

SOLID ADSORBENTS FOR REMOVAL OF HYDROGEN SULPHIDE FROM HOT GAS

by

E. Furimsky and M. Yumura

ABSTRACT

A wide range of solids have been tested as potential adsorbents for H₂S removal from hot gas. These solids can be divided into two main groups, i.e., the adsorbents containing alkaline earth metals and those containing transition metals. Among the former, calcium oxide and naturally occurring materials such as limestone, dolomite and calcium silicate have attracted a great deal of attention. The adsorbents of the second group include iron oxide alone or in combination with some supports, zinc oxide, zinc ferrite and manganese oxide. The materials containing both the alkaline earth metals and transition metals, e.g., manganese nodules, fly ash and the reject from the aluminium industry (red mud) have been evaluated as well.

Authors: Dr. E. Furimsky, Energy Research Laboratories, CANMET, Energy, Mines and Resources, Ottawa, Canada, K1A 0G1.

Dr. Motoo Yumura, National Chemical Laboratory for Industry, Tsukuba, Yatabe, Ibaraki 305, Japan.

INTRODUCTION

Purification is an essential step prior to utilization of combustible gases. In this respect the particulate matter and corrosive components must be removed to avoid detrimental effects on material and the environment. Among the latter, a great deal of attention has been directed to sulphur-containing species, where H_2S is usually the most abundant and the most stable compound.

The formation of H_2S accompanies many industrial processes, e.g., pyrolysis, cracking, hydrocracking, hydrorefining, in which H_2S is usually in the mixture with H_2 , CH_4 and higher hydrocarbons. After H_2S removal these gases could be used as valuable fuels or as a source of petrochemicals. On a commercial scale H_2S is removed by wet scrubbing techniques. This step results in a loss of H_2 bound in H_2S . It would be a significant achievement if H_2S could be decomposed in order to reuse the H_2 . Inevitably, such a route would require a solid catalyst and temperatures higher than those applied in wet purification processes.

Another group of gases containing H_2S are those from gasification. Under reducing conditions, such as those usually applied during moving bed and fluidized bed gasification a substantial portion of S present in the feedstock is converted to H_2S . The H_2S removal is essential prior to utilization of gasification products either as fuel gas or as synthesis gas. In the former, the use in combined cycle power generation has been thoroughly investigated. The present status of this route indicates that the purification at a near gasification temperature is required to make it economically viable.

Continuous efforts have been made to develop a purification technology removing H_2S at high temperatures. This would avoid energy losses associated with cooling the gas prior to purification using current technologies. It is known that in case of gasification products purified at high temperatures and subsequently utilized either as fuel gas or in a combined cycle power generation, the overall energy efficiency may be increased by about 6%.

Hot gas clean-up technologies currently under development are based on two stages, i.e., particulates removal and sulphur compounds removal. The commercial viability of these technologies is influenced by the second stage

which involves the utilization of solid adsorbents. A number of solid materials have been tested and patented as potential adsorbents. Among these calcium oxide, iron oxide, zinc oxide, manganese oxide and numerous minerals and naturally occurring clays containing large quantities of these oxides have been evaluated.

The first review on the status of development of hot gas clean-up technologies was published by IEA Coal Research technical services (1). This review was later updated by Reijnen and van Brakel (2). These reviews emphasize the need for additional research in the area of particulates as well as corrosive components removal from hot gas. The hot gas desulphurization processes have been recently reviewed by Uchida (3) who concluded that processes utilizing solid adsorbents have advantages over those utilizing molten salts. The first attempt to review the agents (solid and liquid) used for the removal of sulphur components from various gases was made by Rosendahl (4).

The purpose of this article is to review published works on different aspects of solid adsorbents for H_2S removal from hot gas. Most of the published information shows that tested adsorbents include the oxides of alkali earth metals and the oxides of transition metals alone or in combination with various supports as well as naturally occurring materials containing these oxides.

It has been established that the efficiency of an adsorbent depends on its affinity to sulphur as well as on its surface structure. To ensure a large number of utilization-regeneration cycles a good adsorbent has to resist structural changes caused by prolonged exposure to high temperatures. The adsorption efficiency is further influenced by chemical composition of purified gases. It appears that the performance of solid adsorbents may be affected by the methods of preparation and pretreatment. The method of adsorbent regeneration is of great importance as well. This review focuses on published information on these aspects of solid adsorbent performance during H_2S removal from hot gas.

COMPOSITION OF GASEOUS PRODUCTS REQUIRING PURIFICATION

Some examples of H_2S containing gas mixtures requiring purification prior to utilization are shown in Table 1. A number of other

S-containing compounds, e.g., COS, CS₂, alkyl sulphides, alkyl mercaptans, etc., may be present in the gas, however the concentrations of such species are known to be significantly lower than those of H₂S. The composition of the produced gas depends on the processing technology and on the properties of the processed feedstock. For example, the high H₂S content gases in Table 1 were produced during coking and hydrocracking of a heavy crude containing about 5 wt % sulphur. The temperature of the produced gases, from the hot gas clean-up point of view one of the most important parameters, would be the highest for the gasification process (≈1000°C) and the lowest for the hydrocracking process (≈400°C).

The removal of S-containing compounds from gasification products is essential regardless of the utilization route. Thus, when a synthesis gas route is chosen, these compounds have to be removed from the raw gas to prevent the poisoning of the water gas shift catalyst. In the gasification-combined cycle power generation route the absence of sulphur in the gas is essential to avoid corrosion of the downstream units and to control sulphur emissions within environmentally acceptable limits.

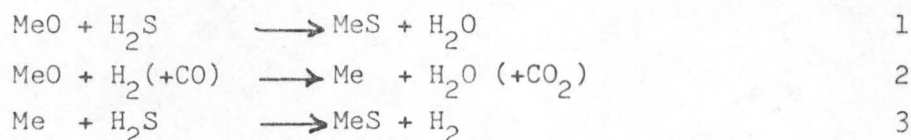
Hydrocarbon containing gases can be a valuable feedstock for the production of H₂ and petrochemicals. In the former case the hydrocarbons are converted to H₂ in the steam reforming process. This process employs a catalyst which may be deactivated by S-containing species if present in the gas. The gas mixtures containing large quantities of C₂ and higher hydrocarbons can be used to produce olefins which are an important feedstock for petrochemical industry. The conversion to olefins may be accomplished via a pyrolytic process. Also in this case purification is necessary to prevent catalyst poisoning.

In hydrotreating operations the gas mixture exiting the reactor may be recirculated to the operation in case that an upgrading of the gas, resulting in H₂ content increase, can be performed. For gases containing high quantities of H₂S such upgrading may be accomplished by removing the H₂S from the gas. When this step is performed at a temperature approaching that of the hydrotreating reactor, the upgraded gas may be directly recirculated without preheating. In industrial practice a number of other hot gases, containing large quantities of S-containing compounds, may be identified. The utilization of such gases is conditional on the removal of these compounds from the gases.

THERMODYNAMIC EVALUATION OF SOLID ADSORBENTS

Preliminary information on the suitability of metal oxides as H_2S adsorbents may be obtained from driving forces of their reactions with H_2S . Thus, very negative free energies of formation for these reactions mean high $\log K$ values indicating high affinities of the metal oxides for H_2S . For the present calculations the data published by Barin and Knacke were used (5). The selection of the metal oxides was based on the abundance of naturally occurring clays and minerals containing Ca, Mg, Ba, Mn, Fe and Zn as well as the attention which has been paid in numerous published works on these metals as potential H_2S adsorbents. These metals or their oxides are known to have a high affinity for sulphur (6). The materials containing these metals may then provide a good base for the preparation of H_2S adsorbents. The inclusion of the oxides of Mo, Co and Ni anticipates the utilization of refinery catalyst being deactivated to the stage that further regeneration is uneconomical. In such a case the pellets of catalyst may be air roasted to remove carbonaceous deposits prior to use as H_2S adsorbent. It is believed that there may be some other metals or metal oxides having a high affinity for sulphur. However, the cost of these materials may be prohibitive.

The approximate reactions which are believed to be important in assessing a material as H_2S adsorbent at high temperatures are:



where Me stands for a metal. It is fair to assume that most of the potential adsorbents will be in an oxidic form. In this case reaction 1 will be the main reaction to take place. However, the frequent presence of H_2 and CO in hot gases, in rather high concentrations, suggests that some reduction of the oxides cannot be ruled out. Thus, reaction 2 may influence the overall rate of H_2S removal. This should not affect H_2S removal when the metal has a high affinity for sulphur, e.g., a large driving force for reaction 3.

The effect of temperature on logK values of reaction 1 for the oxides is shown in Fig. 1. To compare the affinity of the oxides for H_2S the logK values were estimated at $1000^\circ K$ and are shown in Table 2. The chosen temperature is of great interest to hot gas purification. The positive logK values suggest that there is enough driving force for the reaction of the oxides with H_2S with the exception of MgO . The oxides of Mo seems to be the best followed by the oxides of Ni, Zn, Ca, Co and Mn. Among the transition metals oxides the oxides of Fe appear to be at the bottom of the established affinity range.

Relative tendencies of the oxides to be reduced by H_2 can be established from logK values of reaction 2 estimated at $1000^\circ K$. The results in Table 3 show that the oxides of Ca, Mg and Ba as well as those of Zn and Mn are highly resistant to reduction. Thus, during H_2S removal in the presence of these oxides their oxidic forms will play a main role. On the other hand, the oxides of Ni, Co and Mo may be reduced indicating the presence of a metallic form under conditions of hot gas clean-up. For Fe oxides the log K values of reaction 2 at $1000^\circ K$ are close to zero. Then, a coexistence of metallic as well as oxidic forms is possible. It was confirmed that relative resistance of the oxides to reduction by CO was similar to that by H_2 (6).

The reduction of the oxides to metals may not affect H_2S removal. This is supported by the data shown in Table 4, i.e., the positive logK values for reaction 3, with the exception of Co , indicate a high affinity of these metals for H_2S .

Information obtained from thermodynamic calculations indicates the relative probabilities for these reactions to take place. However, since the data are of an equilibrium nature they do not consider the time approach to the equilibrium. For example, large driving forces (large logK values) do not necessarily mean that a given metal or metal oxide will be an efficient H_2S adsorbent. In other words, a favourable logK value must be complemented by favourable kinetics.

In gas-solid reactions, such as in the case of H_2S removal, the surface configuration (surface area, pore volume and pore size distribution) of solid materials is essential in determining the adsorption rate. It is generally established that a high adsorption rate requires a high concentration of adsorption sites on the adsorbent surface. However, the

surface structure may change in the process of H_2S removal, i.e., the oxygen ions are being replaced by larger sulphur ions. This may result in formation of a product layer on the surface of adsorbent particles which will hinder access of H_2S molecules to adsorption sites inside of the particles. Further, the reduction of the surface may be kinetically very favourable due to the small size of H_2 molecules enabling them to penetrate the small pores.

Besides H_2 and CO there may be other species present in gases to be purified at high temperatures which may affect the function of adsorbent. Among these, H_2O and CO_2 are very important. The former may be formed during processes conducted in the presence of H_2 as the product of hydrodeoxygenation as well as during pyrolysis as the product of dehydroxylation. During gasification in the presence of steam some H_2O may end up in the products as well. Under conditions of hot gas clean-up the H_2O , when present in the gas, will shift the equilibrium of reaction 1 to the left and as such decrease the efficiency of H_2S removal. The presence of CO_2 may affect H_2S removal particularly in case of CaO and BaO adsorbents. It was established that CaO and BaO can be converted to their carbonates at temperatures lower than 800° and $1100^\circ C$, respectively. This will diminish the efficiency of these oxides for H_2S removal. With these facts in mind the thermodynamic calculations may be expanded to determine the equilibrium concentrations of H_2S in clean gas. An example of such calculations may be found in the articles published by Proy (7) and Sommers and Last (8). The extent of the reduction of transition metals, i.e., the form of active species at a given temperature may be determined from the H_2O/H_2 and CO_2/CO ratios. An example of the reduction transformations of Fe oxides caused by the presence of H_2 and CO in hot gas was shown by Huttinger and Mingos (9).

PROPERTIES OF SOLID ADSORBENTS

The main function of a solid adsorbent is to decrease the H_2S concentration in the hot gas to the limits required by subsequent utilization processes. To achieve this a solid adsorbent must possess a suitable combination of chemical and physical properties. Among these, affinity for

sulphur surface area, pore volume and pore size distribution and resistance to attrition are perhaps the most important. The adsorbent must also resist crystallographic changes at high temperatures to prevent the loss of active adsorption sites. These losses are caused by sintering of the material. In order to increase the number of adsorption-regeneration cycles an adsorbent should have good regenerability. The available information suggests that the materials evaluated as potential H_2S adsorbents at high temperatures contain alkaline earth metals, transition metals or a combination of both.

ALKALINE EARTH METALS CONTAINING ADSORBENTS

In this group of adsorbents the materials containing Ca have been evaluated most frequently. These materials include CaO, most often prepared by the calcination of limestone, limestone itself, dolomite and others. The low affinity of MgO for sulphur (Table 2) suggests that the Mg containing solids may not be suitable for the adsorbent preparation. On the other hand, the Ba containing solids can be good H_2S adsorbents under certain conditions.

Calcium Oxide

The CaO has a high affinity for sulphur as shown by a large driving force for its reaction with H_2S (Table 2). The reaction will proceed via an exchange of O ions by S ions. The rate of this reaction depends markedly on the availability of the adsorption sites. According to Borgwardt et al. to achieve a high rate of the reaction the CaO has to possess a large surface area and a suitable pore volume and pore size distribution (10). These properties depend on the method of CaO preparation. When CaO is prepared by the calcination of $CaCO_3$, the rate of calcination is of crucial importance. Thus, at high calcination rates a large surface area of the produced CaO can be obtained. However, a temperature increase cannot be used to achieve high calcination rates because of sintering effects. A high rate can be achieved by an efficient withdrawal of CO_2 (calcination product) from the reaction zone. This will result in a shift of calcination equilibrium to the right.

To test CaO as the sulphur adsorbent, Borgwardt et al. used a differential fixed bed reactor (10). The experiments were performed in the temperature range of 600° to 900°C. The two model gas mixtures, i.e., one

containing 5000 ppm H_2S + 45% H_2 and N_2 balance and the other containing 5000 ppm COS + 20% CO and N_2 balance were used. The short residence time given by the experimental arrangements used by these authors required favourable kinetics for efficient H_2S removal. This could be achieved by the use of a small particle size material. In the initial stages of H_2S reaction with CaO a layer of CaS was formed on the outer parts of the particles. Then, the H_2S had to diffuse through this layer to contact the unreacted CaO . These authors applied the grain theory to evaluate the limitations of the reaction, i.e., either chemical reaction control or diffusion control kinetics. For the adsorption controlled by chemical reaction the rate was inversely proportional to the surface area whereas for the diffusion controlled adsorption the rate was inversely proportional to the square of the surface area of the adsorbent. This data treatment was applied to the material ranging in particle size from 1.0 to 9.4 μm (surface area of 5.8 m^2/g to 79 m^2/g). The slope of the reaction rate versus the logarithm of the surface area was - 2.3 for both the chemical reaction and shrinking core model suggesting that in this particle size range the diffusion limitations are quite important. The rate of H_2S and COS adsorption increased with increasing temperature. In the temperature range used the activation energy for both the H_2S and COS adsorption was 31.0 kcal/mol.

The improved H_2S removal with decreasing particle size of CaO was also confirmed by Proy (7). In his work two particle size fractions, 0.8 to 1.25 mm and 4.0 to 6.3 mm, were used in a fixed bed reactor. The gas entering the reactor contained 4700 ppm H_2S . The break through time, i.e., the time at which the H_2S concentration in the exiting reached 75 ppm was 14.3 h and 3.8 h for the 0.8 to 1.25 mm and the 4.0 to 6.3 mm fraction, respectively. The Ca utilization was 80% for the smaller particle size fraction compared with only 18% for the larger fraction. The addition of steam to the gas entering the reactor decreased the rate of H_2S reaction with CaO . This was attributed to the shift of the equilibrium of this reaction to the left. The H_2S adsorption increased with temperature increase up to about 900°C. Further temperature increase resulted in a decrease of H_2S adsorption. The decrease was attributed to less favourable thermodynamics with increasing temperature. The addition of CO_2 to the gas had an inhibitive effect on H_2S removal. The inhibitive effect was

pronounced at temperatures lower than 900°C and was attributed to a possible formation of CaCO_3 which depleted the amount of active CaO species. The effect of particle size on the rate of H_2S reaction with CaO was confirmed by Hasatani et al. (11). Thus, the rate of reaction as well as the utilization of Ca increased with decreasing size of particles.

The 1 to 5 μm particle fraction of CaO prepared by calcination of CaCO_3 at 900°C was used by Yang and Chen to compare the reaction rate of H_2S with that of COS (12). In the temperature range of 500 to 900°C the chemical reaction was observed to be the rate controlling. The rate of COS adsorption was slightly higher than that of H_2S adsorption.

The adsorbent prepared by impregnation of the amorphous carbon by Ca (2 wt % CaO) was investigated by Freund (13). The gas mixture used for this study contained 1000 to 5000 ppm H_2S , 5% H_2 and N_2 balance. In the temperature range of 1127° to 1427°C the adsorption controlled by diffusion, was observed. The estimated apparent activation energy and intrinsic activation energy were 19.6 and 45.5 kcal/mol, respectively.

Barium Oxide

As observed by Proy, the BaO may be a very efficient H_2S adsorbent under properly selected conditions (7). In this case it is the temperature and the presence of CO_2 in the raw gas which are important. Thus, at temperatures lower than 1100°C and in the presence of CO_2 the reaction in which the BaO is converted to BaCO_3 successfully competes with the reaction in which H_2S is consumed. It is therefore essential that the gas purification is performed at temperatures higher than that of BaCO_3 decomposition. Otherwise, the absence of CO_2 in the raw gas would be required for efficient H_2S removal. However, an efficient H_2S removal by BaCO_3 in temperature range of 900°C to 1200°C observed by Kawahara et al. suggests that a partial BaCO_3 decomposition to BaO may yield enough adsorption sites (14).

Calcium Carbonate

Besides being used as the material for the preparation of CaO, CaCO_3 has been directly tested as a potential H_2S adsorbent from hot gas. The CaCO_3 forms usually include the naturally occurring limestone

and dolomite ($\text{Ca Mg}(\text{CO}_3)_2$). Under hot gas clean-up conditions a significant decomposition of CaCO_3 takes place suggesting that the CaO may be a predominant species present in the adsorbent.

Borgwardt and Roache observed that the rate of H_2S adsorption is influenced by the particle size and surface area of CaCO_3 (14) similarly as it was observed for CaO (15). These authors studied a limestone sample in the temperature range of 573° to 870°C using a gas mixture containing 5000 ppm H_2S + 20% CO_2 and N_2 balance. The rate of H_2S adsorption increased when the temperature increased from 573° to 750°C . Further temperature increase resulted in a decrease of H_2S adsorption. The decrease was attributed to the CaCO_3 sintering, which increased the diffusion limitations. Surprisingly, the H_2S adsorption increased when CO_2 concentration in the gas mixture increased. The CaCO_3 could also be converted to CaS in the presence of elemental sulphur. The addition of H_2 to the gas mixture resulted in inhibited H_2S adsorption. The inhibitive effect increased with the increasing particle size of the CaCO_3 .

The efficiency of dolomite for the H_2S removal was investigated by Ruth et al, who observed that the rate of H_2S adsorption depends on the extent of dolomite calcination (16). The half-calcined dolomite was a better H_2S adsorbent than CaCO_3 , CaO and a fully-calcined dolomite. Thus, at 800°C using a gas mixture containing 5% H_2S , the 50% conversion of CaCO_3 to CaS was attained in 15 sec compared with 280 sec for the half-calcined and fully-calcined dolomite, respectively. For CaO and a limestone it took almost 7000 sec to achieve a 30% conversion to CaS . Pulses of small amounts of oxygen, e.g., 0.3% had a dramatic effect on the conversion of CaCO_3 to CaS . However, a prolonged exposure to oxygen had some undesirable effects on the H_2S adsorption. These authors further report that the addition of CO_2 and steam to the raw gas had beneficial effects on the H_2S removal in the presence of the half calcined dolomite.

The high efficiency of half-calcined dolomite for H_2S removal compared with that of uncalcined dolomite was attributed to a favourable development of surface structures during the half calcination (17). For example a thirtyfold increase of surface area and doubling of pore volume were observed. The rate of H_2S reaction using a completely half-calcined dolomite was higher than that of a partially half-calcined dolomite.

The fully calcined dolomite (Ca/Mg ratio 0.84) was used as the adsorbent to purify the gas containing from 0.5 to 5% H_2S and that containing $H_2S + COS$ (H_2S/COS ratio of 20) at 600° to 800°C (18). The kinetics of the H_2S removing reaction was observed to be of the first order. The addition of COS to H_2S had a synergistic effect on the overall sulphur removal, i.e., the rate constant was about 30% higher than the sum of rate constants for the separate removal of COS and H_2S , respectively.

The reactions of H_2S with dolomite and free $CaCO_3$ were compared by Attar and Dupuis (19). These authors observed that at 570°C the $CaCO_3$ as the component of dolomite was completely converted to CaS but only about 3% of the free $CaCO_3$ reacted with H_2S under identical conditions. However, at 700°C the rates of H_2S reaction with free $CaCO_3$ and dolomite were the same. The improved H_2S removal with increasing temperature for free $CaCO_3$ was attributed to its more extensive decomposition to CaO which reacts rapidly with H_2S as well as to the increase of surface area during the decomposition. For dolomite the H_2S removal from the gas was associated with its reaction with Ca-containing species only. Thus, no MgS formation was observed.

Some limitations on using dolomites arise from the presence of alkali metals (20). These metals when present in high quantities induce hot corrosions by accelerating the oxidation and sulphidation of metal. The bulk of sodium and potassium can be released during preheating of the sample at $\approx 850^\circ C$.

It has been emphasized that the formation of the sulphide surface layer hinders the diffusion of H_2S molecules to the adsorption sites. Thus, any process that could destroy the surface layer should enhance the rate of H_2S adsorption. The increased adsorption in the presence of small amounts of O_2 reported by Ruth et al. (16) was attributed to the oxidation of the sulphide ions to sulphate ions which caused the surface layer to break (19). The breaking of the layer resulted from the increase of molar volume during the oxidation. The beneficial effects of small amounts of O_2 on the H_2S removal in the presence of CaO and $CaCO_3$ were also reported by Sommers and Last (8). An efficient H_2S removal achieved on the addition of small amounts of O_2 to the hot cyclone containing a high CaO content dust, observed by Flesch and Velling may be attributed to the same effects (21).

Attempts have been made to decrease the H_2S concentration in the produced gas by trapping the feedstock sulphur in-situ. The Ca-containing materials, i.e., $CaCO_3$ in particular, have been successfully tested as the potential sulphur scavengers. Some examples of this route were reported by Yoo and Steinberg (22) as well as by Pattas and Aldhoch (23). However, this route is not the objective of the present review.

Calcium Silicate

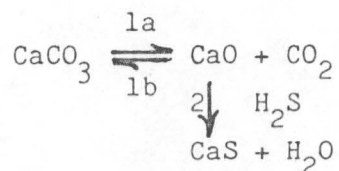
In the search for a naturally occurring material rich in Ca and having a proper pore volume and pore size distribution as well as a large surface area, calcium silicates such as that used for the cement production were tested by Yoo and Steinberg (22). An approximate reaction by which the H_2S removal is accomplished may be written as follows:



Besides the calcium trisilicate these materials contain some Al_2O_3 , Fe_2O_3 , MgO and small quantities of other oxides. The testing of this adsorbent was carried out from $800^\circ C$ to $1000^\circ C$ using the gas mixture containing 5000 ppm H_2S , 12.5% CO , 12.5% H_2 , 8% CO_2 , and N_2 balance. The experimental work was performed in a fluidized bed in two modes, i.e., one in which the adsorbent was used as an in-situ sulphur scavenger during gasification and the other in which the adsorbent was contacted by the gas mixture in order to remove H_2S . The high efficiency of the adsorbent for sulphur removal was confirmed in both modes. In comparison with limestone the performance of the adsorbent was significantly better. This was confirmed by a high resistance to attrition and a good regenerability. Thus, suitable pore volume and size distribution were maintained after repeated adsorption-regeneration cycles. This was attributed to the method of the adsorbent preparation.

Mechanism of H_2S Reaction with CaO and $CaCO_3$ Containing Adsorbents

A tentative mechanism of H_2S reactions with Ca-containing adsorbents may be written as follows;



The adsorbent may contain either CaO or CaCO₃ or a combination of both. When CaO is a predominant species the H₂S removal will proceed via reaction 2. Here, an exchange of O ions by S ions, leading to the formation of CaS and H₂O, takes place. The reaction occurs preferentially on the outer parts of particles. This results in the formation of the sulphide layer which slows down two counteracting processes, i.e., the one in which H₂S diffuses in and the other in which H₂O diffuses out. The decrease of the adsorption rate with time is attributed to these effects. When CO₂ is present in the raw gas reaction 1b may occur as well. However, it is believed that H₂S can successfully compete with CO₂ for the unreacted CaO because of its smaller size. Therefore, the inhibitive effects of CO₂ on H₂S adsorption may be less significant than indicated by thermodynamics.

Also, it is assumed that for adsorbents prepared from CaCO₃-containing material the active species will be some form of CaO. Thus, H₂S removal will be achieved via reaction 2. This requires some decomposition of CaCO₃ to CaO (reaction 1a). It is not necessary to achieve a complete decomposition. In case that a continuous removal of CaO and CO₂ from the system is ensured the H₂S removal (reactions 1a and 2) may take place at temperatures lower than the temperature of CaCO₃ decomposition (≈830°C). Under such conditions a continuous shift of the equilibrium 1 to the right is maintained.

Although the chemistry of CaCO₃ action appears to be simple the formation of CO₂ creates some problems with mass transfer. Thus, the CO₂ must diffuse out from the particles in order to create an adsorption site. The situation becomes more complex after the layer of the sulphide is formed on the outer parts of CaCO₃ particles. It was shown by Attar and Dupuis that after the layer was formed the reaction of H₂S with the adsorbent stopped completely (19). Only after an increase of temperature, which presumably destroyed the layer, could the reaction proceed. To overcome these complications the CaCO₃-containing adsorbent must possess a suitable pore volume and pore size distribution. This can be readily attained during

the preparation of a half-calcined dolomite. Here, the temperature applied ensures the decomposition of MgCO_3 , only leaving CaCO_3 intact. The evolution of CO_2 during preparation results in the formation of large pores which play an important role during the subsequent utilization of this material for H_2S removal from hot gas. A fully-calcined dolomite is known to be less efficient adsorbent of H_2S . This may be attributed to an unsuitable porosity of the material. Thus, to achieve a state of full calcination temperatures in excess of 800°C have to be applied. Under such conditions the sintering of the solid, leading to the decrease of porosity, is quite extensive.

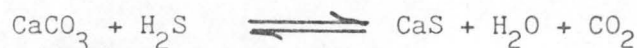
This discussion shows that favourable thermodynamics for the reaction of H_2S with CaO is not sufficient. This must be complemented by favourable kinetics for which the surface structure of an adsorbent is of crucial importance.

In the presence of CaO the H_2S decomposition, yielding H_2 and elemental sulphur occurred in addition to its adsorption (24). Because the CaO is non-reducible (Table 3) the formation of H_2 could not involve the metallic Ca . Then, the decomposition products could arise from some interaction of H_2S with the CaO surface. A speculative mechanism leading to the formation of H_2 and elemental sulphur is depicted in Fig. 2.

Regeneration of Calcium Containing Adsorbents

The conversion of CaS to CaO via its reaction with oxygen appears to be a simple regeneration route. However, this reaction may lead to an uncontrolled temperature increase which may cause undesirable sintering (20). According to Hahn the overheating may be reduced by recirculating a part of the off-gas (25).

To avoid the destructive effects of overheating, other routes for adsorbent regeneration have been evaluated. Some attention attracted the reverse reaction of the equilibrium depicting the use of CaCO_3 as H_2S adsorbent, i.e.;



This approach was studied by Keairns et al during the regeneration of sulphided dolomite using a mixture containing 10% H_2O , 10% CO_2 and

N_2 balance (26). These authors concluded that by increasing the number of sulphidation-regeneration cycles the regenerability of the adsorbent decreased. Thus, after 21 cycles the amount of CaS which could be converted to CaO decreased from 69% to 13%. The decrease of the regenerability was attributed to the enhancement of sintering in the presence of steam (27). Difficulties with regeneration increased with increasing sulphidation temperature. This was accompanied by an increased growth of MgO crystallites on the CaS which then hindered the access of H_2O and CO_2 molecules to CaS during the regeneration cycles (28). Curran et al attributed the decrease of activity on repeated regeneration to crystal growth of $CaCO_3$ and to the segregation of CaS crystallites from MgO leading to a sintered limestone like material (29). Nevertheless, it was confirmed by Morita et al. that the regeneration of sulphided dolomite could be accomplished more readily than that of sulphided limestone (30).

The effect of partial pressure of H_2O and CO_2 on the regeneration of sulphided half calcined dolomite was evaluated by Kan et al. (31). Thus, the regeneration reactions at 15 atm were much faster than those at near atmospheric pressure. Further, the sulphur capacity of the regenerated adsorbent decreased with decreasing steam/ CO_2 ratio. For the ratios of one and higher, little change in the sulphur capacity of the regenerated adsorbent was observed.

The solid deterioration observed during regeneration in the presence of H_2O and CO_2 was diminished significantly when the regeneration of sulphided dolomite was performed in the presence of CO_2 only (32). For example, the Ca utilization after 20 cycles of regeneration in CO_2 was 50% compared with only 20% during the regeneration in H_2O and CO_2 . In addition to sintering the recrystallization of the adsorbent leading to the decrease of crystallographic defects was identified as the cause of the regenerability decrease with repeated regeneration.

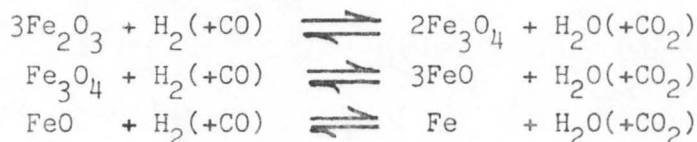
The regeneration of sulphided calcium silicate and sulphided dolomite in CO_2 (30% CO_2 + N_2 balance) was performed at 950°C and 900°C, respectively (22). After three sulphidation-regeneration cycles the adsorbent capacity for sulphur decreased from 54 to 39% compared with 20 to 12% for the calcium silicate and the limestone, respectively.

TRANSITION METALS CONTAINING ADSORBENTS

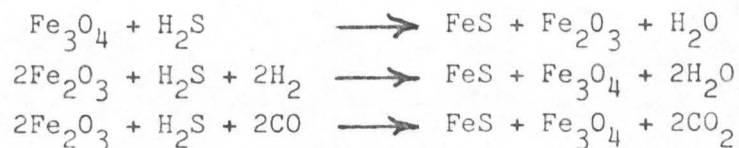
In this group of adsorbents most of the attention has been paid to materials containing Fe, Zn and Mn. These metals and their oxides have a high affinity for sulphur (Tables 2 and 3), but the oxides are less resistant to reduction by H₂ and CO compared with alkali earth metal oxides (Tables 4). Different forms of the adsorbents have been tested, e.g., single oxides, combination of oxides, oxides combined with solid supports and naturally occurring materials having a high content of these metals.

Iron Containing Adsorbents

In these adsorbents the presence of Fe in the form of an oxide is an essential requirement with respect to H₂S removal. In an oxidizing atmosphere the most stable form of Fe oxide is Fe₂O₃. In a reducing atmosphere the Fe₂O₃ can undergo several transformations. The extent of these transformations depends on temperature and on the concentration of reducing species in the hot gas among which H₂ and CO are the most important (33). Following is the set of reactions by which the reduction of Fe₂O₃ can occur:



The extent of these transformations may be estimated by a simple thermodynamic calculation using H₂O/H₂ and CO₂/CO ratios in the temperature range of interest to hot gas clean-up, e.g., 600° to 1100°C. For example when these ratios are higher than 10⁵ the reduction of Fe₂O₃ is not possible. For ratios from 1.0 to about 10⁵ the stable form of Fe oxide is Fe₃O₄. For ratios smaller than about 0.5 a complete reduction to Fe can occur. The composition of most raw gases suggests that during hot gas clean-up the most stable form of Fe oxide will be Fe₃O₄. The reduction of Fe₂O₃ to Fe₃O₄ may be achieved with the direct participation of H₂S as well. This is supported by a rapid increase of SO₂ concentration in the exiting gas during the initial stages of H₂S contact with the fixed bed of Fe₂O₃ (24). The H₂S removal in the presence of Fe₂O₃ and Fe₃O₄ may be described by:



This red-ox cycle may be repeated until all Fe oxides are converted to FeS.

The above discussion suggests that the presence of H_2O and CO_2 in the hot gas may affect the purity of the clean gas by increasing the equilibrium concentration of H_2S in the latter. Further, the consumption of H_2 and CO in the reducing transformations is not welcome as these are usually the most desirable components of the gas. The subsequent reaction of FeS with H_2S yielding FeS_2 could liberate H_2 back into the clean gas. However, experimental results published by Yumura and Furimsky indicate a near stoichiometric conversion of Fe oxides to FeS (24). These authors further observed an increased H_2S decomposition with the increasing level of Fe oxides sulphidation. The decomposition was accompanied by the formation of elemental sulphur. This reaction was attributed to catalytic effects of FeS (34).

Hasatani et al. observed that H_2S removal from hot gas improved with decreasing the Fe_2O_3 particles size (35). They confirmed that Fe utilization for pellets smaller than $1.1 \mu\text{m}$ was at least 90%. The stoichiometric ratio of S to Fe was about 1.0. The activation energy for the H_2S removal was 13.0 kcal/mol.

The Fe_2O_3 based adsorbents for H_2S removal from hot gas have been known for many years. The practical experience with the use of Fe_2O_3 to purify the coke oven gas was described by Reeve (36). The process operated at temperatures approaching 400°C . The raw gas contacted a fluidized bed of particles (-16 to +100 mesh). From 95 to 98% H_2S removal was accomplished. The massive adsorbent attrition, the replacement of fines, plugging and erosion of pipes transporting the adsorbent were identified as the major problems of the process. Some difficulties were also encountered during the regeneration of the sulphur loaded adsorbent. Thus, regeneration in air resulted in an uncontrolled temperature increase which caused extensive sintering. It was further observed by Alkhazov and Amirgulyan, that during the regeneration in air some part of the sulphur of FeS reacts slowly while the other part is totally unaccessible to oxygen (37). This would result in a steady decrease in Fe utilization during successive adsorption-regeneration cycles.

To improve the regenerability and to eliminate the problems described by Reeve attempts have been made to combine Fe_2O_3 with other materials (36). With respect to this fly ash has been successfully tested by Oldaker et al. (38, 39). For example, the addition of small amounts of bentonite (up to 3 wt %) to a combination of 25 wt % Fe_2O_3 and 75 wt % fly ash resulted in a significant improvement of the physical strength of the adsorbent without any detrimental effect on the adsorption capacity. Similar effects were observed when the bentonite was replaced by small amounts of sodium silicate. The regenerability of this adsorbent was very good. Thus, after thirty adsorption-regeneration cycles the adsorption capacity was not affected and the adsorbent showed no signs of physical deterioration. These authors concluded that the temperature of regeneration should not exceed 800°C in order to maintain a long-life adsorbent. However, the fly ash could not accommodate more than 25 wt % of Fe_2O_3 . This determined the upper limits of adsorption capacity of this adsorbent.

The combination of Fe_2O_3 + silica support appears to be an important material for the preparation of solid adsorbents. The results published by Oldaker and Gillmore show that up to 45 wt % Fe_2O_3 can be combined with silica, without affecting the physical strength (40). The higher Fe_2O_3 content results in a higher adsorption capacity of this adsorbent compared with that of the adsorbent prepared from fly ash (39). The physical strength of the silica supported adsorbent could be further enhanced by the addition of a small amount of sodium silicate. Because the fusion temperature of silica is much higher than that of the fly ash operational temperatures as high as 950°C may be applied without detrimentally influencing the adsorbent properties.

The gasifier ash obtained from gasification of Kentucky #9 coal was evaluated as H_2S adsorbent by Schrodt (41). In this coal the pyrite constitutes a large portion of the mineral matter. During gasification the pyrite was converted to Fe_3O_4 rather than Fe_2O_3 . The adsorption capacity of this adsorbent increased with increasing number of adsorption-regeneration cycles. This was attributed to the diffusion of Fe species to the surface of the particles. Thus, after ten adsorption-regeneration cycles a fourfold increase in Fe concentration on the surface of the ash particles was observed. The presence of steam in the raw gas (from 0 to 5.5 vol %) had little effect on the adsorption capacity. The

H_2S reaction with the adsorbent yielded FeS . The FeS_2 was not present. The regeneration in air resulted in the Fe_2O_3 formation. However, a complete conversion of FeS to Fe_2O_3 could not be achieved. This suggests that some portion of sulphur remained in the adsorbent permanently. To overcome the problems with overheating during regeneration the use of diluted air with recycling of some part of coal gas from regeneration is recommended.

The difficulties which arise from the formation of SO_2 during the regeneration of sulphided Fe-containing adsorbents in air may be overcome when the regeneration is performed in steam. In this regard the works published by Tamhankar et al are the most significant (42, 43, 44). Thus, during the regeneration in air + steam mixture a large portion of sulphur trapped in the adsorbent was converted to elemental sulphur. The selectivity for the formation of elemental sulphur increased with increasing concentration of steam in the mixture. For example, for the mixture containing 95% steam and 5% air the selectivity for the formation of elemental sulphur was 75%. The rest of the sulphur was converted to SO_2 and H_2S . When the steam alone was used only H_2S and elemental sulphur were formed. However, the rate of regeneration reactions was rather low.

With the aim to develop an efficient and low cost H_2S adsorbent some materials either disposed from various industrial processes or occurring naturally attracted some attention. Among the former, material disposed from the aluminum industry, so called red mud, appears to have a suitable chemical composition. The solid adsorbent prepared from the red mud was tested at $800^\circ C$. The H_2S removal efficiency of this adsorbent was much better than that of the adsorbent prepared from pure Fe_2O_3 . The high Fe_2O_3 content in the red mud suggests that Fe species account for most of the H_2S removed. In addition to the naturally occurring materials already discussed the $FeCO_3$ (siderite) was tested as the potential H_2S adsorbent (19). This material is known to decompose readily when the temperature approaches $500^\circ C$. The product of the decomposition is FeO which is the active species in H_2S removing reactions. Some manganese nodules have high Fe_2O_3 content as well (Table 5). These materials are discussed below in connection with manganese containing adsorbents and zinc ferrite is discussed in connection with zinc containing adsorbents.

Zinc Containing Adsorbents

Zinc oxide has been used commercially as an H_2S adsorbent perhaps for as many years as iron oxide. The major applications have been in the final desulphurization of hydrocarbon feedstocks for steam-hydrocarbon reforming units as well as the sulphur guard vessel for the protection of the low temperature water gas shift catalysts.

The H_2S reaction with zinc oxide is less complex compared with that with Fe oxides and involves a replacement of O ions by S ions. The simplicity of this reaction stems from the fact that ZnO is by far the most stable form of Zn oxide.

The experience with ZnO as H_2S adsorbent used to purify the gas entering the shift reactor was described by Hawker (42). The proper formulation of surface structure of ZnO was emphasized. For example, for a ZnO sample having a small surface area the reaction with H_2S occurred preferentially on the outer parts of the particles. This prevented Zn utilization under the surface covered with the sulphidation product. In order to increase Zn utilization the ZnO was combined with an alumina support. This, however resulted in the formation of zinc aluminate which is inactive in the reaction with H_2S . Then, a large amount of ZnO would have to be combined with the alumina to obtain an efficient adsorbent. The combinations of ZnO with $Cr_2O_3 + CuO$ and with $CuO + Al_2O_3$ have been tested as well.

The adsorption capacity of an adsorbent prepared from ZnO (containing 80 wt % ZnO) during the clean-up of the raw gas containing 2.7 vol % H_2S at $538^\circ C$ was from 22 to 24 wt % of sulphur (42,46). The clean gas contained less than 10 ppm H_2S . The conversion of ZnO to ZnS decreased the surface area from 3.2 to 1.1 m^2/g and the specific gravity from 6.4 to 3.8 g/cm^3 . The Zn utilization, i.e., the conversion of ZnO to ZnS reached almost 80%.

The performance of ZnO during hot gas clean-up improved in the presence of small amounts of oxygen (9). Under such conditions the conversion of ZnS to $ZnSO_4$ is promoted. In view of the suggestion made by Attar and Dupuis such conversion will change drastically the structure of the ZnS product layer covering the particles (19). The change will result in the reopening of pores and the improvement of access of H_2S molecules to unconverted ZnO inside the particles.

The kinetics of H_2S reaction with ZnO was investigated by Westmoreland et al. (47). Thus, from 300° to 700°C the order of reaction was one and the activation energy 7.2 kcal/mol. They concluded that the use of this adsorbent was limited to a once through adsorption for a hot gas containing small quantities of H_2S . This was attributed to poor regenerability of the spent adsorbent. Moreover, at temperatures approaching 700°C the formation Zn vapour was observed. This is quite surprising as the thermodynamic data show (Table 3) the ZnO is resistant to its reduction.

The low regenerability of ZnO adsorbent was confirmed by Ranade and Harrison (48). For example, the tempering of ZnO at 700°C for 10 h decreased the surface area from 34.4 m^2/g to about 5 m^2/g . The decrease was the result of extensive sintering. The surface area of the sulphided ZnO (80% conversion to ZnS) decreased from 11 m^2/g to 4 m^2/g on tempering at 700°C for 4 h.

During the regeneration of spent ZnO in air an uncontrolled temperature increase may result in significant sintering similar to that observed during the regeneration of other spent adsorbents. Attempts have been made to replace the air by some other oxidizing agents. In this respect the steam was observed to have a dramatic effect on the regeneration rate (49). Thus, at 650°C the rate of regeneration in steam was high and changed little until almost complete conversion of ZnS to ZnO was achieved. At the same time, the rate of regeneration in air was initially very high but slowed down considerably when the conversion of ZnS to ZnO reached about 60%. The difficulties experienced during the regeneration in air were attributed to the formation of $ZnSO_4$. It appears that an optimal temperature and the composition of the air + steam mixture may exist at which the regeneration yields the most active adsorbent.

In order to offset the poor regenerability of ZnO its combination with Fe_2O_3 , i.e., the zinc ferrite ($ZnFe_2O_4$) emerged as a candidate for H_2S removal from hot gas. It is known from metallurgical practice that this material is difficult to reduce thus there would be a lesser probability of elemental Zn volatilization as it was observed previously for ZnO adsorbent (47). Most of the available information on the performance of zinc ferrite was published by the staff of Morgantown Energy Technology Center (50, 51, 52). During three adsorption-regeneration cycles performed at 538°C in the presence of this adsorbent the H_2S removal to less than

6 ppm was achieved. The regeneration was performed by a mixture of equal volumes of steam and air. The surface area decreased from $5.8 \text{ m}^2/\text{g}$ for the initial un sulphided adsorbent to $1.4 \text{ m}^2/\text{g}$ for the final sulphided adsorbent. The analysis of the adsorbent after the third sulphidation run revealed the presence of 28.5% FeS, 38.4% ZnS and 33.0% ZnFe_2O_4 . The effect of temperature (from 318° to 816°C) on the performance of zinc ferrite was investigated in terms of changes in adsorption capacity, breakthrough time and H_2S concentration in the clean gas. The temperature increase to 649°C resulted in increased adsorption capacity and breakthrough time while maintaining very low H_2S concentrations in the clean gas. Further temperature increases to 760°C and 816°C resulted in a gradual decrease of the adsorption capacity and the breakthrough time. The analysis of the adsorbent after the adsorption experiment performed at 816°C revealed the presence of 48.5% FeO, 28.7% ZnS, 17.4% ZnO and 5.3% ZnFe_2O_4 . This suggests that with increasing temperature the role of Fe species of ZnFe_2O_4 in the H_2S removal reactions diminishes.

Manganese Containing Adsorbents

Manganese Oxide

Several oxidation states of manganese oxide are known. In a reducing atmosphere, such as for H_2S containing hot gases the manganese oxides will undergo the following transformations:



According to Westmoreland et al under the conditions of hot gas clean-up the MnO species is the most stable (47). Thus, the higher oxidation states of Mn, if present in the original adsorbent will be reduced to MnO, which is believed to be the active oxide in H_2S removal reactions. These reactions proceed via the exchange of O ions by S ions yielding MnS as the sulphidation product.

The use of manganese oxide based adsorbents for H_2S removal from hot gas was reported by Olsson and Turkdogan (53). At 1000°C the reaction with H_2S was reported to be rapid and the H_2S concentration in the clean gas was in equilibrium with the fixed bed of the adsorbent. The reaction was affected by the particle size of the adsorbent. Thus, the pellets prepared

from the finely divided material were much more efficient adsorbents than those prepared from the coarse material. The formation of the MnS product layer on the outer parts of the adsorbent particles was observed. This resulted in a decrease of the H_2S reaction rate with the unreacted MnO species inside the particles.

A good performance of the manganese oxide based adsorbent from 500° to 800°C was reported by Verfuss (54). At temperatures higher than 800°C the reaction of H_2S with MnO slowed down. This was indicated by the increased content of H_2S in the clean gas as well as by the decreased utilization of Mn. The performance of the adsorbent improved significantly when the MnO was combined with SiO_2 . This combination was, however, chemically less stabil.

The kinetics of H_2S reaction with MnO was investigated by Westmoreland et al. (47). The reaction was observed to be of the first order from 300°C to 800°C. In this temperature range the apparent activation energy for the reaction of H_2S with MnO was about 5.7 kcal/mol. Above 500°C the presence of diffusion limitations was observed.

Manganese Nodules

Vast reserves of these materials occur on the floor of oceans and some lakes. A great potential of manganese nodules for various industrial applications was indicated by Nitta (55). The nodules represent a complex mixture of several metal oxides among which the species containing Mn and Fe are the most important. Some nodules contain relatively large amounts of $CaCO_3$. The relative amounts of Mn-, Fe- and Ca-containing species vary depending on the origin of the nodules. An example of the nodules obtained from the ocean floor and that from the lake floor is shown in Table 5. Here, only the species which are important for the H_2S adsorption are included. Some other active metals may be present as well, however their content is too low to influence H_2S adsorption. The Al_2O_3 and SiO_2 usually account for most of the difference to 100%. These oxides are inactive as they do not react with H_2S .

The alumino-silicate part of manganese nodules possesses a high surface area e.g., the N_2 BET surface area in the range of 100 to 300 m^2/g . This results in the efficient distribution of Mn- Fe- and Ca-containing species ensuring an easy access of H_2S molecules to the adsorption sites. On heating, the manganese nodules undergo sintering which

is accompanied by a surface area decrease. Thus, during prolonged heating at 800°C the surface area of a nodule decreased from 250 m²/g to about 60 m²/g (55). However, even with this decrease the final surface area is about an order of magnitude larger than that of some adsorbents prepared from single oxides.

The chemical changes occurring during heating were described by Van Heacke and Bartlett (56). Thus, the MnO₂, which is believed to be the main form of Mn in manganese nodules will undergo the above transformation. The mineral goethite (FeOOH) is the main form of Fe in the untreated nodules. On heating this species is transferred to Fe₂O₃ and Fe₃O₄. When the heating is performed in a reducing atmosphere the formation of FeO may be observed. As discussed earlier the transformation of CaCO₃ is governed by the thermodynamics of its calcination, which suggests that at temperatures higher than 800°C most of CaCO₃ will be transformed to CaO.

The manganese nodule sample B (Table 5), in the form of pellets having 1.5 mm diameter and 1.5 mm high was tested as H₂S adsorbent by Yumura and Furimsky (57). From 600° to 800°C the adsorption rate was directly proportional to the amount of H₂S flowing through the fixed bed of the adsorbent per unit of time, i.e., the order of the adsorption reaction was one ^(Fig. 3). The impregnation of the sample by Ca (10 wt % Ca) resulted in a 30% increase in the adsorption capacity of the adsorbent. The H₂S adsorption was replaced by the H₂S decomposition as soon as the stage of the adsorbent saturation by sulphur was reached. Increasing the temperature from 600° to 800°C resulted in a fivefold increase of the decomposition rate. The order of the decomposition reaction was about 0.5.

According to Olsson and Turkdogan the regeneration of sulphided manganese oxide based adsorbents may be performed in an oxidic atmosphere at about 1300°C (53). The O₂, CO₂ and H₂O are considered as the oxidizing agents. Such a high temperature may lead to a significant loss of surface area due to sintering and recrystallization, regardless of type of oxidizing agent. However, no particulars related to these effects are revealed by these authors. On the other hand, Verfuss claims that the repeated regeneration of sulphided manganese oxide adsorbent, redistributed on a silica support, resulted in a decrease on Mn utilization during the subsequent sulphidation step (54).

ADSORBENTS CONTAINING OTHER METALS

Besides the adsorbents described in the previous sections other types of materials have been evaluated as potential agents for H_2S removal from hot gas. However, insufficient attention has been paid to these materials. They are V_2O_5 , WO_3 , CuO and MoO_3 (47, 48, 54, 58). One may add to this group some refinery catalysts deactivated to the stage that further utilization is uneconomical. For example, supported catalysts containing Mo, Co and Ni after the coke burn off should still possess a sufficient surface area to achieve an efficient H_2S removal.

COMPARISON OF H_2S ADSORBENTS

The comparison of solid adsorbents for H_2S removal requires the performance evaluation of a series of materials under a wide range of experimental conditions. So far, few studies of this kind have appeared in the scientific literature. An example of a systematic comparison of the adsorbents efficiency is the work performed by the Morgantown Energy Research Center assessing the performance of Fe_2O_3 and ZnO . These studies showed that in the presence of ZnO the equilibrium concentrations of H_2S in the clean gas are very favourable, but its regenerability and adsorption capacity are quite low. On the other hand the adsorption capacity of Fe_2O_3 was much higher. The combination of these two oxides, i.e., zinc ferrite was chosen in anticipation of obtaining the adsorbent possessing high adsorption capacity and good regenerability.

The adsorption capacities and breakthrough times (at 100 ppm H_2S in clean gas) of adsorbents prepared from Fe_2O_3 , CaO , ZnO , Mn-nodule and red mud were estimated by Yumura and Furimsky (24). The results of these experiments are shown in Table 6. Moreover the H_2S adsorption in the presence of Fe_2O_3 , CaO and ZnO was followed in the course of the experiments. The results show that the adsorption capacity of Fe_2O_3 is the largest followed by that of CaO , and ZnO (Fig. 4). When the results were normalized to a unit of surface area the order changed with ZnO being the most efficient followed by Fe_2O_3 and CaO (Fig. 5). The shape of curves in Fig. 4 and 5 indicate a decrease in the adsorption rate with time. The decrease was the most pronounced for CaO and is attributed to the formation of product layer on the outer parts of the particles. This suggests that a proper selection of particle size of the material influencing the formation

of the layer will be the most crucial for the CaO-containing adsorbents.

Initial rates of the H_2S reaction with MnO, CaO, ZnO and V_2O_3 from 300° to 800°C were compared by Westmoreland et al. (47). All the reactions were of the first order in H_2S . The rate of the reaction was highest for MnO followed by CaO, ZnO and V_2O_3 . These authors concluded that among the evaluated oxides MnO was the most suitable for hot gas clean-up.

The regenerability and a thermodynamically attainable equilibrium concentration of H_2S in clean gas were used as the principal criteria to select ZnO, WO_3 , CuO and V_2O_5 from among twelve different oxides (49). It was realized that these oxides have some limitations with respect to the hot gas clean-up with ZnO being very sensitive to structural changes.

REFERENCES

1. Morrison, G.F. "Hot Gas Clean-Up"; Int. Energy Agency Technical Review; 1979.
2. Reijnen, K. and van Brakel, J. "Hot Gas Clean-Up"; Int. Energy Agency Technical Review; 1984.
3. Uchida, H. Nenryo Kyokai-shi; 62, 792; 1983.
4. Rosendahl, F. Erdol und Kohle; 34, 3, 132; 1981.
5. Barin, I. and Knacke, O. "Thermochemical properties of inorganic substances"; Springer-Verlag; 1973.
6. Yumura, M. and Furimsky, E. "Thermodynamic evaluation of metal oxides as potential H₂S adsorbents"; Division Report ERP/ERL 84-01(INT); Department of Energy, Mines and Resources, Canada; 1984.
7. Proy, G. Gluckauf-Forschungshefte; 43, 105; 1982.
8. Sommers, H. and Last, W. Erdol und Kohle; 24. 7, 473; 1971.
9. Huttinger, K.J. and Minges, R. Erdol und Kohle; 37, 11, 493; 1984.
10. Borgwardt, R.H., Roache, N.F. and Bruce, K.R. Environ. Progress; 3, 2, 129; 1984.
11. Hasatani, M., Yajima, I. and Yuzawa, M. Kagaku Kogaku Ronbumshu; 9, 2, 166; 1983.
12. Yang, R.T. and Chen, J.M. Environ. Sci. Techn.; 13, 5, 549; 1979.
13. Freund, H. Ind. Eng. Chem.; Fund.; 23, 338; 1984.
14. Kawahara, T., Nakajima, K., Sato, Y., Kameyama, H. and Yoshida, K. Nihon Kagaku Kaishi; 6, 1071; 1980.

15. Borgwardt, R.H. and Roache, N.F. Ind. Eng. Chem.; Proc. Des. Dev.; 23, 742; 1984.
16. Ruth, L.A., Squires, A.M. and Graff, R.A. Environ. Sci. Techn.; 6, 12, 1009; 1972.
17. Li, K. and Rogan, F.H. "Study of the mechanism of H₂S/dolomite reaction"; DOE Report FE-2408-4; 1977.
18. Kamath, N.S. and Petrie, T.W. Environ. Sci. Techn.; 15, 8, 967; 1981.
19. Attar, A. and Dupuis, F. Ind. Eng. Chem.; Proc. Des. Dev.; 18, 4, 607; 1979.
20. Keairns, D.L., Newby, R.A., O'Neil, E.P. and Archer, D.H. Am. Chem. Soc. Preprints; Div. of Fuels; vol. 21, 91; 1976.
21. Flesch, W. and Velling, G. Erdoel und Kohle; 15, 9, 710; 1962.
22. Yoo, H.J. and Steinberg, M. "Calcium Silicate Cement Sorbent for H₂S Removal and Improved Gasification Process"; Final Report DOE/CH/00016-1494; October 1983.
23. Pattas, E. and Aldhoch, W. Stahl und Eisen; 100, 7, 376; 1980.
24. Yumura, M. and Furimsky, E. Ind. Eng. Chem.; Proc. Des. Dev.; 1985.
25. Hahn, O.J. "Cleanup of Hot Gas"; Proc. of 18th Intersoc. Energy Conv. Eng. Conf.; Orlando, Florida; p.432; 1983.
26. Keairns, D.L., O'Neil, E.P. and Archer, D.H. "Sulphur Emission Control with Limestone/Dolomite in Advanced Fossil Fuel Processing System"; Envir. Aspects of Fuel Conver. Technology; St-Louis, MO; 1974.
27. Peterson, R.D. and Cutler I.B. J. Am. Ceram. Soc.; 51, 21; 1968.
28. Sun, C.C., O'Neil, E.P. and Keairns, D.L. Thermochemica Acta; 26, 283; 1978.

29. Curran, G.P., Pasek, B., Pell, M. and Gonu, E. Am. Chem. Soc. Preprints; Div. of Fuel; vol. 21, 114; 1976.
30. Morita, Y., Noro, T., Hatsuyama, T., Sakamoto, K., Iwasaki, T. and Kikuchi, E. Nenryo Kyokai-shi; 60, 853; 1981.
31. Kan, G.L. Squires, M.A. and Graff, R.A. Am. Chem. Soc. Preprints; Div. of Fuel; vol.21, 129; 1976.
32. Chou, C.L. and Li, K. Chem. Eng. Commum.; 29, 81; 1984.
33. "Chemistry of Hot Gas Clean-Up in Coal Gasification and Combustion"; Report MERC/SP-78/2; 1978.
34. Fukuda, K., Dokiya, M., Kameyama, T. and Kotera, Y. Ind. Eng. Chem.; Fundam.; 17, 4, 243; 1978.
35. Hasatani, M., Yazawa, M., Sugiyama, S. and Wen, C.Y. Kagaka Kogaku Rombumshu; 6, 5, 521; 1980.
36. Reeve, L. Y. Inst. Fuel; 31, 319; 1958.
37. Alkhazov, T.G. and Amirgulyan, N.S. React. Kin. Catal. Lett.; 24, 1, 55; 1984.
38. Oldaker, E.C., Poston, A.M. and Farrior, W.L. "Removal of H₂S from Hot Gas with Iron Oxide-Fly Ash Sorbent"; MERC/TPR-75/1; 1975.
39. Oldaker, E.C., Poston, A.M. and Farrior, W.L. Am. Chem. Soc. Preprints; Div. of Fuels; vol. 20, 4, 227; 1975.
40. Oldaker, E.C. and Gillmor, D.W. Am. Chem. Soc. Preprints; Div. of Fuels; vol. 21, 79; 1976.
41. Schrodt, J.T. "Hot Gas Desulphurization"; ERDA Report ORO-5076-3; 1977.

42. Tamhankar, S.S., Hasatani, M. and Wen, C.Y. Chem. Eng. Sci.; 36, 1181; 1981.
43. Tamhankar, S.S. "Studies on the Regeneration of Sulphided Fe Oxide Adsorbents with Steam + Air Mixtures"; Report DOE/MC/16022; 1982.
44. Tseng, S.C., Tamhankar, S.S., and Wen, C.Y. Chem. Eng. Sci.; 36, 1287; 1981.
45. Hawker, P.N. Hydroc. Processing; 183; April 1982.
46. "Study of High Temperature Gas Clean-Up"; Ebastec Lavalin; Report No. E-8304.
47. Westmoreland, P.R., Gibson, J.B. and Harrison, D.P. Environ. Sci. Techn.; 11, 5, 488; 1977.
48. Ranade, P.V. and Harrison, D.P. Chem. Eng. Sci.; 36, 1079; 1981.
49. Jalan, V. Intern. Gas Res. Conf. Preprints; 128; 1981.
50. Steinfeld, G. "Hot Gas Desulphurization"; DOE/MC-16545-1553; 1984.
51. Schrodt, J.T. "Dynamic Simulation of Fixed-Bed Zinc/Iron Oxide High Temperature Desulphurization Process"; DOE/MC-21582-1500; 1983.
52. Grindley, T. and Steinfeld, G. "Development and Testing of Hot Gas Desulphurization Sorbents"; DOE/MC-16545-1125; 1981.
53. Olson, R.G. and Turkdogan, E.T. U.S. Patent #4,180,549.
54. Verfuss, F. Erdol und Kohle; 37, 2, 82; 1984.
55. Nitta, M. Appl. Catalysis; 9, 151; 1984.
56. Van Hecke, M.C. and Bartlett, R.W. Metall. Transac.; 4, 941; 1973.

57. Yumura, M. and Furimsky, E. Appl. Catalysis; 1985.
58. Morita, Y., Kimura, T., Ogawa, M. and Sakurai, H. Nenryo Kyokai-shi;
57, 917; 1978.

FIGURES CAPTIONS

Fig. 1 - Log K values versus temperature for the reaction of H_2S with the oxides.

Fig. 2 - Tentative transition state for H_2S decomposition in the presence of CaO .

Fig. 3 - Cumulative amounts of H_2S adsorbed (2g of Mn-nodule, 0.1L/min).

Fig. 4 - Cumulative amounts of H_2S adsorbed per one gram of the oxide.

Fig. 5 - Cumulative amounts of H_2S adsorbed (in grams per square meter of the oxide).

Table 1 - Examples of Hot Gases Produced In Different Processes.

Component	Concentration, vol %			
	Gasification	Pyrolysis	Coking	Hydrocracking
H ₂ S	1.1	3.5	8.0	21.0
H ₂	35.7	11.0	23.2	46.5
N ₂ +O ₂	0.5	0.7	0	0.5
CO	44.6	3.3	0.4	tr
CO ₂	18.0	9.0	0.6	tr
CH ₄	0.1	53.0	35.8	12.5
C ₂ +	tr	19.5	32.0	19.5

Table 2 - LogK values for the reaction of metal oxides
with H₂S at 1000°C

Reaction	LogK
CaO + H ₂ S → CaS + H ₂ O	3.36
MgO + H ₂ S → MgS + H ₂ O	-1.79
FeO + H ₂ S → FeS + H ₂ O	2.29
FeO + 2H ₂ S → FeS ₂ + H ₂ O + H ₂	0.58
1/2Fe ₂ O ₃ + 3/2H ₂ S → FeS + 3/2H ₂ O + 1/4S ₂	2.40
1/2Fe ₂ O ₃ + 2H ₂ S → FeS ₂ + 3/2H ₂ O + 1/2H ₂	1.77
1/3Fe ₃ O ₄ + 4/3H ₂ S → FeS + 4/3H ₂ O + 1/6S ₂	1.99
1/3Fe ₃ O ₄ + 2H ₂ S → FeS ₂ + 4/3H ₂ O + 2/3H ₂	0.99
MnO + H ₂ S → MnS + H ₂ O	2.80
ZnO + H ₂ S → ZnS + H ₂ O	3.88
MoO + 2H ₂ S → MoS ₂ + 2H ₂ O	5.2*
MoO ₃ + 3H ₂ S → MoS ₂ + 3H ₂ O + 1/2S ₂	8.7*
CoO + H ₂ S → 1/9Co ₉ S ₈ + H ₂ O + 1/18S ₂	3.10
NiO + H ₂ S → NiS + H ₂ O	4.1*
NiO + H ₂ S → 1/3Ni ₃ S ₂ + H ₂ O + 1/6S ₂	2.76

Table 3 - LogK values for the reaction of
metal oxides with H₂ at 1000°K

Reaction	LogK
CaO + H ₂ → Ca + H ₂ O	-17.73
MgO + H ₂ → Mg + H ₂ O	-15.71
BaO + H ₂ → Ba + H ₂ O	-10.4
FeO + H ₂ → Fe + H ₂ O	- 0.73
1/2Fe ₂ O ₃ + 3/2H ₂ → Fe + 3/2H ₂ O	0.46
1/3Fe ₃ O ₄ + 4/3H ₂ → Fe + 4/3H ₂ O	- 0.31
MnO + H ₂ → Mn + H ₂ O	- 6.21
MnO ₂ + 2H ₂ → Mn + 2H ₂ O	2.8*
1/3Mn ₃ O ₄ + 4/3H ₂ → Mn + 4/3H ₂ O	- 4.65
1/2Mn ₂ O ₃ + 3/2H ₂ → Mn + 3/2H ₂ O	- 3.12
ZnO + H ₂ → Zn + H ₂ O	- 2.76
MoO ₂ + 2H ₂ → Mo + 2H ₂ O	- 1.16
MoO ₃ + 3H ₂ → Mo + 3H ₂ O	4.50
CoO + H ₂ → Co + H ₂ O	1.53
NiO + H ₂ → Ni + H ₂ O	2.26

Table 4 - LogK values for the reaction of
metals with H₂S at 1000°K

Reaction	LogK
Ca + H ₂ S → CaS + H ₂	21.08
Mg + H ₂ S → MgS + H ₂	13.92
Fe + H ₂ S → FeS + H ₂	3.02
Fe + 2H ₂ S → FeS ₂ + 2H ₂	1.31
Mn + H ₂ S → MnS + H ₂	9.07
Zn + H ₂ S → ZnS + H ₂	6.64
Mo + 2H ₂ S → MoS ₂ + 2H ₂	5.9*
Co + 8/9H ₂ S → 1/9Co ₈ S ₈ + 4/9H ₂	-1.58
Ni + H ₂ S → NiS + H ₂	2.4*
Ni + 2/3H ₂ S → 1/3Ni ₃ S ₂ + 2/3H ₂	1.22

Table 5 - Chemical composition of manganese nodules and red mud (wt %)

Component	Sample		
	MNA	MNB	RM
SiO ₂	15.0	35.2	12.0
Al ₂ O ₃	4.8	3.0	22.6
Fe ₂ O ₃	19.5	50.5	29.7
Mn ₃ O ₄	31.8	3.3	-
CaO	25.9	1.2	4.5

MNA manganese nodule from the floor of an ocean

MNB manganese nodule from the floor of a lake

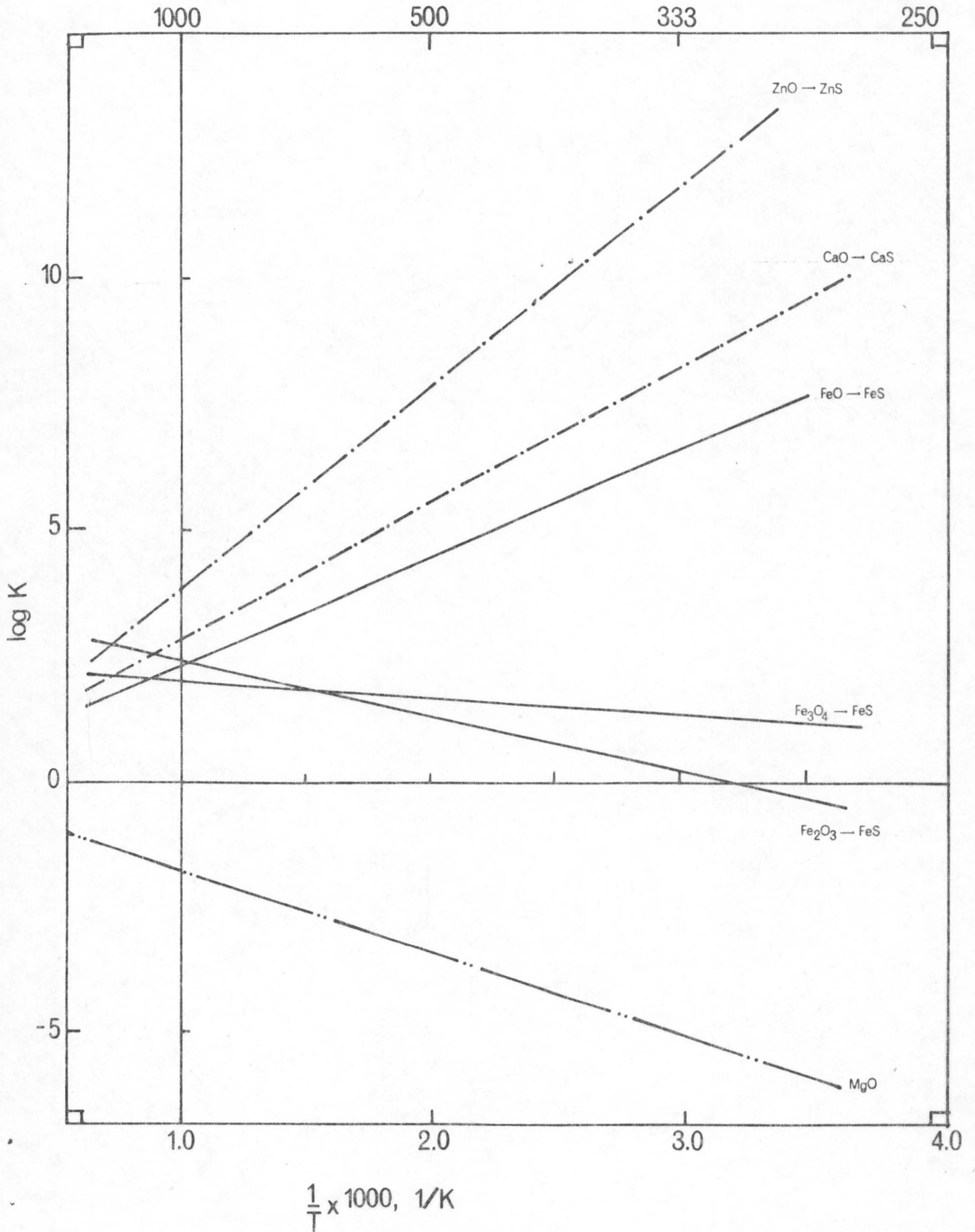
RM red mud

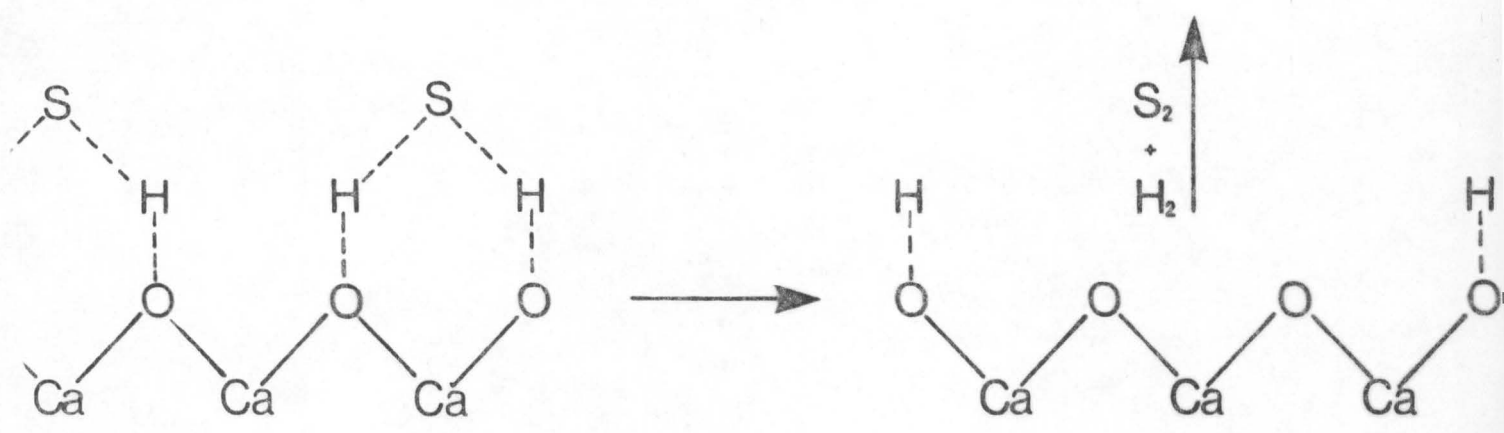
Table 6 - Performance of adsorbents at 800°C *

Adsorbent	Breakthrough time	Adsorption capacity
	min	g H ₂ S/g adsorbent
CaO	15	0.32
ZnO	4	0.25
Fe ₂ O ₃	10	0.45
Manganese nodule	18	0.26
Manganese nodule + 10% CaO	25	0.32
Red mud	22	0.25

* Results obtained at the flow of 0.1 L/min (10% H₂S + N₂)
using 2 g of adsorbents.

TEMPERATURE, K





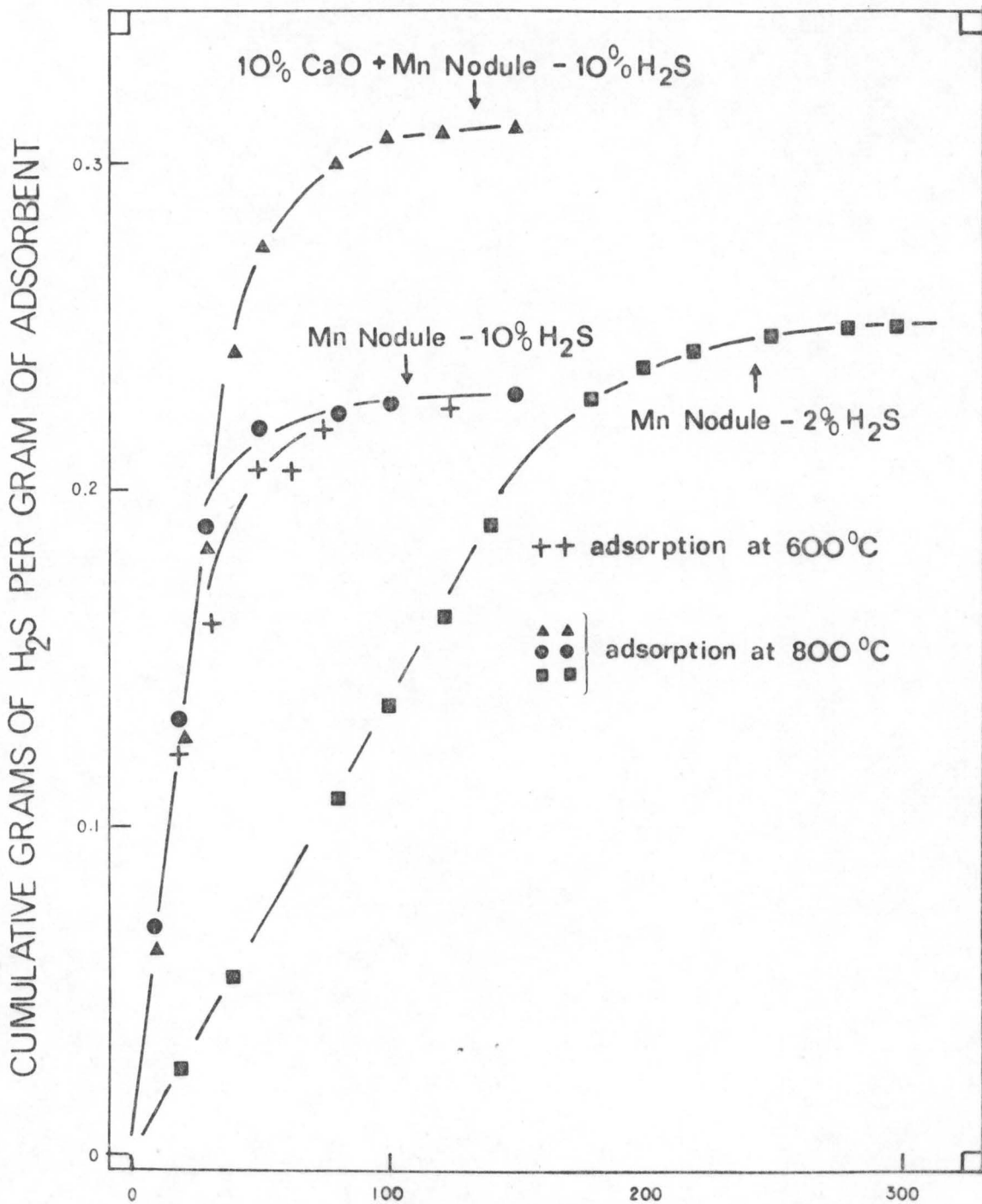


FIG.3 - TIME, min

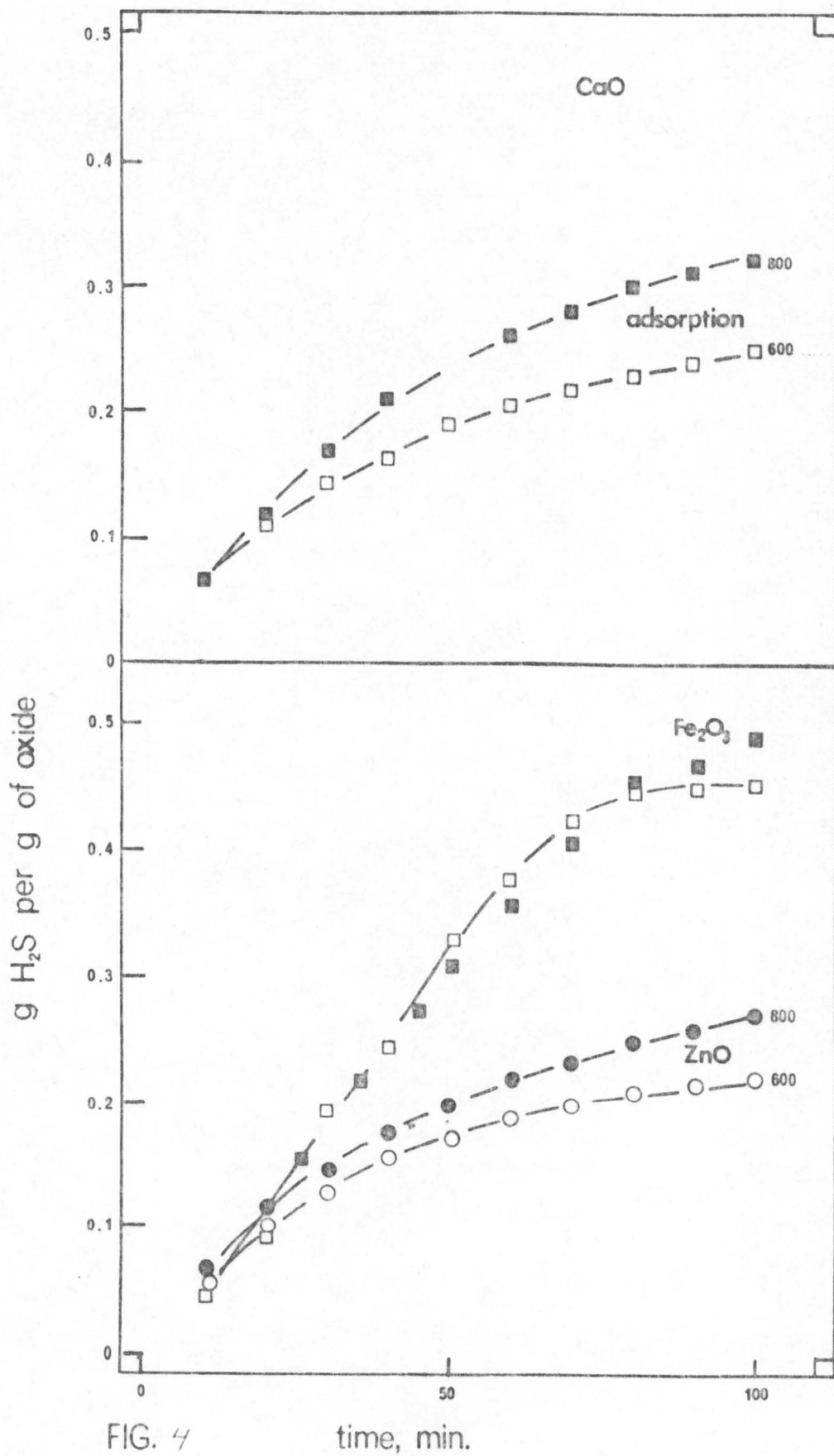


FIG. 4

time, min.

