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DESULFURIZATION OVER METAL ZEOLITES

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ABSTRACT

Metal oxides supported on zeolites have been demonstrated to be effective regenerable desulfurization agents for high temperature removal of hydrogen sulfide from fossil fuels. Metals of interest are iron and zinc. Zeolites of particular interest are commercially available zeolites with high hydrothermal stability such as synthetic mordenite and rare earth stabilized faujasite Y. The metals used as desulfurization agents are introduced by cation exchange. Zinc faujasite Y is of particular interest because of the demonstrated ability to reduce the hydrogen sulfide to several PPM concentration range in the desulfurized fuel in the temperature range of 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 fuel (coal gas or syn gas). 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 advan-

tages 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 (2). The low temperature gas cleanup (LGC) used was the Benefield process (3). 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 (4) 4 gasifier configurations were evaluated, 3 employing entrained flow, by Texaco, Shell-Koppers and by Foster Wheeler/Bituminous Coal Research (FW/BCR) and an Institute of Gas Technology (IGT) fluid bed using 24 variations of air and gas blown gasification with 3 temperatures for desulfurization. Low temperature (150° C) desulfurization was with a Selexol liquid scrubber. Intermediate temperature (540° C) desulfurization was with the METC iron oxide fixed bed. High temperature (820° C) desulfurization used a Conoco half-calcined dolomite in a fluidized bed. All processes met EPA emission standards. The medium and high temperature processes provided an improvement of 6.5% in plant capital cost and 6.1% in electricity cost. The greatest advantage provided was reduced capital cost.

SELECTION OF DESULFURIZATION AGENTS-PRIOR WORK

The elements that have been considered for desulfurization agents have been selected largely on an empirical basis from essentially every group of the periodic table. Westmoreland and Harrison (5) made a systematic examination of candidates for the hot desulfurization of low BTU fuel gases. In their approach, they made use of the free energy minimization method of Van Zeggeren and Story (6) and selected of 11 out of 28 elements considered. The potential candidates for fuel gas desulfurization within the temperature range of 400-1200° C 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 and found MnO to have the most favorable kinetics (7). The initial selection criteria of the particular sulfur removal agents evaluated in more recent studies (8-10) were based on thermodynamic and physical property considerations. Attainable equilibrium H_2S concentrations for typical coal gas compositions at approximately 650° C, typical of hot iron oxide sorbent bed effluents, were considered as was regenerability of the sulfided adsorbents. Of the 42 metals and oxides initially examined, 12 candidates (Fe, Co, Pb, Mo, Cd, W, Zn, V, Mn, Sr, Ba, and Cu) were evaluated in detail, and four candidates (ZnO, Cu, WO_2, and V_2O_3) merited experimental evaluation of their desulfurization and regeneration performance.

A comprehensive review of hot gas (430° C) cleanup processes applicable to sulfur removal, as H_2S from coal gases was prepared by Onursal (11) in 1979. Comment on desulfurization work with an updating since 1979 is appropriate. Initial comments will be made on results obtained with the single component systems Fe, Cu and Zn:

Early work with iron oxides on the Appleby-Frodingham process (12,13) demonstrated excessive sorbent degradation and was abandoned. The MERC iron oxide/silica (fly ash) sorbent (2,14) achieved 200-800 ppm H_2S in coal gases in the temperature range 400-750° C with regeneration at 950° C in air or steam.

Zinc oxide has been widely used commercially for removal of low concentrations of H_2S at low to moderate temperatures but only as a nonregenerable system. Supported ZnO has been evaluated at Giner Inc. (15,16) and by Institute Francais du Petrole (11 page 70) and H_2S levels down to 1 ppm were obtained at bench scale. Evaluations of the IFP ZnO at METC (17) confirmed the low H_2S concentrations but indicated low sulfur loadings relative to unsupported ZnO. More recent work (18) at METC with supported ZnO on zeolites prepared by solution impregnation has been initiated to prepare high temperature sulfur removal sorbents.

Several studies have involved copper sorbents (19-23). Copper supported on silica (22) has been used to desulfurize H_2S/H_2 mixtures over the temperature range 300-1000° C with ultimate application intended for coke oven, producer, and water gases and hydrocarbon vapors. Studies have been conducted by Kennecott Copper Co. (19,23)for Lurgi fuel gases containing H_2, CO and 1-1.5% H_2S in the temperature range 480-510° C . Sulfur removal efficiencies of 80% (to 1500 ppm H_2S) were obtained. Sorbents were regenerated at 816° C 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 (20)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 (21) 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 90-550° C . Regeneration was with air/steam at 370-540° C , but the supports were lacking in stability.

Investigations at METC extending earlier work with Fe oxides

(2, 12-14) indicated that sulfur levels of 2-10 ppm in the temperature range 550-750° C can be achieved for a zinc ferrite sorbent (17) with simulated Lurgi fixed-bed gasifier off-gas. To date this zinc ferrite sorbent of METC has been advanced to the highest stage of development, pilot plant.

However, investigations by Battelle, IGT, MIT, Giner, Research Triangle and Electrochem, and at METC under DOE funding, continue to evalutate promising alternatives for high temperature regenerable desulfurization of coal gases in view of the upper limit of about 700° C for thermal stability and sulfur capture efficiency experienced with zinc ferrite (18). Work at Battelle (24) 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 $CoTiO_3$ in a second bed have been evaluated at IGT (25). Work with oxides of Cu and Zn has been conducted at Giner (26) and work with oxides of Cu and Mn pursued at Electrochem (27). A number of mixed oxides of ZnO, CuO, TiO_2 and MoO_3, notably co-precipitated with alumina have been investigated at MIT (28). Additional studies with mixed oxides of $ZnO/CuO/Fe_2O_3$; ZnO/TiO_2; $CuO/Fe_2O_3/Al_2O_3$ and CuO/Al_2O_3 have been conducted by the Research Triangle Institute (29). Mixed oxide systems have proven superior to single component metal oxides in maintenance of high temperature desulfurization capacity with repetitive sulfidation/oxidation duty cycles due to better thermal stability.

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 zeolite faujasite Y (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 25-60° C with 3 Molar aq. solutions of nitrate salts of the metals. Ion exchanged zeolites were separated from the exchange solutions, dried at 150° C and air calcined at 500° C . The properties of the sorbents are given in Table 1.

The desulfurization performance tests were conducted in a stainless steel bed reactor with 2-12 gr. of adsorbent (20-40 mesh). This bench scale reactor has the capability of handling liquid fuels and gas mixtures for evaluation of high temperature gas/solid reactions. Corrosion resistant alloys must be used to avoid wall effects, but a quartz liner is preferred to eliminate this source of error.

The reactor has been described elsewhere (30). Gas compositions consisted of dry and wet (10-20 Mol% H_2O) H_2 with 200-8000 ppm H_2S. Reaction conditions consisted of 1-2 atms. gas pressure, a 450-650° C temperature range and a space velocity range of 500-10000 hr^{-1}. Tests were conducted to breakthrough concentrations of 20 ppm H_2S. Sulfur concentration in the exit gas was determined with Kitagawa tubes and at intervals of 30-60 min. by absorption in $CdSO_4$ aq. solution and thiosulfate titration (31).

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

The sulfided adsorbents were regenerated with air or simulated fuel cell exhaust gas (11 Mol % O_2) at 450-650° C with periodic measurement of SO_2 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_2S at temperature in the range 450-650° C in a reducing atmosphere are assumed to be:

$$FeO + H_2S = FeS + H_2O \tag{1}$$

$$ZnO + H_2S = ZnS + H_2O \tag{2}$$

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

$$[Zeolite^{2-} + Zn^{2+}] + H_2S = [Zeolite^{2-} + 2H^{+} + ZnS] \tag{3}$$

Limited thermal stability precludes sulfide stoichiometries with sulfur to metal rations 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_2O depending upon whether the gas is air or O_2 blown this is an important consideration. While the water partial pressure of 10 Mole % might raise the H_2S equilibrium concentration from 1-2 to 10 ppm at 650° C there would be an advantage in minimizing the volatility of Zn.

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

$$\mathrm{FeS + 1.5\ O_2 = FeO + SO_2} \tag{4}$$

$$\mathrm{ZnS + 1.5\ O_2 = ZnO + SO_2} \tag{5}$$

$$\mathrm{[Zeolite^{2-} + 2H^{+} + ZnS] + 1.5\ O_2 = [Zeolite^{2-} + Zn^{2+}] + H_2O + SO_2} \tag{6}$$

The expectation is that at the elevated temperature of oxidation most of the sulfur will be evolved as SO_2/SO_3 with minimal sulfate formation if extended exposure to excess oxygen is avoided. The decomposition temperatures of the sulfates, if formed, are relatively high being 500-630 ° C for $FeSO_4$ and 600-840 ° C for $ZnSO_4$ (32).

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 540 ° C the Zn faujasite Y demonstrated a decided advantage in sulfur loading at breakthrough at 20 ppm with H_2S concentration less than 10 ppm prior to breakthrough combined with maintenance of a high BET area of 360 m^2/g. Typical results with wet (15 Mole %) H_2 with 1000 ppm H_2S at 500 ° C over Zn faujasite Y (Fig. 1) show sustained performance for 4 duty cycles with less than 10 ppm H_2S.

TABLE 2
A Comparison of Desulfurization Adsorbents

Adsorbent	Metal	Wt.%	Sulfur Loading Wt.%	Percent.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 540 ° C 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.

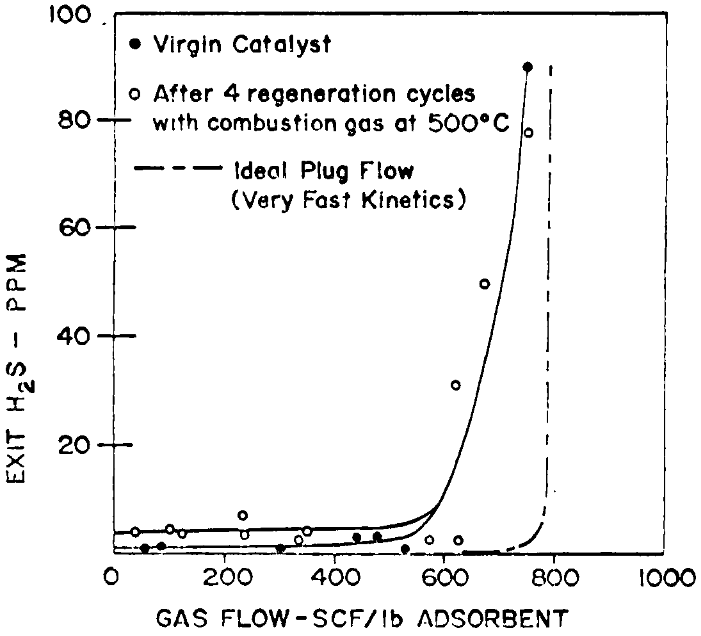

FIG. 1 SULFUR REMOVAL FROM WET (15 MOLE PERCENT H_2O) HYDROGEN WITH 1000 PPM H_2S OVER SUPPORTED ZINC FAUJASITE Y AT 500° C - AND 2000-3500 HR^{-1}

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_2 residual sulfur concentrations before breakthrough appreciably less than equilibrium H_2S 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 (33,34) indicate Lanthanum has potential as a sulfidation adsorbent. 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 (35) for improving the thermal stability of zeolites.

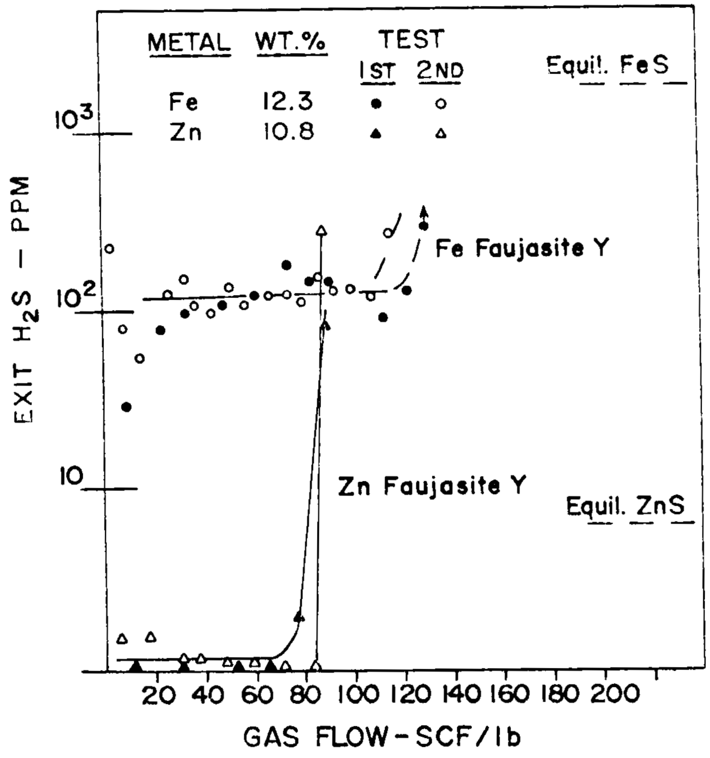

FIG. 2 SULFUR REMOVAL FROM WET (10 MOLE PERCENT H_2O) HYDGROGEN WITH H_2S (7900 PPM) AT 650° C 1500 HR^{-1} SPACE VELOCITY

OXIDATION REGENERATION

Oxidation regeneration at 650 ° C of sulfided Fe and Zn faujasite Y adsorbents with simulated fuel cell exhaust gas (11 Mole % O_2) is essentially complete within 60 minutes (Fig. 3). The extent of residual sulfur retention after regeneration is shown in Table 2.

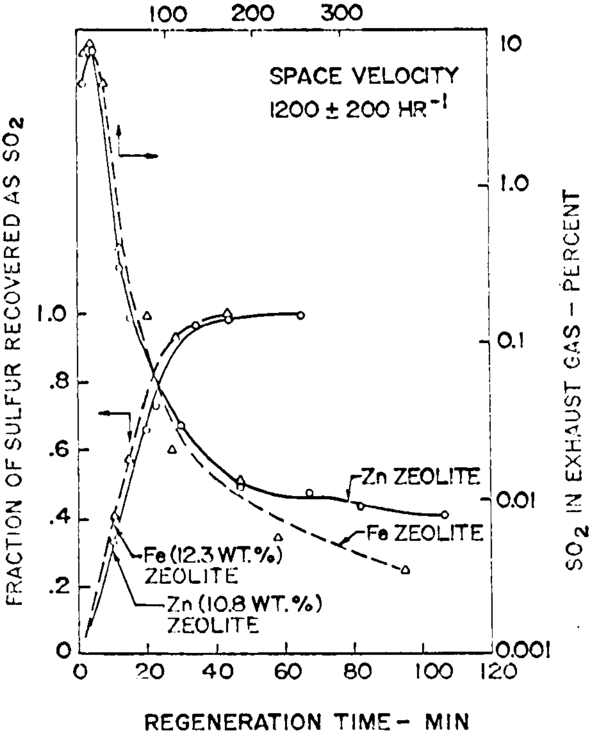

FIG. 3 AIR REGENERATION AT 650° C OF SULFIDED IRON AND ZINC FAUJASITE Y

To complete thermal decomposition of residual $ZnSO_4$ a temperature approaching 800 ° C is necessary for a gas with less than about 15 Mole % O_2. Use of a N_2 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 800 ° C and 650 ° C 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 650 ° C in a reducing atmosphere to minimize losses by volatilization. In the interval between oxidation-regeneration and the next desulfurization cycle the adsorbent exposed to temperatures above 650 ° C is in an oxidized state minimizing volatilization. The sulfur loading capacity of a zinc zeolite sorbent falls short of the values provided by the more successful coprecipitated metal oxides but by accepting shorter duty cycles the superior thermal stability and regenerability of this sorbent offers good prospects for an extended useful life.

CONCLUSIONS

Bench scale evaluations have demonstrated the performance of metal zeolites for high temperature regenerable desulfurization of fossil fuels containing H_2S. 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.

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, notably coal syn gas.

REFERENCES

1. Jones, C.H. and J.M. Donohue , Stone and Webster Eng. Corp., New York, EPRI-AF-416, 151 (1977).

2. Oldaker, E.C. et al, Removal of Hydrogen Sulfide from Hot Low BTU Gas with Iron Oxide-Fly Ash Sorbents, MERC/TPR-75-1 & 2, (1975).

3. Benson, H.E. and S.H. Field, Method of Separating Carbon Dioxide and Hydrogen Sulfide from Gas Mixtures, U.S. Patent 2,886,405 (1959).

4. Robson, F.L. and W.A. Blecher, United Technologies Corp., Hartford, DOE/METC 12050-149 (1981).

5. Westmoreland, P.R. and D.P. Harrison, Environ. Sci. & Tech., Vol.10 p.659 (1976)

6. Vanzeggeren, F. and S.H. Storey, The Computation of Chemical Equilibria, Cambridge Press, London, 1970.

7. Westmoreland, P.R., et al., Environ. Science and Tech., p.488, (1977).

8. Jalan, V. and D. Wu, "Molten Carbonate Fuel Cell Power Plant Desulfurization Systems", NTIS DOE/ET15370, DE 83006804 (1979).

9. Jalan, V., "High Temperature Desulfurization of Coal Gases by Regenerative Sorption", 1981 Int'l Gas Res.Conf.Proceedings, Los Angeles, CA, 291, (1981).

10. Jalan, V., "Studies Involving High Temperature Desulfurization/ Regeneration Reactions of Metal Oxides for the Fuel Cell Program", Giner, Inc., Final Report, Contract No. 31-109-39-5804, ANL-K-83-12, NTIS DE3008714 and DE83008715 (1981).

11. Onursal, A.B. Hot Gas Cleanup Process, EPA-600-7-79-169, (1979).

12. Reeve, L., J. Inst. of Fuel, Vol. 31 319, (1958).

13. Bureau, A.C. and J.J.F. Olden, The Chemical Engineer, Vol. 55, March, (1967).

14. Shultz, F.G. and J.S. Berber, J. Air Pollution Control Assoc., Vol. 20, 93, (1970).

15. Jalan, V., C.S. Brooks, C. Georgakis and M. Desai, Metal Oxide Absorbents for Hydrogen Sulfide Control, p. 360, Proceed. Second Annual Contractors Meeting on Contaminant Control in Hot Coal Gas, NTIS, DOE/METC-82-47, (1982).

16. Jalan, V., Studies Involving High Temperature Desulfurization/ Regeneration Reactions of Metal Oxides for Fuel Cell Development, Giner Inc., NTIS, DOE/METC/16021-1486, (1983).

17. Steinfield, G. and T. Grindley, Development and Testing of Regenerable Hot Coal Gas Desulfurization Sorbents, p.332, Proceed. Second Annual Contractors Meeting on Contaiminant Control in Hot Coal Gas, NTIS, DOE/METC-82-47, (1982).

18. Gasper-Galvin, L., J. Poston and A. Atimtay, p. 563, Proceed. Ninth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, R.A. Johnson and T.P. Dorchak Editors SOE/METC-89/6107 (DE89011707) (1989)

19. Agarwal, J.C., Metal Oxide Hot Gas Desulfurization Process, AIChE Conf. Philadelphia, PA, (1980).

20. Huff, W.J. and L. Logan, AGA Proceed., 18, 359, (1965).

21. Nachod, F.C., U.S. Patent 2,442,982, (1948).

22. Lewis, W.K., U.S. Patent 3,079,223, (1963).

23. Meyer, J.P. and M.S. Edwards, ORNL Rept. TM-6072, (1978).

24. Lyke, S.E. and L.J. Sealock (Battelle Pacific NW Labs) Proceed. 3rd. Annual Contaminant Control in Hot Coal Derived Gas Streams, K.E. Markel Ed., DOE/METC 84-6, NTIS DE84000216, 173, (1983).

25. Anderson, G.L., (IGT), p. 642, Proceed. 7th Annual Gasification & Gas Stream Cleanup Systems Contractors Review Meeting, Vol. 2, M.R. Ghate, K.E. Markel, L.A. Jarr, and S.J. Bossart Eds. Morgantown, W.VA, DOE/METC87/6079-DE87006496, (1987).

26. 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 DE83008715, (1981).

27. Jalan, V., M. Desai, F. Frown, P. 541, Proceed. 9th Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, METC, Morgantown, W.VA, DOE/METC-89/6107, Vol.2, DE89011707, (1989)

28. Flytzani-Stephanopoulos, M., (MIT), p. 726, Proceed.7th Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Vol., 2, M.R. Ghate, K.E. Markel, L.A. Jarr, and S.J. Bossart Eds., Morgantown, W.VA, DOE/METC87/6079-DE87006496, (1987).

29. Harkins, S.M. and S.K. Gangwal, (Research Triangle Inst.), p. 749, Proceed.7th Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Vol. 2, M.R. Ghate, K.E. Markel, L.A. Jarr, and S.J. Bossart Eds. Morgantown, W.VA, DOE/METC87/6079-DE87006496, (1987).

30. Brooks, C.S., Thiophene Hydrodesulfurization over Nickel Mordenite II Kinetics,Surface Technology, 9, 135, (1979).

31. ANSI/ASTM D2385-66, (Reapproved 1976).

32. Mu, J. and D.D. Perlmutter, Ind. Eng. Chem. Process Des. & Dev., 20, 640, (1981).

33. Wheelock, K.S. and C.L. Aldridge, U.S. Patent 3,974,256, (1976).

34. Wheelock, K.S. and R.S. Say, U.S. Patent 4,002,720, (1977).

35. Wilson, R.C., U.S. Patent 3,804,780, (1974).