

APPLICATION OF NICKEL SORBENTS TO REMOVE TRACE
CONTAMINANTS FROM HOT COAL GAS

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INTRODUCTION

Coal gas offers a low cost feed option for efficient generation of electricity using turbines or fuel cells as generators. However, coal derived gases contain contaminants such as sulfur and arsenic compounds, halides, etc., which are known to detrimentally affect the generator performance (1,2,3). These contaminants must be kept below a certain, permissible level for long-term, cost effective operation of a coal gas fueled power plant. Based on contaminant tolerance data for the related catalysts and the limited data available for fuel cell performance, it is desirable that the sulfur and arsenic compounds be reduced to sub-ppm levels. The commercially available low temperature cleanup processes are not cost effective as they require quenching/reheating operations. An energy efficient and economically viable high temperature coal gas purification process to minimize the heat exchange requirements is highly desirable. Several high temperature processes based on regenerative adsorption appear to be capable of removing H_2S from coal gas to a 2-10 ppmv level (4,5,6,7,8), but further reduction to a sub-ppm level is required. This paper describes a regenerable process to achieve this sub-ppm contaminant cleanup using nickel sorbents.

Supported nickel catalysts were investigated for their capability to remove sulfur compounds in coal gas to sub-ppm levels and to study the effect of other contaminants such as arsenic on sorbent performance. This concept is supported by the fact that these contaminants are known poisons towards nickel catalysts, even at low (<10 ppm) concentrations (9,10). The adsorption of sulfur on nickel occurs by reversible, dissociative chemisorption at concentrations of approximately 10 ppmv H_2S or less (11,12). The removal of chemisorbed sulfur has also been studied to recover the activity of nickel catalysts used in processes such as reforming, methanation, etc. (13,14,15). Sorption and regeneration experiments were performed with commercially available dispersed nickel sorbents to determine rate and capacity for sulfur removal from coal gas at high temperatures (500-700°C). A parametric analysis and process design study were performed to develop major guidelines for the trace contaminant removal reactor system.

EXPERIMENTAL METHODS

The coal gas contaminants, sulfur and arsenic, possess strong affinity for many materials of constructions. A test apparatus and analytical techniques capable of handling and monitoring trace amounts of these contaminants in the presence of major coal gas components with good reproducibility were developed.

APPARATUS. The experimental studies were carried out with a bench-scale, isothermal fixed-bed reactor at atmospheric pressure to

establish sulfur and arsenic sorption and regeneration characteristics of the nickel catalysts chosen. The reactor system was constructed of quartz and Teflon to minimize secondary adsorption effects. The model coal gas was simulated via mixing of the appropriate gaseous components, with steam introduced by humidifier evaporation. The gas delivery lines were heated to prevent steam condensation. All components, except H₂S were introduced from compressed gas cylinders (99.999% purity). Trace levels of H₂S (1-10 ppmv) were provided from a certified permeation tube and introduced after the humidifier to prevent dissolution of the H₂S.

ANALYTICAL. The major coal gas constituents were monitored with a microprocessor controlled gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). Trace contaminant measurements at the reactor exit and entry were accomplished with the GC using a photoionization detector (PID). Lower detection limits of 20 ppbv H₂S and 20 ppbv ASH₃ were achieved with this apparatus using appropriate combination of GC columns and operating conditions such as carrier flow rate, oven temperature, etc. Consistent and reproducible measurements were obtained in the presence of H₂O, H₂, CO, CO₂, etc. to establish long-term reliability of the analytical method. When required, gas detector tubes were used to determine certain trace by-products, such as CS₂ and SO₂.

The total adsorbed contaminants and their location on the sorbents were determined with SEM, X-ray fluorescence, and X-ray EDS, supplemented by wet chemical analysis when appropriate. Total arsenic content was determined by spectrophotometric determination with silver diethyl-dithiocarbamate. The physical structural changes in the sorbents were characterized by BET surface area, selective chemisorption, and porosimetry measurements.

SORPTION/REGENERATION CONDITIONS. The preliminary screening of commercial nickel catalysts was performed under a fixed set of most favorable conditions with a constant driving force (P_{H_2S}/P_{H_2}). This was accomplished by using 10 ppmv H₂S in a N₂/H₂ environment at 500°C, 2000 hr⁻¹ space velocity and no carbon species during initial sorption runs. Prior to a sorption run, each sorbent was subjected to a 4-hour reduction period in H₂ at 450°C. Data acquisition was performed with the automated GC/PID system until 1 ppmv H₂S was observed in the exit stream. Sulfur sorption capacity and breakthrough times for 20 and 100 ppb H₂S in the exit coal gas were used for performance comparison purposes. Pre- and post-test analyses were performed to characterize sorbent stability. Two of the most promising sorbents were chosen for further testing with a simulated coal gas. Table 1 illustrates the conditions used for a parametric evaluation of the effects of arsenic and other contaminants on the sulfur sorption characteristics. Various regeneration media such as steam, hydrogen, and air in appropriate combination were also tested at 500-700°C and 500, 5000 hr⁻¹ space velocities to identify a preferred set of regeneration conditions.

RESULTS AND DISCUSSION

Based on input from catalyst manufacturers, consultants, and past experience in applications similar to coal gas, over 120 commercial nickel catalysts were qualitatively assessed for their suitability in removing the trace contaminants regeneratively. From hydrothermal

stability considerations, alumina appeared to be a preferred catalyst support. Ten candidates were chosen for preliminary screening on a comparative basis. All the sorbents were able to purify a dry H₂/N₂ stream from 10 ppmv to less than 20 ppbv H₂S, although breakthrough times varied. Sorbents containing additives such as copper or cobalt, as expected, did provide better regenerability. However, their sulfur sorption capacities were significantly lower and experienced significant losses in surface area. As can be seen in Figure 1, the breakthrough time showed a linear dependence on the nickel content indicating that high nickel contents should be preferred to achieve large sulfur removal capacities. However, the catalysts with high (50-60%) nickel contents showed a greater level of sintering, which may lead to a loss of activity in subsequent sorption cycles. Based on the sulfur sorption capacity, extent of regeneration, and the catalyst stability, two of the candidate sorbents, 3% Ni/14% MoO₃ on alumina (Ni/Mo) and 20% Ni on alumina were selected for further testing.

During preliminary screening with dry gases, the Ni/Mo sorbent exhibited an extremely high sulfur sorption capacity (16,600 ppmwS) and almost complete regeneration. When tested in the presence of a model coal gas, its performance was seriously impaired. As verified by the manufacturer and by elemental analysis, approximately 0.3% sulfur was found in the fresh sorbent. The sulfur evolved as H₂S in the presence of steam in the coal gas. When this sulfur was removed from a fresh sample before testing, the sulfur sorption capacity and the 20 ppbv H₂S breakthrough time decreased to such an extent as to make it unattractive as a trace contaminant cleanup sorbent. Unlike the Ni/Mo sorbent, 20 wt% Ni on alumina maintained the desired sulfur cleanup levels under a variety of operating conditions and changes in the coal gas composition (Table 2). Major observations related to the desirable operating conditions are summarized below.

- The sulfur sorption capacity increased with decreasing space velocity. The breakthrough time behavior suggests that the use of lower space velocities (500-2000 hr.⁻¹) may promote a higher contaminant removal efficiency.
- The sulfur sorption capacity increased slightly with decreasing steam content in the model coal gas. Carbon deposition occurs at lower steam content (~7%) and may be a limiting design parameter.
- Effect of decreasing temperature was to increase sulfur sorption capacity with the largest capacity observed at 500°C (Figure 2).
- In presence of arsine, the sorbent exhibited ~25% reduction in the sulfur sorption capacity, possibly due to a competition between the two contaminants for the available nickel sites (Figure 3).
- Regeneration of the sulfur spent sorbents indicates that chemisorption of sulfur on the nickel surface is reversible depending on the experimental conditions used. With 70% H₂O/30% H₂ as a regeneration medium, 60-80% regeneration may be achieved at 600-700°C. Other regeneration media, such as steam, steam with ~1% air, simulated fuel cell cathode

exhaust, and high steam/hydrogen ratios at 500°C did not provide satisfactory regeneration.

- The structural stability of the nickel sorbents appeared to be affected when relatively high regeneration temperatures (700°C) were used. This resulted in a drop in sorption activity in the next sorption cycle. However, the subsequent sorption/regeneration cycles indicated a stabilization of the sorbent performance (Figure 4).

CONCLUSIONS

This investigation has demonstrated that commercial, supported nickel sorbents are able to remove trace amounts of H₂S from hot coal gas to the desired sub-ppm levels for extended periods of time. The selected sorbent, 20 wt% Ni on alumina, can provide sulfur sorption capacities of 2000-10,000 ppmw S, depending on the operating conditions. All of the sorbents tested are regenerable towards sulfur. Optimum sorption/regeneration conditions exist which may make the application of these sorbents for trace contaminant cleanup of coal gas economically viable. The analytical methods developed for the coal gas cleanup application are capable of measuring sub-ppm levels of H₂S and AsH₃ and reliable for extended period of experimental runs.

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REFERENCES

1. E.J. Vidt, et al., "Evaluation of Gasification and Gas Clean-up Processes for use in MCFC Power Plants," Final Report prepared by Westinghouse-ERC for DOE Contract No. DE-AC21-81MC16220, 1981.
2. TRW, "Monitoring Contaminants in Coal-Derived Gas for Molten Carbonate Fuel Cells," Final Report prepared for Argonne National Laboratory, DOE/METC/82-44, 1981.
3. Morgantown Energy Technology Center, "Advanced Environmental Control Technology," Topical Report, DOE/METC/SP-187.
4. T. Grindley, "Development and Testing of Regenerable Hot Coal Gas Desulfurization Sorbents for Molten Carbonate Fuel Cell Application," DOE/Morgantown Energy Technology Center, IR No. 1133, October 1981; IR No. 1386, November 1982.
5. Katalco, "Catalyst Handbook," Springer-Verlag, New York Inc., 1970.
6. Giner, Inc., a) "Molten Carbonate Fuel Cell Power Plant Desulfurization Systems," DOE Contract No. DE-AC03-78-ET15370; b) "Studies Involving High-Temperature Desulfurization/Regeneration Reactions of Metal Oxides for the Fuel Cell Program," for Argonne National Laboratory, Contract No. 31-109-38-5804; c) Studies Involving High-Temperature Desulfurization/Regeneration reactions

of Metal Oxides for Fuel Cell Development," for DOE/Morgantown Energy Technology Center, DOE, Contract No. DE-AC21-81MC16021.

7. Institute of Gas Technology, a) "Coal Gasification Pilot Plant Support Studies," for U.S. Department of Energy, Contract No. ET-78-C-01-2806; b) "Development of a Hot Gas Cleanup System for Integrated Coal Gasification/Molten Carbonate Fuel Cell Power Plants," for DOE/Morgantown Energy Technology Center, Contract No. DE-AC21-82MC19043.
8. Battelle Pacific Northwest Laboratories, a) "Development of a Solid Absorption Process for Removal of Sulfur from Fuel Gas," for DOE/Morgantown Energy Technology Center, DOE Contract No. DE-AC21-79ET11028; b) "Development of a Hot Gas Cleanup System for Integrated Coal Gasification/Molten Carbonate Fuel Cell Power Plants," DOE/Morgantown Energy Technology Center, Contract No. DE-AC21-82MC19077.
9. J.R. Rostrup-Nielsen, J. Catal., 71, 220 (1968).
10. I.M. Al-Daher and J.M. Salih, J. Phys Chem., 76 (20), 2851-7, 1972.
11. I.E. Den Besten and P.W. Selwood, J. Catal, 1, 93, 1962.
12. J.G. McCarty, and H. Wise, J. Chem Phys., 72, 6332 1980.
13. I. Alstreys, et al., Appl. Catal., 1, 303 1981.
14. J.G. McCarty, et al., Final Report prepared by SRI International for U.S. DOE Contract No. AC21-79MC11323, December 1981.
15. J.R. Rostrup-Nielsen, J. Catal. 21, 171, 1971.

TABLE 1. RANGE OF EXPERIMENTAL PARAMETERS EVALUATED FOR TRACE CONTAMINANT REMOVAL FROM HOT COAL GAS

COMPONENT	RANGE
Model Coal Gas:	
H ₂	15-20 vol%
N ₂	30-50
CO	10-20
CO ₂	5-15
H ₂ O	5-40
Trace Contaminants:	
H ₂ S	1-10 ppmv
AsH ₃	1-10 ppmv
Temperature	500-700°C
Pressure	1 atm
Gas Space Velocity	500-5000 hr. ⁻¹

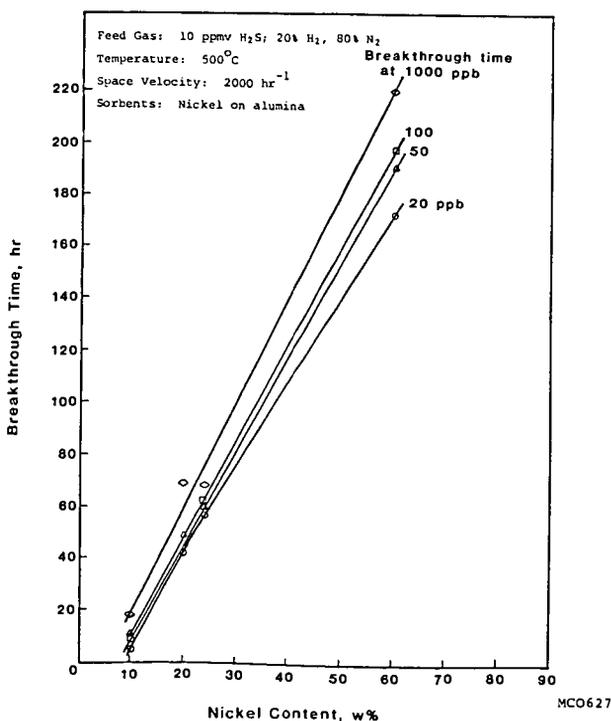
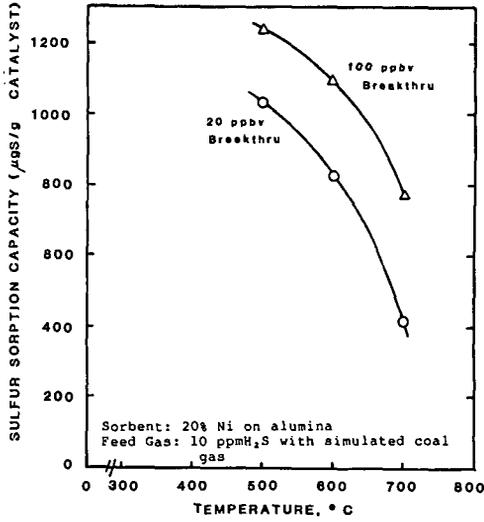


FIGURE 1. THE BREAKTHROUGH TIME SHOWS A LINEAR DEPENDENCE ON THE NICKEL CONTENT

TABLE 2. IMPACT OF OPERATING CONDITIONS ON THE PERFORMANCE OF 20 WT% Ni ON ALUMINA SORBENT

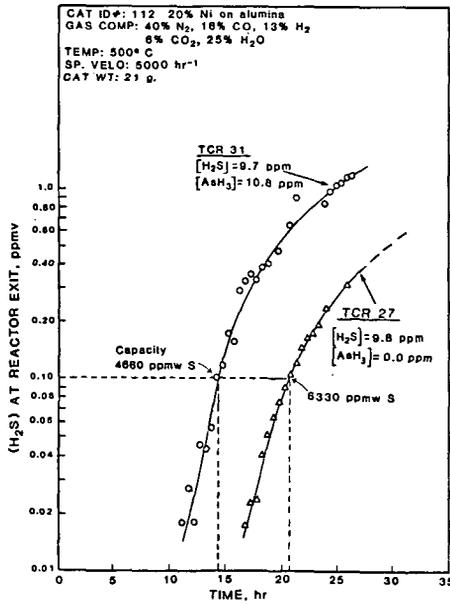
COMPOSITION OF FEED COAL GAS			TEMP °C	SP VEL hr ⁻¹	SULFUR SORPTION CAPACITY g S/g Ni		COMMENTS
H ₂ O %	CO %	N ₂ %			@ 20 ppbv H ₂ S BREAKTHROUGH*	@ 100 ppbv H ₂ S BREAKTHROUGH*	
-	20	-	500	2000	9500	12,500	C-deposition observed; run terminated due to excessive increase in pressure drop. No C-deposition observed No C-deposition observed
7	16	20	500	2150	-	-	
40	10	13	500	2150	7150	9750	Arsenic decreases sulfur sorption capacity.
25	13	16	500	2000	8850	10,650	
25	13	16	500	5000	5200	6200	
25	13	16	600	5070	4150	5500	
25	13	16	700	4900	2100	3900	
25	13	16	500	5000	3850	4650	

*Breakthrough is defined as the time or event at which the specified amount of contaminant is observed in the reactor exit effluent.



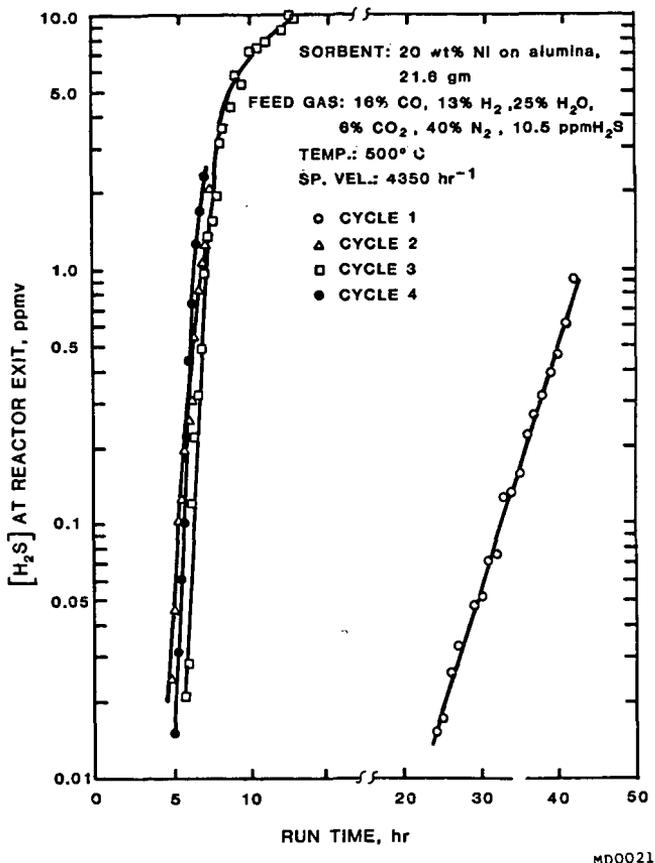
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FIGURE 2. EFFECT OF TEMPERATURE ON SORBENT PERFORMANCE



MC0666

FIGURE 3. EFFECT OF ARSENIC ON SORBENT PERFORMANCE



MD0021

FIGURE 4. EFFECT OF SORPTION/REGENERATION ON SORBENT PERFORMANCE