnS Wt. %	High Temp. Stability Deg. C.
Syn. Mordenite	2.5	8.2	4.0	650
Faujasite Y	4.0	13.2	6.4	650-980

Table 2. A Comparison of Desulfurization Adsorbents

Adsorbent	Metal	Wt. %	Sulfur Loading Wt. %	Percentage of Theoretical Sulfur Loading	Residual Sulfur Wt. %	BET Area Sq. M./Gr.
Faujasite Y (Linde SK 500)	Zn	13.2	4.8	75	1.41	360
ZnO on Alumina (Harshaw AL-0104T)	Zn	11.7	2.4	-	0.71	119
Syn. Mordenite (Norton Zeolon 900)	Zn	10.9	2.4	60	0.51	129
Syn. Mordenite (Norton Zeolon 900)	Fe	14.0	3.7	-	0.33	-

Notes:

- 1) Five tests were conducted with 10.3 cu. cm. of adsorbent bed with 1000 ppm  $H_2S$  in  $H_2$  at 540C and at 2 Atmos. in the space velocity (GHSV) range 4000-9000  $hr^{-1}$  to a breakthrough of 20 ppm  $H_2S$ .
- 2) Oxidation regenerations were conducted with simulated fuel cell cathode exhaust gas with 11%  $O_2$ , 7%  $CO_2$  and 72%  $N_2$ .
- 3) Water partial pressure was 15 Mole % for desulfurization and regeneration.
- 4) ZnO was mounted on alumina by solution impregnation.

Fig.1 SULFUR REMOVAL FROM WET (15 MOLE PERCENT  $H_2O$ ) HYDROGEN WITH 1000 PPMV  $H_2S$  OVER SUPPORTED ZINC FAUJASITE Y AT 500° C

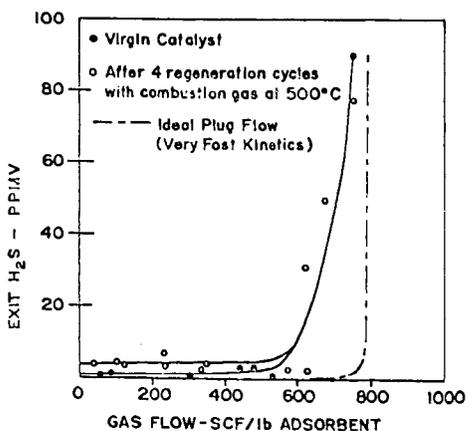


Fig.2 SULFUR REMOVAL FROM WET  
 (10 MOLE PERCENT H<sub>2</sub>O) HYDROGEN  
 WITH H<sub>2</sub>S (7900 PPMV) AT 650°C  
 1500 HR<sup>-1</sup> SPACE VELOCITY

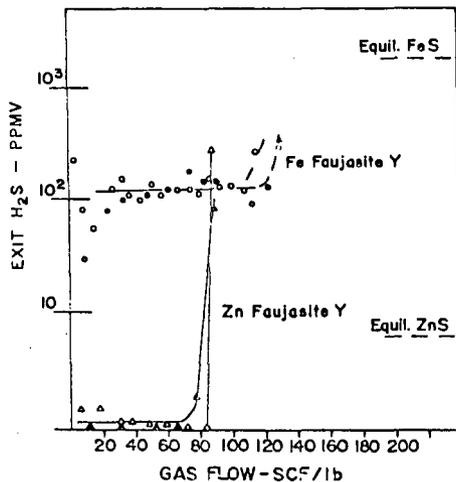


Fig.3 AIR REGENERATION AT 650°C OF  
 SULFIDED IRON AND ZINC FAUJASITE Y

