STELLINGEN

behorende bij het proefschrift

Development of a high temperature steam regenerative H₂S removal process based on alumina supported MnO and FeO

van

J.P. Wakker

In tegenstelling tot datgene wat in veel amerikaanse literatuur vermeld wordt, heeft zinkferriet als acceptor voor hoge temperatuur regeneratieve H₂S verwijdering een beperkte toepasbaarheid.

Hoofdstuk 1 van dit proefschrift

Het vervangen van CFK's door andere middelen dringt weliswaar de snelheid van de afbraak van de ozonlaag terug, maar verhoogt het broeikaseffect.

Het gebruik van schoonmaakmiddelen op natuurlijke basis leidt niet per definitie tot een lagere milieubelasting dan bij het gebruik van synthetische schoonmaakmiddelen.

Het beleid van de overheid dat het gebruik en de ontwikkeling van verven en lakken op waterbasis stimuleert, heeft tot gevolg dat er een aanzienlijk sterkere milieubelasting optreedt dan het geval zou zijn bij het gebruik van verven en lakken op alkyd basis.

Roken zou, gezien de overlast die rokers bij niet-rokers veroorzaken, verboden of alleen op speciale "rookplaatsen" toegelaten moeten worden.
Het in toenemende mate beschikbaar stellen van een bedrijfs- of lease-auto aan werknemers draagt in grote mate bij aan een roekelozer rijgedrag.

Uit het oogpunt van de verkeersveiligheid voor fietser is het niet raadzaam om de geluidsoverlast van stadsbussen te verminderen.

Het argument van het beroepsgoederenvervoer dat invoering van een snelheidsbegrenzer gevaarlijk is omdat de bestuurders de snelheid niet verder zullen kunnen opvoeren in gevallen dat de verkeersveiligheid dat vereist, kan eenvoudig weerlegd worden met de constatering dat dit in de meeste gevallen ook nu reeds onmogelijk is.

De aanschaf en inzet van extra materiaal voor snelheidscontroles zal resulteren in een rustiger verkeersbeeld en een geringere uitstoot van schadelijke stoffen. Tevens zullen rijk en/of gemeentes met het geld dat van de boetes resteert de verkeerseduikatie kunnen verbeteren.

Een uitgebreide dimensie-controle voorkomt fouten bij het opstellen en uitwerken van massa-, impuls- en energiebalansen. De eenheden dienen daarbij nauwkeurig omschreven te worden: ε dimensieloos noemen is ernstig fout, terwijl $m^3/m^3$ verwerpelijk en alleen $m^3_{gast}/m^3_{reactor}$ juist is.

Veel van de technieken die beschikbaar zijn om katalysatoren te karakteriseren hebben een beperkte toepasbaarheid omdat meestal niet onder reaktieomstandigheden gemeten kan worden, of tussen de metingen door geen in-situ reacties uitgevoerd kunnen worden.

De samenhang tussen de factoren die van invloed zijn op het broeikaseffekt wordt nog niet goed begrepen.
In de systeemstudie hoge temperatuur gasreiniging bij KV-STEg-installaties wordt in de conclusie gesteld dat hoge temperatuur gasreiniging, ondanks de rendements winst ten opzichte van conventionele KV-STEg-installaties, niet zonder meer leidt tot lagere kWh kosten. Hierbij wordt ten onrechte voorbij gegaan aan de door het hogere rendement lagere CO₂ uitstoot.


Het invoeren van colleges in blokvorm met aansluitend het tentamen zal bij gelijkblijvende inhoud de studieduur drastisch verkorten.

Alle ambtenaren zouden in plaats van een reiskostenvergoeding voor het woon-werk verkeer een abonnement op het openbaar vervoer uitgereikt moeten krijgen, gekoppeld aan het af te leggen traject woning-werk.

Het feit dat de minister van Economische Zaken het aanbod van Texaco om een elektriciteitscentrale op basis van kolvenvergassing te bouwen in plaats van een gewone kolengestookte centrale heeft afgewezen is in het kader van het huidige milieubewustzijn te verwerpen.
Development of a high temperature steam regenerative H₂S removal process based on alumina supported MnO and FeO

Proefschrift

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Summary and main conclusions

The aim of this study was to develop a process that removes H$_2$S and COS at high temperatures (675 - 1075 K) from fuel gases produced by a coal gasifier. These fuel gases can be used for the production of electricity in a combined cycle power plant, or as a synthesis gas for the production of substitute natural gas (SNG) or chemicals.

The overview of literature on H$_2$S removal (as presented in chapter 1) showed that a number of low temperature H$_2$S removal processes have been developed and used. High temperature processes are in the development stage, but not applied yet. The main attention is concentrated on the development of zinc ferrite, zinc titanate, the mixed metal oxide process and iron oxide on silica. The disadvantages of these processes are the oxidative regeneration and the inevitable H$_2$ consumption. The low stability in highly reducing gases limits the applicability in case of zinc ferrite and zinc titanate. The process described in this thesis can overcome these disadvantages.

In the process discussed in this thesis MnO/γ-Al$_2$O$_3$ reacts with H$_2$S and forms MnS/γ-Al$_2$O$_3$ and H$_2$O. The sulfided material is regenerated with a gas containing steam at the same temperature and pressure. The regeneration off-gas with a high H$_2$S concentration can be used as a feed for a Claus plant to produce elemental sulfur.

Chapter 2 describes the preparation of acceptors with different preparation techniques. Both coprecipitation and sol-gel precipitation do not result in good acceptor materials. The greatest part of the manganese is present as irregenerable manganese crystallites. Pore volume impregnation results in acceptors with the highest capacity and stability. The use of a monolith as a carrier resulted in an acceptor with a high capacity, but has to be investigated further.

Characterization of acceptors prepared by pore volume impregnation (chapter 3) showed that three types of manganese can be distinguished. The first type consists of very reactive but irregenerable manganese oxide crystallites, which can be sulfided only once. The second type is surface MnAl$_2$O$_4$ spinel which can be sulfided and regenerated easily, while the third type is a MnAl$_2$O$_4$ spinel of which the rate of sulfidation and regeneration is limited by the diffusion of Mn$^{2+}$-ions in the γ-Al$_2$O$_3$ support.

Chapter 4 describes the influence of the raw fuel gas composition, temperature
and pressure on the sulfidation behaviour of MnO or FeO on γ-Al₂O₃ acceptors. After an initial deactivation the acceptors can be used over 400 sulfidation-regeneration cycles. Water adversely affects the capacity, whereas CO favours the capacity due to the shift reaction. An increasing pressure does not influence the sulfidation behaviour. Trace compounds can influence the capacity negatively as e.g. HCl, whereas hydrocarbons not influence acceptor performance.

Regeneration of sulfided MnO/γ-Al₂O₃ acceptors is studied in chapter 5. To obtain a regeneration off-gas with a H₂S concentration high enough to be used as feed for a Claus plant (C₁₂S > 15 %v), a regeneration feed gas with a high steam concentration (> 50 %v) must be used. To minimize steam consumption, a relative long residence time (> 1 s) should be applied. Due to the long residence time the regeneration time increases as well, but it is in all cases shorter than the sulfidation time.

During gasification of coal H₂S, COS and other impurities are formed. Using a 200 kWₜₜermal coal gasification plant at ECN Petten the acceptors have been tested under realistic conditions in a bench scale unit (chapter 6). In this way not only the effect of upscaling but also the effect of other impurities in the gas on sulfidation and regeneration behaviour could be studied. The breakthrough capacity was about 0.35 %w S for Mn containing and about 0.20 for Fe containing acceptors. No deactivation was observed during four weeks of continuous sulfidation-regeneration cycles. A regeneration off-gas with high H₂S concentrations (up to 60 %v) was obtained. Used acceptors have been analysed for sulfur capture capacity and contaminants. The distribution of contaminants in the experimental system (coal gasifier and bench scale unit) has been investigated as well.

Chapter 7 presents a mathematical model to describe experimental breakthrough and regeneration curves quantitatively. Diffusion limitation was not observed. The model is based on the kinetics of the reactions taking place on the acceptor surface, viz. a fast sulfur-oxygen exchange reaction between H₂S and manganese oxide, a slow sulfur-oxygen exchange reaction in which sub-surface Mn-ions react, competitive Langmuir adsorption of H₂S, H₂O and CO on the acceptor surface, the water gas shift reaction, COS formation and reaction of the acceptor with COS. Breakthrough curves of different acceptors during sulfidation can be described. The regeneration behaviour of the acceptor is also predicted correctly. However, according to the model the regeneration
proceeds faster and results in a higher H₂S concentration than was measured. The
difference can be explained by side-effects induced by the experimental set-up, in
particular the tubing between the reactor and the analysis system and, to a lesser degree,
by the analysis section itself. The effects induced by the tubing can be incorporated easily
in the model by introducing empty ideally mixed tanks in series.

In chapter 8 advantages and disadvantages of some process schemes for high
temperature regenerative H₂S removal are presented. A process in which the acceptor
is transported from desulfurization reactor to regenerator and back, and which produces
gases with a constant composition seems to be the most advantageous design. Especially
a moving-bed concept should give good results as no mixing of the acceptor bed and
bypassing of acceptor particles by bubbles occurs.

In appendix A a brief economic evaluation is made for a 600 MWₑₑ power plant
based on Shell coal gasification technology. Costs of desulfurization are about Dfl 0.0012
per kWh.
Samenvatting en voornaamste conclusies

Het doel van deze studie was het ontwikkelen van een proces dat bij hoge temperatuur (675 - 1075 K) \( \text{H}_2\text{S} \) en COS kan verwijderen uit stookgassen die door een kolenvergasser geproduceerd worden. Deze stookgassen kunnen gebruikt worden om elektriciteit op te wekken in een KV-STE9 installatie, of als een synthese gas voor de produktie van metaan of chemicaliën.

Het literatuuroverzicht van \( \text{H}_2\text{S} \) verwijderingsprocessen (hoofdstuk 1) laat zien dat een groot aantal lage temperatuur \( \text{H}_2\text{S} \) verwijderingsprocessen is ontwikkeld en wordt gebruikt. Processen die bij hoge temperatuur werken zijn in de ontwikkelingsfase en worden nog niet toegepast. De meeste aandacht wordt gegeven aan de ontwikkeling van zinkferriet, zinktitanaat, het "mixed metal oxide" proces en ijzer op silica. De nadelen van deze processen zijn de oxidatieve regeneratie en het onvermijdelijke \( \text{H}_2 \) verbruik. De geringe stabilitiet van zinkferriet en zinktitanaat in gassen met een hoge CO/\( \text{H}_2 \)-concentratie beperkt de toepasbaarheid hiervan. Het proces dat in dit proefschrift beschreven wordt kent deze nadelen niet.

In het proces dat in dit proefschrift behandeld wordt reageert \( \text{MnO/\gamma-Al}_2\text{O}_3 \) met \( \text{H}_2\text{S} \) en vormt \( \text{MnS/\gamma-Al}_2\text{O}_3 \) en \( \text{H}_2\text{O} \). Het ingezwavelde materiaal wordt bij dezelfde temperatuur en druk geregeneereerd met een gas dat stoom bevat. Het regeneratie-afgas heeft een hoge \( \text{H}_2\text{S} \)-concentratie en kan gebruikt worden als voeding voor een Claus plant om elementaire zwavel te maken.

In hoofdstuk 2 wordt de bereiding van de acceptoren via verschillende technieken behandeld. Zowel coprecipitatie als sol-gel precipitatie resulteren in acceptoren die slecht voldoen. Het grootste deel van het mangaan is aanwezig als mangaankristallietjes die niet geregeneereerd kunnen worden. Porievolume-impregnatie levert acceptoren met de hoogste doorbraakcapciteit en levensduur op. Het gebruik van een monoliet als drager leverde een acceptor met een hoge capaciteit op. Het gebruik van een monoliet moet echter verder onderzocht worden.

Karakterisering van acceptoren die m.b.v. porievolume-impregnatie bereid zijn (hoofdstuk 3) laat zien dat er drie verschillende typen mangaan onderscheiden kunnen worden. Het eerste type bestaat uit zeer reaktieve maar niet regenereerbare
mangaanoxide-kristallietjes. Ze kunnen slechts eenmaal ingezwaveld worden. Het tweede type is een oppervlakte MnAl₂O₄ spinel die makkelijk ingezwaveld en geregenereerde kan worden. Het derde type is een MnAl₂O₄ spinel waarvan de snelheid van de inzwaveling en regeneratie bepaald wordt door de diffusie van Mn²⁺-ionen in de γ-Al₂O₃ drager.


De regeneratie van ingezwavelde MnO/γ-Al₂O₃ acceptoren wordt in hoofdstuk 5 behandeld. Om een regeneratie-afgas te krijgen met een zodanige H₂S concentratie dat het gebruikt kan worden als een voeding voor een Claus plant (C₄H₄S > 15 %v) moet een voeding met een hoge stoomconcentratie (> 50 %v) gebruikt worden. Om het stoomverbruik te beperken is een relatief lange verblijftijd (> 1 s) nodig. De regeneratietijd is in alle gevallen korter dan de inzwavelings tijd.

Tijdens de vergassing van kool ontstaan niet alleen H₂S en COS, maar ook andere verontreinigingen. De acceptoren zijn onder realistische omstandigheden getest in een bench scale unit waarbij gebruik is gemaakt van het gas dat door een bij ECN Petten gesitueerde 200 kW thermisch kolenvergasser geproduceerd werd (hoofdstuk 6). Op deze manier konden zowel het effect van opschaling als van verontreinigingen in het gas bestudeerd worden. De doorbraakcapaciteit was ongeveer 0.35 %w S voor Mn houdende en 0.20 %w S voor ijzerhoudende acceptoren. Er is geen deaktivering waargenomen gedurende vier weken continu bedrijf. Een regeneratie afgas met een hoge H₂S-concentratie (tot 60 %v) werd verkregen. De gebruikte acceptoren zijn getest op ontzwavelingcapaciteit en verontreinigingen. De verdeling van verontreinigingen in de vergasser en ontzwavelingstopstelling is eveneens bekeken.

In hoofdstuk 7 wordt een mathematisch model gepresenteerd dat de experimentele doorbraak- en regeneratie-curves kwantitatief beschrijft. Er is geen diffusie-limitering waargenomen. Het model is gebaseerd op de kinetiek van de reakties die op

In hoofdstuk 8 worden de voor- en nadelen van een aantal processchema’s besproken. Een proces waarin de acceptor van de ontzwavelingsreactor naar de regenerator en terug getransporteerd wordt en gassen met een constante samenstelling produceert lijkt het meest veelbelovend. Een moving-bed systeem lijkt in het bijzonder geschikt te zijn omdat geen opmenging van het acceptorbed en geen doorslip van gas optreedt.

In appendix A wordt een korte economische evaluatie gegeven voor de ontzwaveling van een 600 MWₑₘ elektriciteitscentrale die gebaseerd is op Shell kolenvergassings technologie. De kosten van de ontzwaveling bedragen ongeveer Dfl 0.0012 per kWh.
Introduction

The use of coal for power generation and chemicals production

Coal supplies around the world account for about 72% of all fossil fuels [1]. This fact implies that coal will provide a major source of energy in the future, irrespective of the prevailing oil price. Consequently, it is of vital importance to create and develop the most effective technologies that utilise coal as an independent source of energy, carbon, hydrogen or synthesis gas.

Figure 1 shows the contributions of various energy sources to the production of

![Graph showing contributions of various energy sources to the production of electricity in the world.](image)

*Figure 1. Contributions of various energy sources for the production of electricity in the world [2].*
electricity in the world. Along with the increase of coal consumption in power plants, the associated increase in emissions of gaseous, liquid and solid wastes gives rise to concern. Moreover, coal based electricity generation is expected to contribute an even greater share of the electricity supply in the future [3, 4]. This calls for the development of cleaner technology and operating procedures.

Figure 2. The topping cycle from British Coal [5, 6].

When utilizing coal for electricity production a choice has to be made between direct combustion and more recent techniques like (pressurized) fluidised bed combustion ((P)FBC) and coal gasification. The conventional coal combustion processes, like pulverized fuel combustion (PFC), in general have an overall efficiency of about 37%. More advanced techniques like PFBC can increase the efficiency to about 40 percent and need 10 to 15 percent less investment. This results in some 10 percent cheaper electricity production. The overall efficiency of coal combustion systems is limited by the relatively low temperature of the combustion gases. To obtain a higher efficiency the entrance temperature for the gas turbine must be increased. An interesting alternative to increase the gas temperature at the turbine inlet is developed by British Coal: they use a so-called "topping-cycle". In this system a PFBC and an air blown pressurized fluidized bed gasifier are coupled. Figure 2 gives a schematic flow sheet of the topping cycle. In this
arrangement of gasifier and combustor, 60-80% of the coal is gasified by air. The resulting char is added to the rest of the coal and passed to the combustor. The fuel gas (1275 K) is cleaned and then burned in the combustor off-gases to raise their temperature to a turbine inlet of 1535 K. The efficiency of such a topping cycle is about 45 percent. Due to the increased efficiency (from 37.5 to 45 percent) the CO₂ emission is reduced by 17 percent, and without cost penalty. The main disadvantage of this system is that it can only be used to produce electricity.

Recent studies [7, 8] indicate that in The Netherlands a modern coal combustion power plant has a lower investment but also a lower efficiency than a coal gasification plant. Based on 6000 hour of full load production per year it was concluded that with the present economic and environmental conditions combustion is cheaper. However, developments in coal gasification, gas turbine technology and, not at least, more stringent environmental requirements will lead to more efficient, cleaner and cheaper electricity if coal gasification combined cycle (CGCC) technology is used.

Combined cycle systems, using both gas and steam turbines, offer a significantly higher station efficiency compared with traditional systems. Integration with chemical process technology, adapted from other applications, opens a number of possible routes for coal utilisation, which are capable to meet very stringent environmental standards. An important example of this approach is the Integrated Gasification Combined Cycle (IGCC) power generation system.

The concept of a coal based IGCC power generation system is shown in figure 3. Fuel gas is generated in the gasifier and purified in the gas clean-up system. Clean gas is sent to the gas turbine where it is burned with compressed air to provide a stream of hot high pressure gas and drives the turbine to generate electricity. The exhaust gases from the turbine pass to a waste heat boiler where steam is raised at high temperature and pressure by heat exchange with boiled feed water. The steam passes to the steam turbine which generates electricity. In comparison with PFC, which does not employ a combined cycle system, an IGCC system does have an initial penalty associated with conversion of coal into fuel gas. However, the high efficiency downstream obtained from the combined cycle can more than offset this disadvantage. Other advantages over PFC
Figure 3. Schematic flow sheet of an integrated gasification combined cycle (IGCC) power plant [1].

are [1]:
- excellent environmental performance
- smaller quantity of solid residue
- lower water consumption
- capability of phased construction.

When the techniques described above are used to produce electricity only, efficiencies up to about 45-50 percent [5, 6, 9] can be reached. When it is kept in mind that CO₂ emissions must be reduced and fossil fuel supplies are limited, station efficiencies must be further increased. There are different methods to achieve this goal. First, the economics of power generation can be improved by combining electricity production and supply of heat on a local basis. This option has found to be practical with electricity production in power plants to a scale of about 500 MW [5, 6]. In a combined heat and power station, by-product heat is extracted at a temperature higher than from a power station and used for process or space heating. Although this reduces the electrical output at a given fuel input, the overall thermal efficiency can be raised from
about 37 to about 80 percent. Table 1 gives examples for some of power generation systems.

Table 1. Economics of combined heat and power generation [5]. $1988, based on electricity value $ 16.8/GJ and heat value $ 6.5/GJ.

<table>
<thead>
<tr>
<th>System</th>
<th>Energy Efficiency</th>
<th>Value of energy $/100 GJ of fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Electricity %</td>
<td>Heat %</td>
</tr>
<tr>
<td>PFC (electricity only)</td>
<td>37.5</td>
<td>0</td>
</tr>
<tr>
<td>PFC</td>
<td>28</td>
<td>54</td>
</tr>
<tr>
<td>PFBC</td>
<td>32</td>
<td>52</td>
</tr>
<tr>
<td>IGCC</td>
<td>39</td>
<td>38</td>
</tr>
</tbody>
</table>

Because of the changing need for electricity around the year a coal gasification combined cycle power plants will not always use its full capacity for electric power generation. During periods of low electricity demand the fuel gas produced can be used as a synthesis gas for the production of substitute natural gas (SNG) or chemicals [10].

Poptodorov et al. [11] calculated that the combined production of methanol and electrical energy can raise the overall efficiency from 43 percent, for a conventional set-up, to 57 percent for combined electricity and chemicals production. At the same time the CO₂ production goes down with 25 percent and the amount of fuel used with about 30 percent.

It is clear that the use of coal gasification for electricity production in an IGCC power plant combined with synthesis of methanol or liquid hydrocarbons and eventually the use of heat is a very promising development for future energy production.

Downstream requirements (e.g. protection of the gas turbine) and environmental regulations dictate that the raw fuel gas produced by a coal gasifier must be cleaned before further use. The raw fuel gas contains a lot of impurities such as dust, sulfur compounds (H₂S, COS, CS₂, mercaptans), HCN, NH₃, heavy metals, alkali metals and HCl and HF.
Table 2. Commercial low temperature processes for the removal of H₂S (data obtained from references 12 - 16).

<table>
<thead>
<tr>
<th>Name</th>
<th>Class¹⁾</th>
<th>Sorbent</th>
<th>Operating temperature (K)</th>
<th>Regeneration product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanol amines</td>
<td>CS</td>
<td>methyl diethylamine (MDEA)</td>
<td>300</td>
<td>H₂S</td>
</tr>
<tr>
<td>Girbotol</td>
<td>CS</td>
<td>monoethanolamine (MEA)</td>
<td>295-315</td>
<td>H₂S</td>
</tr>
<tr>
<td>SNPA-DEA</td>
<td>CS</td>
<td>diethanolamine (DEA)</td>
<td>295-315</td>
<td>H₂S</td>
</tr>
<tr>
<td>Econamine</td>
<td>CS</td>
<td>diglycolamine (DGA)</td>
<td>315-355</td>
<td>H₂S</td>
</tr>
<tr>
<td>ADIP</td>
<td>CS</td>
<td>diisopropanolamine (DIPA)</td>
<td>305-315</td>
<td>H₂S</td>
</tr>
<tr>
<td>Benfield, Catacarb</td>
<td>CS</td>
<td>hot potassium carbonate (K₂CO₃ + water)</td>
<td>355-395</td>
<td>H₂S</td>
</tr>
<tr>
<td>Selexol</td>
<td>PS</td>
<td>dimethylether of polyethylene glycol</td>
<td>295</td>
<td>H₂S</td>
</tr>
<tr>
<td>Rectisol</td>
<td>PS</td>
<td>methanol</td>
<td>245-355</td>
<td>H₂S</td>
</tr>
<tr>
<td>Sulfinol</td>
<td>PS</td>
<td>mixture of 2N-diisopropanolamine, sulfolane and water</td>
<td>295-335</td>
<td>H₂S</td>
</tr>
<tr>
<td>Purisol</td>
<td>PS</td>
<td>n-methyl-2-pyrolidone</td>
<td>310-355</td>
<td>H₂S</td>
</tr>
<tr>
<td>CNG</td>
<td>PS</td>
<td>carbon dioxide</td>
<td>220</td>
<td>H₂S</td>
</tr>
<tr>
<td>Stretford</td>
<td>OP/DC</td>
<td>solution of Na-salts of H₂CO₃, anthraquinone-2-sulfonic acid, vanadic acid</td>
<td>295-315</td>
<td>S</td>
</tr>
<tr>
<td>Takahax</td>
<td>OP/DC</td>
<td>solution of Na-salts of H₂CO₃, 1,4-naphtoquinone-2-sulfonic acid</td>
<td>295-315</td>
<td>S</td>
</tr>
<tr>
<td>Townsend</td>
<td>OP/DC</td>
<td>aqueous solution of triethylene glycol</td>
<td>340-395</td>
<td>S</td>
</tr>
<tr>
<td>Iron sponge</td>
<td>DB</td>
<td>hydrated Fe₂O₃</td>
<td>295-315</td>
<td>S</td>
</tr>
</tbody>
</table>

¹⁾ CS = chemical solvent process, PS = physical solvent process, OP/DC = oxidation process/direct conversion process, DB = dry bed process
A wide variety of existing commercial and well developed gas processing systems is available for the removal of sulfur, ammonia and other undesirables from the fuel gas. In general these are low temperature processes involving the use of various liquids with either an organic or aqueous base. Particulates are removed easily by water scrubbing. Consequently, the gas stream must be cooled before admission to the scrubbing towers. This implies the use of waste heat boilers and introduces an unavoidable heat by-pass [1] (the portion of potential energy released from the fuel which does not contribute to power generation in the gas turbine, the energy can be said to by-pass the gas turbine and to be supplied directly to the steam system).

Typical H$_2$S removal systems operating at low temperatures are summarized in table 2. Regeneration of the H$_2$S loaded solvent takes place in a regenerator, where the temperature of the solvent is increased while and the gas pressure is kept low. By stripping with steam the complexes are decomposed and the acid gas components set free. In the direct conversion processes is H$_2$S absorbed in a solvent in which it is oxidized to elemental sulfur. The solvent is transported to a regenerator where the elemental sulfur is extracted from the solvent. Subsequently, the solvent is oxidized and recycled.

To overcome the disadvantages of gas cleaning at low temperatures much attention has been given to the development of hot dry gas cleaning techniques that can be applied directly at the gasifier outlet. In high temperature gas cleaning the following steps can be distinguished: dust removal, desulfurization, removal of halogens, removal of alkali metals and other trace compounds and removal of nitrogenous compounds.

A recent study [17] on coal gasification combined cycle power generation plants using Shell or Texaco technology shows that higher temperatures for gas cleaning can improve the overall efficiency and lead to lower kWh prices if it is allowed to omit SCR (Selective Catalytic Reduction) of NO$_x$. Some results of high temperature gas cleaning compared to low temperature gas cleaning are summarized in table 3.

In this thesis high temperature desulfurization will be discussed. Potential processes for high temperature desulfurization will be discussed in the next paragraph.
Table 3. Calculated overall net efficiencies of a 600 MW_e plant [17].

<table>
<thead>
<tr>
<th>Purification process</th>
<th>Sulfinol (Shell)</th>
<th>Active coal (Cirmac/BF)</th>
<th>FeO/SiO₂</th>
<th>0.8ZnO-TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>315</td>
<td>525</td>
<td>625</td>
<td>875</td>
</tr>
<tr>
<td>Efficiency Shell</td>
<td>43.60</td>
<td>44.54</td>
<td>46.36</td>
<td>46.40</td>
</tr>
<tr>
<td>Efficiency Texaco</td>
<td>42.75</td>
<td>43.68</td>
<td>45.14</td>
<td>45.46</td>
</tr>
</tbody>
</table>

Desulfurization: high temperature processes

A number of metal oxides, mixed metal oxides and supported metal oxides can be used for high temperature regenerative H₂S removal. Evaluations, based on thermodynamic properties, to determine the metal oxides to be used in high temperature removal of H₂S have been carried out by several investigators [18, 19, 20]. Westmoreland [18, 19] showed that the oxides of Ba, Ca, Co, Cu, Fe, Mn, Mo, Sr, W, V, and Zn are thermodynamic feasible candidates. Vanadium oxide and zinc oxide give about 100% desulfurization but their operating temperature is limited to 925 K (V) and 975 K (Zn), due to formation of volatile compounds above these temperatures. Another important factor is the rate of H₂S capture. The results of a comparative study on the intrinsic sulfidation rates of several metal oxides [21] showed that sulfidation of Fe₂O₃ and MnO is much faster than those of other oxides. This result is derived from measurements of initial rates of sulfidation; the order of the reaction with respect to H₂S and metal oxide were assumed to be one. More recently it has been discovered that in general sulfidation is very fast. However, if bulk material is used diffusion rates are often low. Therefore, the dispersion of the metal oxide is a predominant factor. Also, the porosity of the sulfided outer layer is important. The reason that Fe₂O₃ and MnO behave better might well be due to the favourable textural properties.

Under favourable conditions, two metal oxides can react to form a distinct compound, a so-called mixed metal oxide. Examples of the resulting complex oxide are ZnCr₂O₄, TiMg₂O₄ and WNa₂O₄. A mixed metal oxide is called a spinel when its
structure is isomorphous with the natural spinel MgAl₂O₄.

For an oxide of the formula AB₂O₄, there are eight negative charges. The three combinations of the cation charges of A and B which can balance these negative charges are: \(A^{2+} + 2B^{3+}\), \(A^{4+} + 2B^{2+}\) and \(A^{6+} + 2B^{1+}\). The 2-3 spinel (the first example) is by far the most numerous.

Supported metal oxide acceptors have some advantages over unsupported metal oxides for high temperature desulfurization. The support has a large surface area and the metal oxide is spread out on this surface. Since gas-solid reactions only take place at the gas-solid interface, the use of a support will result in a more effective use of the active compound. Moreover, the acceptors can have more desirable mechanical properties, as a high attrition resistance and compression strength.

In some cases, the support can show a strong interaction with the metal oxide dispersed on it. In general three different forms of interaction can be distinguished. First, the metal oxide can retain its chemical identity and the carrier only acts as a dispersing agent. Secondly, it may form a new stoichiometric compound with the support (e.g. aluminate spinel) and, thirdly, it may dissolve into the carrier to give a solid solution. Due to the interaction with the support, the metal oxide can show a different performance than would be expected from bulk thermodynamics of the metal oxide (or the support) itself.

Based on the points discussed above, a lot of different high temperature desulfurization processes are possible theoretically. However, only a few processes get much attention. The advantages and disadvantages of these processes will be discussed.

All processes for high temperature regenerative \(H₂S\) removal can adequately remove \(H₂S\) from the fuel gas produced by a coal gasifier. However, the regeneration route of the materials and the sulfur containing product obtained can differ. Most effective would be a process which produces elemental sulfur during regeneration because no additional process steps are necessary to convert the regeneration product in an environmentally acceptable, saleable product. Such processes are in the development stage and have not been proven yet.
When no elemental sulfur can be made, H₂S becomes the most attractive regeneration product, as it can be converted to elemental sulfur without the use of reducing gases in a Claus plant. In contrast, if SO₂ is formed reducing gases are needed to convert part of the SO₂ into H₂S before it can be converted into elemental sulfur. These reducing gases had better be used to produce electricity in the combined cycle power plant.

The research on zinc ferrite started in the beginning of the 1980's and is a continuation of the research on iron oxide based acceptors. Iron oxide has a limited cleaning depth at high temperatures, whereas zinc oxide provides an excellent cleaning depth. In zinc ferrite the high capacity of iron oxide and the high cleaning depth of zinc oxide are combined.

When zinc ferrite (ZnFe₂O₄) is used a number of reactions are important [22 - 32]. During the sulfidation step two types of reactions take place. The first is reduction of the sorbent:

\[ 3 \text{ZnFe}_2\text{O}_4 + \text{H}_2 \rightarrow 3 \text{ZnO} + 2 \text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \]  \hspace{1cm} (1)

The second is sulfidation of the acceptor:

\[ \text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O} \]  \hspace{1cm} (2)
\[ \text{Fe}_3\text{O}_4 + 3 \text{H}_2\text{S} + \text{H}_2 \rightarrow 3 \text{FeS} + 4 \text{H}_2\text{O} \]  \hspace{1cm} (3)

In the above reactions CO may replace H₂, in which case the product would be CO₂ instead of H₂O.

Other research [53, 55] showed that in the reduction of zinc ferrite (reaction 1) H₂S probably plays a direct role. This has been shown the case for oxides like CoO an MoO₃. Sulfidation of CoO/γ-Al₂O₃ catalysts in H₂S/H₂ is much faster than reduction in H₂. H₂ can only compete with H₂S as a primary reactant when H₂S diffusion is hindered, e.g. in the case of large crystallites [53]. During TPS of MoO₃/γ-Al₂O₃ catalysts it was found that prereduction hinders sulfidation. Therefore, the catalyst not necessarily has to be reduced before sulfidation. An alternative mechanism to reactions (1) to (3) can
be formulated in which the metal oxide (ZnFe₂O₄) reacts with H₂S and forms H₂O. The metal-sulfur bond dissociates, S reacts with H₂ and forms H₂S. The metal oxide is now reduced to ZnO and Fe₃O₄ and can react with H₂S or H₂ [55].

However, in the presence of highly reducing gases (i.e. a coal gas with a large fraction of H₂ or a high CO/CO₂ ratio) Fe₃O₄ is reduced to FeO or Fe, which leads to the formation of iron carbide, Fe₃C. The formation of Fe₃C and other carbides is particularly detrimental for sulfur adsorption and sorbent strength, because Fe₃C reduces the sulfur capacity of the sorbent and induces stresses due to solid density differences. This results in mechanical disintegration of the pellets. To overcome these problems only gases with a low reducing potential are allowed, at an operating temperature limited to 815-925 K. In case of a Texaco or Shell gasifier (oxygen blown) substantial amounts of steam have to be added to the raw fuel gas to lower the reducing potential. The sorbent has a high initial capacity (~30 %w S) but this value rapidly decreases to a stable value of ~10 %w S after 40 cycles [33].

Regeneration of the sulfided sorbent is carried out with a mixture of N₂ and O₂ or steam:

\[
\begin{align*}
ZnS + 2 \text{FeS} + 5 \text{O}_2 & \rightarrow ZnFe_2O_4 + 3 \text{SO}_2 \\
3 \text{ZnS} + 6 \text{FeS} + 3 \text{H}_2\text{O} & \rightarrow 3 \text{ZnO} + 2 \text{Fe}_3\text{O}_4 + 9 \text{H}_2\text{S} + 2\text{H}_2
\end{align*}
\]

When both steam and oxygen are present, Fe₃O₄ will be further oxidized to Fe₂O₃ and ZnFe₂O₄ is formed.

Regeneration is complicated by the tendency to form ZnSO₄ at low temperatures and/or high O₂ and SO₂ concentrations:

\[
\begin{align*}
\text{ZnS} + 2 \text{O}_2 & \rightarrow \text{ZnSO}_4 \\
2 \text{ZnO} + 2 \text{SO}_2 + \text{O}_2 & \rightarrow 2 \text{ZnSO}_4
\end{align*}
\]

To prevent ZnSO₄ formation, regeneration has to be carried out at temperatures between 925 and 1025 K. The amount of ZnSO₄ formed depends upon regeneration temperature: at 925 K significant quantities of ZnSO₄ are formed with high O₂
concentrations only, whereas at 825 K significant amounts of ZnSO₄ are formed with all gas compositions [26]. Its deleterious effect during cyclic sulfidation-regeneration is caused by the reduction of the sulfate during the subsequent sulfidation step:

\[ 2 \text{ZnSO}_4 + 5 \text{H}_2 \rightarrow \text{ZnO} + \text{ZnS} + \text{SO}_2 + 5 \text{H}_2\text{O} \]  

(8)

The reaction results in a temporarily high SO₂ concentration in the cleaned fuel gas. Therefore, regeneration of the sorbent has to be carried out in two steps: first an oxidative regeneration and, second, a reductive regeneration. Another possibility to overcome this problem is regenerating with very low O₂ concentrations at high temperatures (925 - 1025 K).

Due to the strongly exothermic regeneration and ZnSO₄ formation, only low O₂ concentrations can be used. This results in a regeneration off-gas with a low (1 - 3 %v) SO₂ concentration. Other problems are the limited number of cycles the sorbent has been tested (~50) and the hydrogen or carbon monoxide consumption in various stages of the process. Tests carried out with the fuel gas produced by the Texaco gasifier in Montebello [34, 35] clearly showed that zinc ferrite is not applicable right away. Further research is concentrated on the improvement of reactivity and mechanical strength of zinc ferrite and the development of other sorbents, e.g. zinc titanate.

Because zinc ferrite suffers from problems during sulfidation and regeneration, zinc titanate was developed [36, 37]. The addition of titanate [38, 39] reduces the tendency for zinc oxide reduction and subsequent volatilization of metallic zinc, thereby increasing the maximum sorbent operating temperature to about 1035 K. The stabilizing effect is attributed to the formation of mixed metal oxide compounds like ZnTiO₃, Zn₂TiO₄ and Zn₂TiO₃ [40, 41, 42]. Different sorbent formulations (0.8ZnO-TiO₂₂, ZnO-TiO₂, 1.5ZnO·TiO₂ and 2ZnO·TiO₂) have been developed and tested. The reactions occurring during sulfidation are [38, 40]:

\[ \text{Zn}_2\text{TiO}_4 + 2 \text{H}_2\text{S} \rightarrow 2 \text{ZnS} + \text{TiO}_2 + 2 \text{H}_2\text{O} \]  

(9)

\[ \text{ZnTiO}_3 + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{TiO}_2 + \text{H}_2\text{O} \]  

(10)

\[ \text{Zn}_2\text{TiO}_4 + 2 \text{H}_2 \rightarrow 2 \text{Zn} + \text{TiO}_2 + 2 \text{H}_2\text{O} \]  

(11)
ZnTiO$_3$ + H$_2$ → Zn + TiO$_2$ + H$_2$O \hspace{1cm} (12)

Although the rate of zinc loss is lower than for pure zinc oxide, it is not negligible: 2ZnO·TiO$_2$ loses about 7 \% w Zn/1000 hours of operation at 925 K [38]. Further, to minimize the zinc loss the water concentration in the fuel gas must be at least 5 \% v for 0.8ZnO·TiO$_2$ to 20 \% v for 2ZnO·TiO$_2$ [27]. Although the zinc oxides have a high theoretical breakthrough capacity, a sorbent conversions of only 50 - 60 percent are obtained under reaction conditions. The average sulfur loading during the first five sulfidation-regeneration cycles is 7 \% w for 0.8ZnO·TiO$_2$ and 11.5 \% w for 1.5ZnO·TiO$_2$. From the above sorbents 1.5ZnO·TiO$_2$ gives the best compromise between sulfur capacity and zinc loss due to reduction and vaporization.

Regeneration of zinc titanates is simpler than regeneration of zinc ferrite. Regeneration is carried out between 925 K and 1035 K. There is no evidence of ZnSO$_4$ formation due to the high regeneration temperature. Regeneration of the sulfided zinc titanate sorbent is, like zinc ferrite, carried out with a gas with a low oxygen concentration. The regeneration off-gas will have a low SO$_2$ concentration as well. The regeneration reactions are:

\[ x \text{ ZnS} + \text{TiO}_2 + x \text{O}_2 \rightarrow x \text{ZnO-TiO}_2 + x \text{SO}_2 \] \hspace{1cm} (13)
\[ x \text{ ZnS} + \text{TiO}_2 + x \text{H}_2\text{O} \rightarrow x \text{ZnO-TiO}_2 + x \text{H}_2\text{S} \] \hspace{1cm} (14)

The first reaction is much faster than the second. Because no ZnSO$_4$ is formed the regeneration process can be limited to one step.

It is clear that zinc titanate can overcome some of the disadvantages of zinc ferrite. However, because gases with a high water content have been used for testing, it is not clear whether the materials can be used to desulfurize relatively dry gases, e.g. produced by a Shell coal gasifier. Further, the number of cycles the material has been tested is limited and lifetime can not be estimated reliably.

Other processes investigated are based on copper oxide, mixed with various other compounds, e.g. CuO, CuO-Fe$_2$O$_3$, CuO-Fe$_2$O$_3$-Al$_2$O$_3$, CuO/SiO$_2$ and CuO/Al$_2$O$_3$ [31, 37, 39, 43, 44]. After screening tests, none of these sorbents was investigated further because
the copper oxide is reduced from 2+ to 1+ to 0 oxidation state by the reducing gas mixture before sulfidation takes place. The sulfidation equilibrium, however, is much more favourable for the oxidized than for the metallic state of copper.

Copper manganese oxide sorbents (CuMnO$_2$, CuMnO$_4$) [45, 46, 47] do not reduce to metallic copper, have a good sulfidation performance and can be regenerated with a oxygen containing gas. Low SO$_2$ concentrations in the regeneration off-gas are obtained, but no sulfate formation takes place. The processes have to be developed further.

Two processes which possibly can produce elemental sulfur during regeneration are the mixed metal oxide process and a process that uses iron oxide on silica.

The mixed oxide metal process [48] uses two different sorbent materials in series at a temperature between 815 and 925 K. First a cobalt titanate sorbent removes more than 67 % of the H$_2$S. The partially desulfurized fuel gas then comes into contact with a zinc oxide containing sorbent where the sulfur content of the fuel gas can be reduced to less than 20 ppmv. Regeneration is performed countercurrently with pure O$_2$ and a recirculating stream of SO$_2$. The O$_2$ regenerates the zinc oxide containing sorbent. SO$_2$ formed by this reaction is combined with the recirculating stream of SO$_2$ to regenerate the cobalt titanate sorbent. SO$_2$ reacts with the metal sulfide in a Claus like reaction and produces elemental sulfur. The product gas contains both elemental sulfur and SO$_2$. The elemental sulfur is removed from the SO$_2$ by cooling and condensation; the SO$_2$ is recycled.

In a laboratory scale set-up, the process functions satisfactory, but bench scale tests [56] showed that very low space velocities (<300 h$^{-1}$ during sulfidation and 100 h$^{-1}$ during regeneration) were necessary and that the amount of sulfur produced during regeneration was low.

Iron oxide on silica [16, 49] consists of small iron oxide crystallites (<20 nm) on a silica support. The iron oxide (Fe$_2$O$_3$) is reduced to FeO. Between 475 and 975 K FeO reacts with H$_2$S and forms FeS and H$_2$O. The sorbent can be regenerated with O$_2$ or SO$_2$. Regeneration with O$_2$ is strongly exothermic, which makes it necessary to use diluted O$_2$. At low O$_2$ concentrations and plug flow theoretically elemental sulfur can be produced. Practically however, formation of SO$_2$ can not be prevented due to bypassing
of O₂ in the reactor which reacts with the elemental sulfur. Regeneration with SO₂ forms an alternative, but is relatively slow and depends on the temperature. A temperature of at least 875 K should be used. When O₂ is used to regenerate the sorbent, Fe₂O₃ is again obtained; in case of SO₂ Fe₃O₄ is formed. In both cases the next sulfidation will inevitably show a consumption of reducing gases.

The processes discussed so far either produce SO₂ in a low concentration during regeneration or have the possibility to produce elemental sulfur. The processes which produce elemental sulfur did not fulfil the expectations when experiments were carried out in a bench scale unit. All processes require reducing gases due to the oxidative character of the regeneration. Most of the processes need further developments to be applicable on a large scale.

The process developed by the Delft University of Technology (MnO/γ-Al₂O₃, FeO/γ-Al₂O₃) can overcome several of the disadvantages of the above processes and will be discussed in the next paragraph.

**Acceptors based on MnO or FeO on γ-Al₂O₃**

From the work of van der Linde [50] and Soerawidjaja [51] and the foregoing section it can be concluded that MnO or FeO supported by γ-Al₂O₃ has a good perspective for high temperature regenerative H₂S removal. One of the main advantages is the regeneration route: the acceptor is regenerated with steam and H₂S in a high concentration is formed (see chapter 5). This H₂S can be converted to elemental sulfur in a Claus plant without the use of reducing gases.

The fact that MnS/γ-Al₂O₃ and FeS/γ-Al₂O₃ can be regenerated with a gas containing steam, or, in other words, that the following reaction is reversible was unexpected.

\[
\text{MeO/γ-Al₂O₃} + H₂S \rightarrow \text{MeS/γ-Al₂O₃} + H₂O \quad (\text{Me = Mn or Fe})
\]  

(1)

Moreover, van der Linde and Soerawidjaja reported that unsupported MnO, silica supported MnO and molecular sieve 5A supported MnO react rapidly with H₂S but their
products do not hydrolyse with steam up to 875 K. The behaviour of MnO/γ-Al₂O₃ is thus peculiar and deserves an explanation.

Steam regeneration is simply the reverse of the original sulfidation. Thermodynamic calculations [52, 53] of the sulfidation of single metal oxides predicts that regeneration with steam is virtually impossible. Figure 4 shows the thermodynamic equilibrium constants of sulfidation of MnO, FeO, MnAl₂O₄ and FeAl₂O₄. The equilibrium constant of MnO and FeO is 100 or higher. From literature it is known that metal oxides carried by alumina can exhibit strong interaction with the carrier. The metal oxide may form a new stoichiometric compound with the support or dissolve in the carrier to give a solid solution. It is known that Mn and Fe can form MnAl₂O₄ spinel structures at high temperatures [54, 55]. Thermodynamics of MnAl₂O₄ (Me = Mn or Fe) show that the equilibrium constant of sulfidation is about unity in the temperature range studied (see figure 4), thus making steam regeneration possible. Another advantage of the formation of a spinel like structure is the low heat of reaction accompanying sulfidation and regeneration of the acceptor compared with the bulk oxides. Figure 5 shows that sulfidation of MnO and FeO is exothermic, whereas the heat effects involved
Figure 5. Enthalpy changes accompanying the sulfidation of several metal oxides. ▼ = FeO, ▲ = MnO, ♦ = FeAl₂O₄, ● = MnAl₂O₄.

in sulfidation of MnAl₂O₄ and FeAl₂O₄ are negligible.

Outline of the thesis

The preparation of manganese and iron containing acceptors is described in chapter 2. Different preparation techniques are used to obtain the most active acceptor material. Impregnation results in the most active and stable acceptors. Chapter 3 describes the characterization of alumina supported manganese oxide acceptors prepared by pore volume impregnation by means of Temperature Programmed Reduction (TPR) and Sulfidation (TPS), High Resolution Electron Microscopy (HREM) and X-ray Photoelectron Spectroscopy (XPS). The influence of process conditions as temperature, pressure and gas composition is given in chapter 4. Chapter 5 discusses the results of regeneration experiments and the optimization of the regeneration conditions. Testing of the acceptor materials under realistic conditions in a bench-scale unit with a gas produced by a coal gasifier is discussed in chapter 6. The quantitative modelling of sulfidation and regeneration curves is given in chapter 7. Finally, an evaluation
concerning reactor design and economics of the process is given in chapter 8 and appendix A.

References

1. T. Takematsu and C. Maude, Coal gasification for IGCC power generation, IEA Coal Research, March 1991
5. J.S. Harrison, Innovation for the clean use of coal, British Coal, November 1988
7. Comprimo Engineers and Contractors, Elektriciteit uit kolen, poederkoolstoken of vergassen, Dutch summary, 1987
9. H. Goumans and A. Kok, 2e concept Meerjarenprogramma Lange Termijn Onderzoek Fossiele Brandstoffen, November 1990
10. F.P.J.M. Kerkhof and H.A. Droog, Electricity from coal, gasification and combustion alternatives for intermediate load, proceedings of the 7th International Conference and Exhibition on Coal Technology and Coal Trade, 21-23 Nov. 1988, Amsterdam, The Netherlands
13. V. Jalan, Studies involving high temperature desulphurization/regeneration reactions of metal oxides for fuel cell development, final report, DOE/MC/16021-1486 (DE840003096), 1984
16 W.J.J. van der Wal, Ph.D. Thesis, University of Utrecht, 1987
18 P.R. Westmoreland and D.P. Harrison, Environ. Sci. Technol., 10(7)(1976)659-661
21 G.D. Case (ed.), MERC task force, chemistry of hot gas cleanup in coal gasification and combustion, special publication of Morgantown Energy Research Center, Morgantown, USA, 1978
29 M.H. Berggren and D.P. Harrison, Gas stream cleanup papers from DOE/METC sponsored contractors review meeting october 1988 (eds. R.C. Bedick and V.P. Kothari), DOE/METC-89/6099 (DE89000901), Vol. 1, 1989, 63-72
30 T. Grindley, Gas stream cleanup papers from DOE/METC sponsored contractors


32 M.C. Woods, D.P. Harrison, F.R. Groves and K. Jothimurugesan, Proc. of the 8th annual gasification and gas stream cleanup systems contractors review meeting (eds. V.P. Kothari and J.R. Longanbach), 1988, 181-186


34 A.M. Robin, J.C. Wu and M.S. Najjar, Proc. 8th annual gasification and gas stream cleanup contractors review meeting (eds. V.P. Kothari and J.R. Longanbach), DOE/METC-88/6092 (DE88010253), 1988, 21-31


37 S.M. Harkins and S.K. Gangwal, Proc. of the 8th annual gasification and gas stream cleanup systems contractors review meeting (eds. V.P. Kothari and J.R. Longanbach), 1988, 199-203


V. Jalan and M. Desai, Proc. of the 8th annual gasification and gas stream cleanup systems contractors review meeting (eds. V.P. Kothari and J.R. Longanbach), 1988, 45-57


D. Jansen, Deelstudie H₂S/COS verwijdering, ECN, Nederland, Report ECN-C-90-050, October 1990
Preparation of alumina supported manganese or iron containing acceptors for high temperature H$_2$S removal

Abstract

The acceptor materials used for high temperature regenerative H$_2$S removal are prepared by wet impregnation: the breakthrough capacities are about 1 %w sulfur. To increase the breakthrough capacity other techniques like sol-gel precipitation, coprecipitation and pore volume impregnation have been investigated. The use of monoliths as a carrier is tested as well. The results show that the best acceptors are prepared by pore volume impregnation; they have a breakthrough capacity of about 1.5 %w sulfur. The use of monoliths as a carrier is promising but has to be investigated further.

Introduction

The acceptor materials described by Van der Linde [1], Soerawijdaja [2] and Wakker and Gerritsen [3,4] were prepared by wet impregnation. This technique is easy to use and normally results in acceptors with the desired metal loading and sulfidation behaviour. However, this technique is not very reproducible: acceptors prepared in the same way do not always have the same metal loading and sulfidation behaviour. Another disadvantage of the acceptors prepared in this way is their low sulfur loading at breakthrough of the acceptor bed. Only about 1 %w S is captured if a feed gas containing N$_2$, H$_2$ and H$_2$S is used (for experiments with other feed gas compositions see chapter 4). Although the sulfur loading is rather low, the acceptors have a high cleaning
efficiency: the amount of \( \text{H}_2\text{S} \) leaving the acceptor bed before breakthrough is about 0-20 ppm. The acceptors also have a long proven lifetime. They can be used for over 400 sulfidation regeneration cycles.

Because of the low sulfur capture capacity, which may result in large reactors, other preparation techniques have been investigated to prepare the acceptor materials and obtain higher breakthrough capacities. As proposed by Soerawidjaja [2] and discussed in chapter 3, the sulfidation-regeneration behaviour is caused by the formation of a surface manganese aluminate. Consequently, it is important to have a carrier material with a high surface area: in that way more of the active compound can be formed per gram of material. Techniques and materials are needed that result in a material with a high surface area on which the manganese is present in a highly dispersed state with strong interaction with the \( \gamma\text{-Al}_2\text{O}_3 \) carrier. A number of techniques is available to obtain a metal oxide on a support material. Among these techniques are impregnation methods, adsorption from a solution, coprecipitation, deposition methods and the sol-gel method. Also combinations of different techniques can be applied.

Tests with different preparation methods involving various metal support systems showed that the methods can be ordered as a function of interaction between metal oxide and carrier. The interaction decreases according to [9]:

Coprecipitation \( > \) sol-gel precipitation \( > \) adsorptive deposition \( > \) impregnation without adsorption \( > \) dry mixing.

If the product should result in a strong interaction between metal oxide and carrier, methods like coprecipitation and sol-gel precipitation should be used. At the same time it possible to prepare catalysts with high metal contents. In this way the capacity of the acceptors can also be increased.

Coprecipitation of metal ions and carrier results in a good mixing of the compounds. For nickel/alumina catalysts coprecipitation is widely used [11-14]. All compounds are present as a solution, in most cases an aqueous solution: no preshaped carrier is present, both carrier and active compound are formed at the same time. Concentrated metal salt solutions must be mixed and stirred intensively to get a homogeneous mixture. As the name suggests, it is essential that all components precipitate at the same time. The product should precipitate in a finely divided state with
a high surface area.

At a certain metal/aluminium ratio the precipitate forms a so-called M(etal), Al-hydroxotalcite [10, 13]. The hydroxotalcite has a structure consisting of two successive layers: a brucite layer and a so-called inter layer (see figure 1). In the brucite layers the OH⁻ ions are arranged in the closest packing, with the metal ions in the octahedral holes. The interlayer consists of a mixture of H₂O and CO₃²⁻ ions. The stoichiometric composition can be written as: (M²⁺)₆(Al³⁺)₂(OH⁻)₁₀(CO₃⁻)₄H₂O. The hydroxotalcite is the acceptor precursor. After filtration, washing and drying of the hydroxotalcite the hydroxides and carbonates are decomposed in a calcination step. A corresponding mixture of metal oxides with a spinel structure is left. The morphology of the precipitate does not change during this step, nor during subsequent steps, like reduction.

X-ray diffraction spectra of calcined nickel and aluminium containing hydroxotalcites do not show γ-Al₂O₃ lines. This means that γ-Al₂O₃ is amorphous, or present as very little crystallites or dissolved in the metal oxide [11]. Samples prepared at an increasing pH instead of a constant pH do show γ-Al₂O₃ lines. It is concluded that the aluminium ions keep the loosely packed oxygen structure together and that metal is present as little
nickel crystallites in the mesopores of the $\gamma$-Al$_2$O$_3$ carrier [12].

Reaction conditions like pH, temperature, reactants, foreign ions and method of precipitation are very important during precipitation. High surface areas in coprecipitated nickel/alumina catalysts are obtained if at least two of the following conditions are met: pH = 7, low ion concentration, aging of the precipitate, precipitation temperature 335 to 345 K. Samples prepared at pH 7 contain the most ordered crystallite phase [13].

During the preparation of the acceptor by means of sol-gel precipitation both the carrier and the active metal oxide are synthesized. The first step in sol-gel precipitation, which should result in the alumina carrier, is to disperse little boehmite crystals in a fluid phase. Such a system is called a sol. An important physical property of colloidal dispersions is that the particles tend to form aggregates. One of the ways to gelate the sol is by addition of ammonia: the particles coagulate. During this coagulation an open network of crystals is formed in which almost all water is encapsulated. Such a network structure is called a gel. In the ammonia solution the metal ions to be incorporated into the final product can be dissolved. The metal ions diffuse through the solution to the gel and into the gel particles. The metal ions adsorb on the walls of the boehmite particles in the gel. The adsorption proceeds by a stoichiometric ion exchange mechanism in which adsorbing metal ions replace bounded protons [14]:

$$\text{Al-OH} + M^{2+} = \text{AL-OM}^+ + H^+ \quad (1)$$

The ion-exchange causes the acidity of the solution to rise. When the iso-electric pH is reached adsorption stops as an equilibrium is attained. To get a homogeneous distribution of the metal ions it is important to let the metal ions attain equilibrium with the gel for some time. After gelation and in-situ impregnation the particles are filtrated, dried carefully, calcined and reduced to obtain the acceptor material.

Sol-gel precipitation can result in a reactive and mechanically strong sorbent as is shown in the work of Wolff [5] and Duisterwinkel [6]. Their sorbent consists of 8.2 %w CaO on a $\gamma$-Al$_2$O$_3$ support and is used for regenerative desulfurization during fluidized bed combustion of coal.
When impregnation is used to prepare a metal oxide on a carrier the pores of a preshaped carrier are filled with a metal salt solution. The solvent is evaporated and the metal salt is left on the carrier.

Different types of interaction can occur between impregnation solution and carrier. Among these are specific adsorption (the metal ions are adsorbed stronger by the carrier than by the solution) and ion exchange. When the metal concentration in the impregnation solution does not decrease after being contacted with the carrier obviously no interaction occurs. After filling the pores the solvent has to be evaporated in such a way that the precursor salts crystallize in the pores in a finely divided state. They have to be decomposed thermically afterwards.

Two types of impregnation can be distinguished: wet impregnation and pore volume impregnation.

Wet impregnation is carried out with an excess of the impregnation solution. Three processes occur:
- penetration of the solution into the pores
- diffusion of the metal ions through the solution, both inside and outside the particle
- adsorption of metal ions on the walls of the pores
Both penetration and adsorption are relatively fast processes: rate determining is diffusion of the metal ions through the solution [15].

When pore volume impregnation is used, the amount of the solution, containing the active compound, which is added corresponds to the pore volume of the carrier. This method results in a good reproducibility of the metal content of the acceptor. The amount of metal to be added to the carrier can be adjusted accurately but is limited to the solubility of the metal salt in the impregnation solution. Often more then one impregnation step is necessary.

Moreover, by only filling the pores of the carrier with impregnation fluid without letting the solution attain equilibrium with the carrier, it is possible to prepare acceptors with other characteristics than those obtained by wet impregnation. Further it is possible to prepare the acceptor by subsequent impregnations with an impregnation solution with a low metal content, thus preventing the formation of metal clusters or particles.

The techniques used here are sol-gel precipitation, coprecipitation, wet
impregnation and pore volume impregnation. Wet impregnation was also applied to a monolith.

**Experimental**

**Sol-gel precipitation**

![Diagram of sol-gel precipitation process]

*Figure 2. Flow diagram of the set-up for sol-gel precipitation.*

In the first step of preparation, a sol is made by dispersing very fine pseudoboehmite (AlOOHₙH₂O) powder (Pural SB-70) in water, containing nitric acid and urea. The sol (particle size smaller than approximately 30 nm) is then dropped into a nonpolar medium (petrol ether, boiling point 313-333 K) (see figure 2). Since the sol is hydrophobic, the drops will tend to minimize their outer surface area and become spheres. These spheres have a larger specific weight than the petrol ether and sink into a second layer which is a 5 %w solution of ammonia in water. Due to the ammonia the sol gels. This gel is a colloidal solid containing a fluid component; both the solid and the fluid component are highly dispersed. The manganese oxide can be incorporated by adding a manganese salt to the ammonia solution or afterwards by wet impregnation. The
advantage of the first method is the good dispersion of the manganese on the boehmite surface. This method also decreases the number of process stages. The manganese loaded gel is carefully heated to evaporate water. The calcination step is finally carried out at 875 K during 20 hours to decompose the manganese salt and form manganese oxide.

**Coprecipitation**

![Flow diagram](image)

*Figure 3. Flow diagram of the experimental set-up used for coprecipitation.*

Figure 3 gives the flow diagram of the set-up used for preparation of acceptors by coprecipitation. The reactor is filled with 2 l of distilled water. The stirrer, heater, thermometers, pH-electrode and supply tubes for the salt and the base solution are placed in the water. The precipitation is carried out at 343 K and a stirring speed of 450 rpm. After the water is heated the metal salt solution (1l, 1M total (Mn$^{2+}$ + Al$^{3+}$)) is added with a constant flow. The metal salt solution is prepared from a 49/51 %w/w Mn(NO$_3$)$_2$.6H$_2$O solution (BDH, p.a.) and Al(NO$_3$)$_3$.9H$_2$O (Merck, p.a.). By measuring the pH and adding the base solution (NH$_4$HCO$_3$ or Na$_2$CO$_3$) the pH is kept at a constant value of 7. After adding 1 l of the metal salt solution, dosage of both metal salt and base solution is stopped. The solution is left in the reactor for aging and is stirred
continuously. After the desired aging time the coprecipitate is filtrated and washed with 3 l of distilled water of 343 K. The precipitate is dried at 355 K for 20 hours and calcined/activated in air, nitrogen or hydrogen at temperatures up to 1175 K.

**Wet impregnation**

During previous research, the acceptor material was prepared by wet impregnation. The support (γ-Al₂O₃, AKZO/Ketjen 001-1.5E, particle diameters between 0.25 and 0.42 mm or 0.42 and 0.60 mm) is added to the impregnation solution (2M manganese (II) acetate, Merck, p.a. or 1M iron (II) ammonium oxalate, Riedel de Hähn, p.a.) for 16 to 17 hours. 3.3 ml of impregnation solution is used per gram of support material. After impregnation the material is filtrated and dried at ambient temperature for 5 to 6 hours. The material is then calcined in static air at 575 K for 60 hours. The last step in preparation is reductive calcination carried out in-situ in the reactor at 875 K for 6 hours.

**Pore volume impregnation**

Pore volume impregnation is carried out by adding the impregnation solution, with the desired metal content, with the aid of a burette slowly to the carrier material. The carrier is soaked by the impregnation solution until all pores are filled with the solution: the particles then start to stick together and adding of the solution is stopped. The material is dried at 365 K for 16 hours and than calcined in air (flow 100 ml/min STP) at 575 K for 20 hours. Reduction is carried out in-situ in the reactor at 875 K for 6 hours.

**Monolith**

The monolith is supplied by Degussa and provided with an alumina washcoat. Some characteristics of the monolith carrier are listed in table 1. To obtain parts suitable for testing in the experimental set-up the monolith was sawed to pieces with a diameter of 20.6 mm and a length of 42 mm. The manganese is added by wet impregnation to obtain a good distribution of the active metal compound throughout the whole sample. It is not possible to use pore volume impregnation to prepare monoliths: due to capillary forces the long narrow channels of monolith will fill with the impregnation solution as well.
Instrumental

The laboratory set-up is described in detail elsewhere [2, 3]. The apparatus is shown schematically in figure 4. In the gas dosage section oxygen and water are removed.

Table 1. Composition and some characteristics of the monolith

<table>
<thead>
<tr>
<th>Compound</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>22.5 %w</td>
</tr>
<tr>
<td>Si</td>
<td>15.5 %w</td>
</tr>
<tr>
<td>Mg</td>
<td>5.4 %w</td>
</tr>
<tr>
<td>Ce</td>
<td>0.84 %w</td>
</tr>
<tr>
<td>Zr</td>
<td>1.05 %w</td>
</tr>
<tr>
<td>Fe</td>
<td>0.72 %w</td>
</tr>
<tr>
<td>Co, Ba, La, Mo</td>
<td>traces</td>
</tr>
<tr>
<td>Washcoat</td>
<td>10 %w</td>
</tr>
<tr>
<td>Surface area</td>
<td>200 m$^2$/g</td>
</tr>
<tr>
<td>d$_{pore}$ Alumina</td>
<td>5-1500 nm</td>
</tr>
</tbody>
</table>

from all gases, except for H$_2$S which is used without further purification. After passing mass flow controllers the gas flows are mixed and flow to the reactor. The reactor feed contains 10 %v H$_2$ and 1 %v H$_2$S, the balance being N$_2$. The total flow rate is 67.5 $\mu$mol/s. In the reactor three grams of acceptor material are used to remove the H$_2$S from the gas. After breakthrough H$_2$S dosage is stopped and the acceptor material is regenerated. This is done by injecting liquid water into the reactor where it evaporates and is heated to reaction temperature before reaching the acceptor material. The amount of H$_2$S leaving the reactor is measured by a continuous titration system. After regeneration a new acceptance - regeneration cycle is started. The tests are carried out at 875 K.
Figure 4. Flow diagram of the laboratory set-up. $V = \text{valve}$, $ms = \text{molecular sieve}$, $PC = \text{pressure controller}$, $MFC = \text{massflowcontroller}$

**Results and discussion**

**Sol-gel precipitation**

For regenerative $H_2S$ removal a manganese or iron containing acceptor is needed. The preparation has to be carried out with the corresponding metal salt solution. A first attempt has been made by using $KMnO_4$ to prepare the metal salt solution. The maximum solubility of $KMnO_4$ in a 5% $w$ ammonia solution is about 0.4 M. According to Gmelin [7] $Mn(OH)_2$ can be formed and oxidized easily in base solutions when oxygen is present, accompanied by the formation of a gas and a brownish deposition: the manganese ions react in the base solution and form $MnO_2$. Therefore preparation of the ammonia solution took place under nitrogen. The precipitation was also carried out under nitrogen but still some reaction took place because the sol could not be prepared absolutely free of oxygen.

The particles prepared under nitrogen were dried, calcined and tested for their sulfur removal capacity. Particles dried in a microwave oven have a breakthrough capacity of 0.23 %$w$ S, particles dried in an oven at 335 K a breakthrough capacity of 0.28 %$w$ S. The acceptors prepared this way have a low capacity compared to acceptors prepared via wet impregnation, which have a breakthrough capacity of about 1 %$w$ S.

The main problem using sol-gel precipitation is to prepare a manganese or iron
containing ammonia solution. Literature [7, 8] showed that it is not possible to prepare a manganese containing base solution without the formation of Mn(OH)$_2$ and or MnO$_2$ except when carried out in a absolutely oxygen free atmosphere. The same is valid for iron containing ammonia solutions. In all cases a green (Fe(OH)$_2$) or a brown precipitate (Fe$_2$O$_3$) is formed when the reaction is carried out in nitrogen or air respectively.

The only way to solve this problem is to use a coordination compound like Na-EDTA to keep the metal ions in solution. The organic part of this compound is removed during calcination in air, but the sodium incorporated can give rise to some problems during the sulfidation regeneration experiments. The acceptor prepared by using Na-EDTA has a breakthrough capacity of about 1 %w S, but also a low mechanical strength. This still is not an improvement compared to the acceptor prepared by wet impregnation.

In-situ impregnation during sol-gel precipitation is therefore limited to the use of metal compounds that do not form solid precipitates when they are added to the ammonia solution. Wet impregnation of a γ-Al$_2$O$_3$ carrier prepared by sol-gel precipitation does not have the advantages of in-situ impregnation (high dispersion of the metal and strong interaction with the support) and therefore does not result in a better acceptor material.

Coprecipitation

The results of the coprecipitated samples are summarized in table 2. The first part of the table shows the experimental parameters used and the way of activation and calcination. The temperature program is given in the format: heating rate [K/min$^{-1}$]/level at which the temperature is kept constant [K]/time the reactor is kept at that temperature [hours]/heating rate [K/min$^{-1}$]/level at which the temperature is kept constant [K]/time the reactor is kept at that temperature [hours]. Some steps of the program were not carried out and are marked with a - character. Thus 10/475/2/10/775/4 means that the sample is heated with 10 K/min to 475 K and is kept at that temperature during 2 hours. Subsequently, the sample is further heated with 10 K/min to 775 K and is kept at that temperature during 4 hours.

The second part of the table summarizes the H$_2$S removal capacity (% w S) and the corresponding manganese conversion (%). The results can be compared with a sample prepared by wet impregnation.
In table 2 the following codes are used to denote the various samples: P = precipitate, the material obtained after coprecipitation which is not calcined; AP = Activated Precipitate, the material obtained after calcination or activation according to the procedure given in table 2; Imp = a sample which is prepared by wet impregnation.

**Table 2. Preparation and activation of coprecipitated acceptors.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>mol % Mn</th>
<th>Base</th>
<th>pH</th>
<th>T (K)</th>
<th>Aging (h)</th>
<th>Activation and calcination</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gas</td>
</tr>
<tr>
<td>P1</td>
<td>10</td>
<td>NH₄HCO₃</td>
<td>7</td>
<td>345</td>
<td>1.5</td>
<td>N₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5%v H₂</td>
</tr>
<tr>
<td>P2</td>
<td>50</td>
<td>NH₄HCO₃</td>
<td>7</td>
<td>345</td>
<td>1.5</td>
<td>N₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>air</td>
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<td>air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5%v H₂</td>
</tr>
<tr>
<td>P3</td>
<td>30</td>
<td>NH₄HCO₃</td>
<td>7</td>
<td>345</td>
<td>1.5</td>
<td>air</td>
</tr>
<tr>
<td>P4</td>
<td>30</td>
<td>Na₂CO₃</td>
<td>7</td>
<td>345</td>
<td>1.5</td>
<td>air</td>
</tr>
<tr>
<td>P5</td>
<td>50</td>
<td>NH₄HCO₃</td>
<td>3-7</td>
<td>345</td>
<td>1.5</td>
<td>air</td>
</tr>
<tr>
<td>P6</td>
<td>10</td>
<td>Na₂CO₃</td>
<td>7</td>
<td>345</td>
<td>0</td>
<td>5%v H₂</td>
</tr>
<tr>
<td>P7</td>
<td>24</td>
<td>Na₂CO₃</td>
<td>7</td>
<td>335</td>
<td>0.5</td>
<td>5%v H₂</td>
</tr>
<tr>
<td>P8</td>
<td>31</td>
<td>Na₂CO₃</td>
<td>7</td>
<td>335</td>
<td>0.5</td>
<td>5%v H₂</td>
</tr>
<tr>
<td>Imp</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>air</td>
</tr>
</tbody>
</table>

From the second part of the table follows that samples prepared according to literature concerning the preparation of nickel/alumina catalysts by coprecipitation [11-14]
(AP1-1 to AP5-1), can not be regenerated after the first sulfidation. The breakthrough capacity of the second and following cycles is very low.

Table 2. Continued.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (%w)</th>
<th>$S_A$ (m$^2$/g)</th>
<th>Breakthrough capacity (%w S)</th>
<th>Mn conversion (%) at breakthrough</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>Al</td>
<td>First</td>
<td>Stable$^{1)}$</td>
</tr>
<tr>
<td>AP1-1</td>
<td>8.25</td>
<td>24.6</td>
<td>4.19</td>
<td>8.35</td>
</tr>
<tr>
<td>AP1-2</td>
<td>8.46</td>
<td>18.8</td>
<td>4.79</td>
<td>8.71</td>
</tr>
<tr>
<td>AP1-3</td>
<td>8.75</td>
<td>39.4</td>
<td>4.08</td>
<td>1.80</td>
</tr>
<tr>
<td>AP1-4</td>
<td>9.16</td>
<td>42.6</td>
<td>4.85</td>
<td>8.25</td>
</tr>
<tr>
<td>AP2-1</td>
<td>24.2</td>
<td>11.0</td>
<td>158</td>
<td>14.7</td>
</tr>
<tr>
<td>AP2-2</td>
<td>24.5</td>
<td>14.5</td>
<td>191</td>
<td>15.2</td>
</tr>
<tr>
<td>AP2-3</td>
<td>25.1</td>
<td>29.0</td>
<td>149</td>
<td>13.8</td>
</tr>
<tr>
<td>AP2-4</td>
<td>25.7</td>
<td>29.4</td>
<td>193</td>
<td>13.8</td>
</tr>
<tr>
<td>AP2-5</td>
<td>25.7</td>
<td>12.2</td>
<td>62</td>
<td>12.1</td>
</tr>
<tr>
<td>AP2-6</td>
<td>26.9</td>
<td>31.2</td>
<td>168</td>
<td>14.0</td>
</tr>
<tr>
<td>AP3-1</td>
<td>25.2</td>
<td>20.0</td>
<td>217</td>
<td>13.7</td>
</tr>
<tr>
<td>AP4-1</td>
<td>26.0</td>
<td>28.5</td>
<td>153</td>
<td>14.4</td>
</tr>
<tr>
<td>AP5-1</td>
<td>n.d.</td>
<td>n.d.</td>
<td>18</td>
<td>14.9</td>
</tr>
<tr>
<td>AP6-1</td>
<td>7.73</td>
<td>31.6</td>
<td>44</td>
<td>5.51</td>
</tr>
<tr>
<td>AP7-1</td>
<td>19.0</td>
<td>24.2</td>
<td>116</td>
<td>14.5</td>
</tr>
<tr>
<td>AP8-1</td>
<td>23.1</td>
<td>25.0</td>
<td>120</td>
<td>15.7</td>
</tr>
<tr>
<td>Imp</td>
<td>7.1</td>
<td>n.d.</td>
<td>200</td>
<td>1.67</td>
</tr>
</tbody>
</table>

1) Breakthrough capacity after at least 10 cycles; n.d. = not determined

X-ray analysis of the corresponding dried precipitates (P1 to P5, P = Precipitate) shows that in all samples MnCO$_3$ is present with a crystallite size of about 50-80 nm.
Further it is shown that the acceptor precursor, the hydrotalcite, is not formed. X-ray analysis of the activated samples shows that the crystallite size is smaller; about 25 nm. However, compared with the impregnated sample the crystallites are very large. In the impregnated sample the Mn-crystallite size can not be determined because the manganese is present in a very disperse state. We concluded that most of the manganese is present as small crystallites which do not have a strong interaction with the $\gamma$-Al$_2$O$_3$ support and therefore can not be regenerated with a gas containing steam.

The measured composition of the samples shows that not all manganese is incorporated in the sample. At about 30 mol % manganese in the metal salt solution the maximum amount of manganese in the activated samples is obtained. It can also be concluded that the different ways of activating the samples do not result in large differences of sulfur removal capacity, although in literature it is stated that the activation of the precipitated samples is important. Obviously, the simplest way of activation will satisfy our purposes. Using another base solution does not result in large differences either (compare AP3-1 and AP4-1).

As mentioned before, X-ray analysis of the dried precipitates showed that the acceptor precursor, hydrotalcite, is not formed. Therefore samples P6, P7 and P8 were prepared to obtain the right precursor. Baker [13] has found that aging of the precipitate is the most important variable in preparing coprecipitates. As the manganese crystals are too large (about 25 nm) the aging time was lowered from 1.5 hours to zero. In that way growth of manganese crystals during aging is prevented. The results of AP6-1 show that, although the surface area is quite low, the sample is much more active in desulfurization.

Other research [16, 17] showed that addition of some zinc during precipitation can result in the formation of hydrotalcite, because the addition of some foreign ions like Zn$^{2+}$ give a stronger interaction between the manganese ions and the alumina carrier. It is important not to add too much zinc because ZnO can be formed. Under reaction conditions this compound can be reduced to Zn, which will evaporate. As long as the amount of zinc is low enough a stable ZnAl$_2$O$_4$ will be formed. Two samples with different Mn/Zn ratios (1/2 and 1/10, P7 and P8 respectively) have been prepared. From the results it can be concluded that addition of a little zinc results in an acceptor with a breakthrough capacity which is somewhat higher than the one from the impregnated sample.
The use of coprecipitation does not result in a much higher breakthrough capacity. The manganese crystals formed are too large and can not be regenerated with a gas containing steam. Addition of foreign ions like zinc results in a good acceptor.

**Wet impregnation**

Soerawidjaja showed [2] that the use of wet impregnation results in regenerable acceptors if a manganese acetate solution is used for impregnation and the metal content is not exceeding about 9 %w in the final acceptor. This is confirmed by the preparation of other acceptors. The breakthrough capacity of a stabilized acceptor is about 1 %w sulfur. The main disadvantage of this technique is that it is not very reproducible.

Wet impregnation can also be carried out at higher temperatures by heating the impregnation solution to which the carrier is added. An acceptor prepared by heating the solution during two hours at 345 K had a breakthrough capacity of about 1.3 %w S. So heating the impregnation solution can be favourable.

**Pore volume impregnation**

In contrast with to impregnation, pore volume impregnation is a reproducible technique. The amount of metal which is added to the carrier can be calculated easily.

<table>
<thead>
<tr>
<th>Number of impregnations</th>
<th>Metal content (%w Mn)</th>
<th>Breakthrough capacity (%w S)(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Measured</td>
</tr>
<tr>
<td>2</td>
<td>6.97</td>
<td>6.80</td>
</tr>
<tr>
<td>2</td>
<td>7.74</td>
<td>7.35</td>
</tr>
<tr>
<td>2</td>
<td>8.68</td>
<td>7.93</td>
</tr>
<tr>
<td>4</td>
<td>8.5</td>
<td>7.74</td>
</tr>
<tr>
<td>2</td>
<td>9.42</td>
<td>8.68</td>
</tr>
<tr>
<td>2</td>
<td>10.27</td>
<td>9.72</td>
</tr>
</tbody>
</table>

1) After 10 cycles.
before impregnation, and is only limited by the solubility of the metal salt in the solvent (e.g. water).

Table 3 shows the results of some acceptors prepared by pore volume impregnation. The calculated (from the amount of impregnation solution added) and measured (by means of AAS) metal contents are almost the same. The use of pore volume impregnation results in acceptors with a good sulfidation and regeneration behaviour. The breakthrough capacity is higher than the breakthrough capacity obtained with acceptors prepared by wet impregnation. The fluctuations in breakthrough capacity between different metal loadings is not clear yet.

**Monoliths**

The use of monoliths is interesting because they cause a low pressure drop if used in a fixed bed application. The manganese content and breakthrough capacity can be given in two ways: as a function of the weight of the whole sample (carrier + alumina washcoat) or as a function of the amount of alumina present in the sample. The latter gives the activity of the MnO/γ-Al₂O₃ compound.

The monolith can remove the H₂S from the gas stream effectively. The breakthrough capacity of the first sulfidation is high: 34.6 %w S (alumina) or 3.86 %w S (whole sample). The breakthrough capacity of the acceptor after initial deactivation is much lower, 2.48 %w S and 0.277 %w S respectively. This means that a considerable amount of manganese is present as (small) crystals which can not be regenerated. However, if the amount of sulfur captured is related to the amount of alumina present the material is very active. Probably, the additives in the washcoat (see table 1) play a role in the relatively high breakthrough capacity.

**Conclusions**

The attempts made to prepare acceptors with a high breakthrough capacity have resulted in somewhat surprising results. Techniques as sol-gel precipitation and coprecipitation, known from literature to result in acceptor materials with strong interactions between metal oxide and carrier and a high metal content, can not be used due to experimental problems (sol-gel precipitation) or result in acceptors with the same
breakthrough capacity (coprecipitation) as obtained by pore volume impregnation. When coprecipitation is used, addition of zinc during the precipitation results in a acceptor where the manganese has a stronger interaction with the alumina than in the samples without zinc due to the formation of the hydrotalcite: the regenerability of the acceptor is higher.

Preparation of acceptors by means of pore volume impregnation is a convenient method. It results in the best acceptor materials with a long proven lifetime (see chapter 4) while little effort is needed.

A promising development is the use of monoliths provided with an alumina washcoat. Further investigations should concentrate on the effects of additives in the alumina washcoat on the capacity of the acceptor. Addition of additives to standard alumina possibly increases the capacity in applications where normal particles are used.

References

8  D.R. Lide, Handbook of Chemistry and Physics, 72nd edition, CRC Press Inc., USA, 1991
10 P.H.M. de Korte, The influence of the Ni/Al ratio on the properties of coprecipitated nickel/alumina catalysts, Ph.D. Thesis, Delft University of Technology, DUP, 1988
15 J.J.F. Scholten, Katalyse en katalysatoreen, Delft University of Technology, 1989
16 Personal communication, prof. dr. J.J.F. Scholten, dr. Xu Xiaoping, Delft University of Technology, 1990
Characterization of acceptors for high temperature regenerative H₂S removal with TPR, TPS, HREM and XPS

Abstract

Measurements are carried out to give a clear view on the compounds actively involved in the sulfidation-regeneration cycles of Mn/γ-Al₂O₃ acceptors, used for steam regenerative H₂S removal at high temperatures. Up to three different types of manganese oxide can be distinguished. The first type consists of very reactive but irrecoverable manganese oxide crystallites, which can be sulfided only once. The second type is surface MnAl₂O₄ spinel which can be sulfided and regenerated easily, while the third type is a MnAl₂O₄ spinel of which the rate of sulfidation and regeneration is limited by the diffusion of Mn²⁺-ions in the γ-Al₂O₃ support.

Introduction

Soerawidjaja [1] has tried to characterize the acceptors with several techniques. With X-ray spectroscopy he showed that XRD patterns of regenerable acceptors are virtually identical to the γ-Al₂O₃ pattern. The manganese in such acceptors is too highly dispersed to cause any noticeable change in the alumina structure. On the other hand, XRD patterns of irrecoverable acceptors do show several sharp lines, characteristic for MnO. This confirms the supposition that irrecoverable acceptors contain poorly dispersed clusters of MnO.

As MnO is green [2] and regenerable acceptors light cream to light grey other compounds than MnO crystallites must be present on the acceptor surface. Diffuse Reflectance Spectroscopy (DRS) can give information on compounds present on the
acceptor. The DRS spectra of regenerable acceptors derived from manganese (II) acetate do not show a "MnO" peak as do irregenerable acceptors. Moreover, the DRS spectra of acceptors derived from manganese (II) acetate almost completely resemble that of MnAl₂O₄, which provides an indication that the active compound of regenerable acceptors is surface MnAl₂O₄ spinel (or tetrahedral Mn²⁺).

Mössbauer spectroscopy can give information about the oxidation state of metal oxides carried by e.g. alumina. Unfortunately, manganese is not Mössbauer active. Iron containing acceptors show a desulfurization - regeneration behaviour comparable to manganese containing acceptors with a similar metal content. As iron is Mössbauer active, Mössbauer spectroscopy can be used to study the behaviour of iron containing acceptors. Uncalcined material only shows the presence of a Fe³⁺; there is no indication of the presence of Fe²⁺. Reduction with humid hydrogen shows that all Fe³⁺ ions are reduced to Fe²⁺, but not to metallic iron as might be expected at 875 K. The same is observed by other investigators for the reduction of iron oxide on γ-Al₂O₃ [3 - 9]. If the reduced acceptor is exposed to air only two-thirds of the Fe²⁺ ions are oxidized to Fe³⁺. Spectra obtained at different temperatures (295, 77 and 4.2 K) indicate that the iron ions studied are highly dispersed on the alumina support.

The experiments carried out by Soerawidjaja [1] show that acceptors which can be regenerated completely, consist of a surface MnAl₂O₄⁻ or FeAl₂O₄ spinel. A model he developed to describe breakthrough curves takes two different reactions into account: a fast reaction with H₂S in the gas phase and a slow sulfur oxygen exchange in the solid phase. Other sulfidation-regeneration experiments show that acceptors with a high metal content, e.g. 10 %w Mn, contain some irregenerable manganese as the breakthrough capacity decreases sharply between the first and the second sulfidation. The amount of H₂S released during regeneration is much lower then the amount of sulfur captured by the acceptor in the first sulfidation.

To improve understanding of processes taking place on the surface of the acceptor and the formation and occurrence of different manganese phases, Temperature Programmed Reduction (TPR) and Temperature Programmed Sulfidation (TPS) have been used to study the acceptor. TPR can give information about the MnO and MnAl₂O₄
ratio as the reduction of manganese oxide to MnO will take place at an other
temperature than the reduction to MnAl₂O₄, due to different interactions with the γ-
Al₂O₃ support. TPS is a powerful technique to show the differences in activity of various
manganese compounds towards sulfidation. Very interesting differences can be observed
between fresh oxidic, fresh reduced and used/spent samples with a stable sulfidation-
regeneration performance.

Assuming that the main characteristics of the acceptor are already present in the
acceptor precursor, the calcined material, X-ray Photoelectron Spectroscopy (XPS), and
High Resolution Electron Microscopy (HREM) have been used to study differences
between various forms of manganese oxide. Comparison of fresh and used/spent samples
may result in a way to distinguish the sites responsible for fast sulfidation and slow
sulfidation as well.

**Experimental**

**Acceptor preparation**

A series of acceptors with metal contents varying from 0.5 to 10 %w manganese
on γ-Al₂O₃ has been prepared by pore volume impregnation. To prepare the
impregnation solutions manganese (II) acetate (Merck, p.a.) is used. The carrier material
(AKZO/Ketjen, 001-1.5E, particle diameter 0.25 - 0.42 mm) is impregnated one or two
times, depending upon the desired metal content. The solubility of manganese (II)
acetate in water only allows one impregnation step for acceptors with a metal content
below 6 %w Mn. The acceptors are calcined in air (flow rate 67.5 μmol/s) at 575 K
during 20 hours.

**Sulfidation-regeneration experiments**

Sulfidation-regeneration experiments are carried out in the set-up described in the
previous chapter. All experiments are carried out at 875 K.

**Temperature Programmed Reduction (TPR)**

A schematic flow diagram of the TPR apparatus is shown in figure 1. A high
purity mixture of 67 %v H₂ in Ar (flow rate 20.3 μmol/s) is passed over the oxidic sample
in the quartz reactor tube (internal diameter 4-5 mm). The sample is hold on a quartz wool plug. The temperature of the sample (measured inside the reactor) is raised linearly (10 K/min) from room temperature to 1270 K. Subsequently, the sample is kept at 1270 K for 30 minutes. The weight of the samples is always about 150 mg. Water formed by reduction or dehydration is trapped in 3 A and 5 A molsieve columns. Other compounds, such as CO₂ or organic compounds, are trapped as well. After passing the molsieves the gas composition is measured continuously by a thermal conductivity detector (TCD) and a flame ionization detector (FID). The TCD detects all changes in H₂, CH₄ and O₂ pressure. The FID is selective for CH₄. During the experiments no response was observed on the FID. Consequently, only the absolute sensitivity of the TCD has been determined. This was done by TPR of high purity CuO which reduces to metallic Cu; the H₂ consumed was calculated from the TCD signal and resulted in a calibration constant.

**Temperature Programmed Sulfiding (TPS)**

A schematic flow diagram of the TPS apparatus is shown in figure 2. A mixture of 3.3 %v H₂S and 28.1 %v H₂ in Ar is passed over the oxidic sample in the quartz reactor tube with a flow rate of 10.9 μmol/s. The sample (about 100 mg) is hold between two quartz wool plugs. Sulfiding starts at room temperature until H₂S uptake was finished (about 30 minutes). Then the temperature is raised to 1270 K with a rate of 10 K/min. Subsequently the sample is kept at 1270 K for 30 minutes. The H₂S consumption and/or production is determined by a UV-spectrophotometer. After trapping H₂S and H₂O in a 5 A molsieve the H₂ level is determined with a TCD in order to determine its
consumption or production in the reactor. Calibration of the equipment is carried out by sulfiding high purity Co$_3$O$_4$. Both H$_2$S response and H$_2$ response can be obtained from such a measurement.

**High Resolution Electron Spectroscopy (HREM)**

The sample was suspended in ethanol and ground. One drop of the suspension was laid down on a copper grid and the ethanol was evaporated. The HREM measurements were carried out in a Philips CM 30 transmission electron microscope with a resolution of 0.19 nm.

**X-ray Photoelectron Spectroscopy (XPS)**

XPS analysis was performed on a Phi 5400 ESCA system equipped with a hemispherical analyzer. Mg Kα radiation was used for sample excitation. Calibration was performed by correcting for the position of the O 1s line in each spectrum.

The manganese positions at binding energies of 647 and 658 eV were used as a probe to obtain information on the nature of the manganese phase as a function of the metal loading.

Auger electrons can give rise to dominant peaks in the photoelectron spectrum. These Auger peaks, obtained in the region with binding energies between 710 and 630
eV, will be discussed as well.

**Results**

**Sulfidation-regeneration experiments**

![Graph showing breakthrough capacities of acceptors with different metal contents. ▲ = first sulfidation, ▼ = capacity after initial deactivation.](image)

*Figure 3. Breakthrough capacities of acceptors with different metal contents. ▲ = first sulfidation, ▼ = capacity after initial deactivation.*

A series of 12 acceptors, with metal loadings ranging from 0.5 %w Mn to 10 %w Mn have been prepared and tested. Each acceptor has been submitted to 16 sulfidation-regeneration cycles. Figure 3 shows the breakthrough capacity of the first and the breakthrough capacity after 16 sulfidation-regeneration cycles of these acceptors. From this figure it can be concluded that during the first sulfidation the amount of $\text{H}_2\text{S}$ captured till breakthrough almost linearly rises with increasing metal content of the acceptors. The measurements also show that the higher the metal content, the bigger the difference between the first and the breakthrough capacity after 16 cycles becomes. The main part of this deactivation takes place during the first sulfidation: the breakthrough capacity of the second cycle (not shown) is only little higher than the breakthrough capacity after 16 cycles. Obviously the amount of irregenerable manganese increases with
increasing metal content. Another difference can be obtained from the regeneration curves. Figure 4 compares the regeneration curves of an acceptor with a low and a high metal content. The regeneration of 2.0 %w Mn/γ-Al₂O₃ is fast and completed after about 2.5 minutes. The regeneration of 7.9 %w Mn/γ-Al₂O₃ consists of a main part of which the regeneration is fast and completed after about 3.5 minutes, and another part which releases the H₂S slowly from the acceptor during a relatively long time. It is clear that a slow sulfur-oxygen exchange reaction takes place with part of the manganese present in acceptors with higher metal loadings.

**Temperature Programmed Reduction (TPR)**

Results of TPR measurements of acceptors with different metal loadings are shown in figure 5. The TPR pattern of the carrier material is shown as well. On the abscissa the temperature is shown, on the ordinate the hydrogen consumption in arbitrary units. However, the scale used for all patterns is the same, unless otherwise stated. Only TCD signals (H₂ consumption) are shown because the FID signals did not show any peak, indicating that no organic compounds are left on the acceptor.

Two peaks are present in all TPR patterns obtained with manganese containing
acceptors. The second peak, found in the temperature region between 775 and 975 K, changes from sharp (2.0 %w Mn) to broad (9.7 %w Mn). The γ-Al₂O₃ carrier also shows a H₂ consumption in this temperature region. The surface area of the γ-Al₂O₃ peak closely corresponds to the surface area of the high temperature peak of the manganese containing samples, if corrected for the manganese content. The shape of this peak can
be explained by accounting for the catalytic effect of manganese. An increasing amount of manganese on the surface causes the alumina surface exposed to hydrogen to decrease: the hydrogen consumption peak broadens. This means that the high temperature hydrogen consumption can be attributed completely to the carrier material.

So, the reduction of the manganese compounds takes place in the temperature region between 425 and 775 K. The surface area of the corresponding peak increases with increasing metal content of the acceptor. The amount of hydrogen consumed can be used to calculate the oxidation state of the manganese on the acceptor. In acceptors with up to 5.0 %w Mn, all manganese is present as Mn$^{3+}$. In acceptors with a higher metal content part of the manganese is present as Mn$^{4+}$, besides a considerable amount of Mn$^{3+}$. Apparently, the manganese cannot be oxidized to Mn$^{4+}$ during calcination in air when a strong interaction exists between manganese and carrier. At higher metal contents, clusters of manganese are formed with less interaction with the $\gamma$-Al$_2$O$_3$ support. They can be oxidized easier.

Unfortunately, the formation of MnAl$_2$O$_4$ during reduction of the manganese compounds cannot be distinguished from other reduction processes taking place. Presumably, the reduction peak of the manganese oxides is broad because the manganese oxides are not present in a well defined crystal state, but as a disperse manganese oxide with different crystal sizes, different interactions with the carrier and different oxidation states.

Acceptors which have been exposed to 16 sulfidation-regeneration cycles are used for TPR measurements as well. These acceptors are calcined in air (flow rate 67.5 $\mu$mol/s) at 575 K during 1 hour to reoxidize the manganese. This treatment is necessary as the acceptors oxidize to some extent while they are exposed to air after the sulfidation-regeneration experiments. Various types of manganese can be oxidized during this treatment: bulk MnS crystallites which were sulfided during the first sulfidation, or Mn$^{2+}$ ions present in surface and subsurface positions. Figure 6 shows the results of fresh and used samples of 4.3 %w Mn/$\gamma$-Al$_2$O$_3$ and 7.9 %w Mn/$\gamma$-Al$_2$O$_3$. It follows that marked changes took place during the sulfidation-regeneration experiments. The amount of manganese that can be reduced after reoxidation of the acceptor is much lower than that of a fresh acceptor. We conclude that a considerable amount of manganese ions is
Figure 6. TPR patterns of fresh acceptors and acceptors used during 16 sulfidation-regeneration cycles.

diffused into the carrier and formed a new compound, the MnAl$_2$O$_4$ spinel. In case of 7.9 %w Mn only about 30 % of the manganese could be reduced in TPR after being used during 16 sulfidation-regeneration cycles. The reoxidation at 575 K clearly not lasted long enough to let all Mn$^{2+}$-ions diffuse back to the surface of the γ-Al$_2$O$_3$ to be oxidized.

**Temperature Programmed Sulfdation (TPS)**

The TPS patterns of fresh Mn/γ-Al$_2$O$_3$ acceptors with different metal loadings are presented in figures 7 and 8. Both the H$_2$ and H$_2$S signals for 7.9 %w Mn/γ-Al$_2$O$_3$ are shown in figure 7. Figure 8 shows the H$_2$S patterns of seven acceptors and also the H$_2$S pattern of the γ-Al$_2$O$_3$ carrier. Figure 8 only shows the H$_2$S signals.

The sulfidation pattern shown in figure 7 starts with an H$_2$S uptake at room temperature (A). Part of the manganese oxide is sulfided via a fast sulfur oxygen exchange. The sulfidation is fast compared to reduction as during flushing of the reactor at room temperature with an hydrogen mixture before the TPS measurement no reaction takes place. The γ-Al$_2$O$_3$ carrier also adsorbs H$_2$S at room temperature. Directly after the start of the temperature programme a small amount of H$_2$S, physically adsorbed on
the acceptor surface, is desorbed (B). Subsequently, two H₂S consumption peaks are observed at 365 and 525 K, none accompanied by any H₂ consumption (C). These peaks are attributed to the sulfidation of manganese oxides. At 675 K a H₂S production peak is observed, accompanied by a H₂ consumption (D). Magnus [13] showed with TPR-S that this H₂S production is caused by reduction of excess sulfur, probably Sₓ species or elemental sulfur chemisorbed on the acceptor. This sulfur adsorbed on the acceptor surface during H₂S uptake and dissociated at lower temperatures. Finally, a broad H₂S uptake peak is found between 725 and 1250 K (E). This H₂S uptake is attributed to sulfidation of Mn²⁺-ions in subsurface positions and tetrahedrally coordinated Mn²⁺ surface ions, or, in other words, to the sulfidation of MnAl₂O₄ compounds. The MnAl₂O₄ species are relatively stable as is shown by the high sulfidation temperature.

The TPS patterns in figure 8, of acceptors with different metal loadings, show that the shape of the pattern remains constant: only the amount of H₂S consumed or produced changes with metal loading. The quantitative data are listed in table 1. To make interpretation of the data from table 1 easier they are plotted in figures 9. The H₂S uptake at room temperature increases linearly with increasing metal content (curve A).
Figure 8. TPS patterns of acceptors with different metal loadings. Only H$_2$S signals are shown.
Table 1. Quantitative TPS data of the patterns in figure 8.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>μmol Mn/ g acc</th>
<th>H₂S uptake A</th>
<th>H₂S prod. B</th>
<th>H₂S uptake C</th>
<th>H₂S prod. D</th>
<th>H₂S uptake E</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃</td>
<td>0</td>
<td>260</td>
<td>150</td>
<td>0</td>
<td>0</td>
<td>153</td>
</tr>
<tr>
<td>2.0 %w Mn/γ-Al₂O₃</td>
<td>364</td>
<td>497</td>
<td>100</td>
<td>124</td>
<td>24</td>
<td>233</td>
</tr>
<tr>
<td>5.9 %w Mn/γ-Al₂O₃</td>
<td>1074</td>
<td>1340</td>
<td>39</td>
<td>302</td>
<td>77</td>
<td>359</td>
</tr>
<tr>
<td>6.8 %w Mn/γ-Al₂O₃</td>
<td>1238</td>
<td>1600</td>
<td>31</td>
<td>185</td>
<td>87</td>
<td>263</td>
</tr>
<tr>
<td>7.4 %w Mn/γ-Al₂O₃</td>
<td>1347</td>
<td>1600</td>
<td>35</td>
<td>340</td>
<td>90</td>
<td>396</td>
</tr>
<tr>
<td>7.9 %w Mn/γ-Al₂O₃</td>
<td>1438</td>
<td>1650</td>
<td>39</td>
<td>688</td>
<td>101</td>
<td>344</td>
</tr>
<tr>
<td>8.7 %w Mn/γ-Al₂O₃</td>
<td>1584</td>
<td>1670</td>
<td>35</td>
<td>572</td>
<td>101</td>
<td>447</td>
</tr>
<tr>
<td>9.7 %w Mn/γ-Al₂O₃</td>
<td>1766</td>
<td>2160</td>
<td>32</td>
<td>798</td>
<td>123</td>
<td>425</td>
</tr>
</tbody>
</table>

All amounts are given in μmol/g. A: H₂S uptake at room temperature; B: H₂S production at the start of the temperature programme; C: H₂S uptake at 365 and at 525 K; D: H₂S production at 675 K; E: H₂S uptake between 725 and 1250 K.

At the start of the temperature programme the H₂S desorption is strongest for γ-Al₂O₃, although not all H₂S adsorbed at room temperature desorbs. Obviously part of the H₂S dissociated on the alumina surface. When the metal content increases, the amount of H₂S desorbed decreases until a certain stable level is reached (curve B). The H₂S uptake by manganese oxides (curve C) increases with increasing metal content, but no clear relation between H₂S uptake and metal content can be observed. The reduction of the excess sulfur (curve D) shows that the amount of excess sulfur adsorbed on the acceptor at low temperatures increases with increasing metal content. Obviously manganese sites are necessary for the formation and stabilization of excess sulfur. Finally, the H₂S uptake at high temperatures (curve E) increases with an increasing metal content. Even the γ-Al₂O₃ carrier shows some H₂S uptake, probably due to physical and chemical adsorption and some impurities.

TPS measurements have also been carried out with fresh, but reduced samples,
and with acceptors that have been exposed to 16 sulfidation-regeneration cycles. These experiments are carried out with 2.0 %w Mn and 7.9 %w Mn on γ-Al₂O₃ acceptors. The same acceptor material has also been reduced separately at 775 K during 1 hour (2.0 and 7.9 %w Mn) or at 875 K during 16 hours (7.9 %w Mn) in the TPS apparatus to investigate the changes that occur after reduction during the 16 sulfidation-regeneration cycles. The acceptors exposed to the sulfidation-regeneration experiments have been calcined in air as mentioned earlier.

The results of the acceptor with 2.0 %w Mn are not shown as the signals are small due to the low metal content; the results are discussed qualitatively only. When the acceptor is reduced at 775 K the H₂S uptake at room temperature becomes smaller than the one of a fresh acceptor. This uptake is smallest for the acceptor used during 16 sulfidation-regeneration cycles. The H₂S uptake at 365 and 525 K does not change much. The amount of excess sulfur reduced at 675 K decreased, in the sequence fresh, reduced, tested acceptor. This can be caused by a smaller H₂S uptake at room temperature due to diffusion of manganese ions into the carrier, or, in other words, by the formation of MnAl₂O₄. At the same time the formation of MnAl₂O₄ explains why a higher H₂S uptake
is found when the acceptor is reduced or tested at high temperatures.

![Graph showing H₂S uptake vs. temperature](image)

Figure 10. TPS patterns of fresh (A), reduced (775 K = B, 875 K = C) and used (D) 7.9 \%w Mn/\γ-Al₂O₃ acceptors.

The TPS patterns of the acceptor with 7.9 \%w Mn are shown in figure 10. The H₂S uptake or production of every peak is summarized in table 2 as a percentage of the total amount of H₂S involved in the measurements. From figure 10 and table 2 it follows that the H₂S uptake at room temperature decreases with increasing reduction level of the acceptor. At the same time the H₂S uptake at 365 and 525 K decreases. However, the H₂S uptake in the high temperature region between 725 and 1250 K increases strongly: from about 13 \% for the fresh to about 50 \% for the tested acceptor. At the same time
Table 2. The TPS data of 7.9 %w Mn/γ-Al₂O₃. The values correspond with the patterns in figure 10 and are given as a percentage of the total amount of H₂S.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>H₂S uptake A</th>
<th>H₂S prod. B</th>
<th>H₂S uptake C</th>
<th>H₂S prod. D</th>
<th>H₂S uptake E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>57.1</td>
<td>1.6</td>
<td>24.3</td>
<td>3.6</td>
<td>13.4</td>
</tr>
<tr>
<td>Reduced at 775 K</td>
<td>43.6</td>
<td>5.3</td>
<td>23.2</td>
<td>2.2</td>
<td>25.7</td>
</tr>
<tr>
<td>Reduced at 875 K</td>
<td>36.0</td>
<td>4.1</td>
<td>19.0</td>
<td>2.3</td>
<td>38.6</td>
</tr>
<tr>
<td>Tested</td>
<td>36.5</td>
<td>0.9</td>
<td>11.8</td>
<td>1.2</td>
<td>49.6</td>
</tr>
</tbody>
</table>

A: H₂S uptake at room temperature; B: H₂S production at the start of the temperature programme; C: H₂S uptake at 365 and at 525 K; D: H₂S production at 675 K; E: H₂S uptake between 725 and 1250 K.

the peak maximum shifts to a higher temperature, from 915 K to 1075 K. Due to these effects complete sulfidation of MnAl₂O₄ becomes more difficult the longer the acceptor has been used, until a stable performance is reached. Manganese which was easy to sulfide at room temperature is converted into manganese which is difficult to sulfide.

High Resolution Electron Microscopy

A high resolution electron micrograph of a used 7.9 %w Mn/γ-Al₂O₃ acceptor is shown in figure 11. It can be seen that on some places the surface is covered with needle like structures, among large areas without such needles (not on the photograph). EDAX measurements showed that needle free areas contained both aluminium and manganese atoms with a Mn:Al ratio of 1:5 to 1:10. The needles, however, showed a completely different Mn:Al ratio which ranged from 2:3 to 3:2. Relatively much manganese is present in such areas. HREM photographs of a fresh 7.9 %w Mn/γ-Al₂O₃ acceptor show the same needle like structures.

X-ray Photoelectron Spectroscopy

XPS measurements have been carried out with fresh acceptors, acceptors which have been used during 16 sulfidation-regeneration cycles and with two reference materials.
Figure 11. HREM micrograph of a used 7.9 %w Mn/γ-Al₂O₃ acceptor. The length of the bar is 2 nm.

Figure 12. XPS pattern of 9.7 %w Mn/γ-Al₂O₃ used during 16 sulfidation-regeneration cycles.
The results of XPS measurements of different fresh acceptors and the reference materials are summarized in table 3. Figure 12 gives an example of the XPS patterns obtained: the pattern of 9.7 %w Mn/γ-Al₂O₃ which has been used during 16 sulfidation-regeneration cycles is shown. The XPS patterns obtained consisted of two peaks, a main peak and a satellite, at different binding energies. The satellite appears in the XPS patterns due to spin-orbit coupling; the ratio of the surfaces of these peaks should be 3 to 1 in case of manganese. This ratio is about 3 to 1 in case of manganese on alumina and decreases to about 2 to 1 for the reference materials. Both the main peak and the satellite consist each of two sub peaks. Table 3 shows the surface areas of these peaks. In case of MnO₂ the contributions of the sub peaks to the main peak are equal (see sub 1/sub 2). In case of 2.0 %w Mn, sub peak 1 is almost four times bigger than sub peak 2. It looks as if the amount of manganese covered by sub peak 1 minus the amount of manganese in sub peak 2 represents the amount of manganese present in a highly dispersed state on the surface of the acceptor. Therefore, the ratio of highly dispersed manganese and of bulk manganese can be calculated according to: sub peak 1/sub peak 2. It is clear that the amount of highly dispersed manganese decreases when the metal content increases.

Table 3. XPS data of fresh acceptors and reference materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage of the total area</th>
<th>Main/satellite</th>
<th>Sub 1/sub 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Main peak</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sub peak 1</td>
<td>Sub peak 2</td>
<td></td>
</tr>
<tr>
<td>2.0 %w Mn/γ-Al₂O₃</td>
<td>59.2</td>
<td>15.2</td>
<td>2.91</td>
</tr>
<tr>
<td>5.9 %w Mn/γ-Al₂O₃</td>
<td>58.4</td>
<td>19.7</td>
<td>3.57</td>
</tr>
<tr>
<td>9.7 %w Mn/γ-Al₂O₃</td>
<td>50.0</td>
<td>21.5</td>
<td>2.51</td>
</tr>
<tr>
<td>50 %w Mn/SiO₂</td>
<td>40.2</td>
<td>27.0</td>
<td>2.05</td>
</tr>
<tr>
<td>MnO₂</td>
<td>32.7</td>
<td>33.5</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td>Satellite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sub peak 3</td>
<td>Sub peak 4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.0</td>
<td>7.6</td>
<td>3.90</td>
</tr>
<tr>
<td></td>
<td>14.5</td>
<td>7.4</td>
<td>2.97</td>
</tr>
<tr>
<td></td>
<td>20.1</td>
<td>8.4</td>
<td>2.33</td>
</tr>
<tr>
<td></td>
<td>27.4</td>
<td>5.4</td>
<td>1.49</td>
</tr>
</tbody>
</table>
The results of XPS measurements of acceptors used during 16 sulfidation-regeneration cycles are summarized in table 4. From these measurements it follows that the acceptor with the lowest metal content still contains the highest amount of highly dispersed manganese. However, when the data are compared with the data in table 3 it follows that the amount of highly dispersed manganese on the acceptor surface has decreased. This is in agreement with TPR and TPS measurements from which follows

**Table 4. XPS data of acceptors used during 16 sulfidation-regeneration cycles.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage of the total area</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Main peak</td>
<td>Satellite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sub peak 1</td>
<td>Sub peak 2</td>
<td>Sub peak 3</td>
</tr>
<tr>
<td>2.0 %w Mn/γ-Al₂O₃</td>
<td>60.7</td>
<td>20.2</td>
<td>12.3</td>
</tr>
<tr>
<td>5.9 %w Mn/γ-Al₂O₃</td>
<td>57.5</td>
<td>20.6</td>
<td>14.9</td>
</tr>
<tr>
<td>9.7 %w Mn/γ-Al₂O₃</td>
<td>52.2</td>
<td>26.4</td>
<td>14.5</td>
</tr>
</tbody>
</table>

that manganese ions diffuse into the alumina carrier during the sulfidation-regeneration cycles. As XPS is a surface characterization technique most of the information is obtained from the two or three uppermost atomic layers [11]: manganese diffused into the carrier will not be characterized. The results indicate that subsurface MnAl₂O₄ species are formed.

In the XPS patterns also Auger electron features can be observed. Figure 13 shows the XPS patterns and the Auger electron features in the range of 610 to 730 eV. The spectra of bulk manganese compounds (MnO, Mn₃O₄, Mn₂O₃ and MnO₂) are all exactly the same. As an example the pattern of MnO₂ is shown in figure 13. A number of peaks is observed at binding energies of 618 (possibly composed of two peaks), 631, 642, 654 and 669 eV. The peaks at 642 and 654 are the 2p₃/₂ and 2p₁/₂ electrons obtained during the XPS measurements and discussed above. At 618 eV the L₃VV and at 669 eV the L₂M₂₃VV Auger electron transitions of manganese take place [10]. In the spectra of
the alumina carried manganese samples these peaks can be observed among a number of other peaks. In the pattern of the acceptor containing 9.7 %w manganese, clearly manganese oxides are present. The L$_3$M$_{23}$V Auger electron transitions at 669 eV shifted to a higher binding energy of about 678 eV. However, at 666, 690 and 704 eV other peaks are present as well. Reference measurements with the γ-Al$_2$O$_3$ carrier showed that the peak at 690 eV is caused by the γ-Al$_2$O$_3$ carrier. The peaks at 666 and 704 eV either can be caused by the peaks obtained at 642 and 654 eV due to a shift to higher binding energies of part of the manganese atoms, or by Auger electron features of manganese in a binding which is different of that of pure manganese. In both cases, obviously manganese is present in a highly dispersed state on the alumina surface.

In figure 13 also the patterns of 2.0 %w Mn/γ-Al$_2$O$_3$ and 0.5 %w Mn/γ-Al$_2$O$_3$ are shown. The contribution of the two peaks, which are only observed in the alumina carried samples, increases when the metal content decreases. In other words: the amount of bulk like manganese oxides decreases and it looks like if a manganese compound in a highly dispersed state is formed.

When the amount of highly dispersed manganese is compared with the amount of bulk manganese oxide both the 9.7 %w Mn/γ-Al$_2$O$_3$ and the 2.0 %w Mn/γ-Al$_2$O$_3$ have a disperse manganese/bulk manganese ratio of about 0.5. However, when the metal content further decreases the amount of highly dispersed manganese drastically increases as can be seen in figure 13; the value of the disperse manganese/bulk manganese ratio which is about 4, indicating that most of the manganese is present in a highly dispersed state.

When the patterns are obtained from acceptors which have been used during 16 sulfidation-regeneration cycles, the peaks discussed above disappeared. Figure 14 shows the patterns of 9.7 %w Mn for both the fresh and the used acceptor. It is clear that the two peaks disappeared and that the pattern of the used acceptor resembles that of bulk manganese oxide, except the peak caused by alumina. It looks like if the highly dispersed manganese atoms on the alumina surface are dissolved in the carrier and formed a (sub)surface manganese aluminate.
Figure 13. XPS patterns and Auger electron features of MnO₂ and 9.7, 2.0 and 0.5 %w Mn/γ-Al₂O₃.
Figure 14. XPS patterns of fresh and used (16 sulfidation-regeneration cycles) 9.7 %w Mn/γ-Al₂O₃.

Discussion

Sulfidation-regeneration experiments

Depending upon metal loading up to three different types of manganese oxide can be distinguished. Part of the manganese oxide present on the γ-Al₂O₃ carrier has no interaction with the support and is irrecoverable: obviously small MnO crystallites exist. The other part shows strong interaction with the support and can be regenerated with a gas containing steam, at high metal loadings partly by a slow process. Preparation of acceptors with a metal content higher than about 9 %w Mn is useless as the manganese
oxide will not have a strong interaction with the support, unless the surface area of the acceptor can be increased.

**Temperature Programmed Reduction**

Almost no literature is available on TPR of MnO$_2$/γ-Al$_2$O$_3$. Nohman et al. [12] present some TPR results on manganese oxide catalysts, but their experiments are carried out in a way different from the experiments described above: they injected pulses of H$_2$ every other minute in the reactor up to a temperature of 775 K.

The related system FeO$_x$/γ-Al$_2$O$_3$ may give some additional information. Kock [13], Kadkhodayan [14] and Lycourghiotis [15] found that iron oxide reduces to Fe$^{2+}$ and forms interfacial compounds of metal oxide and support. A broad reduction peak at relatively low temperatures is observed (375 - 675 K). The iron strongly interacts with the γ-Al$_2$O$_3$ and makes it difficult to reduce. The different reduction steps (Fe$_2$O$_3$ to Fe$_3$O$_4$ to FeO) can not be distinguished.

Similar observations can be made for the measurements discussed above with the system MnO/γ-Al$_2$O$_3$: the different reduction steps can not be distinguished, nor the formation of MnAl$_2$O$_4$.

**Temperature Programmed Sulfidation**

Since manganese is able to form MnAl$_2$O$_4$ spinel structures at high temperatures it is reasonable to assume that part of the manganese is present as surface MnAl$_2$O$_4$ after calcination at 575 K during 20 hours. The amount of spinel formed depends on the diffusion rate of Mn$^{2+}$-ions into the surface layer at the calcination temperature, i.e. 575 K, and the calcination time used. Whether these species are sulfidable depends on the rate of diffusion back to the surface and the sulfidation temperature applied (see also chapter 4).

From literature [16, 17] it is expected that all manganese compounds are sulfidable. The measurements shown in figure 10 and table 2 confirm this assumption. The amount of MnAl$_2$O$_4$ already present in the fresh calcined acceptor increases when the acceptor is reduced or tested. As the peak maximum in the TPS patterns at the same time shifts to higher temperatures this means that when more MnAl$_2$O$_4$ is converted from a surface MnAl$_2$O$_4$ spinel to a bulk or a subsurface MnAl$_2$O$_4$ spinel it becomes more
difficult to sulfide this compound. This behaviour corresponds with the measurements carried out by Scheffer et al. [18] for NiO/γ-Al₂O₃ and Arnoldy et al. [17] for CoO/γ-Al₂O₃.

The reduction of non-stoichiometric sulfur or excess sulfur (Sₓ or chemisorbed elemental sulfur), observed with all acceptors at 675 K, is discussed extensively by Mangnus [16]. From the observation that the reduction of this type of sulfur only takes place at 675 K, we conclude that it is strongly chemisorbed on the acceptor. TPR measurements of Mn catalysts sulfided at 673 K showed that the reduction of the sulfur species took place at 675 K, near the applied sulfiding temperature. This means that the sulfur species already have been formed during sulfidation. The amount of sulfur species formed decreases with increasing MnAl₂O₄ formation (see table 2). This means that formation of sulfur takes place on manganese oxide sites which, in case of the acceptors studied here, are responsible for the irregenerable amount of sulfur adsorbed.

From table 2 it also follows that, if the amount of MnAl₂O₄ formed increases, H₂S uptake at room temperature and at 365 and 525 K decreases, obviously due to the conversion of manganese oxide into MnAl₂O₄. This observation agrees with the above discussion concerning the formation of excess sulfur.

High Resolution Electron Microscopy

The results of the HREM analysis show that at least two different kinds of manganese oxide are present on the surface of the acceptor. The EDAX analysis showed that clusters of manganese oxide are present. These clusters will have little or almost no interaction with the γ-Al₂O₃ support and can be responsible for the irregenerable part of the manganese that is present on the acceptor (observed during the first sulfidation - regeneration cycle). The other areas with a much lower Mn:Al ratio obviously consist of a disperse manganese oxide with strong interaction with the γ-Al₂O₃ support. It is responsible for the steam regenerable part of the manganese on the acceptor.

X-ray Photoelectron Spectroscopy

The XPS measurements show that the lower the metal content of the acceptors is, the less the manganese oxide present on the acceptor resembles the structure of bulk manganese oxide (MnO₂). From the experiments discussed above it can be concluded
that in acceptors with a low metal content only manganese oxide is observed with a high activity, whereas in acceptors with a higher metal loading, e.g. 9.7 %w Mn, also manganese oxide is found which can not be regenerated, here visualised by the decreasing value of the amount of highly dispersed manganese. XPS patterns of acceptors which have been used during 16 sulfidation-regeneration cycles show that less manganese is present on the acceptor surface. XPS measurements confirm the results of TPR and TPS measurements in which used samples are analyzed: less active manganese is left on the acceptor surface.

Samples in which manganese is present on a γ-Al₂O₃ carrier show other Auger electron transitions than bulk manganese oxides. At a low metal content no Auger electron transitions can be found that represent bulk manganese oxides. When the acceptors have been used during 16 sulfidation-regeneration cycles, the peaks obtained in the patterns of fresh acceptors disappeared and patterns resemble that of manganese oxide. Obviously, manganese ions diffused into the carrier and formed a (sub)surface manganese aluminate.

Conclusions

The measurements discussed in this chapter combined with the results already obtained by Soerawidjaja [1] give a clear picture of the composition of the acceptors in relation to their sulfidation-regeneration behaviour. Acceptors with low metal loadings consist mainly of a surface MnAl₂O₄ spinel, which can be sulfided and regenerated easily. If the metal content is increased to e.g. 7.9 %w Mn three types of manganese oxide can be distinguished. The first is an irrecoverable type of manganese oxide, present as small crystallites which do not exhibit a strong interaction with the support. The second type is a surface MnAl₂O₄ spinel that can be sulfided and regenerated easily. Finally, the third type is also a MnAl₂O₄ compound, but in this case the reaction rate of sulfidation and regeneration is limited by diffusion of Mn²⁺-ions to and from the acceptor surface. According to the TPS measurements the amount of the last type of Mn ions increases during the sulfidation-regeneration experiments until a stable performance is reached.

Better acceptors can be prepared by increasing the surface area of the acceptors: more (surface) MnAl₂O₄ can be formed. Better performance can also be obtained if
during preparation formation of manganese crystallites can be prevented. Unfortunately, the formation a bulk MnAl₂O₄, which shows a slow sulfidation and regeneration performance due to diffusion of Mn²⁺-ions in the support, is inevitable as the diffusion of metal ions into the support is a characteristic of the γ-Al₂O₃ support.

Acknowledgement

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References

2 D.R. Lide (ed.), Handbook of Chemistry and Physics, CRC Press, USA, 1991
9 J.A. Dumesic and H. Topsøe, Advances in Catalysis, 26(1977)121-246
11 A.D. van Langeveld, Ph.D. Thesis, Surface Chemistry of Metals and Alloys,
University of Leiden, 1983


16 P. J. Mangnus, Ph.D. Thesis, chapter 9, University of Amsterdam, Amsterdam, march 1991


The sulfidation behaviour of MnO and FeO on $\gamma$-Al$_2$O$_3$

Abstract

It is important to know what influence the raw fuel gas composition of a coal gasification plant and temperature and pressure have on the sulfidation behaviour of MnO or FeO on $\gamma$-Al$_2$O$_3$ acceptors. Experiments are carried out in a laboratory set-up to determine these influences. The acceptors can be used to remove both H$_2$S and COS between 675 and 1075 K. After an initial deactivation the acceptors can be used over 400 sulfidation - regeneration cycles. Water adversely affects the capacity, whereas CO favours the capacity due to the shift reaction. Trace compounds can influence the capacity negatively as e.g. HCl, whereas hydrocarbons not influence acceptor performance.

Introduction

The composition of a raw fuel gas produced by a coal gasifier can vary over a wide range, depending upon the type of gasifier used (fixed bed, fluidized bed, entrained bed) and the type of coal used. The main compounds produced by a gasifier are CO, H$_2$, CO$_2$, H$_2$O, N$_2$, H$_2$S and COS. The sulfur compounds have to be removed from the fuel gas, dictated by requirements of downstream processes and environmental regulations. The acceptors tested in this chapter are able to remove H$_2$S and COS from the fuel gas according to the following reaction:

$$\text{MeO}/\gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{S} = \text{MeS}/\gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{O} \quad \text{Me} = \text{Mn or Fe}$$ (1)
Also other reactions occur, e.g. the water gas shift reaction and COS formation. COS is removed by direct reaction with the acceptor, or is converted to $\text{H}_2\text{S}$ which reacts with the acceptor according to reaction 1. The performance of the acceptors is strongly dependent upon gas composition and process variables such as temperature. Table 1

*Table 1. The raw fuel gas composition of some coal gasification processes. (Note: n.d. = not determined)*

<table>
<thead>
<tr>
<th></th>
<th>Lurgi</th>
<th>Winkler</th>
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<th>BGC-Lurgi</th>
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<td>1</td>
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<td>20</td>
<td>7</td>
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<td>1875</td>
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<td>28.7</td>
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<td>11.9</td>
<td>5.5</td>
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<td>0.1</td>
<td>1.1</td>
<td>2.1</td>
<td>0.5</td>
<td>0.1</td>
<td>1.5</td>
<td>1.4</td>
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<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>&lt; 1 ppm</td>
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shows the raw fuel gas composition for some coal gasification processes. It can be noticed that there are large differences in gas composition. The hydrogen concentration varies
from 29 to 40 %v, the carbon monoxide concentration even from 16 to 65 %v. Especially the water concentration is expected to have a strong influence on the acceptor performance as water shifts the equilibrium in reaction 1 to the left. Therefore, the acceptor can be regenerated with a gas containing steam. Some processes convert a large part of coal into carbon dioxide, an undesired product. The influence of all these constituents will be discussed in this chapter.

Moreover, the gas produced by a coal gasifier can contain a number of compounds which may deactivate the acceptor or influence the acceptor performance negatively by blocking active sites. Among these compounds are heavy metals, HCl, HF, NH₃, HCN and hydrocarbons. Because it is impractical to add heavy metals in low concentrations to a synthetic gas mixture one best can observe the influence of heavy metals carrying out experiments under realistic conditions (see chapter 6). The amount of HCl and HF present in the raw fuel gas strongly depends on the amount of chlorine and fluorine in the coal used. The expected HCl concentrations for the Shell and Texaco gasification processes, fed with Australian Wambo coal, are 600 and 500 ppm and the HF concentrations 224 and 188 ppm, respectively. Wambo coal only contains 0.05 %w Cl and 0.01 %w F on a dry base [1]; when other coals are used, the concentrations in the coal and thus in the gas phase, can be higher. Tests done with HCl and hydrocarbons will be discussed in this chapter as well.

**Experimental**

**Acceptor preparation**

The acceptor material is prepared by wet impregnation. The carrier (γ-Al₂O₃, AKZO/Ketjen 001-1.5E, ground and sieved, particle diameter 0.25-0.42 mm, surface area 260 m²/g) is added to the impregnation solution (3.3 ml solution/g carrier) and shaken a few times during impregnation. The impregnation time is about 16 hours.

To prepare a manganese containing acceptor a 2M manganese acetate (Merck, p.a.) solution is used. An iron containing acceptor is prepared from an 1M iron (III) ammonium oxalate (Riedel de Hähn, p.a.) solution. After impregnation the material is filtrated, dried at room temperature during 5 to 6 hours and calcined in static air at 575 K during 60 hours. The last step in preparation is reduction, carried out in-situ in the
reactor at reaction temperature. The manganese containing acceptors consisted of 7.10 to 8.23 %w Mn on γ-Al₂O₃ and the iron containing acceptor of 4.64 %w Fe on γ-Al₂O₃. Fresh acceptors have a surface area of 180-200 m²/g and an average pore diameter of 4-5 nm.

Instrumental

The apparatus used to obtain the sulfidation-regeneration cycles is described in detail in chapter 2 and in [12]. The tests are carried out at temperatures between 675 and 1075 K using three grams of acceptor material and a gas mixture containing 1 %v H₂S, 0-70 %v CO, 10-40 %v H₂, 0-15 %v H₂O, the balance being N₂. The total flow rate was always kept at 67.5 µmol/s. When tests are carried out with water in the feed gas, small fluctuations in the H₂S concentration leaving the reactor are observed due to a not completely stable H₂O dosage.

When experiments were carried out at elevated pressure the quartz reactor tube was replaced by a stainless steel (RVS 316) reactor with the same internal diameter. This reactor could only be used up to 725 K because at higher temperatures the steel reacts with H₂S, thus causing incorrect experimental data. Therefore another reactor, made of a ferritic stainless steel (an Al-Cr-Fe alloy), which does not react with H₂S up to temperatures of 1075 K, has been used as well. The internal diameter of this reactor was 12 mm. To obtain the same residence time, 5.1 g acceptor was used and the flow rate was increased to 120.2 µmol/s. The pressure was varied in the range of 0.1 to 0.5 MPa.

Results and discussion

Acceptor deactivation

Whenever a fresh acceptor is tested a stable performance is only obtained after an initial period of deactivation. During this period the sulfur removal capacity decreases with time. As shown in figure 1a the deactivation process is quite strong during the first five to ten sulfidation-regeneration cycles at 875 K; the breakthrough capacity of a fresh manganese containing acceptor decreases from about 1.7 %w S to about 0.8 %w S. As discussed in chapter 3 the decrease in breakthrough capacity between the first and the second cycle is caused by the sulfidation of manganese oxide present as small crystallites
Figure 1. Deactivation of MnO/γ-Al₂O₃ and FeO/γ-Al₂O₃ at 875 K. A, ω = 7.1 %w Mn on γ-Al₂O₃ B, λ = 4.6 %w Fe on γ-Al₂O₃.
which can be sulfided but not be regenerated with steam. TPS measurements showed that the formation of MnAl₂O₄ is relatively slow; not all MnAl₂O₄ is formed after reduction of the acceptor in the reactor. Moreover, part of the MnAl₂O₄ can not be sulfided as its reactivity is too low at 875 K. Only when higher temperatures are applied (e.g. 1075 K) all MnAl₂O₄ can be sulfided. In the next 40 sulfidation-regeneration cycles the deactivation slows down: finally the breakthrough capacity becomes constant at about 0.65 %w S. The decrease in breakthrough capacity during these 40 cycles is caused by a decrease in surface area of the acceptor; the surface area lowers from about 210 to about 140 m²/g. The sulfur capture capacity remains almost constant at this level for at least 300 sulfidation-regeneration cycles. The same change in the breakthrough capacity can be observed for the iron containing acceptor (figure 1b). Due to its lower metal content a fresh acceptor has a breakthrough capacity of about 1 %w S. This value decreases to a stable capacity of about 0.45 %w S. This deactivation is negligibly slow at 657 K, whereas it is much faster and stronger at 1075 K. Deactivation is not caused by an accumulation of sulfur on the acceptor: the amount of sulfur regenerated equals the amount of sulfur captured, except for the first cycle.

**Influence of temperature on acceptor capacity**

The influence of temperature on acceptor capacity can be obtained in two different ways. The first way is to stabilize the acceptor at a certain high temperature, here 875 or 1075 K, and then to measure the breakthrough capacity at lower temperatures, here from 675 to 875 K and from 875 to 1075 K. The results obtained in this way are shown in figure 2 for both the manganese and the iron containing acceptor. In this way the effect of temperature on breakthrough capacity is demonstrated because at all temperatures the tests are carried out with the same, stabilized, material. It is clear that higher temperatures favour the breakthrough capacity. The highest temperature results in the highest breakthrough capacity, but also in the highest deactivation due to excessive sintering of the acceptor. This is shown clearly by the breakthrough capacities at 875 K for the materials stabilized at 875 and 1075 K respectively. The latter has a breakthrough capacity that is about 50% lower than that of the acceptor stabilized at 875 K. The difference in capacity can be explained by the surface area of the acceptor. The
acceptor stabilized at 875 K has a surface area of 141 m²/g and the acceptor stabilized at 1075 K one of 70 m²/g.

When it is supposed that the breakthrough capacity is determined by the equilibrium constant only, the breakthrough capacity can be calculated as a function of temperature. It is necessary to know (to measure) the breakthrough capacity of a stabilized acceptor at a certain temperature. When these calculations are carried out it follows that the breakthrough capacity can be predicted in a small temperature interval (e.g. 100 K) at low temperatures (675 to 875 K): both the calculated and measured breakthrough capacity increase with increasing temperature. However, the results obtained for large temperature intervals (e.g. 400 K) or at high temperatures do not correspond with the measured values. This can be explained with the TPS measurements discussed in chapter 3 which show that the formation of the surface MnAl₂O₄ spinel proceeds during the sulfidation - regeneration experiments. The sulfidation peak of this species obtained with TPS shifts towards higher temperatures (from 925 to 1025 K). This means that at low temperatures only part of the MnAl₂O₄ can be sulfided. Thus, increasing the temperature not only causes the equilibrium constant to become more
favourable but also more of the MnAl₂O₄ to be sulfided. This explains the strong increase in breakthrough capacity when the temperature is increased from 925 to 1075 K. Further, the kinetics of the sulfidation reaction are influenced by increasing the temperature: the rate constants of the intrinsic chemical reaction(s) will become larger. The breakthrough capacity will not increase due to this effect because the reaction rate already is high; the increased diffusion rate of Mn²⁺ ions out of the γ-Al₂O₃ support causes the breakthrough capacity to increase with an increasing temperature.

The second way to study the effect of temperature is to start with a fresh acceptor that was used for a certain number of cycles at a low temperature, here 675 K. Such an acceptor did not deactivate appreciably. The influence of temperature is determined by increasing the temperature (e.g. with steps of 50 K) and measuring the breakthrough capacity. In this case the acceptor will have different characteristics at each temperature (e.g. surface area), but it will more closely correspond to the material which would be used at that temperature in reality. Figure 3 shows the results of these measurements. It is obvious that the breakthrough capacity of an acceptor used for a long time at 875 K will decrease to the value shown in figure 2. At 875 K an optimum is reached between capacity and stability of the acceptor.

The influence of water in the feed gas

The effect of the water concentration in the feed gas on breakthrough capacity is shown in figure 4. The upper line shows the influence of water on an iron containing acceptor, the lower line on a manganese containing acceptor. Because the results obtained have to be corrected for acceptor deactivation and to facilitate comparison of different acceptors (e.g. different metal loadings) breakthrough capacity is shown on a relative scale. The breakthrough capacity with a dry feed gas is used as a reference and given the value one.

As can be seen from figure 4, water strongly decreases acceptor capacity. The influence is strongest at low water concentrations. The presence of 2.8 %v water lowers the breakthrough capacity by almost 40 % for the manganese containing acceptor, a water concentration to 13.8 %v results in a decrease of 75 % in breakthrough capacity. This means that the higher the water concentration is the smaller the effects of an increase in the water concentrations is. The effects of water in the feed gas are less
strong when an iron containing acceptor is used. This effect can be explained by the calculated equilibrium constants of the sulfidation reaction: in case of MnAl₂O₄ the equilibrium constant is about 0.84 at 875 K whereas the equilibrium constant for FeAl₂O₄ is about 2.1 at the same temperature. So, FeAl₂O₄ will be less affected by the presence of H₂O.

The negative effect of water was not surprising because the sulfidation reaction (reaction 1) will shift to the left side if water is added to the feed gas.

More information can be obtained from complete sulfidation curves measured at different water concentrations. On the ordinate a dimensionless gas phase concentration $X_a$ is shown:

$$X_a = \frac{C_a}{C_0}$$  \hspace{1cm} (2)
Figure 4. The influence of the water concentration on breakthrough capacity at 875 K. * = 7.1 %w Mn, α = 4.6 %w Fe on γ-Al₂O₃. Feed: 1%v H₂S, 10%v H₂, x%v H₂O, N₂ bal.

where \( X_a \) = dimensionless gas phase concentration of H₂S (-)
\( C_a \) = gas phase concentration of H₂S (mol/m³)
\( C_0 \) = gas phase concentration of H₂S in the feed (mol/m³)

The abscissa gives the time proceeded after introduction of H₂S in the reactor feed, or in other words, after beginning of the sulfidation.

In figure 5 breakthrough curves are shown of a the manganese containing acceptor. Curve A corresponds to a reference feed gas containing no water. Curves B and C correspond to a feed containing 2.8 and 6.1 %v H₂O respectively. It is clear that the breakthrough capacity decreases as the breakthrough point shifts to a shorter time. The shape of the sulfidation curve changes also. In case of feed containing no water the acceptor keeps on capturing 10 to 20 % of the H₂S present in the feed gas during a long time after breakthrough. When water is added the breakthrough curve resembles more or less a step. After breakthrough almost no H₂S is captured. This effect is strongest at
the highest water concentration. The breakthrough curve closely corresponds to the curve predicted by equilibrium theory [13].

Figure 5. Breakthrough curves at 875 K for different water concentrations. Curve A = 0%v H₂O, B = 2.8%v H₂O and C = 6.1%v H₂O. Acceptor: 7.1%w Mn/γ-Al₂O₃.

The influence of carbon monoxide and hydrogen in the feed gas

As carbon monoxide and hydrogen are the key compounds formed during gasification of coal, their influence on sulfidation behaviour and breakthrough capacity is crucial. The influence of carbon monoxide and hydrogen on breakthrough capacity is shown in figure 6. Again the breakthrough capacity of a feed gas containing N₂, H₂ and H₂S only is used as a reference and given the value one. It is clear that carbon monoxide has a positive effect on breakthrough capacity. The breakthrough capacity can increase by a factor of up to 2.5. When the hydrogen concentration is increased the positive effect of carbon monoxide is less pronounced. A low hydrogen concentration corresponds to a high positive effect of carbon monoxide and a high hydrogen concentration to a less positive effect. As will be discussed later the positive influence of carbon monoxide is smaller at lower temperatures.

The effect of carbon monoxide and the effect of hydrogen on breakthrough
Figure 6. The influence of carbon monoxide and hydrogen concentration on breakthrough capacity at 875 K. * = 7.1 \%w Mn/γ-Al₂O₃, ▲ = 4.6 \%w Fe/γ-Al₂O₃. Relative breakthrough capacity can be explained by the water gas shift reaction:

\[
CO + H₂O ⇌ H₂ + CO₂
\]  \hspace{1cm} (3)

Carbon monoxide consumes the water produced by reaction (1) during sulfidation and increases the driving force for the same reaction by lowering the water concentration in the acceptor.

In literature two mechanisms for the shift reaction are described, the so-called regenerative mechanism and the so-called associative mechanism. The regenerative mechanism [14, 15] proceeds via reduction of the metal oxide with CO and subsequent oxidation with H₂O, e.g. in case of Fe₃O₄ (magnetite):

\[
CO + Fe₃O₄ ⇌ CO₂ + 3 FeO
\]  \hspace{1cm} (4)

\[
H₂O + 3 FeO ⇌ H₂ + Fe₃O₄
\]  \hspace{1cm} (5)
It is not very likely that this mechanism proceeds on the sites used for H₂S removal because it is shown by Soerawidjaja [13] and others [16-22] with Mössbauer spectroscopy that iron carried by alumina, kept in a humid hydrogen atmosphere, will always be present as Fe²⁺: due to the strong metal support interaction neither oxidation with H₂O nor reduction with hydrogen or carbon monoxide to Fe⁰ is possible.

In the associative mechanism reactants absorb on the alumina carrier and form an adsorbed species, surface formate, which decomposes and forms the products of the shift reaction [23]:

\[
\begin{align*}
\text{CO} + * &= \text{CO}^* \\
\text{H}_2\text{O} + * &= \text{HO}^* + \text{H}^* \\
\text{CO}^* + \text{HO}^* &= *\text{COOH}^* \\
*\text{COOH}^* &= \text{CO}_2^* + \text{H}^* \\
\text{CO}_2^* &= \text{CO}_2 + * \\
2\text{H}^* &= \text{H}_2 + 2^*
\end{align*}
\]

It is uncertain which of the steps determines the overall reaction rate. According to Newsome [15] the adsorption of CO is the rate determining step, whereas Udovic [24] states that CO adsorption is fast and reversible and the reaction between CO* and H₂O* is rate determining. Using IR measurements, Amenomiya [25, 26, 27] concluded that the decomposition of the formate complex is rate determining.

As no literature is available on MnO/γ-Al₂O₃ and the measured effects of CO are the same as for FeO/γ-Al₂O₃ it is assumed that the mechanism over both acceptor types will be the same as well.

As is shown in chapter 3, up to three different types of manganese oxide can be distinguished: first small crystallites which can not be regenerated with steam, second a surface MnAl₂O₄ spinel and third a bulk like MnAl₂O₄ compound. The last two types will behave similar towards the shift reaction, namely as described in the above discussion. The first type, however, causes the reaction system to become more complicated. During the first sulfidation these crystallites are converted to manganese sulfide. A number of
sulfur tolerant shift catalysts are described in literature, e.g. molybdenum sulfide on alumina [45]. It is possible that defects in the crystallite structure catalyze the shift reaction, or that some sites are regenerated with steam, and catalyze the shift reaction before they are sulfided again. Due to this complex system the regenerative mechanism can not be excluded beforehand.

It is important to note that Mn/γ-Al₂O₃ is not a real shift catalyst. Compared to Fe₃O₄/Cr₂O₃ turnover frequencies are quite low.

Gas chromatographic analysis of the reactor effluent showed that with both the iron and the manganese containing acceptors the shift reaction is on equilibrium at 875 K. This means that the amount of water converted will be the same. The stronger positive effect for FeO/γ-Al₂O₃ than for MnO/γ-Al₂O₃ is caused by the lower metal loading of the iron containing acceptor: less water will be produced by sulfiding a certain amount of acceptor. As the same CO concentration is present in the feed the result is that the partial pressure of water in the iron containing acceptor will be lower and a stronger positive effect of CO is observed.

The experiments shown in figure 6 were carried out at 875 K. At that temperature the equilibrium constant of the shift reaction is 2.5; lowering the temperature to 675 K causes the equilibrium constant to increase to about 9. Consequently, in principle, the shift reaction is able to convert more water.

Figure 7 shows the effect of CO in the feed gas at different temperatures. It is clear that the positive effect of CO is almost negligible at low temperatures and substantial at high temperatures. Obviously the rate of the shift reaction at low temperatures is too low to let the shift reaction reach equilibrium within the given residence time in the reactor. Therefore, almost no H₂O is converted and H₂S capture is only slightly improved. At high temperatures the reaction rate of the shift reaction is high enough to reach equilibrium. Thus, the shift reaction needs a high temperature or a long residence time to reach equilibrium.

The influence of the hydrogen concentration (figure 6) is easy to explain. Hydrogen and carbon dioxide are products of the shift reaction. Therefore, both hydrogen and carbon dioxide present in the feed gas will lower the amount of water
Figure 7. The influence of temperature and CO concentration on breakthrough capacity. △ v = 3.6 %w Fe/γ-Al₂O₃ ⦿ = 4.6 %w Fe/γ-Al₂O₃

converted via the shift reaction and thus the amount of H₂S captured by the acceptor.

In figure 8 breakthrough curves are shown for the manganese containing acceptor. Curves A, B and C correspond to a feed with 0 %v, 20 %v and 40 %v carbon monoxide, respectively. The breakthrough capacity increases with increasing carbon monoxide concentration as shown in figure 6. The shape of the breakthrough curve does not change dramatically, as was the case with a feed containing water. This behaviour is explained by the fact that carbon monoxide is not involved in the sulfidation reaction itself but only reacts with water produced by the sulfidation reaction. Because the water concentration decreases the equilibrium will shift to the right site and causes the breakthrough capacity to increase: the breakthrough curve shifts to the right. In chapter 7 a model will be discussed explaining the shape of the breakthrough curves under different experimental conditions.

Above results show that the presence of water in the feed gas strongly decreases acceptor capacity whereas carbon monoxide increases acceptor capacity by removing water produced by the sulfidation reaction. If a feed gas contains water it is clear that
Figure 8. Breakthrough curves at 875 K for different carbon monoxide concentrations. Curve 
$A = 0 \%v$, $B = 20 \%v$ and $C = 40 \%v$ CO.

carbon monoxide can convert water into hydrogen and carbon dioxide. Results of 
experiments with a feed gas containing both carbon monoxide and water are shown in 
figures 9 and 10. Figure 9 and 10 show the breakthrough capacity as a function of the 
$H_2O$ concentration at different CO concentrations. It follows from figure 9 that the 
adverse effect of water can be compensated partially if the feed gas contains a substantial 
amount of carbon monoxide. At high water concentrations (e.g. more than 6 \%v) almost 
no positive effect of carbon monoxide is observed anymore. Figure 10 shows that at low 
water concentrations the negative effect of water can be eliminated, or at least 
minimized, if a feed gas with a high carbon monoxide concentration is used.

The usefulness of the acceptors is therefore optimal for gas streams with low 
water contents (up to approximately 5 \%v) and high carbon monoxide concentrations.

The strong effect of water is shown again by the complete breakthrough curves. 
Figure 11 gives breakthrough curves for a feed gas containing 40 \%v carbon monoxide 
and 0, 2.8 and 6.1 \%v water; in figure 12 the curves are given for 6.1 \%v water and 0, 
20 and 40 \%v carbon monoxide respectively. From figures 11 and 12 it can be concluded 
that the effect of carbon monoxide on the breakthrough curves is small, whereas water
results in a drastic change in the breakthrough curve at increasing water concentrations. The breakthrough capacity goes down and the curves become more like a step. An increasing carbon monoxide concentration with a fixed water concentration of e.g. 6.1 %v (figure 12) does not result in a change of the breakthrough curve. Only the breakthrough capacity becomes a little higher as was already shown in figure 6.

![Graph showing the influence of H₂O and CO concentration in the feed gas on breakthrough capacity of 7.1 %w Mn/γ-Al₂O₃ at 875 K.]

*Figure 9. The influence of the H₂O and CO concentration in the feed gas on breakthrough capacity of 7.1 %w Mn/γ-Al₂O₃ at 875 K.*

The effects of pressure on sulfidation behaviour

All experiments described so far are carried out at a pressure of 0.1 MPa. However, a coal gasification plant operates at a considerable higher pressure, up to 4 MPa. Therefore it is necessary to know what influence pressure has on sulfidation behaviour. The influence of pressure on the equilibrium of reaction (1) is expected to be negligible: the same number of gas molecules participates in the sulfidation reaction and in the regeneration reaction. Figure 13 shows the breakthrough capacity as a function of pressure at two different temperatures, 725 and 875 K, and a feed gas containing N₂, H₂ and H₂S. No influence on breakthrough capacity can be observed when pressure is raised to 0.5 MPa. As the shape of the corresponding breakthrough curves remains the same
Figure 10. The influence of the \( H_2O \) and CO concentration in the feed gas on breakthrough capacity of 8.0 \%w \( Mn/\gamma-Al_2O_3 \) at 875 K.

It is concluded that the kinetics of the sulfidation reaction are probably not influenced by increasing the total pressure. Increasing pressure up to 4 MPa will therefore not influence sulfidation behaviour of the acceptor.

When the feed gas contains a significant amount of carbon monoxide the breakthrough capacity increases as described before. Figure 14 shows the relative breakthrough capacity as a function of temperature. It is not surprising that this increase is pressure dependent. At 725 K the breakthrough capacity increases with increasing pressure, whereas at 875 K it is independent of the pressure. In both cases the shape of the breakthrough curve is independent of pressure. The different influence of pressure on acceptor performance at 725 and 875 K was surprising, but can be explained by the shift reaction. At 725 K the equilibrium constant of the shift reaction is about 9 whereas the equilibrium constant at 875 K is 2.5. Theoretically more water can be converted at the lower temperature. However, the shift reaction is relatively slow at 725 K, causing the shift reaction not to attain equilibrium at 0.1 MPa. Increasing the pressure results in more adsorbed species of CO and \( H_2O \) on alumina (see reactions 7 and 8). As, according to different investigators [15, 24-27], the rate determining steps in the shift reaction are
Figure 11. Breakthrough curves of 7.1 %w Mn/γ-Al₂O₃ at 875 K with a feed gas of 40 %v CO and 0, 2.8 and 6.1 %v H₂O (curve A, B and C, respectively).

covered by reactions (7), (8), (9) and (10) the overall reaction rate will increase and a lower partial pressure of water is obtained. These effects are in good agreement with the results shown in figure 7. The same is predicted by empirical relations as the power law relation derived by Bohlbro [29]:

\[-r_{CO} = k_P^{l}P_{CO}^{m}P_{H₂O}^{p}P_{CO₂}^{q}P_{H₂}^{q}\]  

(12)

where \(-r_{CO}\) = intrinsic reaction rate of CO  

k = reaction rate constant  

\(P_x\) = partial pressure of component x  

l, m, p, q = power law exponents

Newsome [15] found different power law exponents for the shift reaction catalyzed by iron oxide on alumina: the values are slightly dependent upon metal loading.

At 875 K the shift reaction reaches equilibrium: therefore no influence of the
Figure 12. Breakthrough curves of 7.1 %w Mn/γ-Al₂O₃ at 875 K with a feed gas of 6.1 % H₂O and 0, 20 and 40 %v CO (curve A, B and C, respectively).

pressure is observed at 875 K. This also means that at a relatively low temperature the positive effect of the shift reaction is stronger than at high temperatures when the shift reaction can reach equilibrium, e.g. caused by a high pressure or a sufficiently long residence time in the reactor.

Table 3. Power law exponents for the shift reaction for some iron oxide on alumina catalyst [15].

<table>
<thead>
<tr>
<th></th>
<th>l</th>
<th>m</th>
<th>q</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 %w Fe/γ-Al₂O₃</td>
<td>0.95</td>
<td>0.30</td>
<td>0.00</td>
</tr>
<tr>
<td>10 %w Fe/γ-Al₂O₃</td>
<td>0.80</td>
<td>0.30</td>
<td>-0.05</td>
</tr>
<tr>
<td>25 %w Fe/γ-Al₂O₃</td>
<td>0.85</td>
<td>0.15</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

Depending upon temperature and gas composition pressure can influence breakthrough capacity. A higher pressure can cause the shift reaction to reach equilibrium. The sulfidation reaction itself is not influenced by pressure.
Figure 13. The influence of pressure on breakthrough capacity of 8.96 %w Mn/γ-Al₂O₃ at 725 (●) and 875 (○) K. Feed gas: 89 %v N₂, 10 %v H₂ and 1 %v H₂S.

Reactor effluent composition in the presence of carbon monoxide in the feed gas

When the gas to be desulfurized contains carbon monoxide, not only breakthrough capacity increases with increasing carbon monoxide concentration, but also marked changes occur in the reactor effluent composition during sulfidation compared with feeds free of carbon monoxide. These changes are the appearance of carbon dioxide and carbonyl sulfide in the reactor effluent. These changes are visualised when figures 15 and 16 are compared. Figure 15 shows the breakthrough curves of a feed containing 1 %v H₂S, 10 %v H₂ and N₂ (balance) only. The reactor effluent contains H₂S and H₂O only. Figure 16 shows the breakthrough curves of a feed containing 1 %v H₂S, 10 %v H₂, 50 %v CO and N₂ (balance): besides H₂O (in a low concentration due to the shift reaction) and H₂S, CO₂ and COS appear in the reactor effluent as well.

Carbon dioxide is formed according to the shift reaction (reaction (3)). As there is no carbon dioxide present in the feed gas it is a direct proof for the occurrence of the shift reaction. The raise in the carbon dioxide concentration corresponds very well with the decrease in the water concentration (figure 16). The temporary increase in the water concentration just before breakthrough is caused by the shift reaction. As the water is
Figure 14. Influence of pressure on relative breakthrough capacity of 8.96 %w Mn/γ-Al₂O₃ at 725 (•) and 875 (○) K. Feed: 39 %v N₂, 10 %v H₂, 50 %v CO, 1 %v H₂S.

produced by the sulfidation reaction, the water production front shifts to the end of the reactor as a function of time. A few minutes before breakthrough the remaining part of the acceptor bed is too small to let the shift reaction reach equilibrium, in other words, the residence time of the gas participating in the shift reaction has become too short. Therefore less water is converted and the water concentration in the reactor exit rises. At the same time the CO₂ concentration goes down.

Carbonyl sulfide is formed due to the reaction between CO and H₂S:

\[ CO + H₂S = H₂ + COS \quad K_{eq} = 0.054 \text{ at } 875 \text{ K} [30] \] (13)

As can be seen from figure 16, COS is not present in the reactor effluent until H₂S breakthrough of the acceptor bed. After breakthrough COS appears in the reactor effluent. The amount of H₂S converted into COS can rise up to about 25 % with high carbon monoxide and low hydrogen concentrations.

The mechanism of COS removal is not completely understood. Thermodynamics [31, 32] of the reaction
Figure 15. Reactor effluent composition of 8.96 %w Mn/γ-Al₂O₃. Feed: 1 %v H₂S, 10 %v \( \text{H}_2 \) \( \text{N}_2 \) balance. \( T = 875 \) K. ◊ = H₂S, ♦ = H₂O.

\[
\text{COS} + \text{MnO}/\gamma-\text{Al}_2\text{O}_3 \rightarrow \text{MnS}/\gamma-\text{Al}_2\text{O}_3 + \text{CO}_2 \quad K_{eq} = 44 \text{ at } 875 \text{ K} \tag{14}
\]

show that it is favourable in the temperature range of 600 to 1100 K. The equilibrium constant decreases from about 112 at 600 K to 30 at 1100 K. So, theoretically the acceptor can remove COS directly from the gas phase. However, when water and hydrogen are present other reactions, which form H₂S, can occur as well:

\[
\begin{align*}
\text{COS} + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{S} + \text{CO}_2 \quad K_{eq} = 8 \cdot 10^{18} \text{ at } 875 \text{ K} \tag{15} \\
\text{COS} + \text{H}_2 & \rightarrow \text{H}_2\text{S} + \text{CO} \quad K_{eq} = 18.5 \text{ at } 875 \text{ K} \tag{16}
\end{align*}
\]

Formally, these reactions are shift reactions. The acceptor might catalyze these reactions.

When reaction (15) and (16) occur, the acceptor would not react with COS but with H₂S. In order to clear the reaction mechanism, experiments have been carried out with a feed gas containing 1.10 %v COS, 11 %v H₂ and N₂ balance. Figure 17 shows the reactor effluent composition as a function of time.
Figure 16. Reactor effluent composition of 8.96 %w Mn/γ-Al₂O₃ Feed: 1 %v H₂S, 10 %v H₂, 50 %v CO, N₂ balance. T=875 K. ◇=H₂S, ◆=H₂O, ▲=CO₂, △=COS.

This figure shows that all COS is converted into H₂S: even after breakthrough no significant amounts of COS appear in the reactor effluent. The amount of CO₂ formed is very low, so in presence of hydrogen COS is converted into H₂S via reaction (16). The H₂S is captured by the acceptor and water is formed. Because now water is present in the gas phase, COS can be hydrolysed via reaction (15) as well. After breakthrough a considerable amount of H₂S leaves the reactor and still about 0.2 %v water is formed, due to a slow sulfdation of the acceptor.

Because no distinction can be made between reaction (14), (15) and (16) the experiment was repeated with a feed gas containing COS and nitrogen only. The breakthrough curves are shown in figure 18. Because no hydrogen is present reaction 16 can not proceed and no H₂S will be produced via this reaction. However, the acceptor always contains hydroxyl groups or even some water due to the steam regeneration. Probably some COS is converted via these OH-groups into H₂S. Subsequently, water is produced via reaction (1).

As the feed does not contain hydrogen or water, the formation of water and H₂S must proceed via the OH groups on the acceptor surface. It can be calculated that a γ-
Figure 17. Breakthrough curves of 8.96 \%w Mn/\gamma-Al_2O_3 with a feed gas containing 1.10 \%v COS, 11 \%v \text{H}_2, \text{N}_2 \text{balance}, T = 875 K. ◇=\text{H}_2\text{S}, ◆=\text{H}_2\text{O}, ◆\text{=}\text{CO}_2, ◆\text{=}\text{COS}.

Al_2O_3 surface contains about 2.7\times10^{18} \text{OH groups} \cdot \text{m}^{-2} at 875 K [46-49]. When it is supposed that one third of the \gamma-Al_2O_3 surface is not covered by manganese oxide, the acceptor has a surface area of 150 m^2 \cdot \text{g}^{-1} and as 6 g of the acceptor were used for the gaschromatographic measurements, a total of 1.30 mmol of OH groups is present. From figure 18 it follows that about 0.45 mmol of hydrogen containing gases were produced. As every \text{H}_2\text{O} and \text{H}_2\text{S} produced consumes two OH groups, it is clear that the acceptor surface contains enough OH groups to produce the amount of hydrogen needed. The above values for the amount of OH groups on the \gamma-Al_2O_3 surface form a lower limit.

Figure 18 shows that only small amounts of COS are converted in that way as only a small amount of water is present in the reactor effluent. The greater part of the COS must have been removed via a direct reaction with the acceptor (reaction (14)). After breakthrough some \text{H}_2\text{S} appears in the reactor effluent. The delay in the appearance of water in the reactor effluent is logical. This effect is already described with the measurements discussed with figure 15.

Surprising is the difference in the amount of COS captured till breakthrough in figures 17 and 18. In figure 17 \text{H}_2\text{S} breakthrough takes place after about 4000 s, in figure
18 COS breakthrough only appears after 9000 s. This means that in the latter case more than twice as much sulfur is captured as the concentration of COS in the feed is the same in both cases. The difference can be explained by the equilibrium constant and the mechanisms of both reactions. At 875 K the sulfidation reaction of the acceptor with H₂S (reaction (1)) has an equilibrium constant of about 1, whereas the sulfidation reaction of the acceptor with COS (reaction (14)) has an equilibrium constant of about 44 at 875 K. Using H₂S as the feed water is produced during sulfidation which at the same time acts as the regeneration agent of the acceptor and thus inhibits the sulfidation reaction, whereas using COS as the feed only carbon dioxide is produced and no water is present during sulfidation.

When in figure 18 the amounts of gases leaving the reactor before and after breakthrough are added, the amount leaving the reactor after breakthrough not sums up to the amount fed to the reactor. This is caused by some decomposition of COS and/or H₂S into elemental sulfur after breakthrough in the quartz reactor exit.

From these experiments it can be concluded that the acceptor can remove COS from the gas phase by a direct reaction between COS and Mn₃Al₂O₄. However, the
experiments show that the contribution of this reaction to the removal of H₂S will be small when H₂ or H₂O are present as well: the COS will be converted into H₂S via reaction 16 or 17 and the OH-groups and subsequently the H₂S will be captured by the acceptor.

The influence of trace compounds in the fuel gas

HCl

The raw fuel gas from a Shell or a Texaco gasifier fired with Wambo coal contains about 600 and 500 ppm HCl respectively [1]. The difference in these concentrations possibly is caused by differences in the gasification processes. Obviously, more chlorine

![Graph](image)

Figure 19. Breakthrough capacity of 8.23 %w Mn/γ-Al₂O₃ as a function of cycle number at 875 K for different HCl concentrations. ∆ = 0.5 %v, v = 1.0 %v, ◇ = 0 %v

leaves the Texaco gasifier as metal salts than is the case with the Shell gasifier. When coal is used with a high chlorine content the HCl concentration in the gas can raise up to 0.5 %v. Figure 19 shows the breakthrough capacity of the acceptor for feeds containing 0, 0.5 and 1.0 %v HCl. It is clear that HCl present in the feed gas has a negative influence on breakthrough capacity. Using 0.5 %v HCl lowers the capacity by
about 30 percent, 1.0%v HCl by about 43 percent. From figure 19 it can also be concluded that the deactivation by HCl is reversible and a function of HCl concentration. If the feed is HCl free the breakthrough capacity is restored. Further it is clear that no accumulation of HCl on the acceptor takes place because the breakthrough capacity remains constant. This means that the HCl is removed from the acceptor during regeneration. Furthermore it is clear that the deactivation caused by HCl does not increase linearly with an increasing HCl concentration: rising the HCl concentration from 0.5%v to 1.0%v does not result in a twice as large reduction of the breakthrough capacity. In the following it will be concluded that the same sites on the acceptor are involved in the reaction with HCl and H₂S.

The exact mechanism of HCl blocking the active sites is not clear yet. Thermodynamic calculations [31, 32] show that not all of the following reactions are important (ΔG values are given at 875 K):

\[
\begin{align*}
\text{MnAl}_2\text{O}_4 + 2 \text{HCl} &\rightleftharpoons \text{MnCl}_2 + \gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{O} & \Delta G_r &= +9 \text{kJ/mol} \ (17) \\
\text{MnO} + 2 \text{HCl} &\rightleftharpoons \text{MnCl}_2 + \text{H}_2\text{O} & \Delta G_r &= -46 \text{kJ/mol} \ (18) \\
\gamma\text{-Al}_2\text{O}_3 + 6 \text{HCl} &\rightleftharpoons 2 \text{Al}_2\text{Cl}_3 + 3 \text{H}_2\text{O} & \Delta G_r &= +305 \text{kJ/mol} \ (19) \\
\text{MnS}/\gamma\text{-Al}_2\text{O}_3 + 2 \text{HCl} &\rightleftharpoons \text{MnCl}_2 + \gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{S} & \Delta G_r &= -98 \text{kJ/mol} \ (20) \\
\text{MnS} + 2 \text{HCl} &\rightleftharpoons \text{MnCl}_2 + \text{H}_2\text{S} & \Delta G_r &= -98 \text{kJ/mol} \ (21) \\
\text{MnCl}_2 + \text{H}_2\text{O} &\rightleftharpoons \text{MnO} + \text{HCl} & \Delta G_r &= +46 \text{kJ/mol} \ (22)
\end{align*}
\]

The negative influence of HCl is not caused by blocking sites of the sulfidation reaction itself. It is likely that sulfided manganese (MnS) reacts with HCl and produces H₂S (reactions (20) and (21)). In that way the breakthrough capacity is lowered because active sites are lost. Theoretically HCl can remove all H₂S from the acceptor when the sulfidation reaction with HCl in the feed proceeds long enough. However, as the sulfidation is stopped when breakthrough of the acceptor bed takes place this will not happen. The reaction scheme is even more complicated because water is formed due to the sulfidation of MnAl₂O₄. Water can react with MnCl₂ and form MnAl₂O₄ back (reaction (17)) to create fresh sulfidation sites. As water is formed during sulfidation of the acceptor it will remove some HCl from the acceptor.
When water is present in the feed gas the negative effect of HCl may be less strong, although water decreases the breakthrough capacity as well. Above reactions of water explain how chlorine is removed from the acceptor during steam regeneration and how a fresh acceptor is obtained for the next sulfidation.

Similar calculations show that these effects should not occur when HF is present in the feed gas. HF does not react with MnAl₂O₄, MnO, γ-Al₂O₃ and MnS in the temperature range studied.

**Hydrocarbons**

Table 3 gives an overview of the experiments and the results carried out with hydrocarbons. The relative breakthrough capacity and the sulfur deficit are averaged over the total number of measurements. In the last two columns the number of sulfidation-regeneration cycles carried out with the corresponding hydrocarbon is shown and whether there is any deactivation within a series of sulfidation-regeneration experiments or not.

**Table 3. Experimental conditions, relative breakthrough capacities and sulfur balances.**

<table>
<thead>
<tr>
<th>Hydrocarbons tested</th>
<th>Concentration in feed gas (%v)</th>
<th>T (K)</th>
<th>q₀,rel</th>
<th>sulfur deficit (%)</th>
<th>number of cycles used</th>
<th>deactivation in series</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>10</td>
<td>875</td>
<td>0.99</td>
<td>-0</td>
<td>81</td>
<td>no</td>
</tr>
<tr>
<td>CH₄</td>
<td>5</td>
<td>875</td>
<td>0.99</td>
<td>-0</td>
<td>14</td>
<td>no</td>
</tr>
<tr>
<td>CH₄</td>
<td>1</td>
<td>625</td>
<td>1.02</td>
<td>-0</td>
<td>24</td>
<td>no</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>10</td>
<td>875</td>
<td>0.99</td>
<td>-0</td>
<td>19</td>
<td>no</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>10</td>
<td>875</td>
<td>1.00</td>
<td>-4</td>
<td>12</td>
<td>no</td>
</tr>
<tr>
<td>C₄H₈</td>
<td>1</td>
<td>625</td>
<td>1.00</td>
<td>-0</td>
<td>35</td>
<td>no</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>2.5</td>
<td>875</td>
<td>1.01</td>
<td>-0</td>
<td>10</td>
<td>no</td>
</tr>
<tr>
<td>C₄H₁₀</td>
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<td>625</td>
<td>1.01</td>
<td>-0</td>
<td>25</td>
<td>no</td>
</tr>
</tbody>
</table>

Figure 20 and 21 give examples of the breakthrough capacity as a function of cycle number, with and without hydrocarbons. From table 3 and figures 20 and 21 it is clear
that lower alkanes do not deactivate the acceptor due to carbon deposition at both temperatures and concentrations up to 10 %v. At 625 K no influence is obtained if alkenes are tested. However, at 875 K some negative influence by propene is observed. Although the breakthrough capacity remains constant, the sulfur deficit of 4 % shows that some H₂S has disappeared during the sulfidation-regeneration cycle. As the same regeneration gas was used in all cases some of the H₂S disappeared during the sulfidation stage. A close inspection of the quartz reactor tube showed that some brownish deposition had taken place at the reactor exit, possibly due to polymerization or vulcanization of H₂S with propene. This means that only 96 % of the H₂S fed to the reactor is captured by the acceptor.

After removing propene from the feed gas the sulfur deficit again becomes about zero, indicating that all H₂S fed to the reactor is captured by the acceptor and has been recovered during regeneration. The breakthrough capacity remains on the same level as the breakthrough capacity found before the tests with propene were carried out. Obviously the effects of propene are non-permanent.

Complete breakthrough curves can give information about the effects of these
hydrocarbons on sulfidation kinetics. When breakthrough curves are compared of a feed gas with 0, 10 and 80 %v CH₄, no differences are observed within experimental tolerations, indicating that the rate of sulfidation is not influenced by the presence of hydrocarbons.

Generally, carbon deposition on catalysts is not only caused by hydrocarbons. Carbon monoxide is well known for its capability to form carbonaceous deposits [37, 38]. However, as already shown, CO improves the performance of the acceptor due to the shift reaction. The reason why neither CO nor hydrocarbons form carbonaceous deposits is explained below.

Most literature concerning carbon deposition on iron or manganese describes tests with foils or single crystals. Less literature is available for iron or manganese on alumina or other alumina carried metal oxides [33-38]. However, in case of iron all mechanisms of carbon formation described attribute the catalytic activity to one or more iron carbides (Fe₂C, Fe₃C, Fe₇C₃), to metallic iron or to the iron - iron oxide interface. It is shown by Soerawidjaja [13] that iron containing acceptors behave in the same way as manganese
containing acceptors. Therefore literature data available on iron on alumina will be used
to explain the characteristics of manganese on alumina.

Four reasons can be given to explain why no carbon deposition or deactivation of
the acceptor material is observed.
1. Iron-oxides on γ-Al₂O₃ are very stable so that completely reduced supported iron
catalysts are rarely observed. As shown by Soerawidjaja [13] using Mössbauer
spectroscopy under reaction conditions, all iron in the acceptor material is present as
Fe²⁺. The same is obviously valid for the system MnO/γ-Al₂O₃. Other investigators [16-
22] report the same for similar systems of FeO/γ-Al₂O₃. This means that it is not
possible to form one of the above catalytic active species because the metal compound
can not be reduced completely. In this way formation of carbon on the acceptor
material is prevented.

2. Water present in the gas phase helps to prevent carbon formation, as reported by
Buyanov [39] and Afanas’ev [40]. During the tests no water was present in the feed
gas, but water is formed in the reactor by the sulfidation reaction (1).

3. It is reported by Baker and Harris [41] that continuous addition of sulfur compounds
to the gas phase inhibits carbon deposition onto Fe₃O₄, Cr₂O₃ and stainless steel.
Particularly effective was thiophene as its larger molecular area could block several
adjacent sites. The same is reported by Durbin and Castle [42] and Kishi and Roberts
[43]. H₂S has been found to reduce the amount of carbon deposited on iron and nickel
surfaces. Kishi and Roberts explain this behaviour by the electron withdrawing effects
of species like sulfur, in the form of dissociatively chemisorbed H₂S. This will diminish
the potential of the surface for back bonding and therefore for dissociative
chemisorption of CO or hydrocarbons. In the experiments described above H₂S is
always present, as the acceptor materials are used for the removal of H₂S from the gas
phase by sulfiding the metal oxide present on the support. So H₂S can help preventing
carbon deposition on the catalyst surface.

4. Special interest has to be paid to the regeneration route of the acceptor material.
When the material is sulfided, i.e. after breakthrough of H₂S from the acceptor bed,
the material is regenerated by injecting water in the reactor at the same temperature
as the sulfidation took place. The metal oxide is formed back and H₂S leaves the
reactor in a high concentration. If any carbon is formed during sulfidation, the carbon
will be gasified during the regeneration [44] and a fresh catalyst is available for the next sulfidation.

From the reasons listed above the most likely ones are those which describe prevention of carbon deposition during sulfidation. This is clear because the breakthrough capacity would decrease if hydrocarbons are added to the reaction mixture. The somewhat lower breakthrough capacity when propene is added to the gas mixture is not permanent. The regeneration step removes the carbonaceous compounds eventually present.

**Conclusions**

Fresh acceptors show an initial deactivation which depends upon temperature. At low temperatures (675 K) deactivation is negligibly slow whereas at higher temperatures (> 875 K) deactivation becomes faster. The main cause for deactivation is loss of surface area of the acceptor.

The breakthrough capacity of the acceptor becomes higher when the temperature increases from 675 to 1075 K. However, due to excessive sintering, prolonged operation at 1075 K is not possible. An optimum between capacity and lifetime of the acceptor is reached at about 875 K.

The feed gas composition influences acceptor performance quite strongly. Water in the feed gas adversely affects the capacity of the acceptor, which is a logical consequence of the fact that the acceptor can be regenerated with steam. On the other hand, CO favours the capacity of the acceptor because it can remove water through the shift reaction. The operation temperature and pressure are important to let the shift reaction reach equilibrium. Increasing pressure causes the shift reaction to reach equilibrium at lower temperatures while the sulfidation reaction itself is not influenced. At higher temperatures the total pressure does not influence the shift reaction and the equilibrium, which is pressure independent, is always reached.

The acceptor effectively removes COS from the feed gas as well. The acceptor can be used to remove both H₂S and COS from the fuel gas.

Trace compounds in the raw fuel gas can influence the breakthrough capacity of the acceptor negatively, as e.g. HCl does, but the effects are small at low concentrations.
Other compounds, such as hydrocarbons, do not influence acceptor performance.

References


13. T.H. Soerawidjaja, Steam regenerative removal of H₂S at high temperatures using metal oxide on alumina acceptors, Ph.D. Thesis, Delft University of Technology,
Delft, 1985

26 Y. Amenomiya, J. Catal., 57(1979)64-71
29 H. Bohlbros, An investigation on the kinetics of the conversion of carbon monoxide with water vapour over iron based catalysts, Ph.D. Thesis, Gjellerup, Copenhagen, 1969
36  D.E. Stobbe, On the development of supported dehydrogenation catalysts based
    on iron oxide, Ph.D. Thesis, University of Utrecht, Nov. 1990
37  J. van Doorn, Carbon deposition on hydrotreating catalysts, Ph.D. Thesis,
    University of Amsterdam, Sept. 1989
39  R.A. Buyanov, V.V. Chesnokov, A.D. Afanas'ev and V.S. Babenko, Kin. Catal.,
    18(1977)839-845
40  A.D. Afanas'ev, R.A. Buyanov and V.V. Chesnokov, Kin. Catal., 23(1982)1042-
    1045
41  R.T.K. Baker and P.S. Harris, Chemistry and Physics of Carbon (eds. P.L. Walker
42  M.J. Durbin and J.E. Castle, Carbon, 14(1976)27
    1720
44  W.L. Holstein and M. Boudart, Fuel, 62(1983)162-165
Regeneration of sulfided MnO/γ-Al₂O₃ acceptors

Abstract

Regeneration of sulfided MnO/γ-Al₂O₃ acceptors is studied in detail. To obtain a regeneration off-gas with a H₂S concentration high enough to be used as feed for a Claus plant (C₃H₂S > 15 %v), a regeneration feed gas with a high steam concentration (> 50 %v) must be used. To minimize steam consumption, a relative long residence time (> 1 s) should be applied. Due to the long residence time the regeneration time increases as well, but is in all cases shorter than the sulfidation time.

Introduction

All processes for high temperature regenerative H₂S removal can adequately remove H₂S from the fuel gas produced by a coal gasifier. The regeneration routes of these materials can differ, and thus the sulfur containing product obtained. In principle, a process which produces elemental sulfur during regeneration would be most attractive: no additional steps in the process are necessary to convert the regeneration product in an environmentally acceptable, resalable product. Some processes can produce elemental sulfur during regeneration. However, they are still in the development stage and have not been proven yet [1-3].

During regeneration most processes produce SO₂ in a low concentration (1-3 %v), e.g. zinc ferrite and zinc titanate [4-6]. To convert the SO₂ into elemental sulfur, part of the SO₂ must be reduced to H₂S before elemental sulfur can be produced in a Claus plant. These reducing gases had better be used in the power plant for the production of
electricity. The low SO₂ concentration itself also complicates the conversion of SO₂ into elemental sulfur. Further, side reactions occurring during regeneration make the whole reaction system more complicated (see chapter 1).

The process discussed here uses MnO/γ-Al₂O₃ as an acceptor for high temperature regenerative H₂S removal. The sulfided product, MnS/γ-Al₂O₃, can be hydrolysed to the starting materials at the same temperature and pressure used during the sulfidation:

\[
\text{MnS/γ-Al₂O₃ + H₂O = MnO/γ-Al₂O₃ + H₂S}
\]  

(1)

The H₂S is formed with a high concentration during a relatively short time compared to the sulfidation. This H₂S can be converted directly into elemental sulfur in a Claus plant if the concentration is high enough. The average H₂S concentration has to be at least 15 %v to use the split flow Claus process [7]. Because no side reactions occur and H₂S is produced in a high concentration, a simple process set-up for the regeneration route can be used.

However, as high temperature, high pressure steam is a relative expensive reactant, the amount of steam used for regeneration has to be as low as possible, whereas at the same time the H₂S concentration has to be high and the regeneration time has to be as short as possible. The above requirements conflict with each other and, therefore, the regeneration has to be optimized. A number of process parameters can be varied to influence the H₂S concentration in the regeneration off-gas and the regeneration time. Among these are the residence time (or space velocity), the steam concentration and the gases used to dilute the steam (N₂, H₂, CO).

**Experimental**

**Instrumental**

The laboratory set-up is described in detail in chapter 2. The composition of the feed gas during the sulfidation of the various experiments is shown in table 1. The total flow rate always was 67.5 μmol/s.

During regeneration different gas compositions have been used and different flow
Table 1. Gas composition during sulfidation. The total flow rate is 67.5 μmol/s.

<table>
<thead>
<tr>
<th>H₂S (%v)</th>
<th>H₂ (%v)</th>
<th>CO (%v)</th>
<th>N₂ (%v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0</td>
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</tr>
<tr>
<td>1</td>
<td>10</td>
<td>50</td>
<td>39</td>
</tr>
</tbody>
</table>

Table 2. Gas composition and flow rates during regeneration.

<table>
<thead>
<tr>
<th>H₂O (%v)</th>
<th>H₂ (%v)</th>
<th>N₂ (%v)</th>
<th>Flow rate (μmol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.8</td>
<td>5.8</td>
<td>86.4</td>
<td>117.4</td>
</tr>
<tr>
<td>12.1</td>
<td>5.8</td>
<td>82.1</td>
<td>117.4</td>
</tr>
<tr>
<td>24.2</td>
<td>5.8</td>
<td>70.0</td>
<td>117.4</td>
</tr>
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<td>48.2</td>
<td>5.8</td>
<td>46.0</td>
<td>117.4</td>
</tr>
<tr>
<td>77.4</td>
<td>5.8</td>
<td>16.8</td>
<td>117.4</td>
</tr>
<tr>
<td>20.0</td>
<td>4.8-22.5</td>
<td>57.5-75.2</td>
<td>30.0/46.0/71.2/141.6</td>
</tr>
<tr>
<td>48.2</td>
<td>3.6-22.8</td>
<td>29.0-48.2</td>
<td>29.6/58.7/117.4/188.4</td>
</tr>
<tr>
<td>75.0</td>
<td>2.8-17.8</td>
<td>7.2-22.2</td>
<td>37.8/75.3/121.0/242.1</td>
</tr>
<tr>
<td>48.2</td>
<td>5.8</td>
<td>40.3</td>
<td>117.4</td>
</tr>
<tr>
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<td>11.5</td>
<td>34.55</td>
<td>117.4</td>
</tr>
<tr>
<td>48.2</td>
<td>17.3</td>
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</tr>
<tr>
<td>48.2</td>
<td>28.8</td>
<td>17.3</td>
<td>117.4</td>
</tr>
<tr>
<td>48.2</td>
<td>32.6</td>
<td>13.4</td>
<td>117.4</td>
</tr>
</tbody>
</table>
rates. They are summarized in table 2. In the reactor three or six grams of acceptor material were used to remove the H₂S from the gas phase and to investigate the regeneration performance. Regeneration is done by injecting liquid water via a capillary into the reactor. It evaporates and is heated to reaction temperature before reaching the acceptor material. The amount of H₂S leaving the reactor is measured by a continuous titration system. After regeneration a new sulfidation-regeneration cycle is started. The tests were carried out at 725 and 875 K and pressures of 0.1 MPa and 0.5 MPa.

Acceptors

Two different acceptors, prepared by wet impregnation of γ-Al₂O₃ (AKZO/Ketjen 001-1.5E) with a 2M manganese (II) acetate solution, have been used for the regeneration experiments. These are 8.23 %w Mn/γ-Al₂O₃ and 8.96 %w Mn/γ-Al₂O₃. Both acceptors have been stabilized during at least 50 sulfidation-regeneration cycles before the regeneration experiments were carried out (for stabilization see also chapter 4). Different particle diameters were applied, viz. 0.15 to 0.25 mm, 0.42 to 0.60 mm and 0.72 to 0.85 mm.

Results

The regeneration curves are strongly influenced by the amount of sulfur present on the acceptor after sulfidation. A higher breakthrough capacity causes the height of the regeneration peak to increase as well. Therefore stabilized acceptors were used to perform the regeneration experiments.

Before the regeneration conditions can be optimized, it has to be checked whether the regeneration is controlled by pore diffusion phenomena or not. Experiments carried out with three different particle diameters, a high steam concentration in the regeneration gas (75 %v) and a flow rate of 121.0 μmol/s showed that no differences that might suggest rate limitation by pore diffusion could be observed. In all cases the height of the regeneration peak, regeneration time and steam consumption was about the same.

Experiments in which the regeneration is carried out counter-currently instead of co-currently showed that there was no difference within experimental tolerations. Normally, it would be expected that regeneration which is carried out counter-currently
Figure 1. Sulfidation profile in the reactor at (curve A) and 15 minutes after breakthrough (curve B), calculated with the model discussed in chapter 7.

would result in the highest regeneration peak as the H₂S which is regenerated can not readsorb on the not completely sulfided acceptor in the reactor exit. Figure 1 shows the expected sulfur loading profile in the acceptor bed at breakthrough (curve A). However, as the sulfidation is not immediately stopped after breakthrough during the experiments, but about 15 minutes later, the sulfur front in the acceptor bed is shifted to the reactor exit (curve B). This means that the sulfur distribution is quite uniform in the acceptor bed before regeneration is started. Practically, however, regeneration must be carried out counter-currently because the last part of the acceptor bed is not loaded with sulfur as sulfidation is stopped before breakthrough has taken place. The model discussed in chapter 7 also predicts a quite uniform sulfur distribution throughout the acceptor bed when sulfidation is continued for about 15 minutes after breakthrough: the differences in sulfur loading are about 10 percent between the inlet- and the outlet side of the acceptor bed.
Figure 2. Regeneration curves with different steam concentrations. Acceptor = 8.23 %\textsubscript{w} Mn/γ-Al\textsubscript{2}O\textsubscript{3} \( T = 875 \) K. Flow rate = 117.4 \( \mu \)mol/s. \( \tau = 0.44 \) s.

Figure 3. Regeneration peak height as a function of steam concentration. Acceptor = 8.23 %\textsubscript{w} Mn/γ-Al\textsubscript{2}O\textsubscript{3} \( T = 875 \) K. \( \tau = 0.44 \) s. Flow = 117.4 \( \mu \)mol/s.
Figure 4. Regeneration peak width as a function of steam concentration. Acceptor = 8.23 \%w Mn/γ-Al₂O₃, T = 875 K, τ = 0.44 s. Flow = 117.4 µmol/s.

Figure 5. t₇₀ and t₉₅ as a function of steam concentration. Acceptor = 8.23 \%w Mn/γ-Al₂O₃, T = 875 K, τ = 0.44 s. Flow = 117.4 µmol/s.
Typical regeneration curves obtained with different steam concentrations are shown in figure 2. The maximum amount of H$_2$S leaving the reactor increases with increasing steam concentration. Further it can be noticed that the regeneration time becomes shorter when the steam concentration increases. However, it is not easy to get quantitative data from these curves. Therefore, the regeneration peak height is given as a function of the steam concentration in figure 3. It has to be emphasized that each point in this and following figures is the average value of at least seven regeneration curves. The reproducibility of the regeneration curves is very high: differences in peak height and peak width are about 2%. Assuming that the regeneration peak resembles a Gauss curve, the width halfway up the peak maximum can be used to give an indication of the regeneration time and also to calculate an average H$_2$S concentration in the regeneration off-gas by dividing the peak maximum by two. Figure 4 shows the width of the regeneration peak as a function of steam concentration. From figure 3 and 4 it follows that regeneration is faster when the steam concentration increases. This effect is strongest at low steam concentrations. The regeneration peak height seems to go asymptotically to a maximum value. The regeneration time decreases asymptotically to a minimum value when the steam concentration increases. Figure 5 shows the time needed to regenerate 70% of the H$_2$S from the acceptor ($t_{70}$) and the time needed to regenerate 95% of the H$_2$S from the acceptor ($t_{95}$). It is clear that the first part of the H$_2$S can be removed from the acceptor easily: increasing the steam concentration hardly causes $t_{70}$ to decrease. The effect of an increasing steam concentration is more pronounced when the time needed to remove 95% of the sulfur is observed. An increasing steam concentration causes $t_{95}$ to decrease from about 1500 s to about 225 s. It also follows from this figure that relatively much steam is needed to regenerate the last part of the acceptor: the time expired between $t_{70}$ and $t_{95}$ (25 percent of the total amount of the sulfur) is much longer than the time expired to regenerate the first 70 percent of the sulfur.

The amount of steam needed to regenerate the acceptor will increase with an increasing degree of regeneration. Figure 6 shows the Relative Steam Consumption (RSC) at $t_{70}$ (RSC$_{70}$) and $t_{95}$ (RSC$_{95}$) as a function of the steam concentration. The RSC is defined as the amount of steam actually used to regenerate the acceptor divided by the amount of steam needed stoichiometrically. The RSC increases almost linearly with an increasing steam concentration, both at $t_{70}$ and $t_{95}$. When 70% of the sulfur is removed
from the acceptor the RSC is about 2 at low steam concentrations and rises to about 7 for high steam concentrations. This means that, although the regeneration time decreases with an increasing steam concentration, the amount of steam needed to regenerate the acceptor increases. The unused amount of steam increases and causes the regeneration costs to increase. The same is observed when the acceptor is regenerated completely. The RSC_{95} rises from about 14 at a low steam concentration to about 21 for a high steam concentration. Therefore, it can be useful not to regenerate the acceptor completely, but only for e.g. 80 to 85 %, in this way decreasing the steam consumption and regeneration costs. Of course the consequence is that the somewhat lower breakthrough capacity makes the use of a larger desulfurization reactor necessary.
Figure 7. Regeneration curves at different superficial residence times. Acceptor = 8.23 %w Mn/γ-Al₂O₃, T = 875 K. C_{steam} = 75 %v.

Figure 8. Regeneration peak height as a function of τ_{sup}, C_{steam} = 20, 48 or 75 %v. Acceptor = 8.23 %w Mn/γ-Al₂O₃, T = 875 K. Flow = 29.6 to 242.1 μmol/s.
The above measurements show the influence of the steam concentration at one particular residence time or space velocity ($\tau_{sup} = 0.44$ s). It is clear that an increasing residence time will cause the RSC to decrease because the steam conversion will increase due to the increased contact time. Figure 7 shows typical regeneration curves obtained at a steam concentration of 75 %v and different superficial residence times. The maximum amount of H$_2$S leaving the reactor increases when the superficial residence time decreases. Further it can be noticed that the regeneration time becomes shorter when the superficial residence time decreases. Figure 8 shows the influence of the superficial residence time ($\tau_{sup}$) on the height of the regeneration peak at three different steam concentrations (20, 48 and 75 %v steam). The longer the residence time is, the lower the regeneration peak becomes. Further, at one residence time the influence of the steam concentration on the peak height can be obtained.

![Graph showing regeneration peak width as a function of $\tau_{sup}$](image)

*Figure 9. Regeneration peak width as a function of $\tau_{sup}$. Acceptor = 8.23 %w Mn/γ-Al$_2$O$_3$, $C_{steam} = 20$, 48 or 75 %v. $T = 875$ K. Flow = 29.6 to 242.1 µmol/s.*
A high steam concentration and a short residence time result in the highest regeneration peak. As already shown above, the width of the regeneration peak increases when the peak height decreases. Figure 9 shows the peak width of the regeneration curves as a function of residence time. The lower the steam concentration and the higher the residence time, the broader the regeneration peak becomes.

![Graph showing time as a function of superficial residence time with different steam concentrations.](image)

*Figure 10. t_{70} and t_{95} as a function of the residence time. Acceptor = 8.23 %w Mn/γ-Al_{2}O_{3}, C_{steam} = 20, 48 or 75 %v. T = 875 K. Flow = 29.6 to 242.1 μmol/s.*

Figure 10 shows the time needed to regenerate 70 and 95 percent of the sulfur from the acceptor. The regeneration time increases with an increasing residence time. In case of a short residence time (about 0.25 %v) and a high steam concentration (75 %v), the acceptor is almost completely regenerated after about 100 s. The regeneration time increases to about 1400 s when a long residence time and a low steam concentration are used.

The RSC at t_{70} and t_{95} is shown in figure 11. It is clear that during experiments with one steam concentration the RSC decreases when the residence time is increased. More of the steam supplied is converted and the steam is used more effectively. To regenerate the acceptor completely still a considerable excess of steam is needed; the RSC_{95} is about 10 at a long residence time and a steam concentration of 20 %v. This
Figure 11. RSC70 and RSC95 as a function of residence time. Acceptor = 8.23 %w Mn/γ-Al2O3 Csteam = 20, 48 or 75 %v. T = 875 K. Flow = 29.6 to 242.1 μmol/s.

rises to about 18 at a steam concentration of 75 %v and the same residence time.

The above results showed the regeneration peaks as an H2S flow versus the regeneration time. When the regeneration off-gas is used as a feed for a Claus plant to produce elemental sulfur the absolute concentration of H2S in the regeneration off-gas is needed for design. This concentration can be calculated from the results shown by taking the total flow rate into account. Figure 12 shows the maximum H2S concentration in the wet regeneration off-gas as a function of residence time and steam concentration. Figure 13 shows the maximum H2S concentration in the dry regeneration off-gas, also as a function of residence time and steam concentration. In the latter case water is removed from the regeneration off-gas by cooling and condensation.

It is clear that, due to high flow rates, the maximum H2S concentration is lowest at short residence times, although the amount of H2S produced per minute has the highest value at short residence times. To obtain high H2S concentrations it is therefore necessary to carry out the regeneration at relative long residence times. At the same time the RSC decreases, but the regeneration time increases. In all cases the regeneration time was shorter than the breakthrough time of the acceptor bed.
Figure 12. The maximum H$_2$S concentration in wet regeneration off-gas as a function of $\tau_{supr}$

Acceptor = 8.23 %w Mn/γ-Al$_2$O$_3$, $C_{steam} = 20, 48$ or $75$ %v. $T = 875$ K.

The average H$_2$S concentration in the regeneration off-gas can be estimated by dividing the maximum H$_2$S concentration by 2, as mentioned before. When the regeneration off-gas is used as feed for a Claus plant to produce elemental sulfur, a high steam concentration and a long $\tau_{supr}$ have to be used. Average H$_2$S concentrations of at least 17.5 %v can be obtained easily.

The regeneration process becomes more complex when a number of other parameters are included. As mentioned in the beginning of this paragraph, the maximum height of the regeneration peak is strongly influenced by the amount of sulfur captured during sulfidation. The experiments shown above are carried out with a sulfidation feed gas containing 1 %v H$_2$S and 10 %v H$_2$, the balance being N$_2$. In chapter 4 it is shown that the breakthrough capacity increases when the feed gas also contains CO. Table 3 summarizes the results of experiments with a sulfidation feed gas containing CO. It is clear that the height of the regeneration peak, and thus the maximum H$_2$S concentration in the dry regeneration off-gas, increases when the amount of sulfur captured increases. The regeneration time remains constant.
Figure 13. The maximum $H_2S$ concentration in the dry regeneration off-gas as a function of $\tau_{sup}$. Acceptor = 8.23 %w Mn/$\gamma$-Al$_2$O$_3$. $C_{steam} =$ 20, 48 or 75 %v. $T = 875$ K.

Table 3. Height and width of the regeneration peak of experiments with CO in the feed gas during sulfidation. Acceptor = 8.23 %w Mn/$\gamma$-Al$_2$O$_3$. $T = 875$ K. Regeneration gas = 48 %v $H_2O$. $\tau_{sup} = 0.49$ s.

<table>
<thead>
<tr>
<th>Feed gas ($%v$ CO)</th>
<th>Breakthrough capacity ($%w$ S)</th>
<th>Regeneration peak maximum ($\mu$mol/min)</th>
<th>Regeneration peak width (s)</th>
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<tbody>
<tr>
<td>0</td>
<td>0.8</td>
<td>950</td>
<td>46</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>1110</td>
<td>47</td>
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</tr>
<tr>
<td>50</td>
<td>1.2</td>
<td>1250</td>
<td>46</td>
</tr>
</tbody>
</table>

Further, the bed length influences the regeneration process. When the amount of acceptor in the reactor is doubled, the regeneration peak height increases from 400 to 610 $\mu$mol $H_2S$/min with the same gas composition and flow rate. When the amount of
Table 4. The influence of bed length and superficial residence time on the regeneration peak maximum. Acceptor = 8.96 %w Mn/γ-Al<sub>2</sub>O<sub>3</sub>, T = 875 K. Regeneration gas = 48.2 %v H<sub>2</sub>O.

<table>
<thead>
<tr>
<th>Bed length (mm)</th>
<th>Flow rate (µmol/s)</th>
<th>Superficial residence time (s)</th>
<th>Regeneration peak maximum (µmol/min)</th>
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<tbody>
<tr>
<td>56</td>
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<td>0.83</td>
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<td>1.56</td>
<td>610</td>
</tr>
<tr>
<td>106</td>
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</tbody>
</table>

acceptor is doubled and the flow rate is increased to keep the residence time constant, the regeneration peak maximum increases from 400 to 1060 µmol H<sub>2</sub>S/min. Table 4 summarizes the effects of bed length and residence time on regeneration peak height. In the first case it can be assumed that the peak height half way the doubled acceptor bed is the same as the peak height at the end of the normal acceptor bed. As not all steam is converted in the normal acceptor bed (RSC > 1, see above) this steam reacts with the remainder of the acceptor bed and the peak height increases. In the second case the overall residence time is kept constant, but the residence time an element of the acceptor bed is decreased and this, according to figure 8, causes the regeneration peak height to increase. So, increasing the bed length with a constant flow rate causes the H<sub>2</sub>S concentration to rise and the steam consumption to decrease. Increasing the bed length with a constant residence time causes, as expected, the maximum amount of H<sub>2</sub>S produced per minute to increase.

When the process is used to desulfurize the raw fuel gas of a coal gasifier, the process will be operated at a considerably higher pressure. An increased pressure does not influence the sulfidation reaction as shown in chapter 4. In view of that result it is expected that the regeneration will not be influenced by an increased pressure. However, some experiments carried out at 0.5 MPa show, compared to the experiments at 0.1 MPa, that the regeneration peak becomes somewhat lower. It is not clear whether the decrease in peak height is caused by the pressure applied during the regeneration process, or by the longer residence time of the gas in the experimental set-up. The first point is not very
likely when the results of the experiments discussed in chapter 4 are taken into account.

When the regeneration gas contains less than 100 %v steam it must be diluted by either nitrogen or a reducing gas. When a reducing gas is needed, either pure hydrogen can be added to the regeneration gas mixture, or part of the cleaned fuel gas. When the cleaned fuel gas is used, CO is present in the regeneration gas as well. In chapter 4 it is shown that CO in a high concentration in the presence of 1 %v H₂S converts up to 25 percent of the H₂S in COS. When CO is present during the regeneration some H₂S will be converted in COS as well. Measurements in which during the regeneration up to 35 %v CO was present, show that the height of the regeneration peak decreases with up to 10 percent. (C_{steam} = 48 %v, \tau = 0.48 s). As COS is an unwanted product in a Claus plant, the use of cleaned fuel gas as a diluent is not recommended.

Discussion

It is shown that complete regeneration of the acceptor with a gas containing steam can be performed easily. In most cases the regeneration time is considerably shorter than the sulfidation time. When a continuous reactor system is used, e.g. a fluidized bed system, the regenerator can be designed smaller than the absorber. The short regeneration time is caused by the high driving force of the regeneration reaction, obtained by the high steam concentrations applied. The results are in agreement with the fact that water inhibits H₂S uptake during sulfidation (see chapter 4) because the regeneration reaction is a fast reaction.

No pore diffusion limitation was observed when particles with different diameters were used. This means that the average pore diameter is large enough to let the steam enter the whole particle and the H₂S to leave the particle. The average pore diameter of freshly calcined material is about 4 to 5 nm. This value increases to about 7 to 8 nm when the material is used at high temperatures for a long time.

The H₂S concentration in the regeneration off-gas can be adjusted to a desired level within certain limits. A low steam concentration generally results in a low H₂S concentration, whereas a high steam concentration results in a high H₂S concentration in the regeneration off-gas. The residence time also influences the H₂S concentration: the
longer the residence time, the higher the $\text{H}_2\text{S}$ concentration.

The measurements with different bed length and flow rates showed that an increasing bed length caused an higher $\text{H}_2\text{S}$ concentration in the regeneration off-gas and a lower steam consumption. From these measurements it follows that the reactors should have a large L/d ratio.

Under realistic conditions, the regeneration not has to be carried out with 100 %v steam. During all experiments described above a few percent $\text{H}_2$ was present in the gas to prevent decomposition of $\text{H}_2\text{S}$ in elemental sulfur and $\text{H}_2$. This elemental sulfur can condensate on cold parts of the tubing and cause problems. To prevent condensation of elemental sulfur in the plant either $\text{H}_2$ has to be added to the regeneration gas, or the whole regeneration section of the desulfurization plant must be kept at a temperature high enough to keep the sulfur in the gas phase, until the sulfur can be condensed at a suitable place. When no hydrogen is added, nitrogen, produced by the oxygen plant needed for the gasifier, can be used as a diluent. In that case formation of elemental sulfur may occur. Theoretically, it is possible to produce elemental sulfur during regeneration when hydrogen can be removed from the regeneration off-gas by e.g. a membrane reactor: the $\text{H}_2\text{S}$ dissociates and forms elemental sulfur.

**Conclusions**

An average $\text{H}_2\text{S}$ concentration of at least 17.5 %v is obtained when the regeneration is carried out with a gas containing 75 %v steam and a superficial residence time of 1 s or more (or a maximum space velocity of about 1250 h$^{-1}$). These values are obtained if the sulfidation was carried out with a feed gas not containing CO. When 50 %v CO is present in the feed during sulfidation, the $\text{H}_2\text{S}$ concentration in the dry regeneration off-gas rises to 22 %v when the regeneration is carried out with 48 %v steam. When the residence time is increased from 1 s to 2 s the regeneration time also increases with an factor 2. The steam consumption decreases by about 15-20 percent when the residence time is increased from 1 s to 2 s. Further it is shown that reactors with a large L/d ratio are most effective with respect to steam consumption and $\text{H}_2\text{S}$ concentration.
References

1 W.J.J. van der Wal, Ph.D. Thesis, University of Utrecht, 1987
Coal gasification: high temperature $H_2S$ removal in a steam regenerative process under realistic conditions.

Abstract

During gasification of coal $H_2S$, COS and other impurities are formed. To remove $H_2S$ and COS a steam regenerative process using MnO or FeO on $\gamma$-Al$_2$O$_3$ acceptors has been developed. The acceptors can be used in the temperature range of 700 - 1100 K. Regeneration takes place at the same temperature with a gas containing steam. Using a 200 kW$_{\text{thermal}}$ coal gasification plant at ECN Petten the acceptors have been tested under realistic conditions in a bench scale unit. In this way not only the effect of upscaling but also the effect of other impurities in the gas on sulfidation and regeneration behaviour could be studied. The breakthrough capacity was about 0.35 %w S for Mn containing and about 0.20 for Fe containing acceptors. No deactivation was observed during four weeks of continuous sulfidation - regeneration cycles. A regeneration off-gas with high $H_2S$ concentrations (up to 60 %v) was obtained. Used acceptors have been analysed for sulfur capture capacity and contaminants. The distribution of contaminants in the experimental system (coal gasifier and bench scale unit) has been investigated as well.

Introduction

As the world oil and natural gas sources are limited quite some research effort is aimed at the utilization of coal to replace oil and natural gas. The positive results of coal
gasification projects of Texaco (demonstration plant in Cool Water, California) [1, 2] and Shell [2, 3, 4] are now available. Also in the Netherlands the application of coal gasification for electricity and chemicals production meets new interests which lead to short and long term research proposals. The long term proposals mainly concern high temperature gas cleaning because this can lead to an improved efficiency and lower the investments in Coal Gasification Combined Cycle (CGCC) power plants [5].

When coal is gasified it reacts with steam and air or oxygen at temperatures in the range of 800 - 2000 K. The raw gas produced by a coal gasifier usually contains a number of impurities, of which sulfur compounds are the major ones. Requirements of either downstream processes or environmental regulations dictate that these impurities must be removed from the gasifier effluent. The principle sulfur compound formed during gasification of coal is \( \text{H}_2\text{S} \), beside smaller amounts of COS, CS\(_2\) and mercaptans. The total amount of \( \text{H}_2\text{S} \) produced can vary between 0.2 and 1.4 \%\text{v}, depending upon the coal type used. After removing the sulfur compounds the gas can be used as a fuel, a synthesis gas or a reducing gas.

Both gasification and combustion of the purified gas are carried out at high temperatures. When purification is carried out at low temperatures (e.g. in case ethanolamines are used, see chapter 1) the raw gas must be cooled before entering the purification unit and reheated prior to combustion. However, when purification is also carried out at high temperatures the cooling and reheating can be eliminated or at least simplified. The overall thermal efficiency of the whole plant will increase. Unfortunately, almost all commercial available processes for the removal of \( \text{H}_2\text{S} \) operate either at a low temperature or can not be regenerated easily (see chapter 1).

\( \text{MnO} \) on \( \gamma\)-\( \text{Al}_2\text{O}_3 \) can remove \( \text{H}_2\text{S} \) from gases at 700 - 850 K, while the sulfided product can be regenerated in the same temperature range using a gas containing steam. In other words, the reaction

\[
\text{MnO/}\gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{S} = \text{H}_2\text{O} + \text{MnS/}\gamma\text{-Al}_2\text{O}_3
\]

(1)
is reversible.

It has been shown by Soerawidjaja [6] that acceptors based on iron behave in the same way. The active compound in the reaction, making steam regeneration possible,
seems to be a surface spinel, MnAl$_2$O$_4$ or FeAl$_2$O$_4$ (see chapter 3).

Previous research was mainly aimed at measurements in a laboratory set-up: capacity and stability, influence of gas composition, process temperature and preparation of the acceptor materials were investigated.

However, a gas produced by a coal gasifier not only contains H$_2$S and COS as contaminants, but also other impurities as dust, heavy metals, HCl, HF, NH$_3$ and HCN as well. To evaluate the acceptor materials on their applicability for high temperature desulfurization it is necessary to test the acceptors under realistic conditions on a somewhat larger scale. Therefore, a bench scale plant consisting of three fixed bed reactors was built. The gas used to test the acceptors was supplied by a cocurrent moving-bed gasifier (200 kW$_{th}$) operated by the Energy Research Foundation (ECN) in Petten, The Netherlands [7].

The research described in this chapter not only concerns the use of a realistic fuel gas, but also involves upscaling: 1 kg acceptor per reactor is used (3 kg acceptor in total) instead of 3 grams in the laboratory set-up. This implies an upscaling with an factor of about 1000. The desulfurization reactors of a 600 MW CGCC power plant will contain 30000 to 150000 kg of acceptor material, depending upon the gasification process used, the sulfur content of the coal, reactor configuration and so on (see chapter 8). This means that upscaling from the bench scale unit to a desulfurization plant concerns a factor of 10000 to 50000, which is the same order of magnitude as upscaling to the bench-scale unit.

**Experimental**

**Acceptor preparation**

During the research carried out in a laboratory set-up approximately 3 g of ground and sieved acceptor material with particle diameters between 0.25 and 0.42 mm is used. Due to the larger scale the particle diameter of the acceptor material had to increase. The γ-alumina extrudates used (Ketjen/Akzo 001-1.5E) have an average length of about 4.8 mm and an average diameter of about 1.7 mm. Because of the increased particle diameter and the larger amount of carrier material the impregnation method had to be changed to maintain the metal content and the sulfur removal capacity.
For laboratory use, the acceptor material was prepared by wet impregnation. The carrier was added to the impregnation fluid (3.3 ml solution/g support) and shaken a few times during impregnation (method 1). The impregnation time could vary between 2 and 16 hours. The material was filtrated and dried for 5-6 hours at ambient temperature. The last step in preparation was calcination in air for about 60 hours at 675 K. For larger amounts of carrier material shaking of fluid and carrier can not be used. The main problem with the large amount of material and coarse extrudates is contacting the impregnation fluid with the carrier in such a way that each particle is filled with the impregnation solution. A number of techniques to improve contacting between fluid and carrier are investigated: stirring the fluid above the particles (method 2), stirring both fluid and solids (method 3) and recycling the fluid through a packed bed of acceptor material (method 4).

Each acceptor batch prepared is analysed for attrition during impregnation, distribution of the metal in and between the particles, metal content (by means of AAS, Atomic Adsorption Spectroscopy) and capacity for H₂S removal. The last property is determined both at laboratory and realistic conditions.

The first two criteria are evaluated qualitatively only. The metal oxide distribution can, because the oxides are dark coloured, be evaluated easily.

**Equipment**

**Laboratory set up**

The laboratory set-up is described in detail elsewhere [11] and in chapter 2. In the gas dosage section oxygen and water are removed from all gases, except for H₂S which is used without further purification. After passing mass flow controllers the gas flows are mixed and flow to the reactor. The reactor feed contains 10 %v H₂ and 1 %v H₂S, the balance being N₂. The total flow rate is 67.5 μmol/min. In the reactor three grams of acceptor material are used to remove the H₂S from the gas phase. After breakthrough H₂S dosage is stopped and the acceptor material is regenerated. This is done by injecting liquid water into the reactor where it evaporates and is heated to reaction temperature before reaching the acceptor material. The amount of H₂S leaving the reactor is measured by a continuous titration system. After regeneration a new acceptation-regeneration cycle is started. The tests are carried out at 875 K.
Pilot plant

The breakthrough capacity and deactivation under realistic conditions are measured in an experimental set up situated at the Energy Research Foundation (ECN) in Petten, The Netherlands. This set up can be divided into two main parts: the coal gasifier [7] and the equipment in which the acceptor materials for high temperature regenerative H₂S removal can be tested.

The gasifier is a cocurrent moving bed gasifier of 200 kW<sub>th</sub>. Both coal and air needed for gasification flow from top to bottom through the gasifier. As the blower is situated after the gasifier this implies that the whole system is operated at a pressure less than atmospheric pressure. Consequently, the desulfurization plant had to be equipped with a pump to suck to fuel gas through the reactors. The major advantage of this is the larger safety.

Because the gasifier is a cocurrent moving bed type, the hydrocarbons and tars formed in the upper part of the coal bed are converted in the lower parts of the coal bed: only small amounts of hydrocarbons will leave the gasifier. The coal bed can be divided into three zones (from top to bottom):

1. The pyrolysis zone. In this zone devolatilisation of the coal takes place. Light hydrocarbons and heavy tar products are formed.

2. The oxidation zone. Tar and hydrocarbons are converted in the oxidation zone by the air which is led into the reactor just above the coal bed. Moreover, part of the coal is converted into CO<sub>2</sub> and H₂O to produce the heat needed by the reactions in the reduction zone. The temperature rises quickly to a level of about 1600 - 1900 K.

3. The reduction zone. The products of the oxidation zone, CO<sub>2</sub> and H₂O, react with coal to form CO and H₂. Because these reactions are relatively slow the reduction zone covers the greatest part of the coal bed.

The fuel gas exit is situated at the bottom of the reduction zone. The fuel gas leaves the reactor at about 1000 K and flows to the cyclones. The gasifier is built for research purposes and produces a fuel gas that can be used to test the acceptor materials. The unused gas is flared.

The equipment in which the acceptor materials are tested is shown schematically in figure 1. The following parts can be distinguished: pretreatment of the fuel gas,
pretreatment of regeneration and flush gas, reactor section, gas analysis and process control and data acquisition.

The fuel gas leaves the cyclones with a temperature of about 900 K. As the gas cools down during its transport to the desulfurization unit it is reheated electrically to 875 K. The hot gas passes through a silicon carbide filter (86 %w SiC, 7 %w SiO₂, 7 %w Al₂O₃) to remove most of the dust present in the gas. The dust content decreases from about 1 g/Nm³ to about 20 mg/Nm³. The gas then flows to the reactor section.

The equipment is designed in such a way that H₂S can be removed continuously. Three reactors are required (R1, R2 and R3). During operation one reactor is in the acceptation stage (R1), a second in the regeneration stage (R2) while the third reactor (R3) is flushed. After H₂S breakthrough of the reactor in the acceptation stage all reactors are switched to their next stage (acceptation to regeneration, regeneration to flush, flush to acceptation).

Each reactor is filled with 1 kg of acceptor material, MnO or FeO on γ-Al₂O₃.

Figure 1. Schematic flow sheet of the plant for testing acceptor materials under realistic conditions.
The temperature is kept at about 875 K by a heating jacket. The raw fuel gas is sent through the reactor from top to bottom. Regeneration and flushing takes place in the opposite direction. In this way the removal of H$_2$S from the acceptors is faster and more complete (after sulfidation most of the H$_2$S is accumulated in the top of the acceptor bed). For regeneration a mixture of H$_2$O, N$_2$ and H$_2$ is used. Flushing is done with a N$_2$, H$_2$ mixture.

The H$_2$S concentration in the raw fuel gas, the cleaned fuel gas and the regeneration off gas are measured because they are needed to calculate breakthrough capacities and mass balances. Moreover, the CO$_2$, CO, CH$_4$ and H$_2$O concentrations in the raw fuel gas are measured. A Beckmann gas chromatograph is used for the measurement of the H$_2$S, CO, CO$_2$ and CH$_4$ concentrations in the raw fuel gas, a Radas H$_2$S monitor for the H$_2$S concentration in the cleaned fuel gas (by means of UV absorption) and a Metrohm titration unit for the amount of H$_2$S regenerated. This titration unit is the same as the used in the laboratory set up. From time to time the H$_2$O concentration in the raw fuel gas is measured separately.

The plant is automated by an AT personal computer, equipped with a Keithley 570 interface running under the software package Asyst. The system has the following tasks:

- control of the acceptance - regeneration cycles in the three reactors, using 12 channels
- data acquisition of three different channels (GC, monitor and titration unit) and filing of the data gathered
- presentation of the data in such a way that mass balances and breakthrough capacities can be calculated and the course of the breakthrough capacity as a function of time can be shown.

Results and discussion

Acceptor preparation

Table 1 shows the necessity of improving contact between impregnation fluid and carrier material. Shaking the fluid from time to time (method 1) results in a poor distribution of the metal oxide, a low metal content and a low capacity (batch 1). Stirring
the fluid only (method 2) results in a lot of attrition. This attrition could be lowered by stirring with a lower speed, but applied to larger quantities the contact is influenced negatively. The results of batch 3 show that stirring of both fluid and solids (method 3) results in a large attrition. The results of batch 4 show that, in contrast with method 1, 2 and 3, method 4 (recycling the impregnation fluid through a packed bed of

**Table 1. Results of acceptor preparation and characterization.**

<table>
<thead>
<tr>
<th>Batch</th>
<th>Metal</th>
<th>Preparation</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Mn</td>
<td>0.02</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.07</td>
<td>bad</td>
</tr>
<tr>
<td>2</td>
<td>Mn</td>
<td>0.02</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.07</td>
<td>good</td>
</tr>
<tr>
<td>3</td>
<td>Mn</td>
<td>0.02</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.07</td>
<td>good</td>
</tr>
<tr>
<td>4</td>
<td>Mn</td>
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<td></td>
<td></td>
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<td>good</td>
</tr>
<tr>
<td>5</td>
<td>Mn</td>
<td>1.08</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.54</td>
<td>good</td>
</tr>
<tr>
<td>6</td>
<td>Mn</td>
<td>1.80</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.94</td>
<td>good</td>
</tr>
<tr>
<td>7</td>
<td>Mn</td>
<td>1.80</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.00</td>
<td>good</td>
</tr>
<tr>
<td>8</td>
<td>Mn</td>
<td>2.00</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.00</td>
<td>good</td>
</tr>
<tr>
<td>9</td>
<td>Mn</td>
<td>1.90</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.30</td>
<td>good</td>
</tr>
<tr>
<td>10</td>
<td>Fe</td>
<td>1.90</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.30</td>
<td>good</td>
</tr>
<tr>
<td>11</td>
<td>Fe</td>
<td>1.50</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.00</td>
<td>good</td>
</tr>
</tbody>
</table>

acceptor material) improves contact between carrier and impregnation fluid. Attrition,
metal distribution, metal content and capacity correspond with previous work [6, 8]. Batches 5 to 9 and iron containing batches 10 and 11 confirm these observations. Decreasing impregnation time from about 18 hours to 2 to 3 hours has no influence on breakthrough capacity. Only batches 5 - 11 are used in the tests under realistic conditions.

**Gas composition**

When West German brown coal is used the average fuel gas composition of the gas produced by the coal gasifier is given in table 2.

*Table 2. Average fuel gas composition for West German brown coal.*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (%v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>16.6</td>
</tr>
<tr>
<td>H₂</td>
<td>17.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>12.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>5.0</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.5</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.06</td>
</tr>
<tr>
<td>N₂</td>
<td>balance</td>
</tr>
<tr>
<td>dust</td>
<td>20 mg/Nm³</td>
</tr>
</tbody>
</table>

As can be seen in table 2, the H₂S concentration is quite low, due to the low sulfur content (0.35 %w) of the West German brown coal used. This value is not representative, e.g. in case of a Shell coal gasifier the H₂S concentration is expected to range from 900 to 3400 ppm. For that reason some H₂S is added to the gas stream just before the gas enters the ceramic filter. The H₂S concentration is raised to about 3000 - 5000 ppm.

Because the gas composition is known, the breakthrough capacity of the acceptor material under realistic conditions can be estimated on the basis of the measurements done in the laboratory set-up. Manganese and iron containing acceptors will have a
breakthrough capacity of about 0.40 %w sulfur and about 0.25 %w sulfur respectively.

**Sulfidation - regeneration experiments**

Batches 6, 9 and 10 were tested continuously during four weeks under realistic conditions in reactors 2, 3 and 1 respectively. Each reactor was submitted to about 50 sulfidation - regeneration cycles. The measurements which are most reliable with respect to their mass balances are discussed below.

Examples of measured sulfidation and regeneration curves are given in figures 2 and 3. It is clear that during the sulfidation stage almost all H$_2$S is captured. The gas leaving the reactor contains only about 20 ppm H$_2$S. In some cases a cleaning depth of less then 1 ppm H$_2$S is observed. The H$_2$S concentration leaving the reactor is influenced by the fuel gas composition. A high H$_2$O concentration causes a somewhat higher H$_2$S concentration in the cleaned fuel gas. However, a cleaning efficiency of more then 99% can be obtained under realistic conditions.

In figures 4, 5 and 6 the breakthrough capacities, and the CO- and water concentrations are shown as a function of sulfidation-regeneration cycle number. The CO and water concentrations shown in the figures represent average values obtained during the corresponding sulfidation cycle. Most of the water concentrations in the figures were not measured quantitively but result from equilibrium calculations, in which it is supposed that thermodynamic equilibrium between CO, CO$_2$, H$_2$ and H$_2$O is reached at the desulfurization reactor inlet [9]. As the measured points (the crosses in the figures) are
somewhat higher than the calculated values, the calculated points only indicate concentration qualitatively.

The breakthrough capacity $q_b$ is calculated according to:

$$q_b = \frac{\text{flow}_{H_2S, \text{in}} \times t_b \times M_S}{W_{\text{acc}}} \times 100\%$$  (2)

where $q_b$ = breakthrough capacity (%w sulfur)
(flow$_{H_2S, \text{in}}$ = H$_2$S flow entering the reactor (mol/s)
$t_b$ = breakthrough time (s)
$M_S$ = molar weight of sulfur (g/mol)
$W_{\text{acc}}$ = weight of the acceptor in the reactor (g)

The amount of H$_2$S released during regeneration is determined directly by the titration unit: it measures the cumulative amount of H$_2$S formed. The H$_2$S concentration in the regeneration off-gas can be calculated by taking the first derivative of the
measured data. An example of these curves is shown in figure 3.

The breakthrough capacity is fluctuating quite strongly in all figures, and so does the amount of sulfur regenerated. It can be noticed easily that the breakthrough capacities follow the CO concentration line. A high CO concentration corresponds to a high breakthrough capacity. This effect of CO is not surprising because CO consumes water by the water gas shift reaction:

\[ CO + H_2O \rightarrow CO_2 + H_2 \]  

(3)

In this way the local water concentration is lowered and the acceptor can capture more H₂S. The opposite happens when the CO concentration decreases. The strong fluctuations in gas composition are caused by the coal gasifier which could not be operated easily under steady state conditions.

From figures 4 to 6 it can also be concluded that the average breakthrough capacity remains almost constant. This means that the use of a realistic fuel gas does not result in a fast deactivation of the acceptor material.
Figure 6. Breakthrough capacity of FeO/γ-Al₂O₃, batch 10 (*), and the CO (∆) and the calculated H₂O (v) concentration at 875 K. + = measured H₂O concentration.

In table 3 the results of measurements with batches 6, 9 and 10 are summarized.

Table 3. Average breakthrough capacities of fresh and used acceptors at 875 K.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Batch</th>
<th>Capacity after 16 cycles (%w S)¹</th>
<th>Capacity under realistic conditions (%w S)²</th>
<th>Capacity after use (%w S)³</th>
<th>Standard deactivation (%)⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO/γ-Al₂O₃</td>
<td>6</td>
<td>0.84</td>
<td>0.21</td>
<td>0.39</td>
<td>54</td>
</tr>
<tr>
<td>MnO/γ-Al₂O₃</td>
<td>9</td>
<td>0.79</td>
<td>0.19</td>
<td>0.35</td>
<td>56</td>
</tr>
<tr>
<td>FeO/γ-Al₂O₃</td>
<td>10</td>
<td>0.60</td>
<td>0.23</td>
<td>0.35</td>
<td>42</td>
</tr>
</tbody>
</table>

¹) model gas, typically after 16 sulfidation-regeneration cycles, feed 1 %v H₂S and 10 %v H₂, N₂ balance.
²) coal gas, typically 100 - 200 cycles.
³) model gas, after testing under realistic conditions.
⁴) (column 3 - column 5)/column 3 * 100 %
For the manganese containing batches 6 and 9 it is clear that the breakthrough capacity is lower than the capacity predicted from the laboratory experiments. The breakthrough capacity of the iron containing acceptor under realistic conditions better corresponds to the value expected from laboratory experiments. The same trend is shown by the tests carried out with used/spent acceptors under laboratory conditions. The breakthrough capacity of the used batches 6 and 9 is about 55 percent lower than the capacity of fresh acceptors. In case of the iron containing acceptor (batch 10) the breakthrough capacity is about 40 percent lower. Part of the decline in activity can be explained by the fact that the given breakthrough capacity of fresh acceptors are values obtained after 15 sulfidation - regeneration cycles. In chapter 4 it is shown that the acceptors reach a stable capacity only after about 50 cycles. Between cycle 15 and 50 the breakthrough capacity goes down with 25 to 30 percent. So due to the use of a realistic fuel gas in case of both manganese containing acceptors a deactivation of about 25 to 30 percent is left which can not be explained by laboratory measurements. In case of the iron containing acceptor this is about 15 percent.

It is assumed that the relatively strong deactivation of batches 6 and 9 is caused by introductory experiments carried out with these materials while testing several sections of the bench scale unit. Batches 6 and 9 were exposed to temperatures of about 1000 K and subsequent oxidizing and reducing atmospheres.

Table 4 shows specific surface areas of the fresh and the used acceptors.

**Table 4. Surface areas of fresh and used acceptor.**

<table>
<thead>
<tr>
<th>Batch</th>
<th>Fresh</th>
<th>Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>231</td>
<td>141</td>
</tr>
<tr>
<td>9</td>
<td>234</td>
<td>132</td>
</tr>
<tr>
<td>10</td>
<td>241</td>
<td>98</td>
</tr>
</tbody>
</table>

From these data it is concluded that the high temperatures the acceptors were exposed
to not caused the relatively strong deactivation of the manganese containing acceptors. It is more likely that the exposure to air at high temperatures caused sintering of the active compound on the acceptor.

The sulfur balance is an important parameter to check whether the acceptor material is completely regenerated or not. A sulfur deficit indicates an accumulation of sulfur on the acceptor.

The sulfur deficit can be calculated from the amounts of sulfur accepted and regenerated. The sulfur deficit is defined as the amount of sulfur fed to the reactor minus the amount of sulfur leaving the reactor during sulfidation and regeneration divided by the amount of sulfur fed to the reactor during sulfidation. The amount of sulfur slipped through the reactor during sulfidation is calculated from the breakthrough curves:

$$\text{SD} = \frac{\text{flow}_{\text{H}_2\text{S}, \text{in}} \cdot t_{\text{acc}} - (Q_{\text{sl}} + Q_{\text{reg}})}{\text{flow}_{\text{H}_2\text{S}, \text{in}} \cdot t_{\text{acc}}}$$ (4)

where

- \(Q_{\text{reg}}\) = amount of \(\text{H}_2\text{S}\) produced during regeneration (mol)
- \(t_{\text{acc}}\) = total acceptation/sulfidation time (s)
- \(Q_{\text{sl}}\) = amount of \(\text{H}_2\text{S}\) slipped through the reactor during sulfidation (mol)

Sulfur deficits for the experiments shown in figures 4 to 6 are shown in figure 7. The average value of the sulfur deficit for all experiments is about zero. This means that the acceptor material can be regenerated completely under realistic conditions.

During the second test period three other acceptor batches were tested. Batches 7, 8 and 11 are tested in reactor 1, 3 and 2 respectively during two weeks of continuous use. As expected the breakthrough capacities of the manganese containing acceptors are higher than the capacities of the acceptors tested during the previous period. Both iron containing acceptors (batches 10 and 11) show almost the same capacity.
Regeneration behaviour is much better. The $\text{H}_2\text{S}$ concentration in the regeneration off gas is higher due to some changes in the equipment: the regeneration gas is supplied to the reactor at a higher temperature and has a higher steam concentration.

The influence of gas composition on breakthrough capacity induces the same effects as in figures 4 to 6. Therefore, only breakthrough capacities of batches 7, 8 and 11 are shown in figure 8. Figure 9 shows the sulfur deficit of the corresponding experiments. Because of more accurate analysis methods and an optimized regeneration procedure sulfur deficits are much closer to zero than those shown in figure 7 for tests done in the previous testing period.

It is clear that the fresh acceptors show the same initial deactivation in the bench scale unit as they do in the laboratory set-up (see chapter 4). After the initial deactivation the average breakthrough capacity remains almost constant and is only slightly influenced by the gas composition because of a relatively stable run of the gasifier. In table 5 the results of the measurements with batches 7, 8 and 11 are summarized.
Figure 8. Breakthrough capacities of MnO/γ-Al2O3, batch 7 (*), MnO/γ-Al2O3, batch 8 (△) and FeO/γ-Al2O3, batch 11 (σ) at 875 K.

Table 5. Average breakthrough capacity of fresh and used/spent acceptors

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Batch</th>
<th>Capacity after 16 cycles (%w S)(^1)</th>
<th>Capacity under realistic conditions (%w S)(^2)</th>
<th>Capacity after use (%w S)(^3)</th>
<th>Standard deactivation (%)(^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO/γ-Al2O3</td>
<td>7</td>
<td>0.74</td>
<td>0.36</td>
<td>0.62</td>
<td>16</td>
</tr>
<tr>
<td>MnO/γ-Al2O3</td>
<td>8</td>
<td>0.94</td>
<td>0.33</td>
<td>0.68</td>
<td>28</td>
</tr>
<tr>
<td>FeO/γ-Al2O3</td>
<td>11</td>
<td>0.55</td>
<td>0.21</td>
<td>0.36</td>
<td>35</td>
</tr>
</tbody>
</table>

\(^1\) model gas, typically after 16 sulfidation-regeneration cycles, feed 1 %v H2S and 10 %v H2, N2 balance.

\(^2\) coal gas, typically 100 - 200 cycles.

\(^3\) model gas, after testing under realistic conditions.

\(^4\) (column 3 - column 5)/column 3 * 100 %

From table 3 and 5 it follows that acceptor performance (capacity, deactivation) is strongly influenced by temperature. The deactivation of the acceptor in the second testing
Figure 9. Sulfur deficits of MnO/$\gamma$-Al$_2$O$_3$ batch 7 (*), MnO/$\gamma$-Al$_2$O$_3$ batch 8 (△) and FeO/$\gamma$-Al$_2$O$_3$ batch 11 (□) at 875 K.

period is caused mainly by the deactivation until the 50th cycle. It is therefore important not to exceed the operation temperature of the acceptor (e.g. 875 K) as this will cause sintering and deactivation of the acceptor. Secondly it is better not to expose the acceptor to an oxidizing atmosphere at high temperatures because it can cause formation of manganese particles. This is caused by the tendency of the manganese ions to diffuse out of the alumina carrier when they are exposed to air at high temperatures. Due to the high temperatures the oxidized manganese ions on the acceptor surface will form small crystallites (see also chapter 3).

It is shown that the breakthrough capacity obtained under realistic conditions can be predicted from laboratory experiments if gas composition and temperature are known. So it is possible to estimate the breakthrough capacity for any coal gasification process without doing measurements. A breakthrough capacity of about 0.4 %w S as found during the above measurements seems to be low, but using the Shell coal gasification process a higher breakthrough capacity (about 1.5 %w S) will be found because of its favourable gas composition (60-65 %v CO, little H$_2$O (1-3 %v) [4])
Contaminants

Lifetime of the acceptors could, among others, be influenced by contaminants present in the fuel gas. Some of these contaminants are NH₃, HCN, halogens and heavy metals. To get an impression of the distribution of these compounds through the experimental system (gasifier and bench scale unit) and on the acceptors, samples of coal, ash, gas and acceptors have been analysed for their contents of heavy metals and halogens. Table 6 shows the composition of the West German brown coal used for gasification and the bottom and cyclone ashes of the gasifier.

Table 6. Trace compounds in the West German brown coal used, and in the bottom and cyclone ashes of the gasifier.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr (ppm)</th>
<th>Cu (ppm)</th>
<th>Pb (ppm)</th>
<th>Mn (ppm)</th>
<th>Ni (ppm)</th>
<th>Zn (ppm)</th>
<th>V (ppm)</th>
<th>Cl (%w)</th>
<th>F (ppm)</th>
<th>S (%w)</th>
<th>Fe (%w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>coal</td>
<td>bdl¹</td>
<td>bdl¹</td>
<td>168</td>
<td>bdl¹</td>
<td>0.7</td>
<td>1.8</td>
<td>0.03</td>
<td>21</td>
<td>0.30</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>det. limit</td>
<td>3</td>
<td>5</td>
<td>13</td>
<td>5</td>
<td>4</td>
<td>0.7</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.003</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>bottom ash</td>
<td>1.2</td>
<td>0.2</td>
<td>bdl¹</td>
<td>314</td>
<td>2.4</td>
<td>3.5</td>
<td>3.8</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.08</td>
</tr>
<tr>
<td>cyclone ash</td>
<td>13.8</td>
<td>3.8</td>
<td>3</td>
<td>716</td>
<td>8.7</td>
<td>11.1</td>
<td>7.8</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2.21</td>
</tr>
<tr>
<td>det. limit</td>
<td>0.9</td>
<td>0.2</td>
<td>3</td>
<td>0.1</td>
<td>0.13</td>
<td>0.2</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3 ppm</td>
</tr>
</tbody>
</table>

¹) bdl = below detection limit
n.d. = not determined, n.a. = not available

It is clear that the concentration of heavy metals rises downstream the gasification plant. The gasifier uses about 50 kg coal an hour and produces 2.5 kg bottom ash an hour. Because both coal composition and the composition of the bottom ash are known it can be calculated that about 10% of the contaminants in the coal are recovered in the bottom ash. The finest ash (cyclone) has the highest concentration of heavy metals but the amount of cyclone ash is much too low to recover all heavy metals present in the coal. The remainder of the mineral matter leaves the reactor as finely divided material, fly-ash, suspended in the raw fuel gas. A number of elements volatilize and show up in the raw fuel gas as well [2]. This implies that dust carried by the gas stream to the
desulfurization plant contains a lot of heavy metals and that part of the metals is present in the gas phase, not bounded to dust. These compounds may deactivate the acceptor and in that case be present on used acceptors.

The concentrations of $\text{SO}_4$, $\text{HCl}$ and $\text{HF}$ in the fuel gas entering the desulfurization plant are 3, 20 and 1 ppmw at $10^5 \text{ Pa}$ respectively. The $\text{HCl}$ and $\text{HF}$ concentrations are quite low compared to the expected values for the Shell and Texaco gasification processes (the expected $\text{HCl}$ concentrations are 600 and 500 ppm and the $\text{HF}$ concentrations 224 and 188 ppm respectively [2]). However, experiments done in the laboratory set-up show that, although 0.5 %v $\text{HCl}$ has a negative influence on breakthrough capacity, it does not result in a permanent deactivation of the acceptors. Obviously, $\text{HCl}$ is removed from the acceptor during the regeneration stage (see chapter 4).

The composition of the iron containing acceptor (batch 10) used during the first testing period was determined by means of nuclear activation analysis. The results are summarized in table 7.

Table 7. Composition of $\text{FeO}/\gamma-\text{Al}_2\text{O}_3$ batch 10, after 4 weeks of continuous use under realistic conditions at 875 K.

<table>
<thead>
<tr>
<th></th>
<th>Na ppm</th>
<th>Mg ppm</th>
<th>Al %w</th>
<th>Ca ppm</th>
<th>Cr %w</th>
<th>Mn ppm</th>
<th>Fe ppm</th>
<th>Co ppm</th>
<th>Ni ppm</th>
<th>Mo ppm</th>
<th>Cl ppm</th>
<th>Cu ppm</th>
<th>Pb ppm</th>
<th>Zn ppm</th>
<th>V ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>102</td>
<td>&lt;100</td>
<td>47.5</td>
<td>&lt;0.1</td>
<td>22.8</td>
<td>121</td>
<td>10.5</td>
<td>6.7</td>
<td>34</td>
<td>268</td>
<td>&lt;30</td>
<td>&lt;400</td>
<td>20</td>
<td>&lt;7</td>
<td>&lt;15</td>
</tr>
</tbody>
</table>

Table 7 shows that no accumulation of heavy metals or halogens on the acceptor occurred. Most of the contaminants are present in the ash. The remainder is carried by the gas stream as dust and fed to the desulfurization plant. Most of this dust is removed by the ceramic filter. Obviously, compounds entering the reactor leave the reactor with the cleaned fuel gas or are removed from the acceptor during the regeneration stage which is carried out countercurrently.
Conclusions

Preparing large amounts of acceptor material can be performed by recycling the impregnation fluid through a packed bed of carrier material. The acceptor materials have a metal content, metal distribution and sulfur capture capacity corresponding to those of previous work. After an initial deactivation, as expected from laboratory experiments, the use of a realistic fuel gas does not deactivate the acceptors. The capacity of the acceptors is low, but corresponds to the values estimated from laboratory experiments and the given gas composition. The cleaning depth is good, in most cases less then 20 ppm H₂S leaves the reactor before breakthrough. This corresponds to cleaning efficiency of more then 99 % with a H₂S concentration of 5000 ppm in the fuel gas. During regeneration the average H₂S concentration in the regeneration off-gas is high enough to be fed to a Claus-plant.

Acknowledgement

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References

1 E.O. Gerstbrein and V.R. Shorter, 7th International Conference & Exhibition on Coal Technology & Coal Trade, C2, 21 - 23 Nov. 1988, Amsterdam, The Netherlands
g-installaties, NOVEM, Nov. 1990
1988, Amsterdam, The Netherlands


7 D. Jansen, Beschrijving van 200 kW kolenvergasser, internal report, ECN, Petten, 1988


Modelling

Abstract

A mathematical model has been developed to describe experimental breakthrough and regeneration curves quantitatively. Diffusion limitation was not observed. The model is based on the kinetics of the reactions taking place on the acceptor surface, viz. a fast sulfur-oxygen exchange reaction between H₂S and manganese oxide, a slow sulfur-oxygen exchange reaction in which sub-surface Mn-ions react, competitive Langmuir adsorption of H₂S, H₂O and CO on the acceptor surface, the water gas shift reaction, COS formation and reaction of the acceptor with COS. Breakthrough curves of different acceptors during sulfidation can be described. The regeneration behaviour of the acceptor is also predicted correctly. However, according to the model the regeneration proceeds faster and results in a higher H₂S concentration than was measured. The difference can be explained by side-effects induced by the experimental set-up, in particular the tubing between the reactor and the analysis system and, to a lesser degree, by the analysis section itself. The effects induced by the tubing can be incorporated easily in the model by introducing empty ideally mixed tanks in series.

Introduction

In contrast to the previous chapters which deal with experimental results and their interpretation, this chapter deals with predicted breakthrough and regeneration curves. Specifically, results aimed at the quantitative description of breakthrough and regeneration behaviour with a mathematical model will be presented.

Soerawidjaja [1] developed a model based on sorption and exchange reactions. His
model was found to describe the breakthrough of manganese containing acceptors with a feed gas containing $\text{H}_2\text{S}$ and/or $\text{H}_2\text{O}$ in $\text{N}_2/\text{H}_2$ quite accurately. It is used as a basis of the model described in this chapter.

In an ideal fixed bed reactor, it is assumed that not only the local mass flow rate but also the fluid properties, temperature, pressure and compositions are uniform over any sectional area. Deviations from this idealized flow pattern can be caused by channelling and/or backmixing of fluid, or by stagnant regions in the reactor. In the elementary treatment of fixed bed reactors, longitudinal dispersion, i.e. mixing by diffusion and other processes in the direction of flow, is neglected. When a gas-solid system is modelled the hydrodynamics of the reactor system have to be verified. Also the mass/energy production and transfer in- and outside the porous solid have to stay within certain limits.

A number of rules of thumb are summarized by Wolff [2] to determine the influence of the topics mentioned above. It follows that the pressure drop in the acceptor bed is about 1900 Pa. Experiments discussed in chapter 4 showed the absence of pressure effects up to pressures of 0.5 MPa. The influence of pressure drop can therefore be neglected in the modelling work. The existence of axial dispersion is negligible if $\text{Bo} > 20$. Calculations showed that $\text{Bo} = 500$ when an average particle diameter of 0.33 mm is used. The velocity profile differs less than 20 % from the assumed uniform profile for $\frac{d_{\text{bed}}}{d_{\text{particle}}}$ ratios of more than 30. It is generally assumed that the tube diameter should be at least 20 particle diameters wide. In the tubular reactor used in this work $\frac{d_{\text{bed}}}{d_{\text{particle}}}$ is about 27. So, we conclude that no axial or radial dispersion occurs.

From thermodynamic calculations (see chapter 1) it follows that the heat effects of the sulfidation and the regeneration reaction are negligible. However, when the feed contains CO (and possibly $\text{H}_2\text{O}$) the shift reaction will proceed on the acceptor surface as well (see chapter 4). As the shift reaction is an exothermic reaction ($\Delta H_r = -205 \text{ kJ/mol at 875 K}$), the amount of heat produced in the acceptor can cause a temperature rise. Due to the low flow rates ($67.5 \mu\text{mol/s}$) the amount of heat produced is small and will be transported from the acceptor bed fast enough and therefore will not influence the measurements. The heat effect of the shift reaction, however, must be taken into account when large reactors are modelled, as is e.g. the case in a coal gasification combined cycle power plant.
Experiments at 875 K, a flow rate of 67.5 \( \mu \text{mol/s} \) and particle sizes between 0.25 and 0.42 mm, 0.42 and 0.60 mm, and 0.60 and 0.85 mm showed that neither the shape of the breakthrough curves nor the breakthrough capacity of the acceptor was influenced. The same is observed for the regeneration curves. This was interpreted as an indication that the rates of sulfidation and regeneration are not limited by pore diffusion. This conclusion is based on the expectation that, if pore diffusion is the rate limiting step, the breakthrough capacity would be significantly influenced by the particle size, it would increase with decreasing particle sizes.

Beside the points mentioned above, showing that the fixed bed reactor used can be assumed to be an ideal fixed bed reactor, the flow pattern in the tubing between reactor and analysis section may influence the measurements. When a pulse of tracer, with a width smaller than the residence time of the gas in the tubing, is fed to the tubing, it will be disturbed and become broader and lower. To what extent this effect influences the measurements of breakthrough curves depends upon flow rate, the height of the \( \text{H}_2\text{S} \) concentration and on the rate of the concentration change. The effect of the tubing can be included in the model by adding a number of empty ideally mixed tanks in series. The number of tanks in series can be estimated when the Bodenstein number is known. The tubing between reactor and analysis section is kept at 373 K. It can be calculated that the Reynolds number is about 20 to 30 (depending upon the flow rate applied during regeneration) and the Schmidt number is about one. According to the model of Taylor and Aris [15] the corresponding Bodenstein number is 10 to 20 (depending upon flow rate). The number of tanks needed to describe an empty tubular reactor can be approximated by \( N = \text{Bo}/2 \) [16]. This means that the tubing between reactor and analysis section can be simulated by 5 to 10 equal empty tanks in series.

**Model**

Based on a qualitative interpretation of the breakthrough curves of \( \text{H}_2\text{S} \), \( \text{H}_2\text{O} \), \( \text{CO}_2 \) and \( \text{COS} \) (see figure 1 and 2), obtained with a 8.96 \%w \( \text{Mn}/\gamma\text{-Al}_2\text{O}_3 \) acceptor, it is proposed that the following processes take place during sulfidation:

- \( \text{H}_2\text{S} \) uptake by a fast oxygen-sulfur exchange (the principal process)
Figure 1. Reactor effluent composition of 8.96 %w Mn/γ-Al₂O₃. Feed: 1 %v H₂S, 10 %v H₂, N₂ balance. T = 875 K. ◊ = H₂S, ♦ = H₂O.

Figure 2. Reactor effluent composition of 8.96 %w Mn/γ-Al₂O₃. Feed: 1 %v H₂S, 10 %v H₂, 50 %v CO, N₂ balance. T = 875 K. ◊ = H₂S, ♦ = H₂O, ▼ = CO₂, △ = COS.
- H$_2$S uptake by a slow oxygen-sulfur exchange. This reaction must be taken into account because after H$_2$S breakthrough a considerable amount of H$_2$S is captured during a long time (see figure 1 and 2). This is caused by diffusion of manganese ions out of the alumina support to the acceptor surface where they react with H$_2$S. The rate of this reaction is limited by the diffusion of the Mn$^{2+}$-ions in the support (see also chapter 3).

- competitive Langmuir adsorption of H$_2$S, H$_2$O and CO on the acceptor surface
- the water gas shift reaction (see chapter 4)
- COS formation (see chapter 4)
- reaction of COS with the acceptor via an oxygen-sulfur exchange reaction

During regeneration a feed gas containing H$_2$O, H$_2$ and N$_2$ is used; no CO, CO$_2$ or COS is present. The model used to describe the regeneration process is therefore based on a simplified version of the model derived for the sulfidation reaction and includes the next processes:

- H$_2$O uptake by a fast sulfur-oxygen exchange (the principal process)
- H$_2$O uptake by a slow sulfur-oxygen exchange
- competitive Langmuir adsorption of H$_2$S and H$_2$O on the acceptor surface

Because the model used to describe the sulfidation is very similar to the regeneration model, only the model for sulfidation of the acceptors will be derived in this chapter. Results of both the sulfidation and the regeneration model will be discussed later.

The kinetic model is composed of the following elementary steps (A = H$_2$S or S, B = H$_2$O or O, C = CO, D = CO$_2$, E = H$_2$, F = COS, S$_1$ = fast exchangeable manganese sites, S$_2$ = slow exchangeable manganese sites and S$_3$ = sites in Langmuir adsorption isotherms). Below each reaction the concentrations of the components involved are shown. For the gas phase C$_A$ is used, for the solid phase Q$_1$ or q$_i$:

1. Fast oxygen-sulfur exchange:

$$A (g) + S_1B (s) = S_1A (s) + B (g)$$

$$C_A (Q_1 - q_1) \quad q_1 \quad C_B$$
Q₁ represents the number of sites (mol/mᵢ³) which react via the fast oxygen-sulfur exchange; q₁ represents the number of sulfided Q₁ sites. The equilibrium constant is Kᵣ and the rate constant of the forward reaction kᵣ. The rate of the forward reaction is r₁, and of the backward reaction r₂.

\[ r₁ = kᵣ Cₐ (Q₁ - q₁) \] (2)

\[ r₂ = \frac{kᵣ Cₐ q₁}{Kᵣ} \] (3)

2. Slow oxygen-sulfur exchange:

\[ S₁A (s) + S₂B (s) = S₂A (s) + S₁B (s) \] (4)

\[ q₁ \quad (Q₂ - q₂) \quad q₂ \quad (Q₁ - q₁) \]

Q₂ represents the number of sites (mol/mᵢ³) which react via the slow oxygen-sulfur exchange; q₂ represents the number of sulfided Q₂ sites. The equilibrium constant of this reaction is (Kᵣ) assumed to be unity. The rate constant is kₛ. Note that the terms "fast" and "slow" mean that kᵣ is supposed to be much larger than kₛ. The rate of the forward reaction is r₃, and of the backward reaction r₄.

\[ r₃ = kₛ q₁ (Q₂ - q₂) \] (5)

\[ r₄ = kₛ q₂ (Q₁ - q₁) \] (6)

3. Competitive Langmuir adsorption isotherms of A, B and C with equilibrium constants Kₐ, Kₐ and K₉ respectively. It is assumed that the effect of CO₂ and H₂ is negligible:

\[ A (g) + S₃ (s) = S₃A (s) \] (7)

\[ Cₐ \quad (Q₃ qₐ qₐ qₐ) \quad qₐ \]
\[ \text{B (g)} + \text{S}_3 \text{ (s)} = \text{S}_3\text{B (s)} \quad (8) \]
\[ \text{C}_B \left( \frac{Q_3-q_A^*q_B^*q_C}{q_B^*} \right) = q_B \]
\[ \text{C (g)} + \text{S}_3 \text{ (s)} = \text{S}_3\text{C (s)} \quad (9) \]
\[ \text{C}_C \left( \frac{Q_3-q_A^*q_B^*q_C}{q_C^*} \right) = q_C \]

\( Q_3 \) represents the number of Langmuir adsorption sites (mol/m\(^3\)).

The net changes in the adsorption equilibria are \( r_A, r_B \) and \( r_C \).\)

\[ r_A = \frac{dq_A}{dt}; \quad r_B = \frac{dq_B}{dt}; \quad r_C = \frac{dq_C}{dt} \quad (10-12) \]

Reactions 7 to 9 are assumed to reach equilibrium instantaneously; the equilibria are described by [5]:

\[ q_A = \frac{K_A C_A}{1 + K_A C_A + K_B C_B + K_C C_C} Q_3 \quad (13) \]

\[ q_B = \frac{K_B C_B}{1 + K_A C_A + K_B C_B + K_C C_C} Q_3 \quad (14) \]

\[ q_C = \frac{K_C C_C}{1 + K_A C_A + K_B C_B + K_C C_C} Q_3 \quad (15) \]

4. The water gas shift reaction:

\[ \text{B (g)} + \text{C (g)} = \text{D (g)} + \text{E (g)} \quad (16) \]

\[ \text{C}_B \quad \text{C}_C \quad \text{C}_D \quad \text{C}_R \]

\( K_{\text{wgs}} \) is the equilibrium constant and \( k_{\text{wgs}} \) the reaction rate constant of the forward reaction; \( r_5 \) and \( r_6 \) describe the rates of the forward and the backward reaction, respectively.

\[ r_5 = k_{\text{wgs}} C_B C_C \quad (17) \]
\[ r_6 = \frac{k_{ggs} C_D C_E}{K_{ggs}} \]  

(18)

5. \textbf{COS formation:}

\[ A \ (g) + C \ (g) \rightarrow E \ (g) + F \ (g) \]  

(19)

\[
\begin{align*}
C_A & & C_C & & C_E & & C_F \\
K_{scos} & & & & & & \\
\end{align*}
\]

\[ K_{scos} \] is the equilibrium constant and \( k_{scos} \) the reaction rate constant of the forward reaction; \( r_7 \) and \( r_8 \) describe the rates of the forward and the backward reaction, respectively.

\[ r_7 = k_{scos} C_A C_C \]  

(20)

\[ r_8 = \frac{k_{scos} C_E C_F}{K_{scos}} \]  

(21)

6. \textbf{A fast reaction of the acceptor with COS. As the COS removal can proceed via different routes (see chapter 4) for simplicity only one reaction is taken into account in the model. In this case COS reacts directly with the acceptor and is not hydrolysed and converted to \( H_2S \) first.}

\[ F \ (g) + S_1 B \ (s) \rightarrow S_1 A \ (s) + D \ (g) \]  

(22)

\[
\begin{align*}
C_F & & (Q_1-q_1) & & q_1 & & C_D \\
\end{align*}
\]

\[ K_{fcos} \] is the equilibrium constant and \( k_{fcos} \) the reaction rate constant of the forward reaction; \( r_9 \) and \( r_{10} \) describe the rates of the forward and the backward reaction, respectively.

\[ r_9 = k_{fcos} C_F (Q_1-q_1) \]  

(23)
\[ r_{10} = \frac{k_{i, \text{cos}} C_D q_1}{K_i \text{cos}} \]  

(24)

Mass balances for all compounds have to be set up over a certain element of volume and over a certain element of time. As the composition varies with the position in the reactor, a differential element with volume \( dV \) must be used and the equations integrated. Likewise, as the composition changes with time, the balance must also be made over a differential element of time. Consequently, the mass balances of the fixed bed reactor result in a set of partial differential equations. These equations either must be solved numerically. To do so the tubular reactor is simulated by a number of tanks-in-series model. When the tanks-in-series approximation is used, the partial differential equations become a set of normal differential equations. In total \( N_{\text{tanks}} \) times 8 differential equations (the number of independent equations resulting from the reactions assumed) have to be solved numerically simultaneously.

In each tank the same 8 differential equations are solved. These equations will be derived for one arbitrary tank in the series, having a volume of \( V_R / N_{\text{tanks}} \).

The mass balances (in = out + conversion + accumulation) can be set up for all components, resulting in:

\[
\begin{align*}
\phi_v C_{A, \text{in}} &= \phi_v C_A + (r_1 - r_2 + (r_7 - r_8) \epsilon) V_R + V_G \frac{dC_A}{dt} \\
\phi_v C_{B, \text{in}} &= \phi_v C_B + (r_2 - r_1 + (r_5 - r_6) \epsilon) V_R + V_G \frac{dC_B}{dt} \\
\phi_v C_{C, \text{in}} &= \phi_v C_C + ((r_5 - r_6 + r_7 - r_8) \epsilon) V_R + V_G \frac{dC_C}{dt}
\end{align*}
\]  

(25)  

(26)  

(27)
\[
\phi_v C_{D, \text{in}} = \phi_v C_D + ((r_6 - r_5) \epsilon + (r_{10} - r_9)) V_R + V_G \frac{dC_D}{dt} \tag{28}
\]

\[
\phi_v C_{E, \text{in}} = \phi_v C_E + (r_6 - r_5 + r_8 - r_7) \epsilon V_R + V_G \frac{dC_E}{dt} \tag{29}
\]

\[
\phi_v C_{F, \text{in}} = \phi_v C_F + ((r_8 - r_7) \epsilon + (r_9 - r_{10})) V_R + V_G \frac{dC_F}{dt} \tag{30}
\]

\[
\frac{dq_1}{dt} = (r_1 - r_2) + (r_4 - r_3) + (r_9 - r_{10}) \tag{31}
\]

\[
\frac{dq_2}{dt} = (r_3 - r_4) \tag{32}
\]

\[
\frac{dq_A}{dt} = \left( \frac{dq_A}{\partial C_A} \right) \frac{\partial C_A}{\partial t} + \left( \frac{dq_A}{\partial C_B} \right) \frac{\partial C_B}{\partial t} + \left( \frac{dq_A}{\partial C_C} \right) \frac{\partial C_C}{\partial t} \tag{33}
\]

\[
\frac{dq_B}{dt} = \left( \frac{dq_B}{\partial C_A} \right) \frac{\partial C_A}{\partial t} + \left( \frac{dq_B}{\partial C_B} \right) \frac{\partial C_B}{\partial t} + \left( \frac{dq_B}{\partial C_C} \right) \frac{\partial C_C}{\partial t} \tag{34}
\]

\[
\frac{dq_C}{dt} = \left( \frac{dq_C}{\partial C_A} \right) \frac{\partial C_A}{\partial t} + \left( \frac{dq_C}{\partial C_B} \right) \frac{\partial C_B}{\partial t} + \left( \frac{dq_C}{\partial C_C} \right) \frac{\partial C_C}{\partial t} \tag{35}
\]

To ease the numerical solution, to prevent computer overflow and/or underflow and to simplify the interpretation of the calculated results, the following dimensionless quantities are introduced:

Dimensionless concentrations in the gas phase:

\[
X_A = \frac{C_A}{C_0}; \quad X_B = \frac{C_B}{C_0}; \quad X_C = \frac{C_C}{C_0}; \quad X_D = \frac{C_D}{C_0}; \quad X_E = \frac{C_E}{C_0}; \quad X_F = \frac{C_F}{C_0} \tag{36-41}
\]
Dimensionless concentrations in the solid phase:

\[
y_1 = \frac{q_1}{Q_1}; \quad y_2 = \frac{q_2}{Q_2}; \quad y_A = \frac{q_A}{Q_3}; \quad y_B = \frac{q_B}{Q_3}; \quad y_C = \frac{q_C}{Q_3}
\]  

(42-46)

The ratio of the gas volume compared to the reactor volume (porosity):

\[
\epsilon = \frac{V_G}{V_R}
\]

(47)

Dimensionless time:

\[
\Theta = \frac{t v V_G C_0}{L V_R Q_0} - \frac{t \phi v C_0}{N V_R Q_0}
\]

(49)

in which: \(C_0\) = reference gas phase concentration, typically the \(H_2S\) inlet concentration (mol m\(^{-3}\)); \(Q_0\) = reference capacity of the acceptor (assigned a value of 140 mol m\(_r\) m\(^{-3}\)); \(t\) = time on stream (s); \(v\) = gas velocity (m\(_r\) s\(^{-1}\)); \(L\) = length of the acceptor bed (m\(_r\)).

The expressions for the forward and backward reaction rates can now be written as:

\[
r_1 = k_f C_0 X_A Q_1 (1-y_1)
\]

(49)

\[
r_2 = \frac{k_f C_0 X_B Q_1 y_1}{K_f}
\]

(50)

\[
r_3 = k_s Q_1 Q_2 y_1 (1-y_2)
\]

(51)

\[
r_4 = k_s Q_1 Q_2 y_2 (1-y_1)
\]

(52)

\[
r_5 = k_{wgs} C_0^2 X_B X_C
\]

(53)

\[
r_6 = \frac{k_{wgs} C_0^2 X_D X_E}{K_{wgs}}
\]

(54)
\[ r_7 = k_{\cos} C_0^2 X_A X_C \]  
(55)

\[ r_8 = \frac{k_{\cos} C_0^2 X_E X_F}{K_{\cos}} \]  
(56)

\[ r_9 = k_{t, \cos} C_0 X_F Q_1 (1 - y_1) \]  
(57)

\[ r_{10} = \frac{k_{t, \cos} C_0 X_D Q_1 y_1}{K_{t, \cos}} \]  
(58)

Introducing the new relations for \( r_1 \) to \( r_{10} \) in the mass balances for components A to F and \( q_1 \) and \( q_2 \), and multiplying by \( N \cdot V_R \cdot Q_0 / (\phi, C_0) \) results in:

\[ N Q_0 (X_{A, \text{in}} - X_A) - \frac{N V_R k_{t} Q_1 Q_0}{\phi_v} \left( X_A (1 - y_1) - \frac{X_B y_1}{K_t} \right) \]  
(59)

\[ N V_R k_{\cos} C_0 \epsilon Q_0 \left( X_A X_C - \frac{X_E X_F}{K_{\cos}} \right) = Q_3 \frac{dY_A}{d\Theta} + \epsilon C_0 \frac{dX_A}{d\Theta} \]

\[ N Q_0 (X_{B, \text{in}} - X_B) + \frac{N V_R k_{t} Q_1 Q_0}{\phi_v} \left( X_A (1 - y_1) - \frac{X_B y_1}{K_t} \right) \]  
(60)

\[ N V_R k_{wgs} C_0 \epsilon Q_0 \left( X_B X_C - \frac{X_D X_E}{K_{wgs}} \right) = Q_3 \frac{dY_B}{d\Theta} + \epsilon C_0 \frac{dX_B}{d\Theta} \]

\[ N Q_0 (X_{C, \text{in}} - X_C) - \frac{N V_R k_{wgs} \epsilon C_0 Q_0}{\phi_v} \left( X_B X_C - \frac{X_D X_E}{K_{wgs}} \right) \]  
(61)

\[ N V_R k_{\cos} C_0 \epsilon Q_0 \left( X_A X_C - \frac{X_E X_F}{K_{\cos}} \right) = Q_3 \frac{dY_C}{d\Theta} + \epsilon C_0 \frac{dX_C}{d\Theta} \]
\[ \frac{d y_1}{d \Theta} = \frac{N V_R k_{f_1} Q_0}{\phi_v} \left( X_A (1 - y_1) - \frac{X_B y_1}{K_f} \right) - \frac{N V_R k_s Q_1 Q_2 Q_0}{\phi_v C_0} \left( X_f (1 - y_1) - \frac{X_D y_1}{K_{f_{cos}}} \right) \]

\[ \frac{d y_2}{d \Theta} = \frac{N V_R k_s Q_1 Q_2 Q_0}{\phi_v C_0} \left( y_1 (1 - y_2) - y_2 (1 - y_1) \right) \]

To simplify equations 59 to 66 new dimensionless groups are introduced:

Capture 1 = \( X_A (1 - y_1) - \frac{X_B y_1}{K_f} \)
Exchange \(- y_1 (1 - y_2) - y_2 (1 - y_1) - y_1 - y_2\) \quad (68)

Shift \(- X_B X_C - \frac{X_D X_E}{K_{wgs}}\) \quad (69)

Cos \(- X_A X_C - \frac{X_E X_F}{K_{cos}}\) \quad (70)

Capture2 \(- X_F (1 - y_1) - \frac{X_D y_1}{K_{l, cos}}\) \quad (71)

\[ k_1 = \frac{V_R k_{l} Q_1}{\phi_v} - \frac{\tau k_{l} Q_1}{N} \] \quad (72)

\[ k_2 = \frac{V_R k_{s} Q_1 Q_2}{\phi_v C_0} - \frac{\tau k_{s} Q_1 Q_2}{C_0 N} \] \quad (73)

\[ k_3 = \frac{V_R k_{wgs} \epsilon C_0}{\phi_v} - \frac{\tau k_{wgs} \epsilon C_0}{N} \] \quad (74)

\[ k_4 = \frac{V_R k_{cos} \epsilon C_0}{\phi_v} - \frac{\tau k_{cos} \epsilon C_0}{N} \] \quad (75)

\[ k_5 = \frac{V_R k_{l, cos} Q_1}{\phi_v} - \frac{\tau k_{l, cos} Q_1}{N} \] \quad (76)

\[ \text{Cap1} = k_1 \times \text{Capture1} \] \quad (77)

\[ \text{Exc} = k_2 \times \text{Exchange} \] \quad (78)

\[ \text{Shi} = k_3 \times \text{Shift} \] \quad (79)

\[ \text{Coss} = k_4 \times \text{Cos} \] \quad (80)

\[ \text{Cap2} = k_5 \times \text{Capture2} \] \quad (81)

and
\[ \lambda_1 = \frac{NQ_0}{Q_1}; \quad \lambda_2 = \frac{NQ_0}{Q_2}; \quad \lambda_3 = \frac{NQ_0}{Q_3}; \quad \epsilon^* = \frac{\epsilon C_0}{Q_3}; \quad \epsilon^{**} = \frac{\epsilon C_0}{NQ_0} \] (82-86)

By introducing equations 67 to 86 in mass balances 59 to 66 these can be simplified to:

\[ \lambda_3 (X_{A, in} - X_A) - \text{Cap} - \text{Coss} \]
\[ \left( \frac{\partial y_A}{\partial X_A} + \epsilon^* \right) \frac{\partial X_A}{\partial \Theta} + \left( \frac{\partial y_A}{\partial X_B} \right) \frac{\partial X_B}{\partial \Theta} + \left( \frac{\partial y_A}{\partial X_C} \right) \frac{\partial X_C}{\partial \Theta} \] (87)

\[ \lambda_3 (X_{B, in} - X_B) + \text{Cap} - \text{Shi} \]
\[ \left( \frac{\partial y_B}{\partial X_A} \right) \frac{\partial X_A}{\partial \Theta} + \left( \frac{\partial y_B}{\partial X_B} + \epsilon^* \right) \frac{\partial X_B}{\partial \Theta} + \left( \frac{\partial y_B}{\partial X_C} \right) \frac{\partial X_C}{\partial \Theta} \] (88)

\[ \lambda_3 (X_{C, in} - X_C) - \text{Shi} - \text{Coss} \]
\[ \left( \frac{\partial y_C}{\partial X_A} \right) \frac{\partial X_A}{\partial \Theta} + \left( \frac{\partial y_C}{\partial X_B} \right) \frac{\partial X_B}{\partial \Theta} + \left( \frac{\partial y_C}{\partial X_C} + \epsilon^* \right) \frac{\partial X_C}{\partial \Theta} \] (89)

\[ \frac{dX_D}{d\Theta} = \frac{(X_{D, in} - X_D) + \text{Shi} + \text{Cap2}}{\epsilon^{**}} \] (90)

\[ \frac{dX_E}{d\Theta} = \frac{(X_{E, in} - X_E) + \text{Shi} + \text{Coss}}{\epsilon^{**}} \] (91)

\[ \frac{dX_F}{d\Theta} = \frac{(X_{F, in} - X_F) + \text{Coss} - \text{Cap2}}{\epsilon^{**}} \] (92)

\[ \frac{dy_1}{d\Theta} = \lambda_1 (\text{Cap} - \text{Exc} + \text{Cap2}) \] (93)

\[ \frac{dy_2}{d\Theta} = \lambda_2 \text{Exc} \] (94)
Expressions for the partial derivatives in equations 87 to 89 can be found by writing the Langmuir adsorption isotherms (equations 13, 14 and 16) in a dimensionless form and calculating partial differentials. This results in the following relations, in which $K_a = K_{A0}$, $K_b = K_{B0}$, $K_c = K_{C0}$ and $d = (1 + K_a X_A + K_b X_B + K_c X_C)^2$:

\[
\frac{\partial y_A}{\partial X_A} = \frac{K_a (1 + K_b X_B + K_c X_C)}{d}; \quad \frac{\partial y_A}{\partial X_B} = \frac{-K_a K_b X_A}{d}; \\
\frac{\partial y_A}{\partial X_C} = \frac{-K_a K_c X_C}{d}; \quad \frac{\partial y_B}{\partial X_A} = \frac{-K_b K_a X_B}{d}; \\
\frac{\partial y_B}{\partial X_B} = \frac{K_b (1 + K_a X_A + K_c X_C)}{d}; \quad \frac{\partial y_B}{\partial X_C} = \frac{-K_b K_c X_B}{d}; \\
\frac{\partial y_C}{\partial X_A} = \frac{-K_a K_c X_C}{d}; \quad \frac{\partial y_C}{\partial X_B} = \frac{-K_b K_c X_C}{d}; \\
\frac{\partial y_C}{\partial X_C} = \frac{K_c (1 + K_a X_A + K_b X_B)}{d};
\]

(95-103)

In equation 87 to 89 three variables $\partial X_A/\partial \Theta$, $\partial X_B/\partial \Theta$ and $\partial X_C/\partial \Theta$ are present. To solve these equations each of these variables must be written independent of the other variables. Rearranging the three equations and solving for $\partial X_A/\partial \Theta$, $\partial X_B/\partial \Theta$ and $\partial X_C/\partial \Theta$ results in:

\[
\frac{dX_A}{d\Theta} = \frac{e (lo - kp) + g (ip - lm) + h (km - io)}{q}
\]

(104)

\[
\frac{dX_B}{d\Theta} = \frac{e (jp - ln) + f (lm - ip) + h (in - jm)}{q}
\]

(105)

\[
\frac{dX_C}{d\Theta} = \frac{e (kn - jo) + f (io - km) + g (jm - im)}{q}
\]

(106)

in which:

\[
e = \lambda_3 \left( X_{A_{in}} - X_A \right) - \text{Cap} - \text{Cap2}
\]

(107)
\[ f = \frac{\partial y_A}{\partial X_A} + \epsilon^*; \quad g = \frac{\partial y_A}{\partial X_B}; \quad h = \frac{\partial y_A}{\partial X_C} \quad (108-110) \]

\[ i = \lambda_3 (X_{B, in} X_B) + \text{Cap - Shi} \quad (111) \]

\[ j = \frac{\partial y_B}{\partial X_A}; \quad k = \frac{\partial y_B}{\partial X_B} + \epsilon^*; \quad l = \frac{\partial y_B}{\partial X_C} \quad (112-114) \]

\[ m = \lambda_3 (X_{C, in} - X_C) - \text{Shi - Cos} \quad (115) \]

\[ n = \frac{\partial y_C}{\partial X_A}; \quad o = \frac{\partial y_C}{\partial X_B}; \quad p = \frac{\partial y_C}{\partial X_C} + \epsilon^* \quad (116-118) \]

\[ q = g(jp - ln) + h(kn - jo) + f(lo - kp) \quad (119) \]

When sulfidation is started by passing a dry feed containing 1 %v H₂S through a fully regenerated acceptor bed, the initial conditions of the above equations are:

\[ \Theta \leq 0: X_A = X_B = X_C = X_D = X_E = X_F = 0 \text{ in all tanks} \]

\[ y_1 = y_2 = 0 \text{ in all tanks (all manganese is present as MnO)} \]

\[ \Theta > 0: X_A = 1 \text{ in feed} \]

\[ X_B = X_C = X_D = X_E = X_F = 0 \text{ in feed} \]

Differential equations 90 to 94 and 104 to 106 have been solved numerically for 30 tanks in series with the RR Runge Kutta Package, obtained from the Reactor Research Foundation, Delft, The Netherlands [6]. This package solves sets of stiff and/or non-stiff first order differential equations simultaneously. It uses an IBM-PC or compatible computer and Turbo Pascal (a registered trademark of Borland International, Inc.). In a modified form, the package can be used on a VAX/VMS system to shorten calculation times.

A short summary of the principles of the solution method used in the package is:

1. The equations may be stiff or non-stiff, or even vary in stiffness during the course of integration, but must have the same independent variable.
2. Embedded integration codes are used. This means that the code not only determines the value of the dependent variable(s) at the end of a step, but also provides an estimation of the local error in the result obtained.

3. The non-stiff code (or non-stiff integrator) uses an embedded explicit Runge Kutta method of order 4, according to Merson [7] and May [8]. The error is estimated by comparing with an order 3 result.

4. The stiff integrator uses an embedded implicit "W-method" of order 3, according to Shintani [9]. The error is estimated by comparing with an order 2 result.

5. At the start of each step an estimation is made of the maximum stepsize that will give a stable solution using the non-stiff integrator. The value of this stepsize is called "stable stepsize".

6. At the end of each step the estimated local error is compared with a tolerance specified by the user. If the estimated local error is larger the step is rejected and a smaller stepsize chosen, otherwise the step is accepted.

7. If the step is accepted the stepsize proposed for the next step is obtained by multiplying the current stepsize with a factor ranging from 1 to 5, depending upon:
   - the ratio of tolerated and estimated error in the last step(s)
   - the current value of the stable stepsize.

8. The first step will always be calculated with the non-stiff integrator. The first stepsize tried is the stable stepsize.

9. Before all subsequent steps the new proposed stepsize is compared with the stable stepsize. If the proposed stepsize is less than 2 times the stable stepsize, the non-stiff integrator and stable stepsize are chosen. If the proposed stepsize is more than 2 times the stable stepsize the stiff integrator is used with the proposed stepsize.

The above RR-Runge Kutta Package is included in a program which optimizes estimated values of a given number of parameters by comparing the calculated and the experimental breakthrough curves. The optimization procedure used is a Simplex routine, while the best fit is obtained using the least-squares method [10].
Results of modelling

Sulfidation

The model given above contains 15 parameters. Nine parameters can be measured separately, be calculated with thermodynamic data or be found in literature ($K_p$, $K_A$, $K_B$, $K_{wgs}$, $k_{wgs}$, $K_{cos}$, $k_{cos}$, $K_{f,cos}$ and $Q_3$). To improve parameter estimation two situations have been analyzed.

First, the model is used to describe the experiments with a feed gas containing $H_2S$, $H_2$ and $N_2$ only (see figure 1). In that case only 4 parameters remain: $k_p$, $k_s$, $Q_1$ and $Q_2$. After having obtained these 4 parameters, the model is extended and used to describe experiments with a feed gas containing CO as well. In that case 7 new parameters are needed of which 5 are obtained from literature data ($K_{wgs}$, $k_{wgs}$, $K_{cos}$, $k_{cos}$ and $K_{f,cos}$), so 2 remain. The already obtained 4 parameters are left unchanged! Finally, the parameters are used unchanged to predict the regeneration curves. This implies a final test of all parameters.

Thermodynamic calculations [13, 14] (see also chapter 1) show that $K_A = 1$ at 875 K. The sorption parameters of $H_2O$ and $H_2S$ on the acceptor surface were obtained from data on $H_2O$ adsorption and $H_2S$ desorption. Water adsorption measurements on a 8.0 \%w $Mn/\gamma-Al_2O_3$ acceptor resulted in the following values of the parameters $K_B$ and $Q_3$ at 875 K: $K_B = 12.36 \text{ m}^3\text{mol}^{-1}$; $Q_3 = 168 \text{ mol} \cdot \text{m}^{-3}$. The equilibrium constant ($K_A$) of $H_2S$ adsorption could be obtained by measuring the amount of $H_2S$ desorbed when a completely sulfur saturated acceptor was flushed by an inert stream (88 \%v $N_2$, 12 \%v $H_2$). From the measurements, and using the value of $Q_3$ obtained with the $H_2O$ adsorption measurements, the following value $K_A$ at 875 K was found: $K_A = 1.36 \text{ m}^3\text{mol}^{-1}$

Moreover, some physical boundaries to the values of $k_p$, $k_s$, $Q_1$ and $Q_2$ can be given. As $k_f$ is the rate constant of the fast oxygen-sulfur exchange reaction and $k_s$ of the slow one, $k_f >> k_s$. When the values of $Q_1$ and $Q_2$ are added it should not exceed the amount of manganese present on the acceptor.

The parameters $k_p$, $k_s$, $Q_1$ and $Q_2$ are found for a 8.96 \%w $Mn/\gamma-Al_2O_3$ acceptor. The optimum fit is shown in figure 3, in which the solid line corresponds to the simulated data and the symbols give the experimental data. It resulted in the following values of the
parameters at 875 K:

\[ k_i = 0.4 \, \text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}; \quad Q_1 = 392 \, \text{mol}\cdot\text{m}^{-3}; \quad k_s = 7\times10^{-7} \, \text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}; \quad Q_2 = 272 \, \text{mol}\cdot\text{m}^{-3}. \]

The value of \( k_s \) is in the same order of magnitude as the value of diffusion of Mn\(^{2+}\) ions in the alumina carrier. This is in accordance with observations in chapter 3.

In order to be sure that the tubing between reactor and analysis section does not disturb the measured breakthrough curve, the modelled breakthrough curve is fed to 1, 10, 25 or 100 empty tanks in series. Figure 4 shows the breakthrough curve obtained with the sulfidation model, and the ones obtained after being submitted to the empty tanks in series. It can be seen that the shape of the curves remains unchanged, the curves only shift to a higher breakthrough time due to the residence time in the tubing. So, during modelling of the sulfidation, the effect of tubing can be neglected, except for a shift in time.

When a feed is used which also contains CO the parameters, \( K_{f,\text{CO}} \), \( K_{w,\text{CO}} \), \( K_{\text{CO}} \), \( k_{f,\text{CO}} \), \( k_{w,\text{CO}} \), and \( k_{\text{CO}} \) are needed as well. Most of these parameters can be calculated from
thermodynamic data or found in literature. The equilibrium constant of the shift reaction, $K_{\text{wgs}}$, is 2.54 at 875 K. According to Kohl and Riesenfeld [12] the equilibrium constant of COS formation, $K_{\text{cos}}$, is 0.054 at 875 K. This value is close to the values calculated from figures 5 and 6 ($K_{\text{cos}} = 0.06$ to 0.07). It is reported by Case [11] that COS formation rapidly attains equilibrium. Thus, COS formation is assumed to be in equilibrium. In order to be consistent with the fact that both of the above reactions rapidly attain equilibrium, the rate constants were assigned a relatively large value: $k_{\text{wgs}}$ and $k_{\text{cos}} = 0.4$ m$^3$·mol$^{-1}$·s$^{-1}$ (this value can be changed in a relative wide range and still obtain the same results). The equilibrium constant of the reaction between the acceptor and COS is calculated from thermodynamic data [13, 14]: $K_{\text{f,cos}} = 6$ at 875 K. As this reaction is fast and the rate of COS capture at least equals the rate of H$_2$S uptake $k_{\text{f,cos}}$ is given the same value as $k_f$. Last, the equilibrium constant of the Langmuir adsorption of CO on the acceptor surface must be estimated. As discussed in chapter 4, H$_2$O produced by the sulfidation reaction is adsorbed by certain sites on the surface, with the result that no H$_2$O was found in the reactor effluent initially during sulfidation when a relatively dry feed gas is used. When this feed contains CO, however, water appeared in the reactor effluent earlier, but in a low concentration because it has been converted partially to CO$_2$.
by the shift reaction. As CO was adsorbed on the same sites as H₂O, thus diminishing the
capacity of the acceptor for H₂O adsorption, the equilibrium constant of CO adsorption,
Kₐ, must have the same order of magnitude as Kₐ: Kₐ = 10 m³·mol⁻¹ at 875 K.

With the above values of the parameters, which are summarized in table 1,
experiments with a feed containing 25 %vol CO and 50 %vol CO are simulated.

<table>
<thead>
<tr>
<th>Table 1. The model parameters at 875 K.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kₐ (dimensionless)</td>
</tr>
<tr>
<td>kₐ (mₐ⁻³ mol⁻¹ s⁻¹)</td>
</tr>
<tr>
<td>Q₁ (mol mᵣ⁻³)</td>
</tr>
<tr>
<td>kₛ (mᵣ⁻³ mol⁻¹ s⁻¹)</td>
</tr>
<tr>
<td>Q₂ (mol mᵣ⁻³)</td>
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<tr>
<td>Kₐ (mₐ⁻³ mol⁻¹)</td>
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<tr>
<td>Kₛ (mₐ⁻³ mol⁻¹)</td>
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<tr>
<td>Q₃ (mol mᵣ⁻³)</td>
</tr>
<tr>
<td>Kᵣᵣ (dimensionless)</td>
</tr>
<tr>
<td>kᵣᵣ (mₐ⁻³ mol⁻¹ s⁻¹)</td>
</tr>
<tr>
<td>Kᵣ₢₢ (dimensionless)</td>
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<tr>
<td>kᵣ₢₢ (mₐ⁻³ mol⁻¹ s⁻¹)</td>
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<tr>
<td>Kᵣᵣ (dimensionless)</td>
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<tr>
<td>kᵣᵣ (mₐ⁻³ mol⁻¹ s⁻¹)</td>
</tr>
<tr>
<td>Kᵣ (dimensionless)</td>
</tr>
</tbody>
</table>

Figure 5 shows the experimental data (the symbols in the figure) and the
simulated data (the solid lines) in case a feed containing 25 %vol CO is used. Figure 6
shows the same results of an experiment in which the feed contained 50 %vol CO. In both
cases the behaviour of the experimental data is described accurately by the model. Even
the increase in the water concentration just before breakthrough takes place is predicted
by the model. An explanation of this effect is given in chapter 4.

In case of a feed containing CO the results of the model calculations are almost the same as the ones shown in figures 4 and 5. However, in case of a feed containing H₂S only, the shape of the breakthrough curve is not predicted correctly and should be optimized.

When the optimization routine mentioned before is used, an accurate description is obtained when Kᵣ is increased to 3.6 and Q₁ decreased to 226 mol·m⁻¹. Figure 6 shows the experimental and simulated breakthrough curves for Kᵣ = 3.6 and Q₁ = 226 mol·m⁻¹. The remaining parameters are left unchanged. In that case the results of the measurements shown in figure 4 and 5 can only be predicted when Q₁ is increased to 335 (25 %v CO) or 392 mol·m⁻¹ (50 %v CO). If one can find a reason to explain an increase in the number of sites showing a fast oxygen-sulfur exchange when the CO concentration is increased, a value of Kᵣ is 3.6 can be used.

Obviously, with the Simplex routine it is possible to find an optimum fit which not necessarily holds for all experimental conditions. Therefore, different optimization
Figure 6. Simulated and experimental breakthrough curves at 875 K. Acceptor: 8.96%w Mn/γ-Al₂O₃. Feed: 1%v H₂S, 50%v CO, 10%v H₂, N₂ balance.

routines should be used in the model.

Regeneration

In modelling regeneration curves, the sulfidation cycle that precedes the regeneration involved was simulated as well. This was necessary because sulfidation is stopped after breakthrough of the acceptor bed. At the end of the sulfidation the concentrations in all tanks (X_A, X_B, X_C, X_D, X_E, X_F, y_1 and y_2 in 30 tanks) are saved and read into the regeneration model before regeneration is started.

In modelling the regeneration, experiments are simulated that use a gas containing 20.0, 48.2 or 75.0%v steam in a N₂/H₂ mixture. Figure 8 shows the effect of the steam concentration on regeneration time and H₂S concentration in the regeneration off-gas according to the model. In all cases the parameters used to calculate the regeneration curves were the same as the parameters needed to obtain an optimum description of the sulfidation curve. It is clear that the highest steam concentration results in the highest H₂S concentration and the shortest regeneration time. When the steam concentration decreases the H₂S concentration obtained during regeneration decreases and the
regeneration time increases. In all cases the $\text{H}_2\text{S}$ concentration in the regeneration off-gas is almost as high as the steam concentration in the feed. The same trend in the $\text{H}_2\text{S}$ concentration as a function of steam concentration is observed during the experiments described in chapter 5.

Increasing the residence time during the regeneration experiments resulted in a decreasing regeneration peak height (see chapter 5, figure 6). When the model is used to predict the regeneration peak for e.g. 75 %v steam and different residence times the curves in figure 9 are found. In this figure regeneration curves at superficial residence times of 0.24 and 1.53 s are shown. When the residence time increases the height of the regeneration peak decreases and the regeneration peak width increases. This trend is the same as the one observed during the regeneration experiments.

However, when the results of an experimental regeneration curve are compared with a simulated one a considerable difference in the $\text{H}_2\text{S}$ concentration and the regeneration time is found. Figure 10 shows the experimental and simulated regeneration curves for a regeneration gas containing 75 %v steam and a superficial residence time of 1.53 s. Experimentally, the maximum $\text{H}_2\text{S}$ concentration is about 15 %v, while the
Figure 8. Simulated regeneration curves for different steam concentrations. Curve A = 75.0 %v, B = 48.2 %v and C = 20.0 %v steam.

Figure 9. Simulated regeneration curves at different superficial residence times. The superficial residence time is 0.24 s (A), 0.48 s (B), 0.77 s (C) and 1.53 s (D).
Figure 10. Simulated and experimental regeneration curve. \( C_{steam} = 75 \% \text{v}, \tau = 1.53 \text{ s} \).

The simulated regeneration curve shows a much higher \( H_2S \) concentration of almost 75 \%v, and a shorter regeneration time. The experimental regeneration curve could not be approached better by changing the model parameters.

This discrepancy can be explained by the experimental set-up: when a high and narrow regeneration peak is led through the tubing and valves from the reactor to the analysis section, the regeneration peak can become lower and broader. Experiments in which the tubing between reactor and analysis section is replaced by a single straight tube showed that the maximum regeneration peak height increased with up to 20 percent. The effects of the tubing can be included in the model by adding a number of empty ideally mixed tanks in series.

With the calculated values of \( \text{Re}, \text{Sc} \) and \( \text{Bo} \), in case of the experimental regeneration curve shown above, a model with 8 tanks in series must be used to describe the tubing between reactor and analysis section. The height of the simulated regeneration peak decreases to about 35 \%v \( H_2S \). The results of this approximation are shown in figure 11. In case other flow rates are used during regeneration the number of tanks
needed varied between 5 and 10.

Further, the automatic burette used to inject the water into the reactor has more dead time than may be expected from the residence time of the gas in the reactor. In case of 48.2 v% steam and a superficial residence time of 0.44 s in the acceptor bed, it takes about 60 s before any steam is observed in the reactor exit after starting regeneration of a freshly regenerated acceptor. The calculated dead time from the capillary to the reactor exit, however, is only 20 s. Obviously, water evaporates from the capillary during drying and sulfidation subsequent to the regeneration. It will take some time to refill the capillary and to produce steam. In the meantime, gas without or with a small amount of steam is flowing through the reactor and removes physically bounded H₂S, may be even some chemically bounded H₂S.

Lastly, the response time of the analysis section influences the regeneration peak height and width negatively. The H₂S must react with the CdSO₄ solution and the decrease of the pH must be registered by the pH-electrode before the base solution can be added. However, the effect of the response time is small compared to the dead time.
involved in making the regeneration gas and the effect of the tubing. The effect of the response time of the analysis section might be incorporated in the model by adding one empty tank to the model. The effect of the response time, however, is neglected in the model.

The points discussed above lead to the recommendation to build an experimental set-up in which the regeneration gas is produced continuously at a high temperature (e.g. 875 K). When the regeneration gas is not used it should be vented. When the acceptor is regenerated, the regeneration gas can be fed directly to the reactor by switching a valve. Further, the tubing between reactor exit and analysis section should be shortened considerably.

Conclusions

The model derived in this chapter is able to describe the phenomena taking place during sulfidation. However, when some of the parameters of experimental breakthrough curves are fitted with the Simplex routine, a parameter set is obtained which only describes the measurement used for the fit and not necessarily other experiments. Therefore, a program should be developed in which different optimization techniques are used.

The H$_2$S concentration in the simulated regeneration curves is much higher than the H$_2$S concentration obtained during the measurements. The difference between simulation and experiment can be explained by side effects induced by the experimental set-up. The effect of the tubing between reactor exit and analysis section on the regeneration curve is quite strong and is described by adding 8 empty ideally mixed tanks in series to the model.

References

York, 1970, p. 467
11 G.D. Case, Chemistry of Hot Gas Cleanup in Coal Gasification and Combustion, Morgantown Energy Research Center, Morgantown, West Virginia, 1978
16 C.M. van den Bleek and A.W. Gerritsen, St75, Reaktorkunde II, Handout course Chemical Reaction Engineering, Department of Chemical Engineering, Delft University of Technology, Delft, The Netherlands, 1988
Nomenclature

**Capitals**
A = H₂S or S  
B = H₂O or O  
C = CO  
D = CO₂  
E = H₂  
F = COS

**Symbols**
\( C_{i,\text{in}} \) = inlet gas phase concentration of component i (mol m⁻³)  
\( C_i \) = gas phase concentration of component i (mol m⁻³)  
\( C_0 \) = reference gas phase conc., typically the H₂S inlet concentration (mol m⁻³)  
\( d \) = denominator  
\( e\text{-q} \) = elements in equations 104-106, defined by equations 107-119  
\( K_r \) = equilibrium constant (-)  
\( k_f \) = forward reaction rate constant (m⁶ g⁻³ mol⁻¹ s⁻¹)  
\( K_s \) = equilibrium constant (-)  
\( k_g \) = forward reaction rate constant (m⁶ g⁻³ mol⁻¹ s⁻¹)  
\( K_A \) = Langmuir adsorption equilibrium constant of component A (m⁶ g⁻³ mol⁻¹)  
\( K_B \) = Langmuir adsorption equilibrium constant of component B (m⁶ g⁻³ mol⁻¹)  
\( K_C \) = Langmuir adsorption equilibrium constant of component C (m⁶ g⁻³ mol⁻¹)  
\( K_{\text{WGS}} \) = equilibrium constant of the shift reaction (-)  
\( k_{\text{WGS}} \) = forward reaction rate constant of the shift reaction (m³ g⁻¹ mol⁻¹ s⁻¹)  
\( K_{\text{CO}_2} \) = equilibrium constant of the COS formation (-)  
\( k_{\text{CO}_2} \) = forward reaction rate constant of the COS formation (m³ g⁻¹ mol⁻¹ s⁻¹)  
\( K_{\text{COS}} \) = equilibrium constant of COS uptake by the acceptor (-)  
\( k_{f,\text{COS}} \) = forward reaction rate constant of COS uptake (m³ g⁻¹ mol⁻¹ s⁻¹)  
\( L \) = length of the acceptor bed (m)  
\( N \) = number of tanks (-)  
\( Q_0 \) = reference capacity of the acceptor (mol m⁻³)  
\( Q_1 \) = stoichiometric capacity of the solid phase of component 1 (mol m⁻³)  
\( Q_2 \) = stoichiometric capacity of the solid phase of component 2 (mol m⁻³)  
\( Q_3 \) = stoichiometric capacity of the solid phase of component 3 (mol m⁻³)  
\( q_i \) = concentration of component i in the solid phase (mol m⁻³)  
\( r_i \) = reaction rate (the dimension depends upon i)  
\( S_1 \) =  
\( S_2 \) =  
\( S_3 \) =  
\( t \) = time (s)  
\( v \) = gas velocity (m/s)  
\( V_R \) = volume of the reactor (m³)  
\( V_G \) = gas volume in the reactor (m³)  
\( X_i \) = dimensionless gas phase concentration of component i (-)  
\( y_i \) = dimensionless solid phase concentration of component i (-)  
Capture, Exchange, Shift, Cos, Capture2, k₁, k₂, k₃, k₄, k₅, Cap, Exc, Cos = dimensionless groups
Greek
\[ \epsilon = \frac{V_G}{V_R} = \text{bed porosity (m}_g^3/\text{m}_r^3) \]
\[ \epsilon^* , \epsilon^{**} = \text{dimensionless groups (-)} \]
\[ \lambda_i = \text{dimensionless groups (-)} \]
\[ \phi_v = \text{volumetric flow rate (m}_g^3 \text{ s}^{-1}) \]
\[ \Theta = \text{dimensionless time (-)} \]
\[ \tau_{sup} = \text{superficial residence time (s)} \]

Subscripts
A = H\textsubscript{2}S or S
B = H\textsubscript{2}O or O
C = CO
D = CO\textsubscript{2}
E = H\textsubscript{2}
F = COS
Evaluation

Introduction

In the previous chapters the influence of preparation methods and process conditions on the sulfur removal capacity, regenerability and breakthrough behaviour were discussed. In this chapter advantages and disadvantages of some process schemes for high temperature regenerative $\text{H}_2\text{S}$ removal will be presented with regard to the use of $\text{MnO}/\gamma-\text{Al}_2\text{O}_3$.

It has to be emphasized that high temperature gas cleaning not only involves desulfurization, but also removal of dust, halogens, alkali metals, heavy metals, $\text{NH}_3$ and HCN. The removal of other than sulfur compounds has recently been described by Alderliesten et al. [1] and will not be discussed in this chapter.

Fixed bed process

The flow diagram of a fixed bed high temperature desulfurization process based on $\text{MnO}/\gamma-\text{Al}_2\text{O}_3$ is shown in figure 1. The conditions shown in this figure are based on the assumption that the unit is an integral part of a coal gasification combined cycle (CGCC) power plant, based on Shell coal gasification technology. The unit consists of a fixed bed desulfurizer - regenerator system R1 to R3 which is operated in a batch swing mode. As the regeneration time is much shorter than the sulfidation time (see chapters 4 and 5), two reactors can be used to desulfurize the raw fuel gas while the third reactor is regenerated. The sulfidation of the two reactors is not started at the same time, but with a difference of 50 percent of the breakthrough time. In this way the acceptor beds can be regenerated subsequently without loss in desulfurization capacity [2]. The clean
gas leaving the adsorber (cleaning efficiency > 99.5 %) can be sent directly to the combined cycle unit because its sulfur content is low enough. When the gas is to be used in a fuel cell or as a synthesis gas, a zinc oxide guard bed should be installed downstream the adsorber to lower the H₂S concentration from about 20 ppmv to less than 1 ppmv.

The regeneration of a sulfur-saturated bed is carried out at a temperature and pressure similar to those applied during desulfurization. As discussed in chapter 5, it is possible to obtain a regenerator off-gas with a high H₂S concentration (> 17.5 %v). To concentrate the H₂S and to remove the remaining steam the regeneration off-gas is cooled by passing it through a heat recovery system. The H₂S is separated from water in a gas liquid separator and sent to a Claus unit. The water leaving the separator contains some H₂S and some elemental sulfur. The H₂S is stripped with the feed air of the Claus unit and the elemental sulfur is filtered.

The main disadvantages of using fixed bed reactors for high temperature desulfurization are summarized below. Due to the relatively low breakthrough capacity of the acceptor (about 1.5 %w S at 875 K) relatively large amounts of acceptor have to be used. For a 600 MWₑ power plant, based on Shell coal gasification technology, three
reactors each containing 16 m\(^3\) acceptor are needed when a breakthrough time of 10 minutes is applied. The pressure drop in these reactors will be about 0.3 MPa when extrudates with a length of 4.8 mm and a diameter of 1.7 mm are used and the length of the acceptor bed is 8 m. However, because the composition of the reactor off-gases are changing as a function of time (especially during regeneration) and the reactors have to be flushed after regeneration, the use of buffer vessels to get a gas with an average composition as a function of time is inevitable. These vessels make the whole set-up more expensive as they have to be designed to operate at the same temperature and pressure as the sulfidation and the regeneration. Another option is the use of a large number of reactors, each shifted in the start of the sulfidation compared to the other reactors to obtain a constant gas composition. This option will be even more expensive than the use of buffer vessels.

When three fixed bed reactors are used in the way described above, desulfurization of the raw fuel gas of a 600 MW\(_e\) power plant, based on Shell coal gasification technology (\(C_{\text{H}2S, \text{in}} = 0.3 \% v [1]\)), will cost about 0.0012 DFl/kWh (see Appendix A). The exact cost could not be calculated as the implementation in the whole plant (gasifier, Claus etc.) was not possible due to lack of data and suitable computer programs. It is difficult to compare the costs of desulfurization with the costs of other processes, as in most cases a price of electricity per kWh is given. Alderliesten et al. [1] calculated an electricity price of about 0.036 Dfl/kWh for a CGCC power plant with high temperature gas cleaning. With respect to this price the calculated cost of high temperature desulfurization of about 0.0012 Dfl/kWh seems to be reasonable.

The rates of sulfidation and regeneration are high. The low breakthrough capacity causes the desulfurization reactors to become large when a fixed bed set-up is used. Therefore, it is logical to develop a continuous reactor system where the solids (the acceptor) are transported from the adsorber to the regenerator and back. A fluidized bed system can eliminate the disadvantages of a fixed bed system as it operates continuously [3-4].
Fluidized bed system

Figure 2 shows the desulfurizer and the regenerator section of a fluidized bed desulfurization plant schematically. The sulfur saturated acceptor particles are lifted by a stream of high pressure steam into the regenerator. The freshly regenerated particles flow to the desulfurizer by gravity. The low capacity of the acceptor is not much a problem because a high circulation rate of the solids between desulfurizer and regenerator is possible. The high sulfidation and regeneration rates make it possible to use relatively small reactors. Due to its continuous operation, the fluidized bed system ensures a feed with a constant composition to both the gas turbine and the Claus plant [5-8].

![Diagram of fluidized bed desulfurization system](image)

Figure 2. Flow diagram of a fluidized bed desulfurization system.

However, some preliminary calculations showed that the sulfur removal efficiency of this system is lower than that of a fixed bed system because of extensive mixing of the acceptor bed and the bypassing of acceptor particles by bubbles. Therefore, it is necessary to use a staged fluidized bed to desulfurize the raw fuel gas.

In order to judge the suitability of the acceptor to be used in a fluidized bed system, commercially available γ-Al₂O₃ carrier materials developed for the use in...
fluidized beds should be impregnated and tested for sulfur removal capacity. It is not likely that these materials will suffer from pore diffusion resistances because the average particle diameters are about 80 μm.

One of the main advantages using of MnO/γ-Al₂O₃ in a fluidized bed system over other processes (discussed in chapter 1) is that both the sulfidation and regeneration are carried out in a reducing atmosphere, whereas the other processes use a oxidative regeneration. Oxidative regeneration makes the use of a fluidized bed system more complicated because the gas phases of sulfidation and regeneration have to be separated in order to prevent formation of explosive gas mixtures.

Because a fluidized bed system operates continuously, it eliminates the disadvantageous fuel gas hold-up and the changing reactor off-gas composition featured by the fixed bed swing process.

When a fluidized bed system is used an interesting type is an interconnected fluidized bed (IFB) [9] which eliminates transport of solids through tubing. In a IFB the

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*Figure 3. Schematic flow diagram of an Interconnected Fluidized Bed (IFB) for high temperature regenerative H₂S removal.*
transport of solids is performed by differences in fluidization velocities of the fluidized beds involved. Figure 3 shows a schematic flow diagram for high temperature desulfurization using MnO/γ-Al₂O₃ in an IFB.

In the first bed the raw fuel gas is desulfurized. Part of the acceptor is moved to the next, small, bed as it flows over the wall separating the two fluidized beds due to the higher fluidization velocity in the first bed. The second bed is only used to transport the acceptor to the regenerator and is fluidized by part of the cleaned fuel gas. After being regenerated in the third reactor the acceptor is transported to the fourth reactor. In the fourth reactor the remaining water (left on the acceptor after regeneration) is removed before it is recycled to the first reactor where the raw fuel gas is desulfurized. The fourth reactor is fluidized by nitrogen, e.g. produced by the oxygen plant.

**Moving-bed system**

As already mentioned before it is likely that, when fluidized beds are used, staged

![Diagram](image)

*Figure 4. A flow diagram of a moving bed system for high temperature regenerative H₂S removal.*
fluidized beds are needed because of extensive mixing and bypassing of uncleaned fuel gas. Therefore, a moving bed can combine the advantages of both fixed bed and fluidized bed operation. Figure 4 shows a flow diagram of the moving bed concept as developed by General Electric for high temperature desulfurization [11-13]. In the moving bed the acceptor moves slowly downwards by gravity, countercurrently to the fuel gas flowing upwards. Sulfided acceptor material is removed from the adsorber and fed to the top of the regenerator which is also a slowly moving bed. Regenerated sorbent is recycled to the top of the adsorber. The moving bed design has the advantages of a nearby steady-state operation and of minimal sorbent damage, if compared to fluidized beds.

**Monolith reactors**

\[ \text{MnO/Al}_2\text{O}_3 + H_2\text{S} \rightarrow \text{MnS/Al}_2\text{O}_3 + H_2\text{O} \]

![Diagram of Monolith Reactor](image)

\[ \text{MnS/Al}_2\text{O}_3 + H_2\text{O} \rightarrow \text{MnO/Al}_2\text{O}_3 + H_2\text{S} \]

*Figure 5. Schematic presentation of a monolith reactor for high temperature regenerative H_2S removal.*
A new development is the use of monolith reactors. As mentioned in chapter 2, a monolith with an alumina washcoat, impregnated with manganese, can desulfurize the fuel gas effectively. Monoliths are expensive and therefore can only be used in applications where the material has a proven long lifetime. In chapter 4 it is shown that after an initial deactivation the acceptor can be used over 400 sulfidation - regeneration cycles without loss in activity. This also will apply to the use of a monolith as a support.

An example of a monolith reactor is shown in figure 5. The monolith is mounted in a rotating vessel. From the left side the raw fuel gas enters the reactor and is desulfurized. The cleaned fuel gas leaves the reactor on the other side. At the same time the reactor slowly rotates and the sulfided part comes in the stream with the regeneration gas. Regeneration is carried out countercurrently. The regenerated part of the monolith is than used to desulfurize the raw fuel gas. In this way a system is obtained which can operate continuously.

References

ginstallatie, Nov. 1990, NOVEM, 90-310
2. G.R.M. Breembroek and A.M.G. Groenendaal, Internal Report, January 1991, Department of Chemical Engineering, Delft University of Technology, Delft, The Netherlands


Appendix A

Economic evaluation

A brief economic evaluation of high temperature H₂S removal using MnO/γ-Al₂O₃ will be made in this appendix for the fixed bed set-up discussed in chapter 8. The electrical power plant considered is based on Shell coal gasification technology and can deliver 600 MW electrical power. The overall efficiency of the plant is assumed to be 43%. The composition of the raw fuel gas produced by the Shell coal gasifier [1] is shown in table 1.

Table 1. The composition of the raw fuel gas produced by a Shell gasifier [1].

<p>| | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>CO</td>
<td>64 %v</td>
</tr>
<tr>
<td>H₂</td>
<td>32 %v</td>
</tr>
<tr>
<td>CO₂</td>
<td>1 %v</td>
</tr>
<tr>
<td>CH₄</td>
<td>0 %v</td>
</tr>
<tr>
<td>N₂ + Ar</td>
<td>0.7 %v</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.5 %v</td>
</tr>
<tr>
<td>H₂S + COS</td>
<td>0.3 %v</td>
</tr>
</tbody>
</table>

With the results discussed in chapter 4 it can be calculated that at 875 K the breakthrough capacity of 8.2 %w MnO/γ-Al₂O₃ will be about 1.5 %w S. Before the size of the reactors can be calculated, the amount of raw fuel gas to be desulfurized must be known. According to Kerkhof and Droog [2] 44.0*10¹⁵ J of coal/year is needed to feed a 600 MW electrical power plant. This equals 1.40*10⁹ J of coal/s. The efficiency of a gas fired combined cycle unit can be assumed to be 55% [3]. In that case a stream containing 1.09*10⁹ J/s must be desulfurized. The Lower Heating Value (LHV) of this
gas is $11.3 \times 10^6$ J/m$^3$ (STP) [4], so that $1.09 \times 10^9 / 11.3 \times 10^6 = 96.54$ m$^3$/s (STP) must be treated. This equals 3.95 kmol gas/s or 77.65 kg gas/s. Figure 1 summarizes the values mentioned above.

From table 1 it follows that the raw fuel gas contains 0.3 %v $\text{H}_2\text{S} + \text{COS}$. With the above mentioned flow rate about 0.38 kg S/s must be removed from the gas stream. If it is assumed that the sulfidation time of each reactor is 10 minutes, in that time 228 kg S must be captured. The breakthrough capacity of the acceptor is 1.5 %w S; 15.2 ton acceptor is needed. For safety reasons 10 percent more acceptor material is used. As two reactors are used to desulfurize the gas, each reactor must contain 8.4 ton acceptor. The estimated reactor density of this material is 600 kg/m$^3$, which results in reactors each having a volume of 14 m$^3$. Reactors with an internal diameter of 1.5 m and a height of 8 m can be used.

Regeneration of the sulfided acceptor bed is carried out counter-currently with a gas with a high steam concentration and a relatively long residence time (see chapter 5). No hydrogen is added to the regeneration gas because the system is kept at a temperature high enough to prevent condensation of elemental sulfur formed due to dissociation of $\text{H}_2\text{S}$. As is often done [5] it is assumed that the costs for the $\text{H}_2\text{S}$ recovery from the regeneration off-gas in a Claus plant equals the profits of the S produced.
Between sulfidation and regeneration and between regeneration and sulfidation the reactors are flushed by a reactor volume of nitrogen (supplied by the oxygen plant needed for the gasifier).

The investments needed for a chemical plant can be divided into various parts:

\[ I_t = I_p + I_a + I_i + I_c \]

in which

- \( I_t \) = the total investment
- \( I_p \) = the investments in process equipment
- \( I_a \) = the investments in auxiliary equipment
- \( I_i \) = the investments in licenses, start-up etc.
- \( I_c \) = the investments in capital, cash, site and supplies

According to the method of Lang [6], \( I_p \) and \( I_a \) can be calculated: \( I_p + I_a = \$ 15 \times 10^6 \). \( I_i \) and \( I_c \) can be estimated when \( I_p \) and \( I_a \) are known because \( I_p \) is about 64 percent and \( I_a \) about 16 percent of the total investment \( I_t \) [7]. This results in a total investment of about \( 19 \times 10^6 \$ \). With an exchange rate of Dfl 1.77 per dollar, the total investment is about Dfl 34 \times 10^6 \.

The semi-variable costs cover cost of maintenance and wages: Dfl 1.7 \times 10^6 \$ a year.

The variable costs cover costs for feedstocks and additives, e.g. the acceptor,

<table>
<thead>
<tr>
<th>Cost sort</th>
<th>Mfl/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depreciation + interest</td>
<td>3.7</td>
</tr>
<tr>
<td>Semi-variable</td>
<td>1.7</td>
</tr>
<tr>
<td>Variable</td>
<td>5.5</td>
</tr>
<tr>
<td>Overhead</td>
<td>0.7</td>
</tr>
<tr>
<td>Total</td>
<td>11.6</td>
</tr>
</tbody>
</table>

Table 2. Total yearly costs of the plant for high temperature desulfurization plant.
steam, boiler water etc. The price of the acceptor is estimated to be Dfl 15 per kg. The variable costs are about Dfl 5.5*10^6 a year.

Plant overheads can be estimated by taking 75 % of the wages and 50 % of the maintenance [7]. This results in a plant overhead of Dfl 0.7*10^6 a year.

Linear depreciation of the plant in 10 years results in a cost centre of Dfl 3.4*10^6 per year, plus 10 % interest which results in Dfl 0.34*10^6 a year.

The total yearly costs are summarized in table 2.

In this economic study 77.65 kg fuel gas has to be desulfurized each second. Because both the amount of gas to be desulfurized and the total yearly cost are known, the cost of desulfurization per kg gas or per kWh can be calculated. This results in Dfl 0.0048 per kg gas or Dfl 0.0012 per kWh.

References


2 F.P.J.M. Kerkhof and H.A. Droog, Lecture C1 in 7th International Conference & Exhibition on Coal Technology & Coal Trade, RAI, Nov. 21-23, 1988, Amsterdam, The Netherlands

3 A. Lezuo, K. Riedle and E. Wittchow, BWK, 41(1/2)(1989)13-22


6 Z. Olujic, Handout of the course: A preliminary process cost estimation method, Delft University of Technology, Delft, 1988

7 A.G. Montfoort, Handout of the course: De chemische fabriek, Volume 2, Delft University of Technology, Delft, 1989
Dankwoord

De afgelopen vier en een half jaar waarin dit proefschrift tot stand is gekomen heeft een hoop energie gekost. Zonder de hulp en steun van veel mensen was dit dan ook een zeer zware opgave geweest.

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