

INTRODUCTION

FUEL-BOUND NITROGEN COMPOUNDS IN COAL GAS STREAMS

Fuel-bound nitrogen compounds such as ammonia and hydrogen cyanide are formed during gasification of coal and these compounds are readily converted to oxides of nitrogen (NO_x) during combustion of coal gas. U.S. coals contain from 0.5 to 2 wt% nitrogen on a dry basis [Chen et al., 1982]. The nitrogen in coal is chemically combined with the carbon in polycyclic aromatic rings [Axworthy, 1975]. Such chemical structures possess strong C-N bonds. At gasification temperatures, C-C bonds are readily broken, but the C-N bonds survive. Thus, HCN is the initial nitrogen-bearing gaseous product of pyrolysis [Solomon et al., 1982]. In a gasifier, the oxygen potential and the temperature near the inlet are sufficiently high to convert the HCN, through an NH_x intermediate, to NO and N_2 . As the gases travel through the bed, oxygen is depleted and the NO is converted back to HCN and to NH_3 . This general mechanistic pathway has been suggested by a number of investigators [Haynes, 1977; Smith et al., 1982] and has been confirmed by Highsmith et al. [Highsmith et al., 1985] in experimental measurements in a pilot-scale gasifier.

Fuel-bound nitrogen compounds become an undesirable contaminant in coal gas destined for high-temperature applications such as the generation of electricity in gas-fired turbines. In this use, during combustion the NH_3 is readily oxidized to NO_x (fuel- NO_x), a highly undesirable and difficult-to-remove atmospheric pollutant. Unlike the formation of NO_x from atmospheric nitrogen (thermal NO_x), the oxidation of fuel-bound nitrogen occurs at temperatures as low as 800°C ; thus small decreases in flame temperature do not prevent the formation of fuel-bound NO_x . In molten carbonate fuel cell applications (MCFC), when the anode exhaust gas is burned with air to supply CO_2 for the regeneration of the carbonate electrolyte, the fuel NO_x formed can react with the electrolyte to form relatively volatile nitrates that lead to loss of electrolyte by evaporation [TRW, 1981]. Thus, removal of NH_3 from coal gas is highly desirable before the coal gas is used in these applications.

The concentration of fuel-bound nitrogen compounds in coal gas depends on factors such as temperature, pressure, residence time, and coal rank. Chen et al., [1982] who studied the combustion of a variety of coals in an oxygen-deficient atmosphere, found that low rank coals

avored the formation of ammonia. An extensive examination of nitrogen compounds in the product gas of coal gasifiers was reported by Kilpatrick [1986]. In this study, conducted from 1977 to 1981, gas samples taken from working gasifiers producing low- and medium-Btu gas were analyzed for a number of chemical components, including NH_3 and HCN. The results revealed levels of NH_3 in the range 180 to 3100 ppm, depending on the type of gasification process, and they confirmed that NH_3 is a major nitrogen-bearing contaminant in coal gas. The concentration of HCN is typically an order of magnitude less than that of NH_3 .

Haldipur et al. [1989] reported the concentration of NH_3 found in the KRW air-blown fluidized-bed pilot plant gasifier. The gasifier was operated at about 1100°C and limestone was used for in-bed desulfurization. The ammonia concentration was measured by scrubbing an aliquot of coal gas with an acid solution and analyzing the extract with a gas chromatograph. The NH_3 concentration varied from 20 to 340 ppm, corresponding to a coal nitrogen conversion ranging from 0.6% to 8.8%. The fate of the remainder of the nitrogen present in the coal was not reported.

Kurkela and Ståhlberg [1992] measured the concentration of NH_3 and HCN in fluidized-bed gasifiers operating with peat, brown coal, and wood sawdust. The concentration of NH_3 varied from about 500 to 9000 ppm depending on the type of fuel and the operating pressure. Similarly, the HCN level in the gas stream varied from about 10 to 200 ppm. Generally, the NH_3 levels were found to be highest with peat, moderate with brown coal, and low with wood sawdust feeds.

PREVIOUS STUDIES

Thermal decomposition of NH_3 to its elements, N_2 and H_2 , is highly desirable as a method of removal, because such a reaction would not introduce any additional contaminants into the coal gas stream. Because of this reaction's high activation energy ($92 \text{ kcal} \cdot \text{mol}^{-1}$) (Yamura and Asabe, 1981) it is ineffective for reducing NH_3 levels at temperatures typical of hot coal gas streams. A catalyst is required, and hence, research efforts must focus on catalytic decomposition of ammonia.

Because of great interest in ammonia synthesis, the reverse reaction, catalytic decomposition of ammonia, has been examined by many investigators over the last 50 years. Most of these studies are related to the development of highly active catalysts such as bulk iron and promoted bulk iron formulations used in ammonia synthesis and they were devoted mainly to understanding reaction mechanisms and optimizing reaction conditions for high yields of ammonia. Such studies are of little importance to the hot coal gas cleanup conditions because steam, carbon

monoxide, and hydrogen sulfide present in the coal gas are highly detrimental to the activity of the iron catalyst.

Nearly all kinetic studies of the decomposition of ammonia suggest that the decomposition occurs through successive dehydrogenation of adsorbed NH_x species to form surface adstates of nitrogen atoms and hydrogen atoms. The adstates then combine and desorb to form gaseous nitrogen and hydrogen. At low concentrations of NH_3 and high temperatures, the rate is limited by the rate of dissociative adsorption of NH_3 on the catalyst surface. At high concentrations of NH_3 and low temperatures, the desorption of product nitrogen molecules determines the overall rate.

The activity of the catalyst is related to the bond between the nitrogen adstate and the catalyst surface (Tamaru, 1961). If this bond is too weak, there is little driving force for dissociative adsorption of NH_3 . At the opposite extreme, where the binding energy of the nitrogen adstate is strong, solid-state interactions such as dissolution and nitride formation are favored over associative desorption of nitrogen atoms. Indeed, the observed ammonia decomposition rate was found to be proportional to the heat of formation of the highest oxide of a metal (assumed to be proportional to the heat of formation of nitrides); the metals that form oxides with moderate heats of formation exhibit the highest activities. Such metals include ruthenium, cobalt, iron, and nickel. Strong nitride-forming metals such as tungsten were found to have very low activities.

Krishnan, et al. (1988) studied the removal of fuel-bound nitrogen compounds in simulated coal gas streams using a laboratory scale reactor. This study investigated several catalysts including supported nickel catalysts, zinc ferrite sorbents containing NiO or CuO additives, and a MoS_2 catalyst at 550° and 800°C under simulated coal gas compositions representative of fixed-, fluidized-, and entrained-bed gasifiers. HTSR-1, a catalyst proprietary to Haldor-Topsøe A/S, Copenhagen, Denmark, exhibited excellent activity, even in the presence of 2,000 ppm of H_2S , and high temperature stability. G-65*, an SRI catalyst, demonstrated superior activity in the temperature range 550° to 650°C at H_2S levels below 10 ppm. The presence of impurities such as HCl and HCN did not affect the catalyst performance in the temperature range studied. Tar contaminants can lead to carbon deposits that are easily removed at 800°C.

Other oxide and sulfide catalysts also have shown some activity for NH_3 decomposition (Krishnan et al., 1988). An MoS_2 catalyst reduced NH_3 levels from about 5000 ppm to 1500 ppm at 790°C. Ni- and Cu-doped zinc ferrite sorbents exhibited initial activity for NH_3 decomposition at 550°C, but the activity could not be sustained as the sulfide is absorbed by the sorbent.

A few other studies have also been performed on the catalytic decomposition of ammonia under simulated coal gas conditions. The Institute of Gas Technology (1983) reports that, although zinc- and iron-based catalysts were more effective in decomposing NH_3 , the catalysts exhibited a four- to six-fold decrease in catalytic activity on exposure to a feedgas containing H_2S . Similarly, a study by Engelhard Corporation (Farruto, 1986) found that a catalyst containing nominally NiO and MnO_2 supported on a proprietary alumina exhibited very high activity for ammonia decomposition but deactivated in the presence of steam and H_2S . A marked decrease in catalytic activity was noted when the steam and H_2S concentrations exceeded 10% and 10 ppm, respectively; steam was more deleterious than H_2S .

Cooper and Lungström (Cooper et al., 1989; Cooper and Ljungström, 1988) studied the decomposition of NH_3 over silica and calcined and sulfated limestone materials. In the temperature range 840° to 960°C , the activities of these materials were found to be moderate in a fluidized-bed reactor and a stream of NH_3 and Ar. The presence of H_2 reduced the rate of decomposition, as expected. The rate constants for NH_3 decomposition on these materials are significantly lower than the value (220 s^{-1}) found for the HTSR-1 catalyst.

The effect of water vapor and hydrocarbons on the rate of decomposition of NH_3 by CaO , MgO , and dolomite was investigated by Björkman and Sjöström (1991). Steam and hydrocarbons that can form carbonaceous material on the catalysts inhibited the decomposition. At 900°C , in a mixture of 0.1% NH_3 , 8% steam and 91.9% He, the extent of conversion of NH_3 was less than 10% in comparison to a >90% conversion in a mixture of 0.1% NH_3 and 99.9% He.

Leppälahti et al. [1991] also investigated the conversion of nitrogen compounds from a peat gasifier over several inexpensive materials such as dolomite, limestone, iron sinter, and ferrous dolomite. The gas stream used in these tests contained only about 100 ppm of H_2S . Limestone, dolomite, and silicon carbide had very little catalytic effect. But, ferrous materials such as iron sinter and ferrous dolomite decomposed NH_3 and organic nitrogen compounds at temperatures 900°C . About 80% of the feed NH_3 (2250 ppm) dissociated on these materials. But they were not as effective as nickel catalysts which decomposed nearly 100% of feed NH_3 under the same conditions.

Krishnan et al. (1990) performed a preliminary cost estimate for the process of catalytic removal of fuel-bound nitrogen from hot coal gas streams. The gas stream was assumed to be from a KRW gasifier operating in air-blown mode with 2000 ppm NH_3 present. Removal of 90% of the fuel-bound nitrogen was the design objective. The catalytic unit is of a fixed-bed type and placed downstream of the particle removal equipment but upstream of the desulfurization units.

The operating pressure, temperature, and space velocity are 225 psia, 750°C and 2500 h⁻¹, respectively. For a plant capacity of 100 MW_e, the catalytic unit consists of two refractory-lined fixed-bed reactors with an internal diameter of 4 m and a height of 8.3 m. The capital cost is estimated to be \$1,237,000. The operating cost including catalyst replacement every four years, labor, maintenance, and cost of capital is estimated to be about 0.1¢/kWh, a very modest burden on the cost of electricity. A change in the capital recovery factor from 25% to 15% will decrease the cost of catalytic removal of fuel-bound nitrogen by about 20%. A 25% change in the catalyst cost will change the annual operating cost by about 9%.

SIMULTANEOUS REMOVAL OF AMMONIA AND HYDROGEN SULFIDE

Coal gas streams contain several impurities that need to be removed. Providing a separate reactor and process stage for each impurity would be economically impractical. Combined removal of H₂S and NH₃ in one process step would minimize capital and operating costs. Ayala [1993] claimed that addition of metal oxides such as MoO₃ to zinc oxide-based sorbents would decompose NH₃ while removing H₂S at about 530°C. Recently, Jothimugerasan et al. (1995) reported that zinc titanate sorbents containing additives such as Ni, Mo, and W compounds were able to remove H₂S and NH₃ simultaneously. At a temperature of 700°C, the H₂S level was reduced from 1% to 75 ppm while about 50% conversion of feed NH₃ (0.18%) was observed.

Zinc titanate sorbents have proven to be durable for hot coal gas desulfurization applications. Hence, they are ideal candidates to be used as supports for the active NH₃ decomposition formulations. The integration of the catalyst and the sorbent may be accomplished in several ways: physical mixing of catalyst and sorbent particles, precipitation of the catalyst formulation on to the sorbent, or wet impregnation of the sorbent with the catalytic material.

The catalyst-sorbent mixture must be able to survive the oxidative regeneration conditions. Under these conditions, many of the candidate NH₃ decomposition catalyst surfaces are likely to be converted to the oxides or sulfates. For example, the equilibrium partial pressure of oxygen for conversion of Ni to NiO at 800°C is 1×10^{-14} atm which is well below the partial pressure of oxygen in the regeneration atmosphere. Similarly, we expect that Mo, Co, Ni, and W and their respective sulfides will be converted to oxides during the sorbent regeneration process step.

For the catalyst-sorbent mixture to be useful in long-term applications, the volatility of the catalyst under oxidizing conditions must be negligibly small. Thermodynamic calculations indicate that Mo₃O₉ and Mo₄O₁₂ species have appreciable vapor pressures ($\sim 6 \times 10^{-4}$ atm) at 1000 K, and thus they would likely disappear from the bed at an unacceptably high rate. However, formation

of molybdates may lower the vapor pressure of the molybdenum oxides significantly. Also, oxides of Ni, Co, and W have significantly lower vapor pressures, less than 1×10^{-10} atm, at 1000 K.

The densities of MoS_2 , WS_2 , NiS and CoS are lower than their corresponding oxides. Hence, cyclic sulfidation-oxidation steps may lead to volume changes that are detrimental to the physical integrity of the catalyst-sorbent mixture. However, if the fractional quantity of the catalyst is small in comparison to the sorbent, then changes in the catalyst particle volume may not have a significant effect on the strength of the catalyst.

SCOPE OF THE REPORT

The objective of the proposed program is to identify and test, at a laboratory-scale, various catalysts that will both decompose NH_3 and remove H_2S in the hot coal gas desulfurization environment. The program consists of three tasks:

- A. Submission of NEPA information and development of a test plan
- B. Catalyst selection, synthesis, and testing
- C. Data analysis.

In Task A, the information necessary for the preparation of the NEPA document was submitted. A test plan was also submitted previously to select and evaluate various catalysts in a laboratory scale reactor. This report provides the results of Tasks B and C. The next chapter describes the thermodynamic calculations made to determine (a) the equilibrium decomposition of NH_3 and (b) the stability of the catalysts and sorbents under various conditions. The experimental procedures used for testing the activity catalysts and sorbents are described next. The observed results and their interpretation are presented next followed by a summary of conclusions and recommendations.

THERMODYNAMIC CALCULATIONS

Thermodynamic calculations were performed to determine the concentrations of NH_3 in equilibrium with coal gas streams typical of two gasifiers: Texaco's entrained-bed unit (Texaco) and METC's Gasifier Product Improvement Facility (GPIF). The Texaco gasifier is operated in an oxygen-blown mode whereas the GPIF gasifier performs in an air-blown mode. The concentrations of NH_3 and other components are substantially different in the respective product streams of these gasifiers (Table 1).

TABLE 1
PRODUCT GAS COMPOSITION (VOL %) IN TEXACO AND GPIF GASIFIERS

<u>Component</u>	<u>Texaco Gasifier</u>	<u>GPIF Gasifier</u>
H_2	31.1	12.5
CO	45.7	21.6
H_2O	12.5	25.0
CO_2	10.0	2.39
H_2S	0.5	0.13
NH_3	0.18	0.34

The equilibrium partial pressure of NH_3 as a function of temperature in the product gas of these respective gasifiers at total pressures of 1 and 20 atm are illustrated in Figures 1 and 2. As expected, the partial pressure of NH_3 decreases with increasing temperature at a total pressure of 1 atm. However, at 20 atm, the equilibrium partial pressure of NH_3 is low at 500°C, but increases at higher temperatures. A maximum level in NH_3 partial pressure is attained in the temperature range 600° to 800°C depending on the gas composition. At very high temperatures, the equilibrium partial pressure is decreased even at 20 atm total pressure.

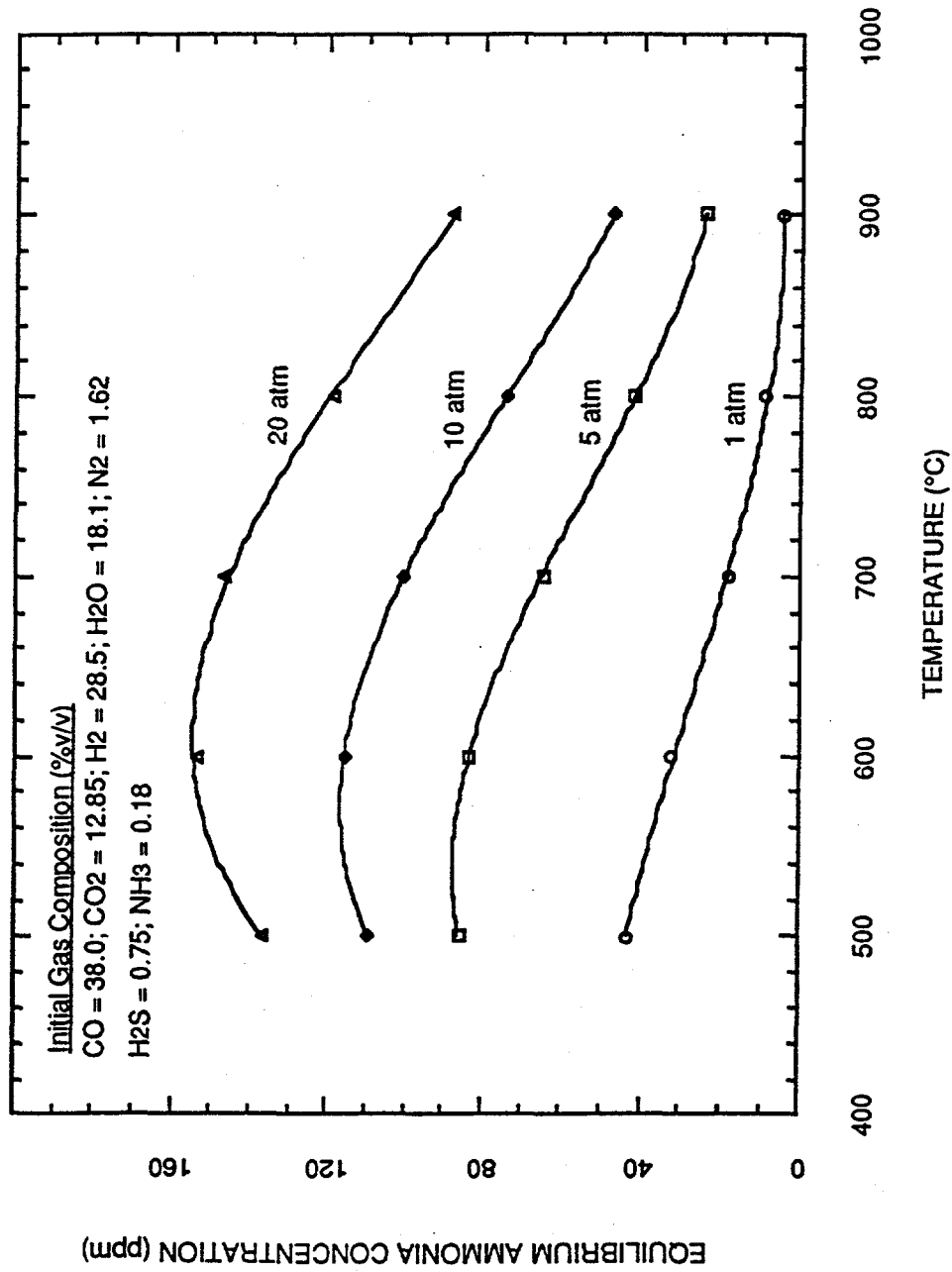


Figure 1. Equilibrium concentration of ammonia as a function of temperature and pressure in a Texaco coal gasifier gas stream.

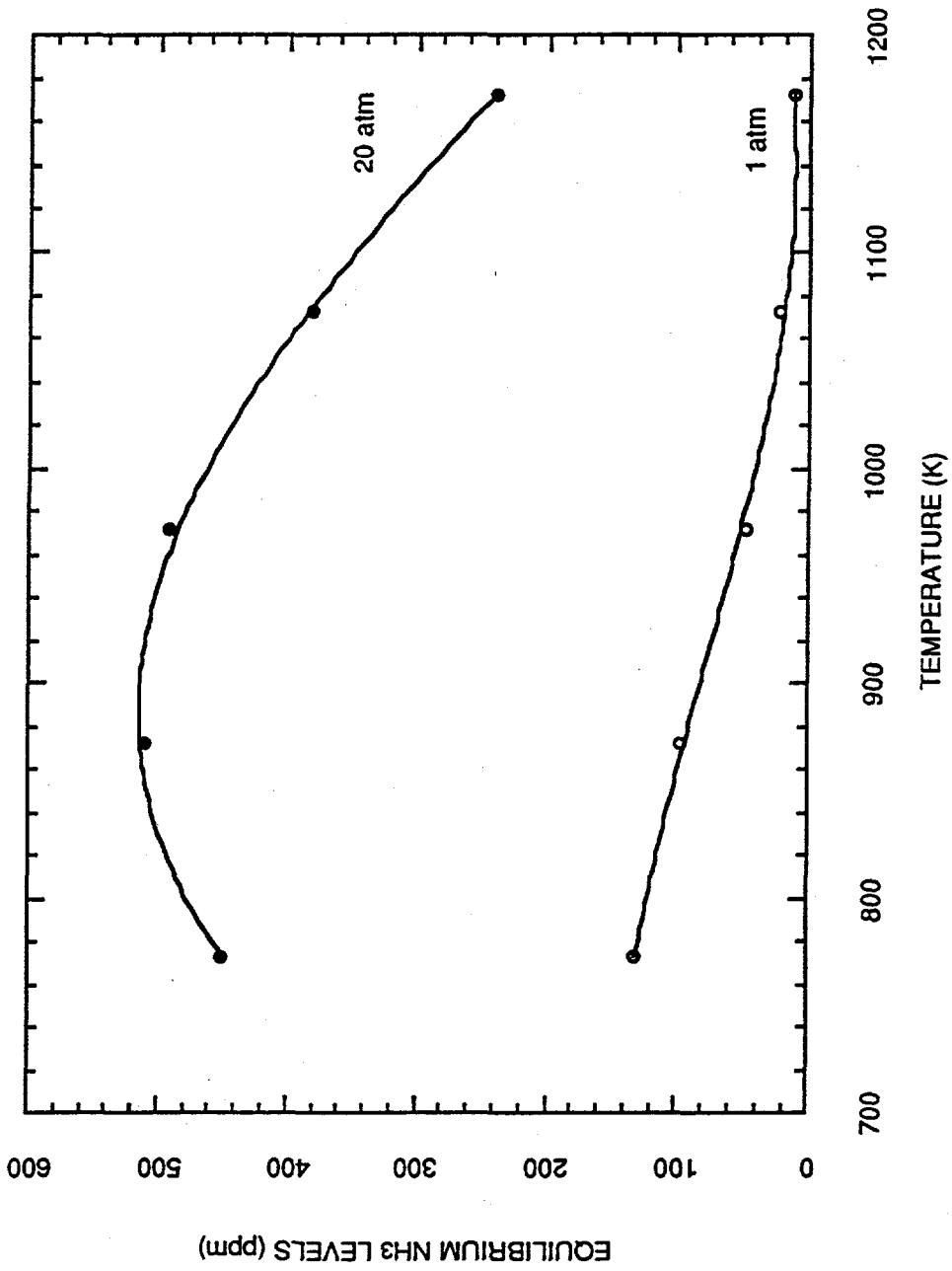


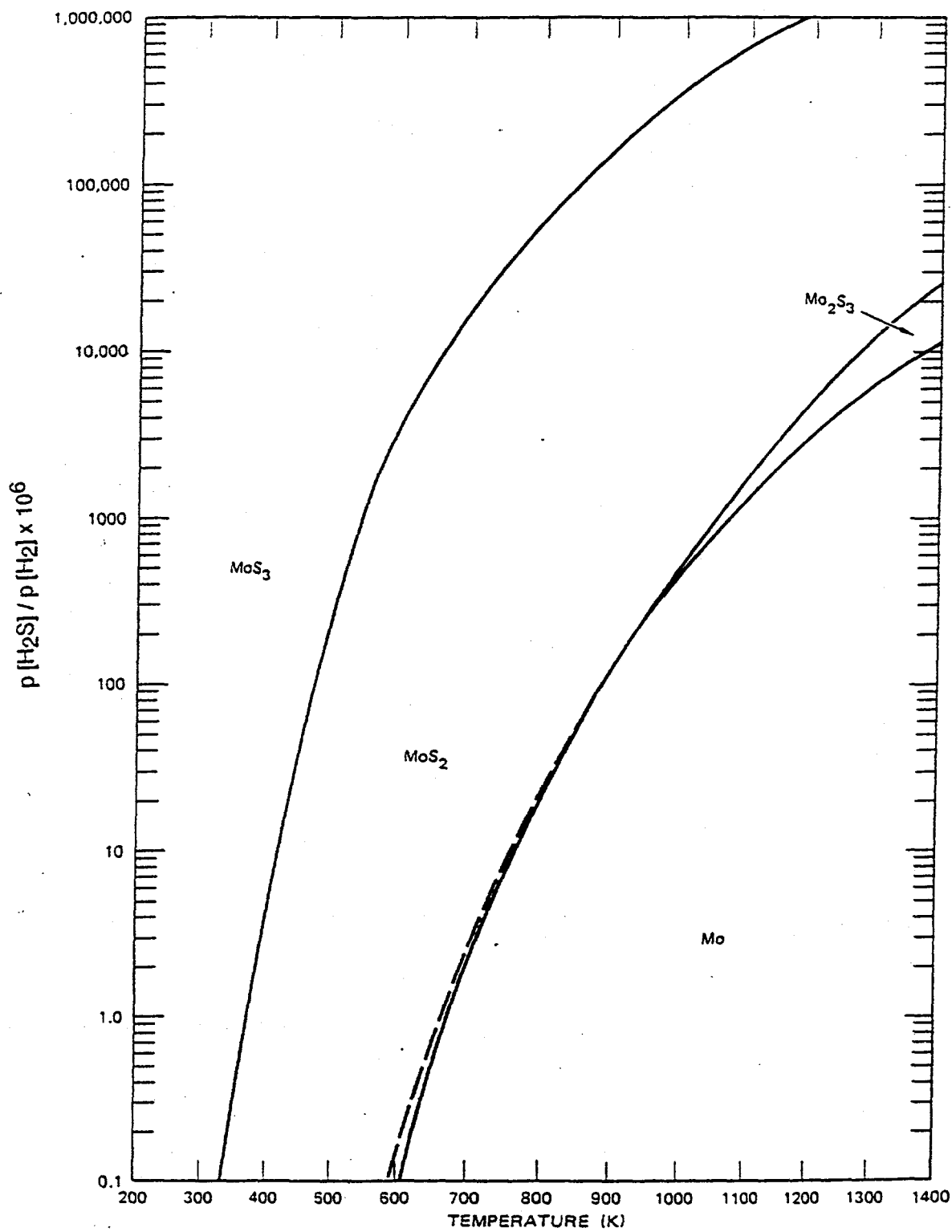
Figure 2. Equilibrium levels of ammonia as a function of temperature and pressure in GIF's air-blown gasifier stream.

The low NH_3 partial pressure calculated for the Texaco gasifier stream at 500°C appears to be due to the formation of CH_4 , a process that reduces the partial pressure of H_2 . Thermochemically, the extent of decomposition of NH_3 is inversely proportional to the partial pressure of H_2 . Because the formation of CH_4 is thermodynamically favored at lower temperatures and higher pressures, the process is beneficial to the decomposition of NH_3 under such conditions. Table 2 shows the equilibrium partial pressures of CH_4 and H_2 as functions of temperature at a total pressure of 20 atm..

TABLE 2
CALCULATED EQUILIBRIUM PARTIAL PRESSURES OF CH_4 , AND H_2 AT A
TOTAL PRESSURE OF 20 ATM IN A TEXACO GASIFIER STREAM

<u>Temperature ($^\circ\text{C}$)</u>	<u>% CH_4</u>	<u>% H_2</u>
500	28.1	2.6
600	23.4	6.45
700	15.7	13.4
800	7.63	22.2
900	2.31	28.7
1000	0.47	30.6

Nickel and MoS_2 based catalysts have been shown to be effective in decomposing NH_3 in the presence of H_2S in simulated coal gas streams. The activity of the sulfide based catalysts for NH_3 decomposition may depend on whether the catalyst can be kept in the sulfided state. Our thermodynamic calculations indicate that MoS_2 will be stable at 723°C at a $p(\text{H}_2\text{S})/p(\text{H}_2)$ ratio higher than 0.5×10^{-3} (Figure 3). At the same temperature, WS_2 will be stable at ratios higher than 1×10^{-3} (Figure 4). The product gas streams from both Texaco and GPIF gasifiers contain more than enough H_2S to keep these sulfides in stable conditions. However, after passage through a zinc titanate sorbent the concentration of H_2S will decrease substantially. Under equilibrium conditions in this environment, the sulfides may be reduced to metals as the stable phases.



SA-1945-75

Figure 3. Stability of molybdenum sulfides in hydrogen.

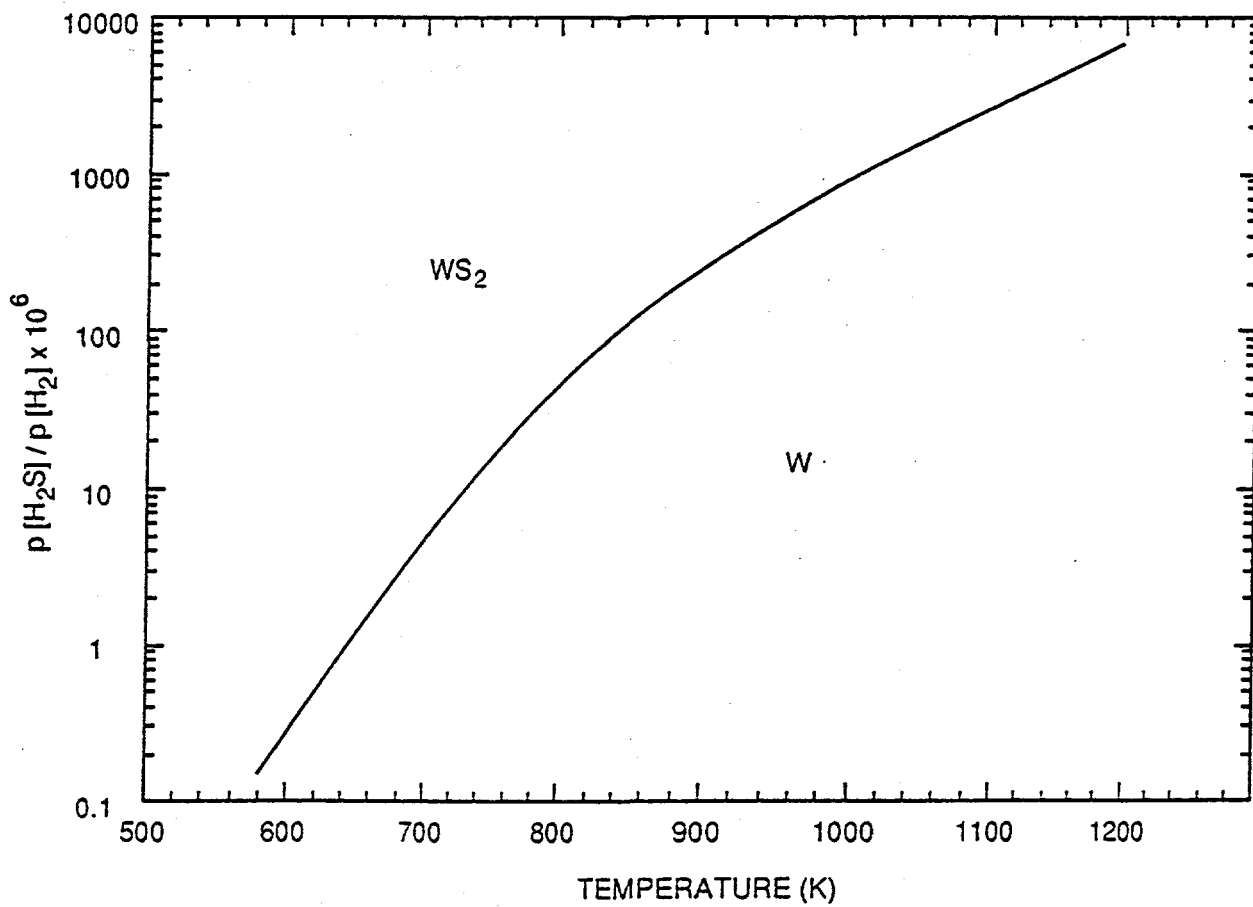


Figure 4. Stability of tungsten disulfide in hydrogen

Combining both the desulfurization sorbent and NH_3 decomposition catalyst in the same unit requires that the catalyst not only function in the presence of H_2S but also must survive the oxidative regeneration of the sulfided sorbent. During this process step, the loss of active components by volatilization must be minimized. To predict the possible extent of loss by vaporization, we calculated the equilibrium vapor pressures of several metal oxides as a function of temperature (Table 3). Of the oxides considered, only the molybdenum oxides have significant vapor pressure at temperatures above 600°C . Detailed calculations (Table 4) indicated that Mo_3O_9 , Mo_4O_{12} , and Mo_5O_{15} are the dominant vapor species in the temperatures range $525\text{--}825^\circ\text{C}$ in equilibrium with solid MoO_3 .

TABLE 3
EQUILIBRIUM PARTIAL PRESSURES OF METAL OXIDE VAPORS IN THE
PRESENCE OF 2% O_2 AT 625° AND 725°C

Oxide Vapor	$p(\text{MO})$ at 625°C (atm)	$p(\text{MO})$ at 725°C (atm)
CoO	2.7×10^{-23}	6.9×10^{-20}
CuO	8.7×10^{-18}	3.7×10^{-15}
FeO_2	1.4×10^{-20}	5.8×10^{-18}
ZnO	3.8×10^{-17}	1.2×10^{-14}
NiO	2.3×10^{-22}	3.2×10^{-19}
W_2O_6	1.6×10^{-21}	7.0×10^{-12}
Mo_3O_9	4.4×10^{-6}	2.9×10^{-4}
Mo_4O_{12}	4.1×10^{-6}	3.5×10^{-4}

TABLE 4

CALCULATED PARTIAL PRESSURES OF SPECIES OVER MoO₃(c) IN PRESENCE OF PURE O₂ AT
0.02 ATM TOTAL PRESSURE

Species	Partial Pressure (atm)				
	700 K	800 K	900 K	1000 K	1100 K
<u>Vapor Species</u>			MoO ₃ (c)		
Mo	1.21 x 10 ⁻⁸¹	1.23 x 10 ⁻⁶⁸	1.53 x 10 ⁻⁵⁸	1.84 x 10 ⁻⁵⁰	6.11 x 10 ⁻⁴⁴
MoO	4.76 x 10 ⁻⁶²	7.35 x 10 ⁻⁵²	5.89 x 10 ⁻⁴⁴	1.21 x 10 ⁻³⁷	1.34 x 10 ⁻³²
MoO ₂	5.48 x 10 ⁻³⁹	2.76 x 10 ⁻³²	4.30 x 10 ⁻²⁷	5.97 x 10 ⁻²³	9.86 x 10 ⁻²⁰
MoO ₃	5.93 x 10 ⁻¹⁹	1.76 x 10 ⁻¹⁵	8.52 x 10 ⁻¹³	1.16 x 10 ⁻¹⁰	3.98 x 10 ⁻⁹
Mo ₂ O ₆	3.01 x 10 ⁻¹⁴	3.63 x 10 ⁻¹¹	8.59 x 10 ⁻⁹	6.52 x 10 ⁻⁷	8.76 x 10 ⁻⁶
Mo ₃ O ₉	2.20 x 10 ⁻¹¹	2.19 x 10 ⁻⁸	4.42 x 10 ⁻⁶	2.92 x 10 ⁻⁴	2.20 x 10 ⁻³
Mo ₄ O ₁₂	9.37 x 10 ⁻¹²	1.45 x 10 ⁻⁸	4.07 x 10 ⁻⁶	3.46 x 10 ⁻⁴	2.02 x 10 ⁻³
Mo ₅ O ₁₅	1.10 x 10 ⁻¹³	4.04 x 10 ⁻¹⁰	2.20 x 10 ⁻⁷	3.13 x 10 ⁻⁵	1.76 x 10 ⁻⁴
O	5.02 x 10 ⁻¹⁷	1.12 x 10 ⁻¹⁴	7.54 x 10 ⁻¹³	2.17 x 10 ⁻¹¹	3.09 x 10 ⁻¹⁰
O ₂	2.00 x 10 ⁻²	2.00 x 10 ⁻²	2.00 x 10 ⁻²	1.93 x 10 ⁻²	1.56 x 10 ⁻²
O ₃	1.45 x 10 ⁻¹⁷	3.14 x 10 ⁻¹⁶	3.44 x 10 ⁻¹⁵	2.34 x 10 ⁻¹⁴	7.81 x 10 ⁻¹⁴
Σ p(Mo) (atm)	3.15 x 10 ⁻¹¹	3.68 x 10 ⁻⁸	8.72 x 10 ⁻⁶	6.70 x 10 ⁻⁴	4.41 x 10 ⁻³
<u>Solid Phases</u>					
Mo(c)	No	No	No	No	No
MoO ₂ (c)	No	No	No	No	No
MoO ₃ (c)	Yes	Yes	Yes	Yes	No
Mo ₄ O ₁₁ (c)	No	No	No	No	No
Mo ₈ O ₂₃ (c)	No	No	No	No	No
Mo ₉ O ₂₆ (c)	No	No	No	No	No

Addition of another metal oxide can suppress the vaporization of molybdenum oxide, just as the presence of titanium oxide in zinc titanate sorbents decreases the vaporization of zinc. We calculated the equilibrium partial pressures of molybdenum oxide vapors in the presence of copper, cobalt, iron, nickel, and zinc oxides (Table 5). Appendix A describes the results of thermodynamic calculations with several molybdates and tungstates. Copper oxides were effective in decreasing the vaporization of molybdenum oxides by about four orders-of-magnitude. Other oxides do not promote the formation of the corresponding molybdates, and hence, no reduction in the equilibrium vapor pressures of molybdenum oxides is achieved.

TABLE 5

TOTAL PRESSURE OF Mo-CONTAINING SPECIES OVER $\text{MoO}_3(\text{c}) + \text{MMoO}_4(\text{c})$
IN THE PRESENCE OF PURE O_2 AT 0.02 ATM TOTAL PRESSURE

Oxide	Total Pressure of Mo-Containing Species (atm)				
	700 K	800 K	900 K	1000 K	1100 K
$\text{MoO}_3(\text{c})$	3.15×10^{-11}	3.68×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	4.41×10^{-3}
$\text{CuMoO}_4(\text{c})$	1.17×10^{-15}	2.34×10^{-12}	8.04×10^{-10}	8.10×10^{-8}	3.30×10^{-6}
$\text{Fe}_2\text{O}_3 + \text{MoO}_3(\text{c})$	3.15×10^{-11}	3.68×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	5.45×10^{-3}
$\text{NiO} + \text{MoO}_3(\text{c})^1$	4.94×10^{-15}	1.11×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	4.41×10^{-3}
$\text{Co}_3\text{O}_4 + \text{MoO}_3(\text{c})$	3.15×10^{-11}	3.68×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	5.05×10^{-3}
$\text{ZnO} + \text{MoO}_3(\text{c})$	3.15×10^{-11}	3.68×10^{-8}	8.72×10^{-6}	6.70×10^{-4}	4.41×10^{-3}

¹ At temperatures below 800K, NiMoO_4 was the equilibrium solid phase.