CHAPTER 3

Adsorption and Absorption of $H_2S$

1 Introduction

The hydrogen sulfide that is removed by adsorption and/or absorption processes originates from a number of anthropogenic sources. These include sewerage and municipal waste gases, and refinery processing gas streams. The processing gas streams include those arising from hydrodesulfurisation of organosulfides and other hydrefining processes (see Chapter 2), and other refinery operations such as catalytic cracking and hydrocracking.

Catalytic cracking involves the breakdown of heavy oils into lighter fractions for processing into petrol and fine chemicals using a zeolite catalyst at a pressure of $ca. 0.2-0.3$ MPa and a temperature of $ca. 520-540 \degree C$.\textsuperscript{1} Hydrocracking combines hydrogenation and catalytic cracking. It is used for breaking down heavy gas and vacuum oils which contain large amounts of polycyclic aromatic hydrocarbons into lighter fractions such as jet fuel. The hydrogen minimises coking and thus deactivation by hydrogenating coke precursors which build up on the surface of the catalyst. A zeolite supported Ni-Mo catalyst can be used for hydrocracking, and the operating conditions are usually $ca. 200-400 \degree C$ at a hydrogen pressure of $1-10$ MPa, according to the feedstock used.\textsuperscript{1} Hydrogen sulfide is formed after cracking and hydrocracking by the breakdown of sulfur-containing molecules present in the oil feedstocks at the operating temperatures and pressures of the cracking plants.

The problem of removing hydrogen sulfide from the wide variety of feedstocks discussed above is complicated by the fact that hydrogen sulfide is not found in isolation. Thus, in sewerage and municipal waste gases it is accompanied by methane, whereas in refinery gases hydrogen sulfide is found together with methane, hydrogen and higher hydrocarbons, and traces of nitrogen-, oxygen- and metal-containing species which have not been completely removed during processing. Nevertheless, the reduction in concentration of hydrogen sulfide from percentage to ppm levels in these process streams is readily achieved. Routes to this include: absorption in liquids such as alkanolamine,
ammonia solution and alkaline salt solutions; and oxidation of \( \text{H}_2\text{S} \) using iron(III) oxide, activated carbon or a Claus process. These processes are described in this chapter. The challenging problem is to remove the last traces of \( \text{H}_2\text{S} \) from the process stream. This is important since, as stated in Chapter 1, a few ppm of sulfur can corrode pipelines, poison catalysts used in fuel processing and can ultimately be emitted into the atmosphere as acid rain. A number of materials have been identified that are effective at completely removing \( \text{H}_2\text{S} \) from feed streams at high temperatures, but the ultimate goal is to develop materials that can remove \( \text{H}_2\text{S} \) at room temperature. This has the advantage that the materials can be readily transported to the process stream, even if it is in an inaccessible location such as an oil platform, and plant operating costs are kept to a minimum. Materials developed for either high or low temperature removal of \( \text{H}_2\text{S} \) are described in Section 3. The high surface area materials used to remove gases such as \( \text{H}_2\text{S} \) from feedstocks are referred to as ‘sorbents’ since adsorption of the gas onto the surface of the solid is followed by absorption of the sulfur into the bulk of the solid. Thus, the removal of \( \text{H}_2\text{S} \) is generally a two-stage process, the sulfur level being reduced to 2–3 ppm by an absorption or oxidation step in the first stage, and then in the second stage the sulfur content of the feedstock is reduced effectively to zero by sorption using a high surface area active solid sorbent. Many of these sorbents are also effective at higher concentrations of \( \text{H}_2\text{S} \). Traces of organic sulfur compounds are left in feedstocks after processing and these compounds are much less chemically reactive than \( \text{H}_2\text{S} \) and are therefore only partially eliminated by some of the adsorption/absorption processes described below.

### 2 Absorption into a Liquid

When \( \text{H}_2\text{S} \) is absorbed in a liquid, it can either dissolve or react chemically. Liquids used for absorption include alkanolamines, aqueous ammonia, alkaline salt solutions and sodium and potassium carbonate solutions.\(^2\)

#### Absorption in Alkanolamine

Monoethanolamine, \( \text{HOCH}_2\text{CH}_2\text{NH}_2 \), is one of the most widely used alkanolamines for \( \text{H}_2\text{S} \) removal. The function of the hydroxyl group is to decrease the vapour pressure and increase the water solubility of the alkanolamine, and the amine group makes an aqueous solution of the compound basic so that it can neutralise acidic gases such as \( \text{H}_2\text{S} \). Monoethanolamine reacts with \( \text{H}_2\text{S} \) to form the amine sulfide and hydrosulfide,\(^1\) *i.e.*:

\[
2\text{HOCH}_2\text{CH}_2\text{NH}_2 + \text{H}_2\text{S} \rightleftharpoons (\text{HOCH}_2\text{CH}_2\text{NH}_3)_2\text{S} \tag{3.1}
\]

\[
(\text{HOCH}_2\text{CH}_2\text{NH}_3)_2\text{S} + \text{H}_2\text{S} \rightleftharpoons 2\text{HOCH}_2\text{CH}_2\text{NH}_3\text{HS} \tag{3.2}
\]

A schematic diagram of the plant used for \( \text{H}_2\text{S} \) absorption using an aqueous
solution of monoethanolamine is shown in Figure 3.1. The sulfur-containing feedstock stream is passed up through an absorber bed. The monoethanolamine solution flows countercurrently to the gas stream. Absorption columns contain either packing or trays in order to increase the interfacial contact and hence mass transfer between the wash solution and the gas stream. Packing can be either random or ordered, and one of the commonest types of packing material is the Raschig ring (Figure 3.2); this is widely used in monoethanolamine absorption towers. The packed column is usually cylindrical, and it contains a support plate for the packing material and a multi-exit distributor for dispensing the absorbent liquid onto the top of the packing. A schematic diagram of a packed absorption tower is shown in Figure 3.3. Alternatively, the packed column can contain trays and one of the most commonly used
types is the bubble cap. A schematic diagram of this is given in Figure 3.4. In the bubble cap absorber column, the absorber liquid cascades down the column in a series of layers whereas the feedstock vapour bubbles up through each of the layers. Mass transfer then takes place at the surfaces of the bubbles.
The monoethanolamine solution that collects at the bottom of the absorber bed is sulfur rich whereas the cleaned feedstock stream passing out of the top of the absorber contains only minute traces of sulfur. The used monoethanolamine solution passes next, via a heat exchanger, to the top of a stripping column (Figure 3.1). The role of the stripping column is to reverse the absorption operation by transferring the sulfur back into the gas phase, thus regenerating the clean monoethanolamine solution. The stripping column is often packed to aid mass transfer. The sulfur as \( \text{H}_2\text{S} \) is cooled to remove water vapour. The water vapour can then be fed back into the plant to prevent the ethanolamine solution from becoming too concentrated. \( \text{H}_2\text{S} \) can then be isolated for further processing. Heat is extracted from the clean monoethanolamine emerging from the bottom of the stripping column and used to heat the \( \text{H}_2\text{S} \)-rich monoethanolamine exiting the absorption column. The clean monoethanolamine is then cooled further by heat exchange with air or water and fed back into the top of the absorber, thus completing the unit operation. Absorption in Ammonia Solution

Alkanolamine processes are only really suitable for the purification of gas feedstocks that contain \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) as the only impurities. They cannot be used for the purification of coal gas, for example, which contains COS, \( \text{CS}_2 \), HCN, pyridine bases, thiophene, mercaptans, ammonia and traces of nitric oxide in addition to \( \text{CO}_2 \) and \( \text{H}_2\text{S} \) impurities, since the alkanolamine will either react with these impurities or form non-recoverable residues. \( \text{H}_2\text{S} \) can be removed from coal gas feedstocks by absorption in aqueous ammonia at room temperature using an absorption column similar to that described above for alkanolamine absorption. The reactions involved are:

\[
\text{NH}_3(\text{aq}) + \text{H}_2\text{S} \rightleftharpoons [\text{NH}_4]^+ + [\text{HS}]^- \quad (3.3)
\]
\[
2\text{NH}_3(\text{aq}) + \text{H}_2\text{S} \rightleftharpoons 2[\text{NH}_4]^+ + \text{S}^{2-} \quad (3.4)
\]

\( \text{H}_2\text{S} \) was generally found to be present as \([\text{HS}]^-\) ions in solution. The sulfide concentration (\( \text{S}^{2-} \)) was negligible except at very high pH (> 12). Absorption in Alkaline Salt Solutions

Alkaline salt solutions formed from sodium or potassium and a weak acid anion such as carbonate or phosphate have been used in regenerative \( \text{H}_2\text{S} \) removal. They can be used to absorb \( \text{H}_2\text{S}, \text{CO}_2 \) and other acid gases. The weak acid acts as a buffer, preventing the pH from changing too rapidly on absorption of the gases.

The Seaboard process was introduced in 1920 by the Koppers Company and was the first regenerative liquid process for \( \text{H}_2\text{S} \) removal which was developed for large scale industrial use. In this process, \( \text{H}_2\text{S} \) is absorbed at room
temperature into a solution of dilute sodium carbonate in an absorber column similar to the one described for monoethanolamine. The gas stream containing the H\textsubscript{2}S flows countercurrently to the sodium carbonate solution in the absorber column. The reaction can be represented as:

\[
\text{Na}_2\text{CO}_3 + \text{H}_2\text{S} \rightleftharpoons \text{NaHCO}_3 + \text{NaHS} \tag{3.5}
\]

The H\textsubscript{2}S is then regenerated in a separate column using a countercurrent flow of low pressure air. The regenerated H\textsubscript{2}S is oxidised by combustion to SO\textsubscript{2} and vented into the atmosphere. 85–95% of the H\textsubscript{2}S can be removed from the gas stream by this process. It has the advantage that it is simple and economical to operate, but the disposal of the extracted sulfide as sulfur dioxide is environmentally damaging. The oxidation step is also accompanied by further oxidation of some of the H\textsubscript{2}S to thiosulfate which is retained in the stripping column and hence contaminates recycled sodium carbonate, lowering its H\textsubscript{2}S absorption capacity. Any HCN which may be present in the feedstock, especially if it is coal gas, is also absorbed by the Na\textsubscript{2}CO\textsubscript{3} solution and is oxidised in air in the stripping column to NaSCN by reacting with NaHS, \textit{i.e.}:

\[
2\text{NaHS} + 2\text{HCN} + \text{O}_2 \rightarrow 2\text{NaSCN} + 2\text{H}_2\text{O} \tag{3.6}
\]

Koppers Company later developed a vacuum distillation process which allowed the H\textsubscript{2}S to be recovered rather than combusted by operating at low pressure and using steam as the stripping vapour.\textsuperscript{2}

A number of processes have also been developed for absorption at elevated temperature. One of these is the Benfield process.\textsuperscript{2} This process uses hot potassium carbonate and can remove 90% of the H\textsubscript{2}S from a feedstock and, to a lesser degree, carbonyl sulfide, carbon disulfide, and mercaptans. It can also be used to remove CO\textsubscript{2}, SO\textsubscript{2} and HCN. The Benfield process is still used today, and there are several hundred plants located throughout the world. The reactions involved are:

\[
\text{K}_2\text{CO}_3 + \text{H}_2\text{S} \rightleftharpoons \text{KHCO}_3 + \text{KHS} \tag{3.7}
\]

\[
2\text{KHCO}_3 \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} + \text{K}_2\text{CO}_3 \tag{3.8}
\]

It is essential to have some CO\textsubscript{2} in the gas stream to prevent the KHS from being converted to K\textsubscript{2}S which is non-regenerable, \textit{i.e.}:

\[
2\text{KHS} \rightleftharpoons \text{K}_2\text{S} + \text{H}_2\text{S} \tag{3.9}
\]

Carbonyl sulfide present in the feedstock is readily hydrolysed to H\textsubscript{2}S and CO\textsubscript{2}:

\[
\text{COS} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2\text{S} \tag{3.10}
\]
Carbon disulfide is first hydrolysed to carbonyl sulfide:

\[ \text{CS}_2 + \text{H}_2\text{O} \rightleftharpoons \text{COS} + \text{H}_2\text{S} \quad (3.11) \]

and then further hydrolysed as in equation 3.10. The two stage hydrolysis makes carbon disulfide removal considerably less efficient than that of carbonyl sulfide.\(^2\) The Benfield process has been modified further in recent years and it has been reported that it can reduce \(\text{H}_2\text{S}\) levels in the exit gas to \(< 1\) ppm. This is accomplished by using two hot \(\text{K}_2\text{CO}_3\) solutions of different concentrations and carrying out the purification step in two stages.

### 3 Removal of \(\text{H}_2\text{S}\) by Oxidation

#### Claus Process

The Claus process is used to recover sulfur from feedstocks containing high concentrations (ca. 1–4 wt%) of \(\text{H}_2\text{S}\). In this reaction, some of the \(\text{H}_2\text{S}\) is oxidised in air to \(\text{SO}_2\) at ca. 550 °C.

\[ \text{H}_2\text{S} + 1.5\text{O}_2 \rightleftharpoons \text{H}_2\text{O} + \text{SO}_2 \quad (3.12) \]

The remaining \(\text{H}_2\text{S}\) then reacts with the \(\text{SO}_2\) at ca. 400 °C over an alumina catalyst forming sulfur.

\[ 2\text{H}_2\text{S} + \text{SO}_2 \rightleftharpoons 3\downarrow + 2\text{H}_2\text{O} \quad (3.13) \]

This method cannot be used to reduce the sulfur content of gas feedstocks to ppm levels as equation 3.13 is equilibrium limited.\(^2\) Further complications arise from the reaction of \(\text{H}_2\text{S}\) with \(\text{CO}_2\) present in the feedstock which form COS and \(\text{CS}_2\) in the high temperature oxidation stage of the process. The alumina catalyst slowly becomes deactivated by deposition of carbonaceous material from hydrocarbons present in the feedstock and sulfate formed by overoxidation of \(\text{H}_2\text{S}\). The catalyst can be regenerated by oxidising these carbonaceous deposits.\(^2\)

#### Superclaus Process

A recent extension of the Claus process is the development of the Superclaus process.\(^4\) The bulk of the \(\text{H}_2\text{S}\) is removed in a conventional Claus process, then the remainder is removed by selective oxidation in oxygen to sulfur on a catalyst comprised of a mixture of iron and chromium oxides supported on \(\alpha\)-\(\text{Al}_2\text{O}_3\). The alumina support has a low surface area and wide pores. The catalyst prevents overoxidation of the sulfur to \(\text{SO}_2\), it is insensitive to high water vapour concentration and excess \(\text{O}_2\), and it is highly selective for \(\text{H}_2\text{S}\) oxidation (other compounds in the process gas such as COS, \(\text{CS}_2\), \(\text{H}_2\) and CO are not oxidised). In this manner, this process can be used to increase sulfur recovery to > 99%.
Iron Oxide Process

This process was introduced in England in the 19th century, and is used in coal gas purification. \(^2,5,6\) \(\text{H}_2\text{S}\) is allowed to react with hydrated iron(III) oxide at room temperature, to form hydrated iron(III) sulfide. The absorbent is exposed to air whereupon the sulfide is oxidised to elemental sulfur and ferric oxide is reformd. The regenerated oxide can then be reused to react with more \(\text{H}_2\text{S}\). After several sulfiding/oxidation cycles the iron oxide becomes deactivated due to the surface becoming covered with elemental sulfur and the material must be discarded. The deposited sulfur can either be burned to \(\text{SO}_2\) and used for sulfuric acid manufacture, or recovered by solvent extraction and recrystallisation. The reaction takes place at ca. 55°C under alkaline conditions since the hydrated ferric sulfide loses its water of crystallisation and is converted to \(\text{FeS}_2\) and \(\text{Fe}_8\text{S}_9\) in acid or neutral conditions. \(\text{FeS}_2\) and \(\text{Fe}_8\text{S}_9\) are converted to iron(II) sulfate and polysulfides so that the hydrated iron(III) oxide cannot then be regenerated.

The hydrated iron(III) oxide is either used unsupported, supported on wood shavings, or as natural bog ore which is comprised of hydrated iron oxide combined with peat. Sodium hydroxide is added to maintain the alkalinity.

An extension of this process is the use of iron oxide suspensions in aqueous \(\text{Na}_2\text{CO}_3\) in which the \(\text{H}_2\text{S}\) reacts with \(\text{Na}_2\text{CO}_3\) at room temperature. \(^2\) The sodium hydrogensulfide and sodium hydrogencarbonate formed in this process react with hydrated iron(III) oxide to form the sulfide.

\[
\text{H}_2\text{S} + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{NaHS} + \text{NaHCO}_3 \tag{3.14}
\]

\[
\text{Fe}_2\text{O}_3\cdot3\text{H}_2\text{O} + 3\text{NaHS} + 3\text{NaHCO}_3 \rightleftharpoons \text{Fe}_2\text{S}_2\cdot3\text{H}_2\text{O} + 3\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O} \tag{3.15}
\]

The hydrated iron oxide can be regenerated by oxidation.

\[
2\text{Fe}_2\text{S}_3\cdot3\text{H}_2\text{O} + 3\text{O}_2 \rightleftharpoons 2\text{Fe}_2\text{O}_3\cdot3\text{H}_2\text{O} + 6\text{S} \tag{3.16}
\]

Most of the sulfide is precipitated out as elemental sulfur, but some is further oxidised to thiosulfate.

Activated Carbon Process

This process uses activated carbon as a catalyst to promote the oxidation of \(\text{H}_2\text{S}\) to sulfur at ambient temperatures. \(^2\) The sulfur can then be extracted using ammonium sulfide and the carbon reused. It has a limited lifetime, however, due to the deposition of tar and polymeric materials on the surfaces of the carbon particles.
4 Removal of \( \text{H}_2\text{S} \) and Other Sulfur Compounds Using Solid Sorbents

High Temperature Sorbents

Most of the work carried out to date on the development of absorbents for \( \text{H}_2\text{S} \) removal has been on materials that are used at temperatures in excess of 300 °C. Westmoreland and Harrison investigated the thermodynamic feasibility of using various metal oxides for the desulphurisation of gas feedstocks and identified the oxides of Fe, Mo, Zn, Mn, Ca, Ba, Sr, Cu, W, Co and V as being suitable for desulphurisation when used at temperatures greater than 300 °C.\(^7\) Westmoreland \textit{et al.} also studied the initial rates of reaction between \( \text{H}_2\text{S} \) and \( \text{MnO} \), \( \text{CaO} \), \( \text{ZnO} \) and \( \text{V}_2\text{O}_3 \) over the temperature range 300–800 °C using a thermobalance reactor.\(^8\) The hydrogen sulfide concentration in the feed was varied from 1.9 to 7.0% by volume. All the reactions were first order with respect to \( \text{H}_2\text{S} \) and obeyed the Arrhenius equation. Further studies were then carried out with single pellets of \( \text{ZnO} \) and 1–4 mol\% \( \text{H}_2\text{S} \) in which sulfidation was allowed to proceed to completion.\(^9\) Under these conditions mass transfer and diffusion effects would be observed in addition to adsorption and absorption, whereas mass transfer effects were unimportant in measurements of the initial rates carried out previously. The reaction was rapid and went to completion over the temperature range 600–700 °C.

High temperature \( \text{H}_2\text{S} \) absorption studies have also been carried out using zinc titanate.\(^10\) The rate of formation of sulfide and saturation coverage of sulfide on \( \text{ZnO} \) and zinc titanate were similar at 720 °C, but the sulfide coverage on \( \text{TiO}_2 \) was much lower. Jalan’s group studied the initial rate of sulfidation of \( \text{ZnO} \) at 650 °C and found that the uptake was low.\(^11,12\) He attributed this to pore blocking and sintering of the \( \text{ZnO} \) at this reaction temperature. The \( \text{ZnO} \) could be regenerated using a mixture of steam and air at 650 °C but the pore structure was damaged by this treatment. Yumuru and Furimsky looked at the reaction of \( \text{H}_2\text{S} \) with iron(III) oxide, calcium oxide and zinc oxide over the temperature range 600–800 °C.\(^13\) A feed gas of 10% \( \text{H}_2\text{S} \) in nitrogen was used, and \( \text{H}_2\text{S} \), \( \text{H}_2 \) and \( \text{SO}_2 \) concentrations exiting from the sorbent bed were determined with respect to time. The sulfur uptake/gram of sorbent at 600 and 700 °C followed the sequence \( \text{Fe}_2\text{O}_3 > \text{CaO} > \text{ZnO} \), whereas the sulfur uptake per unit surface area followed the order \( \text{ZnO} > \text{Fe}_2\text{O}_3 > \text{CaO} \). Each oxide interacted with \( \text{H}_2\text{S} \) differently. \( \text{H}_2\text{S} \) decomposed during adsorption as well as reacting to form the sulfide in the case of \( \text{CaO} \), indicating that the decomposition of \( \text{H}_2\text{S} \) may be catalysed by \( \text{CaO} \). The predominant reaction of \( \text{H}_2\text{S} \) with \( \text{ZnO} \) was the formation of \( \text{ZnS} \), but some decomposition was observed as the reaction proceeded, indicating that in this case \( \text{ZnS} \) may catalyse the decomposition of \( \text{H}_2\text{S} \). Sulfur dioxide was detected in the exit gas in the early stages of the reaction of \( \text{Fe}_2\text{O}_3 \) with \( \text{H}_2\text{S} \). A redox reaction route was proposed in which the iron(III) oxide was converted to iron(II) oxide.
The removal of $\text{H}_2\text{S}$ by decomposition has also been described using bimetallic supported ruthenium catalysts.\footnote{14} The catalysed decomposition was carried out in a fluidised bed reactor over the temperature range 610–730°C and at a pressure of 160 kPa. The best catalyst was comprised of 0.5% MoS$_2$/0.5% RuS$_2$/γ-Al$_2$O$_3$. This was a very clean reaction, as the sulfur was recovered for sale, and the hydrogen could be recycled for use in hydrodesulfurisation or other hydrotreating processes.

**Low Temperature Sorbents**

Comparatively little work has been carried out on sorbents for low temperature desulfurisation. The main advantage of removing $\text{H}_2\text{S}$ at low temperatures is that processing costs are substantially reduced. The use of hydrated iron oxides for $\text{H}_2\text{S}$ removal at ambient temperatures has already been discussed (see iron oxide process). These absorbents are extremely efficient, but iron sulfide is pyrophoric in air and has therefore recently been replaced by zinc oxides in Europe.\footnote{15,16} ZnO absorbs $\text{H}_2\text{S}$ stoichiometrically at 350°C, but the rate of reaction decreases rapidly as the temperature is lowered. The rate of reaction is strongly dependent on the morphology as well as the metal oxide used, and this has been demonstrated by the recent development of a high surface area ZnO with an improved $\text{H}_2\text{S}$ uptake.\footnote{17}

Stirling et al.\footnote{18} investigated the initial rate of reaction of $\text{H}_2\text{S}$ with ZnO and ZnO doped with ca. 5 wt% CuO, Fe$_2$O$_3$ or Co$_3$O$_4$. The doped materials were prepared by one of two routes: (i) impregnation of ZnO with copper(II), iron(III) or cobalt(II) nitrate salts; (ii) precipitation of the zinc oxide or doped zinc oxides from their nitrate salts with base. These precursors to the oxides were then calcined at 350°C for 16 hours to form the oxides. The extent of reaction (calculated from the ratio of the number of moles of $\text{H}_2\text{S}$ absorbed to the number of moles of $\text{H}_2\text{S}$ required for complete conversion of the oxide to sulfide) was higher for all the absorbents prepared by a precipitation route and this could at least partly be attributed to the fact that higher surface areas were obtained for the materials prepared by the precipitation rather than the impregnation route. The best absorbent was the 5 wt% CuO/ZnO prepared by the precipitation route. The $\text{H}_2\text{S}$ absorption was found to be proportional to surface area, and it was concluded that the main role of the dopant was to increase the surface area of the zinc oxide.

\[
\text{H}_2\text{S} \rightarrow \text{H}_2 + \frac{1}{2}\text{S}_2 \tag{3.17}
\]
\[
2\text{Fe}_2\text{O}_3 + \text{H}_2\text{S} \rightarrow 4\text{FeO} + \text{H}_2 + \text{SO}_2 \tag{3.18}
\]
\[
2\text{Fe}_2\text{O}_3 + \frac{1}{2}\text{S}_2 \rightarrow 4\text{FeO} + \text{SO}_2 \tag{3.19}
\]
\[
\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{FeO} + \text{H}_2\text{O} \tag{3.20}
\]
Davidson, Lawrie and Sohail studied the rates of reaction of H$_2$S in nitrogen over the concentration range 0.05–0.8% H$_2$S in N$_2$ with ZnO and a series of doped zinc oxides at temperatures of 0–45°C.\textsuperscript{19} The initial rates varied considerably, and this could be attributed to differences in the morphology of the ZnO particles induced by doping. They identified three stages for the reaction of H$_2$S with the ZnO and doped zinc oxides. In the first stage, the rate of reaction was fast. The H$_2$S diffused to the ZnO surface and reacted to form a surface sulfide and water. A second fast reaction stage then occurred in which the rate of reaction was controlled by the diffusion of water out of the pellet. During this process, water was adsorbed and desorbed continuously within the body of the solid. At high conversions, a pseudo steady state conversion of the oxide was established. This proceeded at a slower rate and was thought to involve the diffusion of Zn$^{2+}$ to the surface to react with the sulfide and H$^+$ from the adsorbed H$_2$S to hydroxylated zinc oxide forming water.\textsuperscript{20} The hydroxylated surface was formed by a hydration step preceding H$_2$S adsorption at the pseudo steady state conversion. It was thought that this cation diffusion mechanism was more likely to occur than the transport of bulk ZnO to the reaction interface which would be difficult at the low temperatures at which this reaction was studied. The reaction was strongly promoted by water and independent of zinc oxide conversion and H$_2$S partial pressure at pseudo steady state conversion.

A series of mixed Co/Zn oxides have been prepared by a precipitation route and used to measure the initial rates of absorption of H$_2$S from a 2% H$_2$S in nitrogen feedstock at 30°C.\textsuperscript{21,22} The H$_2$S absorption capacity was found to increase with increase in cobalt concentration, with the reaction being virtually stoichiometric when pure Co$_3$O$_4$ was used. Cognion\textsuperscript{23} used a 5% CuO/ZnO absorbent over the temperature range 200–370°C for the desulphurisation of a feedstock containing H$_2$S and some organosulfides. The copper was found to absorb H$_2$S and, in the presence of hydrogen, it hydrogenated some sulfur compounds. The copper also acted as a promoter for ZnO, enabling it to remove less active organosulfides such as CS$_2$ by exchange reactions, \textit{i.e.}:

\[
\text{CS}_2 + 2\text{ZnO} \rightarrow \text{CO}_2 + 2\text{ZnS} \tag{3.21}
\]

Holliman \textit{et al.} synthesised feroxyhyte ($\delta$-FeOOH) and used it to measure the initial rate of H$_2$S uptake from 2% H$_2$S/N$_2$.\textsuperscript{24} 80% of the feroxyhyte was converted to iron(II) sulfide. On initially exposing the sample to air at room temperature, an amorphous hydrated iron oxide species formed and the sulfide was oxidised to sulfur. After several days, the amorphous oxide recrystallised as goethite ($\alpha$-FeOOH).

A method has been developed for the simultaneous removal of COS and H$_2$S from coke oven gas.\textsuperscript{25} $\alpha$-FeOOH is partially dehydrated at \textit{ca.} 200°C and then used for desulphurisation at 40–60°C in a stream of 50–100 ppm of H$_2$S and/or 50–100 ppm of COS. The COS is hydrolysed to H$_2$S and this is stabilised as iron sulfide on the surface of the iron oxide:

\[
\text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2 \tag{3.22}
\]
Two active sites were identified in the partially dehydrated $\alpha$-FeOOH:\(^{25}\)
(i) Fe$_2$O$_3$ which was active for H$_2$S absorption; and (ii) Fe$_2$O$_3$$\cdot$H$_2$O which was active for COS hydrolysis and H$_2$S absorption. H$_2$S formed from the hydrolysis of COS and H$_2$S present in the feedstock would then react with Fe$_2$O$_3$$\cdot$H$_2$O:

$$\text{Fe}_2\text{O}_3\cdot\text{xH}_2\text{O} + 3\text{H}_2\text{S} \rightarrow \text{Fe}_2\text{S}_3 + (3+x)\text{H}_2\text{O} \quad (3.23)$$

H$_2$S would also react at the Fe$_2$O$_3$ site:

$$\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow 2\text{FeS} + 3\text{H}_2\text{O} + \text{S} \quad (3.24)$$

The main reaction occurring at this site would however be:

$$\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow \text{Fe}_2\text{S}_3 + 3\text{H}_2\text{O} \quad (3.25)$$

A different approach to low temperature H$_2$S removal is to use an adsorbent to 'concentrate' the H$_2$S and then to desorb and combust it.\(^{26}\) A zeolite molecular sieve 13X was found to be effective in removing H$_2$S from a feedstream of 10 ppm H$_2$S in helium at 25°C. Activated carbon was found to be a better adsorbent if the feedstream also contained 0.9% water. The adsorbed sulfide was then oxidised to sulfur in the presence of oxygen. Low temperature (25°C) oxidation over the activated carbon can be carried out in the presence of oxygen provided that only small amounts of H$_2$S are involved and that the feedstream contains some moisture. The reaction was thought to take place in the water that had condensed in the pores. It was proposed that the H$_2$S, present as HS$^-$ in solution in the pores, would be oxidised to sulfur using dissociatively adsorbed oxygen on the carbon. In the absence of moisture and/or at high concentrations of H$_2$S, the sulfide can be oxidised over the temperature range 150–250°C to SO$_2$ and SO$_3$ using a monolith supported platinum or palladium catalyst. These high temperature oxidation experiments were carried out using a feed gas of 1.8% methane, 21% oxygen, 20 ppm H$_2$S and the balance as nitrogen in order to simulate emissions from sewerage gases which contain methane. The methane would not be oxidised at these temperatures, but it is important to study the interaction of H$_2$S with sorbents and catalysts in the presence of all the gases likely to be present in a feedstock in order to obtain a realistic assessment of sorption capacity/reactivity in industrial conditions. With the continuing worldwide interest in emission control, it is likely that this will be a fruitful area of research for many years to come.

5 Conclusions

Although much progress has been made in the development of sorbents that can remove H$_2$S at low temperatures (and indeed attention is now also focusing on the interactions of gases in these materials), the mechanisms for the low temperature diffusion of ions through the solids are still poorly understood and differ for many of the sorbents studied. Generally, sorption is accompanied
by reaction with the conversion, for example, of a metal oxide to a metal sulfide and water.

In broad terms, the interaction of adsorbed $\text{H}_2\text{S}$ with the solid can proceed by either a pore or a lattice diffusion mechanism. $\text{H}_2\text{S}$ is dissociatively adsorbed on the surface of the solid, forming $\text{H}^+$ and $\text{HS}^-$. If pore diffusion predominates, the sorption capacity will be limited by the rate of diffusion of $\text{HS}^-$ to fresh surface (oxide) sites in the pores. Pore size and pore accessibility as the reaction proceeds will therefore be important. Pore diffusion is likely to be rate limiting if the sorbent particles are large (ca. 2.5–3.5 mm) since it will take longer for the $\text{H}_2\text{S}$ to diffuse into the centre of a particle. Pore diffusion has been found to be rate limiting in high temperature studies of the reaction of $\text{H}_2\text{S}$ with zinc oxide.\( \text{9} \)

In lattice diffusion, $\text{HS}^-$ will react with oxide at the surface to form a surface sulfide and water. The reaction can then be controlled by one or more diffusion routes. The oxide from the bulk of the lattice can replenish the depleted surface oxide and water can diffuse to the surface, and/or $\text{HS}^-$ can diffuse into the oxide lattice. The reaction will cease either when all the oxide has reacted or when an inert sulfide shell forms which limits the diffusion process. In reality, bulk diffusion of anions is unlikely at the low temperatures used in these studies and surface reconstruction may occur on reaction. Thus, measurements of the reaction of $\text{H}_2\text{S}$ (0.05–0.8% in $\text{N}_2$) with $\text{ZnO}$ over the temperature range 0–45 °C taken when the reaction was operating at pseudo steady state conversion, indicated that a water promoted cation diffusion mechanism operated at these low temperatures\( \text{19} \) (see previous discussion of low temperature sorbents). The occurrence of reconstruction on reaction is illustrated by the studies of the initial rates of reaction of $\text{H}_2\text{S}$ with the mixed $\text{Co}_3\text{O}_4$/ZnO materials discussed there. Reconstruction and oxide segregation occurred in these mixed oxide materials when they were used as sorbents for $\text{H}_2\text{S}$.\( \text{22} \) The spinel $\text{ZnCo}_2\text{O}_4$, which was present at the surface of these mixed oxides, oxidised the $\text{H}_2\text{S}$ to sulfur. Both $\text{Co(II)}$ and $\text{Co(III)}$ were detected at the surface by XPS after sulfidation whereas only $\text{Co(III)}$ was present initially (i.e. in the surface spinel $\text{ZnCo}_2\text{O}_4$). It was proposed that the oxides segregated in the presence of $\text{H}_2\text{S}$ and were then sulfided. The following equations are consistent with the observed XPS data:

\[
\begin{align*}
3\text{ZnCo}_2\text{O}_4 + \text{H}_2\text{S} &\rightarrow 3\text{ZnO} + 2\text{Co}_3\text{O}_4 + \text{H}_2\text{O} + \text{S} \\
\text{Co}_3\text{O}_4 + \text{H}_2\text{S} &\rightarrow 3\text{CoO} + \text{H}_2\text{O} + \text{S} \\
\text{CoO} + \text{H}_2\text{S} &\rightarrow \text{CoS} + \text{H}_2\text{O} \\
\text{ZnO} + \text{H}_2\text{S} &\rightarrow \text{ZnS} + \text{H}_2\text{O}
\end{align*}
\] (3.26) (3.27) (3.28) (3.29)

Interestingly, analysis of the sulfided samples by transmission electron microscopy revealed the presence of microcrystalline membraneous sheets which linked the particles together. Micrographs of the oxides before and after sulfidating are shown in Figure 5.14 (see Chapter 5). The sheets contained cobalt, zinc and sulfur and analysis by electron energy loss spectroscopy
(EELS) showed that they were zinc rich. The surface segregation and formation of the membraneous sheets was attributed to surface reconstruction occurring on sulfiding the mixed oxides.

Several theoretical models have been proposed for the reaction of solids with gases. The two most common models are the shrinking core and the grain model. The shrinking core model assumes that the $\text{H}_2\text{S}$ diffuses through a gas film which surrounds a spherical particle of sorbent to the oxide surface where it reacts. The oxide 'core' then shrinks as the reaction proceeds. The $\text{H}_2\text{S}$ must continually diffuse through the sulfided sorbent to unreacted oxide. The rate-controlling step could be the diffusion of $\text{H}_2\text{S}$ through the gas film, the diffusion of $\text{H}_2\text{S}$ through the sulfided sorbent or the reaction of $\text{H}_2\text{S}$ with the oxide at the sulfide/oxide interface, but it is generally found that the gas film does not offer much resistance to mass transfer and so one of the latter two steps are rate limiting. The grain model more effectively represents the sulfidation reaction and has been used to model the kinetics of the reaction of $\text{H}_2\text{S}$ with $\text{ZnO}$ and zinc ferrites at high temperatures. In the grain model, it has been assumed that each sorbent particle is spherical and that it contains cylindrical pores. The diffusion of the $\text{H}_2\text{S}$ through the pores of the particle was assumed to be much greater than that through the sulfide film which formed at the reaction interface. The reaction takes place at the sulfide/oxide interface and is assumed to be first order. The model allows the surface area, porosity and diffusion coefficients to be varied during the sulfidation process so that it is in accord with changes in the material as the reaction proceeds. The grain model correctly predicted the observed changes in concentration of $\text{H}_2\text{S}$ with respect to time for the reaction of $\text{H}_2\text{S}$ with zinc ferrites at $540^\circ\text{C}$ and for the reaction of $\text{H}_2\text{S}$ with $\text{ZnO}$ over the temperature range $600-700^\circ\text{C}$. Sorption kinetics are discussed in more detail in Chapter 7.

6 References

7 P.R. Westmoreland and D.P. Harrison, Environ. Sci. Technol., 1976, 10(7), 659.