STEAM-REGENERATIVE REMOVAL OF H₂S AT HIGH TEMPERATURES USING METAL OXIDE ON ALUMINA ACCEPTORS
STEAM-REGENERATIVE REMOVAL OF H₂S AT HIGH TEMPERATURES USING METAL OXIDE ON ALUMINA ACCEPTORS

Proefschrift

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Tatang Hernas Soerawidjaja

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scheikundig ingenieur

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Kepada:
Endang, Aakh, dan Adi
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SUMMARY

The regenerative removal of H$_2$S from high-temperature industrial gaseous stream has been studied by various research institutions since about 1970. The main incentive for developing this kind of process is the potential improvement in thermal efficiency of a coal gasification combined cycle power plant.

Most hot gas desulfurization processes developed to date use a solid metal or metal oxide as a sulfur removal agent (acceptor). The exhausted acceptor is usually regenerated by oxidation using air-nitrogen mixture. Since non-oxidative regeneration of the acceptor with steam is conceptually more advantageous, a process containing such a step has been selected as the subject of this thesis.

The starting point was Van der Linde's finding that when manganese or iron oxide appropriately dispersed on a $\gamma$-Al$_2$O$_3$ support is used as a H$_2$S removal acceptor, steam regeneration is, in principle, possible. Bulk thermodynamic calculations presented in this thesis indicate that the active component of this type of acceptor is not free oxide but a surface MnAl$_2$O$_4$ or FeAl$_2$O$_4$ spinel.

A substantial part of the present work was devoted to an investigation on the influence of preparation methods on the steam-regenerability, composition and structure of acceptors. To that end, their acceptation-regeneration performance was studied in a bench-scale fixed-bed experimental unit at 400 to 600°C and atmospheric pressure. The most efficient way to prepare steam-regenerable acceptors based on manganese is found to be by wet impregnation of $\gamma$-Al$_2$O$_3$ with a concentrated manganese acetate solution. When the nitrate salt of manganese is used, repeated impregnation of the $\gamma$-Al$_2$O$_3$ with dilute solutions must be applied to produce steam-regenerable acceptors with sufficiently high manganese content (8 wt%). On the other hand, a single impregnation of $\gamma$-Al$_2$O$_3$ with a concentrated nitrate solution leads to an irregenerable acceptor. Zinc, iron, and cobalt behave similarly to manganese in the sense...
that they also form steam-regenerable acceptors when appropriately dispersed on γ-A12O3.

In line with the conclusions drawn from bulk thermodynamic calculations, characterization of the acceptors by X-ray diffraction, diffuse reflectance spectroscopy and Mössbauer spectroscopy provides evidence that the active component of a steam-regenerable acceptor is a surface aluminate spinel, whereas an irreversible acceptor consists of clusters of free oxide on the surface of the alumina support. No significant differences in the behaviour of the acceptors are found to result from the use of different type of γ-Al2O3.

When fresh steam-regenerable acceptors are applied to desulfurize gases in a cyclic process, stable performance is obtained after an initial period of deactivation. The breakthrough capacity of a stable acceptor containing about 8 wt% Mn is roughly 1 wt sulfur at 600 °C. The rate of deactivation depends only on the operating temperature; it is negligibly slow at 400 °C and becoming faster as the temperature is higher. The main cause of deactivation presumably is recrystallization of surface spinel resulting in a decrease of reactivity and/or loss of surface area.

The breakthrough capacity of the acceptor doubles when the temperature is increased from 400 to 600 °C. This improvement is not only due to more favourable kinetics but also to a more favourable equilibrium. Acceptors capacity is only slightly affected by the H2S concentration; it is somewhat lower at higher concentrations. On the other hand, the capacity of the acceptor is adversely affected by the presence of water vapour in the feed gas, a logical consequence of the fact that the acceptor can be regenerated with steam. This negative influence of water is, however, less noticeable when the feed gas contains carbon monoxide, because the latter consumes water via the well-known shift reaction.

The main reaction occurring during acceptance of H2S is a rapid equimolar sulfur-oxygen exchange reaction between the gas and the solid phase to produce H2O. During regeneration the same reaction proceeds in the opposite direction. The molar ratio of sulfur to manganese in a completely converted acceptor is roughly 1:2. Additionally, relatively small amounts of H2O as well as H2S are adsorbed by the acceptor.

These facts are used to formulate a simple description of the overall process of H2S acceptance, i.e., a reversible sulfur-oxygen exchange reaction consuming two moles of manganese per mole of sulfur removed. A dynamic model based on this reaction only affords a useful approximation of the fixed-bed behaviour of the acceptor in the temperature range investigated if the feed gas is dry. When the feed contains water vapour, the model fails to predict the observed behaviour of the acceptor. This inadequacy is ascribed to the fact that it neglects the phenomena of H2O and H2S adsorption.

A model which takes sorption into account was also developed. By comparison of experimental and simulated breakthrough curves this more complex model was shown to be valid under a wider range of conditions. Accurate estimation of model parameters is, however, not yet possible owing to the presence of experimental as well as computational obstacles. Means to avoid or to eliminate these obstacles in subsequent work are suggested.

A brief evaluation study has shown that high-temperature desulfurization processes based on a steam-regenerable acceptor can have a number of important advantages compared to existing ones. To improve the feasibility of these processes, further studies are required to produce acceptors having a sulfur removal capacity significantly higher than 1 wt% S at 600 °C.
SAMENVATTING

De regeneratieve verwijdering van H₂S uit industriële processtromen bij hoge temperaturen wordt sinds ongeveer 1970 door verschillende research instellingen bestudeerd. Het belangrijkste doel daarbij is de verbetering van het thermische rendement van een met kolen gestookte energiecentrale waarin kolenvergassing gevolgd wordt door energie opwekking in verbrandingsturbines.

De meeste processen die tot nu toe ontworpen werden om zwavel te verwijderen gebruiken een metaal of metalloxyde als middel om het zwavel af te vangen (acceptor). De beladen acceptor wordt gewoonlijk geregenereerd door oxydatie met een stikstof-lucht mengsel. Aangezien niet-oxydatieve regeneratie van de acceptor met stoom conceptueel aantrekkelijker is werd voor deze promotie als onderwerp een proces gekozen dat een dergelijke stap omvat.

Hierbij is uitgegaan van het door Van der Linde gevonden verschijnsel dat na dispergeren van mangaan- of ijzer-oxyde op γ-alumina het in principe mogelijk is deze stoffen als acceptor te gebruiken en met stoom te regenereren. In dit proefschrift opgenomen thermodynamische berekeningen geven aan dat de actieve component van een dergelijke acceptor niet het vrije oxide, maar een oppervlakte spinel Mn₃Al₂O₆ of Fe₃Al₂O₆ is.

Een belangrijk deel van het voorliggende werk is gewijd aan het onderzoek van de invloed van bereidingsmethoden op de samenstelling van de verkregen acceptoren, hun structuur en de regeneratie mogelijkheden. Hiertoe is het acceptatie-regeneratie gedrag bestudeerd in een vastbed opstelling bij 400 - 600 °C en atmosferische druk. De efficiënte manier om door stoom regenereerbare acceptoren te maken blijkt acetaat oplossing te zijn. Bij gebruik van het nitraatzuur van mangaan is herhaalde impregnatie met een verdunde oplossing noodzakelijk om tot door stoom regenereerbare acceptoren te komen met een redelijk mangaanhalte (8 gewt.). Een enkele impregnatie met een geconcentreerde mangaannitraat oplossing leidt daarentegen tot een niet-regenereerbare acceptor. Ook voor zink, ijzer en cobalt geldt dat zij door stoom regenereerbare acceptoren kunnen vormen indien de dispersie op γ-Al₂O₃ aangepast wordt.

Karakterisering van de acceptoren met behulp van röntgendiffractie, reflectiespectroscopie en Mössbauer spectroscopie streven de thermodynamische berekeningen en tonen aan dat de actieve component van door stoom regenereerbare acceptoren een oppervlakte spinel is, terwijl een niet-regenereerbare acceptor uit clusters van het vrije oxide op de alumina drager bestaat. Het gebruik van verschillende typen γ-Al₂O₃ heeft niet geleid tot significante verschillen in het gedrag van de verkregen acceptoren.

Bij toe passage van door stoom regenereerbare acceptoren in een cyclisch proces blijkt na enige deactivering een stabiele werking verkregen te worden. De doorbraak capaciteit van een stabiele acceptor met 8 gewt% mangaan bedraagt bij 600 °C ongeveer 1 gewt% zwavel. De snelheid waarmee deactivering optreedt is afhankelijk van de temperatuur; bij 400 °C is deze verwaarloosbaar en neemt langzaam toe met de temperatuur. De belangrijkste oorzaak is waarschijnlijk herkristallisatie van de acceptoren.

Bij verhogen van de temperatuur van 400 naar 600 °C verdubbelt de doorbraak capaciteit van de acceptor. Deze toenname wordt niet alleen veroorzaakt door snellere reacties maar ook door een gunstiger ligging van het evenwicht. De capaciteit wordt slechts in geringe mate beïnvloed door de H₂S concentratie en is wat lager bij hogere concentraties. Anderzijds wordt de capaciteit van de acceptor ongunstig beïnvloed door waterdamp in de voeding; een logisch gevolg van het feit dat de acceptor met stoom geregengereerd kan worden. Deze negatieve invloed van water vermindert aanzienlijk als de voeding koolmonoxide bevat omdat daarmee de bekende shiftreactie optreedt.

Tijdens de acceptatie van H₂S is de voornaamste reactie een snelle equimolaire uitwisseling tussen gas en vaste stof van zwavel met zuurstof onder vorming van H₂O. Tijdens regeneratie vindt de omgekeerde reactie plaats. In een geheel
beladen acceptor bedraagt de molaire verhouding van zwavel tot mangaan ongeveer 1 op 2. Naast uitwisseling vindt ook adsorptie van relatief kleine hoeveelheden H2S en H2O plaats. Een eenvoudig model voor de H2S verwijdering bestaat uit een omkeerbare zwavel-zuurstof uitwisseling waarin 2 moleculen mangaan verbruikt worden per molecuul zwavel die wordt afgevangen. Wordt op deze reactie echter een dynamisch model gebaseerd dan blijkt dat dit slechts tot een bruikbare benadering in het onderzochte temperatuur traject leidt als de voeding droog is. Zodra de voeding water bevat is dit model niet in staat het gevonden gedrag van de acceptor te verklaren. Deze tekortkoming wordt toegeschreven aan het feit dat het model geen rekening houdt met de adsorptie van H2O en H2S. Een model dat deze adsorpties wel in rekening brengt blijkt de doorbraakcurves in een wijder gebied goed te kunnen voorspellen. Zowel door experimentele als rekentechnische moeilijkheden is echter een nauwkeurige schatting van de modelparameters nog niet mogelijk. Wegen om deze moeilijkheden in komend onderzoek te vermijden of te elimineren worden voorgesteld.

Een eenvoudige evaluatie heeft aangetoond dat ontzwalingsprocessen die bij hoge temperatuur werken en gebaseerd zijn op door stoom regenererbare acceptoren een aantal belangrijke voordelen kunnen hebben in vergelijking met de bestaande processen. Teneinde de toepassingsmogelijkheden te vergroten is nodig onderzoek nodig om acceptoren te beschrijven die significant meer dan 1 gew% zwavel kunnen opnemen bij 600 °C.

CHAPTER 1
INTRODUCTION

1.1. The need to remove H2S from the product gas of coal gasifiers.

Considerable effort is presently being made in many parts of the world to utilize coal to replace the dwindling supplies of natural gas and petroleum. One of the main routes to achieve this goal is coal gasification. In this process, coal reacts with steam and air or oxygen at temperatures in the range of 500 to 1500 °C. The gas produced, which contains hydrogen and carbon monoxide as the key components and has a heating value ranging from 4 to 20 MJ/m3, may be used as a fuel gas, as a synthesis gas for the manufacture of chemicals, or as a reducing gas in the metallurgical industries. Table 1.1. shows two typical compositions of the raw product gas from a modern gasifier, i.e. the Shell-Koppers gasifier.

The raw gas produced by the gasifier generally contains a number of impurities, of which the major ones are sulfur compounds and particulates. These are undesirable and requirements of either downstream processes or environmental regulations usually dictate that they must be removed from the gasifier effluent.

The principal sulfur compound formed during the gasification of coal is H2S with lesser portions of COS, CS2, and mercaptans. Table 1.2. shows the distribution of sulfur in the raw product gas from several gasification processes. It is clear from this table that the removal of sulfur from the gasifier product gas practically means the removal of H2S, because the sulfur in the form of this compound accounts for more than 90 % of the total sulfur presents in the gas. A recent survey indicates that the H2S content of the product of various gasification processes is usually between 0.4 and 1.4 %.v.

The required extent of sulfur removal from the gasi-
Table 1.1. Typical compositions of the raw product gas from the Shell-Koppers gasification process.

<table>
<thead>
<tr>
<th>Gasifying medium</th>
<th>steam + O₂</th>
<th>steam + air</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>62.2 %v</td>
<td>22.7 %v</td>
</tr>
<tr>
<td>H₂</td>
<td>28.0</td>
<td>8.3</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>2.7</td>
<td>4.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.4</td>
<td>4.9</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Traces (COS, HCN, NH₃, NO)</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>N₂, Ar</td>
<td>3.5</td>
<td>59.0</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Heating value, MJ/Nm³</td>
<td>11.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>1400</td>
<td>1400</td>
</tr>
<tr>
<td>Pressure, MPa</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Data of reference (2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2. Distribution of sulfur in the raw product gas of various coal gasifiers. (in %-weight of the total sulfur in the gas).

<table>
<thead>
<tr>
<th>Gasification process</th>
<th>Lurgi</th>
<th>Synthane</th>
<th>MERC³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur as : H₂S</td>
<td>95.0</td>
<td>94.9</td>
<td>91.5</td>
</tr>
<tr>
<td>COS</td>
<td>2.4</td>
<td>2.6</td>
<td>6.5</td>
</tr>
<tr>
<td>CS₂</td>
<td>0.3</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Mercaptans</td>
<td>2.0</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Thiophenes</td>
<td>0.3</td>
<td>1.3</td>
<td>0.8</td>
</tr>
<tr>
<td>SO₂</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Reference</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
</tr>
</tbody>
</table>

³Morgantown Energy Research Center.

The idea to desulfurize gas at high temperatures arose initially when considering desulfurization as an integral part of the "coal gasification combined cycle power generation technology". The gasification step and the combustion of the purified gas are both carried out at high temperatures. If the gas purification steps are carried out at low temperatures, the raw gas must be cooled before entering the purification unit and reheated prior to combustion. This cooling and reheating task can be eliminated or, at least, simplified, if purification is also carried out at a high temperature. An even more important result is that the overall thermal efficiency of the whole plant will increase. Analyses done by Stone and Webster Engineering Corp. for the United States Electric Power Research Institute (EPRI) showed that the use of high
Table 1.4. Examples of commercial processes for the removal of H₂S from gases.

<table>
<thead>
<tr>
<th>Class of process</th>
<th>Sorbent</th>
<th>Process designation</th>
<th>Operating temp., °C</th>
<th>Regeneration product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutralisation processes</td>
<td>Solution of monoethanolamine (MEA)</td>
<td>Girbotol</td>
<td>20 - 40</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>Solution of diethanolamine (DEA)</td>
<td>SNPA-DEA</td>
<td>20 - 40</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>Solution of diethylene glycol (DEG)</td>
<td>Econamine</td>
<td>40 - 80</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>Solution of diisopropanolamine (DIPA)</td>
<td>ADIP</td>
<td>30 - 40</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>Activated solution of K₂CO₃</td>
<td>Benfield</td>
<td>80 - 120</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>Activated solution of K₂CO₃</td>
<td>Catarcab</td>
<td>80 - 120</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>Solution of Na-salts of H₂CO₃, Anthraquinone 2-sulfonic acid, vanadyl acid</td>
<td>Stretford</td>
<td>20 - 40</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>Solution of Na-salts of H₂CO₃ and 1,4-naphthoquinone 2-sulfonic acid</td>
<td>Takahax</td>
<td>20 - 40</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>As₂O₃-activated solution of K₂CO₃</td>
<td>Vetrocoke</td>
<td>40 - 140</td>
<td>S</td>
</tr>
<tr>
<td>Physical or physical-chemical solvent processes</td>
<td>Dimethylether of polyethylene glycol</td>
<td>Selexol</td>
<td>0 - 30</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>Solution of n-methyl-2-pyrolidone</td>
<td>Purisol</td>
<td>0 - 40</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>Rectisol</td>
<td>-70 - -20</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>Solution of diisopropanolamine + sulfolane (tetrahydrothiophene dioxide)</td>
<td>Sulfinol</td>
<td>20 - 60</td>
<td>H₂S</td>
</tr>
<tr>
<td>Dry purification processes</td>
<td>Iron oxide (Fe₂O₃)</td>
<td>-</td>
<td>15 - 80</td>
<td>SO₂</td>
</tr>
<tr>
<td></td>
<td>Zinc oxide (ZnO)</td>
<td>-</td>
<td>250 - 400</td>
<td>*</td>
</tr>
</tbody>
</table>

*Condensed from Refs. 12, 13, and 14

*Not regenerated; used as “guard bed”
Table 1.5. Estimated thermal efficiencies of coal gasification combined cycle power plants(18).

<table>
<thead>
<tr>
<th>Purification process</th>
<th>Benfield</th>
<th>MERC</th>
<th>Benfield</th>
<th>MERC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas turbine inlet temperature, °C</td>
<td>1066</td>
<td>1066</td>
<td>1316</td>
<td>1316</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gasification process</th>
<th>Thermal Efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lurgi (O$_2$)</td>
<td>29.4 35.4 32.4 39.9</td>
</tr>
<tr>
<td>Lurgi (air)</td>
<td>31.0 37.0 34.5 41.2</td>
</tr>
<tr>
<td>BGC Slagging (O$_2$)</td>
<td>36.5 37.5 39.6 40.6</td>
</tr>
<tr>
<td>Foster-Wheeler (O$_2$)</td>
<td>35.4 36.6 37.8 39.3</td>
</tr>
<tr>
<td>Foster-Wheeler (air)</td>
<td>38.0 38.4 40.8 41.6</td>
</tr>
</tbody>
</table>

$^{f}$Thermal efficiency (%) = \[
\frac{(\text{Delivered kW})(3412.75)(100)}{\text{(lb/hr coal)}(\text{HHV, Btu/lb coal})}
\]

Table 1.6. Estimated capital requirements of 1000 MW gasification combined cycle power plants(18).

<table>
<thead>
<tr>
<th>Purification process</th>
<th>Benfield</th>
<th>MERC</th>
<th>Benfield</th>
<th>MERC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas turbine inlet temperature, °C</td>
<td>1066</td>
<td>1066</td>
<td>1316</td>
<td>1316</td>
</tr>
<tr>
<td>Gasification process</td>
<td>Capital requirements, $/kW $^f$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lurgi (O$_2$)</td>
<td>1117 739 1046 703</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lurgi (air)</td>
<td>1000 667 916 642</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BGC Slagging (O$_2$)</td>
<td>643 629 629 606</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foster-Wheeler (O$_2$)</td>
<td>670 679 658 657</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foster-Wheeler (air)</td>
<td>619 616 604 597</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{f}$Mid-1975 dollars.

Table 1.7. Estimated cost of electricity for 1000 MW gasification combined cycle power plants(18).

<table>
<thead>
<tr>
<th>Purification process</th>
<th>Benfield</th>
<th>MERC</th>
<th>Benfield</th>
<th>MERC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas turbine inlet temperature, °C</td>
<td>1066</td>
<td>1066</td>
<td>1316</td>
<td>1316</td>
</tr>
<tr>
<td>Gasification process</td>
<td>Power costs, Mills/kWh $^f$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lurgi (O$_2$)</td>
<td>60.2 43.7 55.5 40.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lurgi (air)</td>
<td>55.0 40.5 50.7 37.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BGC Slagging (O$_2$)</td>
<td>39.9 39.0 38.0 36.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foster-Wheeler (O$_2$)</td>
<td>41.4 41.1 39.8 39.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foster-Wheeler (air)</td>
<td>38.4 38.1 36.7 36.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{f}$Based on : Delivered coal cost of $2.00/MMBtu. Mid-1975 dollars with no escalation included and operating load factor of 70%.

The reasons that only modest improvements are obtained by using the MERC process are(18):

1. The regeneration reaction of the MERC process, i.e. reaction (2), is highly exothermic and, if not controlled carefully, can cause the fusion of the adsorbent bed. To avoid this danger, the MERC process uses nitrogen-enriched air for regeneration. As a consequence of this, the off-gas from the regeneration stage tends to be low in SO$_2$ content and its treatment resembles that of stack gas.

2. The conversion of the regeneration product (SO$_2$) into elemental sulfur in the Claus plant requires the valuable component of the fuel gas (hydrogen).
3. The unnecessary reduction of iron oxide during the acceptation stage, i.e. reaction (1), represents an extra penalty because it consumes H₂ and/or CO.

The single cause of these drawbacks is the oxidative regeneration used by the MERC process. It is thus clear that an alternative, and better, method of acceptor regeneration is desirable.

In the above discussion, the need for removing H₂S at high temperature has been presented in the context of the treatment of coal gasification products. The potential applicability of hot gas desulfurization processes is, however, not limited to this industrial sector. Examples of other possible applications are:

- Desulfurization of steam reformer feedstocks(6,19). Because sulfur compounds strongly poison the reforming catalyst, the sulfur content of natural gas or naphtha feedstock to a steam reformer must be reduced to less than 1 ppmv. Desulfurization temperatures as high as 500 °C (the inlet temperature of the reformer) are possible. Presently, a zinc oxide guard bed is used for this purpose.

- Desulfurization of recycle/make-up hydrogen in the petroleum refineries(20-22). In many hydrogenative conversion processes applied to petroleum fractions, e.g. hydrocracking, heavy gas-oil hydrogenation and catalytic reforming, the excess hydrogen separated from the product stream and recycled to the reactor usually contains H₂S, which results from the reaction of hydrogen with the sulfur compounds in the oil. To prevent accumulation of H₂S in the recycle gas, this must be removed.

- Desulfurization of coke oven gas(23). The fluidized-bed Appleby-Frodinham process, which operates at about 400 °C, is an example of this application. It reduces the sulfur content of coke oven gas from 1 - 2 %w down to less than 1 ppm.

1.3. Aim of the present study.

During his study on the use of manganese oxide on γ-Al₂O₃ as an acceptor for SO₂ removal from flue gas, Van der Linde(24) came to the conclusion, and provided evidence, that MnO on γ-Al₂O₃ can remove H₂S from gases at 400 - 550 °C and that the sulfided product formed can be hydrolized back to MnO on γ-Al₂O₃ at the same temperature using a gas containing 50 % steam. In other words, the reaction

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

is reversible. This finding is interesting, because it implies that MnO on γ-Al₂O₃ might be used as an acceptor in a high temperature regenerative H₂S removal process which does not have the weaknesses of the iron oxide process mentioned in the previous section. Moreover, Van der Linde also reported that unsupported MnO, silica-supported MnO, and molecular sieve 5A supported MnO react rapidly with H₂S but their products, unlike the sulfided product of MnO on γ-Al₂O₃, do not hydrolize with steam, at least up to 600 °C. The behaviour of MnO on γ-Al₂O₃ is thus peculiar and deserves an explanation.

The aim of the present study is therefore:

- to investigate whether other metal oxides, such as iron and zinc oxide, can behave like manganese oxide when supported by γ-Al₂O₃. The results of this work may also help in explaining the behaviour of MnO on γ-Al₂O₃.

- to study the relation between the method of preparation and the properties of MnO on γ-Al₂O₃ acceptors.

- to test and compare the desulfurization and regeneration performance of the various acceptors prepared and to select the best acceptor(s) in terms of sulfur removal capacity and regenerability.

- to study the dynamic performance of the selected acceptor(s) during the sulfur acceptation-regeneration cycles and the influence of process conditions (temperature, gas composition) on acceptor performance.

- to make a preliminary estimate of the feasibility of high temperature removal of hydrogen sulfide on the basis of the experimental data obtained.
1.4. Outline of thesis.

In chapter 2, general information is provided about the use of supported and unsupported metal oxides as sulfur removal acceptors. The interaction between a support and a metal oxide dispersed on it is also discussed. Chapter 3 describes the equipment and experimental techniques used to study acceptor performance as well as the method of acceptor preparation, analysis, and characterization. In chapter 4, data on the sulfur removal capacity and steam-regenerability of a variety of acceptors are presented, together with some discussion about the relation of these performance data with the composition and/or structure of the acceptors.

Chapter 5 contains data and discussion on how process variables such as temperature and composition of the treated gas affects the sulfur breakthrough capacity of the acceptors. The quantitative modelling of the breakthrough curves to extract the process parameters is the subject of chapter 6. Finally, chapter 7 presents a brief evaluation, comparing the process studied here with those described in the literature.

References.

CHAPTER 2

METAL OXIDES AS SULFUR REMOVAL ACCEPTORS

2.1. Introduction

Although the use of metal oxides as sorbents (or acceptors) for \( \text{H}_2\text{S} \) removal dates back to the middle of the nineteenth century (1), most of the high temperature \( \text{H}_2\text{S} \) removal processes based on metal oxides were developed in the last decade and, in fact, all of them are still in an early stage of development. Section 2.2. reviews recent work in this area of application.

A possible explanation of the peculiar behaviour of MnO on \( \gamma\text{-Al}_2\text{O}_3 \) with respect to sulfidation (cf. section 1.3.) is based on the assumption that the MnO reacts with the \( \gamma\text{-Al}_2\text{O}_3 \) support to form aluminate. In section 2.3. the structure and sulfidation thermodynamics of this compound is considered. Finally, section 2.4. discusses the possibility and the consequences of aluminate formation on the surface of gamma-alumina, with the aid of some data taken from the literature.

2.2. Single metal oxides.

2.2.1. Thermodynamics.

Thermodynamic evaluation of metal oxide for use in high temperature removal of \( \text{H}_2\text{S} \) has been carried out by several investigators (2,3,4). The most extensive study is that of Westmoreland and Harrison (2). Using a free energy minimization technique (5), they investigated the desulfurization potential of the oxides of 28 elements under the conditions listed in Table 2.1. They assumed all gases to be ideal and condensed species to form pure phases. An element is considered as a thermodynamically feasible acceptor if, after being contacted with the sulfur-containing gases and allowed
Table 2.1. Conditions used in the thermodynamic screening study of Westmoreland and Harrison (2).

<table>
<thead>
<tr>
<th>Temperature range</th>
<th>Pressure</th>
<th>Gas composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 - 1200 °C</td>
<td>2.0 MPa</td>
<td>N₂ 35 - 44 mol-%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO 8 - 33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂ 5 - 37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂O  4 - 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO₂ 1 - 20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂S 0.7 - 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>COS 0.02 - 0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₄  0 - 16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH₃  0 - 0.04</td>
</tr>
</tbody>
</table>

To reach equilibrium, it removes at least 95% of the sulfur initially present in the gas phase. According to this study the elements can be divided in the following groups:

1. Elements rejected because their oxides or carbonates are stable relative to the element and unreactive throughout the temperature range include Al, Ce, Cr, K, Li, Mg, Na, Ti, Zr. Note that the oxides of some of these elements, in particular aluminum oxide, are normally used as high area supports for adsorbents and catalysts.

2. Elements rejected because their excess metal oxide can be reduced to a low-melting metal: Bi, Cd, Pb, Sn.

3. Elements rejected because inadequate desulfurization potential (< 95%) even though their equilibrium is in favour of the sulfided state: Ag, La, Ni, Sb.

4. Thermodynamically feasible candidates: Ba, Ca, Co, Cu, Fe, Mn, Mo, Sr, W, V, Zn.

The results of the thermodynamic studies by other investigators (3,4), who used different gas compositions, are generally in agreement with the above results of Westmoreland and Harrison.

Two of the 11 thermodynamically feasible elements give essentially 100% desulfurization. These are vanadium (V) and zinc (Zn). Their possible operating temperatures are, however, limited. Vanadium oxide can only be used below 650 °C because above this temperature vanadium sulfide (i.e. the sulfidation product) is a liquid. The appreciable vapor pressure of zinc above 700 °C prevents the use of zinc oxide above this temperature.

Fig. 2.1 shows the possible operating temperature and the stable solid phases of the thermodynamically feasible acceptors.

2.2.2. Kinetics.

Another important factor in the selection of accep-
tors is the rate of H$_2$S capture. The result of a comparative study on the sulfidation rates of several metal oxides is shown in Fig. 2.2. This result is derived from measurements of initial rates of sulfidation; the order of the reaction with respect to the H$_2$S and the solid oxide were assumed to be one.

It can be seen from Fig. 2.2 that Fe$_2$O$_3$ and MnO are superior to other oxides. Sulfidation of MnO is 5-10 times faster than that of CaO or ZnO, but 10-50 times slower than that of Fe$_2$O$_3$. Activation energies of sulfidation vary from 12 kJ/mol for Fe$_2$O$_3$ to 37 kJ/mol for V$_2$O$_3$.

2.2. Processes

As has been pointed out in the beginning of this chapter, all high temperature H$_2$S removal processes are still in the development phase. Table 2.2. lists some examples.

The calcium-based processes use calcined dolomite instead of limestone. Due to its more porous structure, calcined dolomite sulfides faster than (calcined) limestone. The acceptation reaction of the Conoco process, which uses semi calcined dolomite, is:

$$H_2S(g) + CaCO_3 \cdot MgO(s) \rightarrow CaS \cdot MgO(s) + H_2O(g) + CO_2(g) \quad (1)$$

The regeneration reaction is the reverse of this reaction. Acceptation is carried out at 900 °C where equilibrium favours the formation of MgO, CaS, CO$_2$, and H$_2$O from H$_2$S and MgO, CaCO$_3$. Regeneration is done at lower temperature where the reverse is true.

The problems facing calcium based processes are:
1. coke formation and deposition in the acceptor bed,
2. corrosion and
3. sintering/deactivation of acceptor.

The main cause of the last two problems is the acceptation temperature, which is quite high.

The acceptation step of the processes based on the oxides of a transition metal can be represented by the following irreversible reaction:

$$M_{ox}(s) + (x-y) H_2(g) + y H_2S(g) \rightarrow MS_y(s) + x H_2O(g) \quad (2)$$

where M = metal and $x \geq y$. The regeneration step is:

$$MS_y(s) + (y \cdot \frac{1}{2}) O_2(g) \rightarrow M_{ox}(s) + y SO_2(g) \quad (3)$$

This oxidation reaction is highly exothermic (ΔH$^o$ = -420 ± 125 kJ/mol SO$_2$ formed) and, as has been pointed out in chapter 1, is the main cause of problems associated with
the use of transition metal oxides as regenerable acceptors for \( \text{H}_2\text{S} \) removal. These problems are discussed further in the next paragraph.

2.2.4. Discussion.

The elements that pass thermodynamic screening can be classified into two groups: the alkaline earth metals and the transition metals. The thermodynamic limitation that alkaline earth metals are applicable only above 800 °C is, perhaps, the major drawback of this group. The ability of the transition metals to desulfurize effectively at 400 - 700 °C is advantageous for two reasons:

1. Many applications, especially those in the petroleum refining and petrochemical industries, require a desulfurization temperature not higher than 500 - 600 °C. (cf. examples at the end of section 1.2.)

2. Even though a desulfurization temperature as high as 1000 °C will be possible in modern coal gasification combined cycle power plant, the optimum operating temperature of hot purification units in such plants would probably not be higher than 600 - 700 °C. This is because, at high temperature, the loss due to material of construction problems can outweigh the saving due to operating at higher thermal efficiency.

The regeneration method presently applied with the transition metals is, in turn, the major drawback of this group. Its highly exothermic nature makes temperature very difficult to control, while its oxidative nature results in a regeneration product (i.e. \( \text{SO}_2 \)) which is less attractive than that of the alkaline earth-based processes (i.e. \( \text{H}_2\text{S} \)). Moreover, during this regeneration process the transition metal is unnecessarily oxidized to a higher valence.

It should be clear from the above that a more ideal situation will result if an alternative, and better, regeneration method is found for transition metal acceptors. One of the most popularly cited alternative regeneration procedure

---

### Table 2.2. Examples of dry processes for the removal of \( \text{H}_2\text{S} \) at high temperatures

<table>
<thead>
<tr>
<th>Process</th>
<th>Status of development</th>
<th>Acceptance temp.(°C)</th>
<th>Regeneration method</th>
<th>Regeneration temp.(°C)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conoco</td>
<td>terminated</td>
<td>&gt; 816</td>
<td>H2-CO2</td>
<td>600-700</td>
<td></td>
</tr>
<tr>
<td>U.S. Steel</td>
<td>in progress</td>
<td>538-816</td>
<td>Air</td>
<td>47-649</td>
<td></td>
</tr>
<tr>
<td>Shell</td>
<td>in progress</td>
<td>538-816</td>
<td>Air</td>
<td>58-816</td>
<td></td>
</tr>
<tr>
<td>MRSC</td>
<td>in progress</td>
<td>20-25</td>
<td>O2-containing</td>
<td>816</td>
<td></td>
</tr>
<tr>
<td>Koppers</td>
<td>in progress</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IFP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U.S. Steel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eneller</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Climax</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IMR</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mgo-CaCO3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mgo-CaO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu/CuO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na2O-Al2O3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn2O5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---


is the use of steam to remove sulfur from the acceptor bed in
the form of H2S(3). However, steam-regeneration is simply the
reverse of the original sulfidation and the thermodynamics of
sulfidation of single metal oxides (cf. paragraph 2.2.1) pre­
dicts that regeneration with steam is virtually impossible(3).

It is with respect to this problem that the
findings of Van der Linde(8) are important and interesting.
As has been discussed in section 1.3., he noticed that, in
contrast with pure manganese oxide, the γ-Al2O3-supported MnO
used in his investigation can remove H2S and is capable of
being regenerated with steam. The next two sections represent
an attempt to explain this observation of Van der Linde.

2.3. Complex oxides: the aluminate spinels.

2.3.1. General.

Under favourable conditions, two metal oxides can
react to form a distinct compound. Examples of the resulting
complex oxides are ZnCr2O4, TiMg2O4, and WNa2O4. A complex
oxide may be called a spinel when :
- its formula can be written as AB2O4 and
- its structure is isomorphous with the natural spinel (magnesium aluminate, 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: (A2+ +
2 B3+), (A6+ + 2 B3+), and (A6+ + 2 B3+). These result in
a 2-3 spinel, a 4-2 spinel, and a 6-1 spinel. The three exam­
ples of a complex oxide given above are in fact a 2-3 spinel,
a 4-2 spinel, and a 6-1 spinel. The 2-3 spinel is by far the
most numerous(9-12).

The aluminate spinels are 2-3 spinels (B3+ = Al3+).
Some of them are found in nature; these are(12) MgAl2O4 (the
spinel itself), FeAl2O4 (Hercynite), MnAl2O4 (Galaxite), and
ZnAl2O4 (Gahnite).

2.3.2. Structure. (9-12)

The unit cell of a spinel \( \text{MgAl}_2\text{O}_4 \) contains 32 oxygen
ions in cubic close packing, see Fig. 2.3., and corresponds
to the formula \( \text{Mg}_{\frac{\text{Al}_{2}\text{O}_4}}{2} \) or \( \text{Al}_{\frac{\text{Mg}_{2}\text{O}_4}}{16} \). This unit cell con­
tains 32 octahedral holes and 64 tetrahedral holes, in which
8 M2+ ions and 16 Al3+ ions are arranged. In one limiting
mode of distribution, 8 out of the 64 tetrahedral holes are
occupied by M2+ ions and 16 out of the 32 octahedral holes
are occupied by Al3+ ions. Spinel with this type of distri­
bution are called normal. Examples of normal spinels are(11,
12) : Co-, Fe-, Mg-, Mn-, and ZnAl2O4. In the other limiting
mode of cation distribution, 8 tetrahedral holes are occupied
by trivalent cations. The remaining 8 trivalent cations and
all 8 divalent cations occupy 16 octahedral holes. Such a spi­
nel is called inverse. Between these two limiting cases (nor­
mal and inverse spinels), various degrees of inversion are ob­
served. NiAl2O4 is an example of a partly inverted spinel (a
bout 76% of the Ni2+ ions occupy octahedral holes(11)).

It is worthy of note that the position of the M2+
ion in the aluminate spinel \( \text{MgAl}_2\text{O}_4 \) is different from that in

Fig. 2.3. The structure of spinels.
Large circle : oxygen ion
Small circle,
black : octahedral cation
white : tetrahedral cation
its simple oxide MO (except for M = Zn). In the simple oxide
MO, all the M2+ ions occupy octahedral holes/10/. For M =
transition metal, this difference of environment result in
difference in behaviour with respect to light absorption
and/or reflection. Thus, the colour of MnO, FeO, and CoO is,
respectively, green, black, and olive green, whereas the co­
lor of MnAl2O4, FeAl2O4, and CoAl2O4 is, respectively, dark
cream, grey-green, and ultramarine blue/12/.

2.3.3. Thermodynamic of sulfidation.

Using available thermodynamic data/13,14/, equili­
brum constants and enthalpy changes were calculated for the
following reaction scheme:

\[
\text{MAl}_2\text{O}_4(s) + \text{H}_2\text{S}(g) \rightleftharpoons \text{MS}(s) + \gamma\text{-Al}_2\text{O}_3(s) + \text{H}_2\text{O}(g)
\]  

(4)

\[
K = \frac{a_{\text{MS}}a_{\gamma\text{-Al}_2\text{O}_3}a_{\text{H}_2\text{O}}}{a_{\text{MAl}_2\text{O}_4}a_{\text{H}_2\text{S}}}
\]  

(5)

where M = Mn, Fe, or Ni; a is activity; \( p \) is partial pressure.
The results are shown in Figs. 2.4. and 2.5.. For the purpose
of comparison, the equilibrium constants and enthalpy changes
of sulfidation of MnO and FeO, reaction (6) and eq. (7), are
also shown in these figures.

\[
\text{MO}(s) + \text{H}_2\text{S}(g) \rightleftharpoons \text{MS}(s) + \text{H}_2\text{O}(g)
\]  

(6)

\[
K = \frac{a_{\text{MS}}a_{\text{H}_2\text{O}}}{a_{\text{MO}}a_{\text{H}_2\text{S}}}
\]  

(7)

As can be seen in Fig. 2.4., the thermodynamic equilibrium
constants for the sulfidation of Mn- and FeAl2O4 in the tem­
perature range of 700 to 1000 °C are close to unity (log \( K \)
about zero), while those of MnO, FeO, and NiAl2O4 are large.
(greater than 100). This means that the sulfidation of MnAl$_2$O$_4$ and FeAl$_2$O$_4$ is reversible, whereas that of NiAl$_2$O$_4$, MnO, and FeO is irreversible (the equilibrium positions are much in favour of the sulfided state). Thus, if MnS or FeS is in a good contact with γ-Al$_2$O$_3$, the presence of steam will remove sulfur from the solid phase in the form of H$_2$S, a phenomenon which does not occur when only MnS or FeS is present.

Fig. 2.5. shows that, whereas the sulfidation of MnO, FeO, and NiAl$_2$O$_4$ is somewhat exothermic, the sulfidation of Mn- or FeAl$_2$O$_4$ involves a negligible heat effect; it is slightly endothermic.

Due to lack of data, the thermodynamics of the sulfidation of ZnAl$_2$O$_4$ and CoAl$_2$O$_4$ were not calculated. The use of ZnAl$_2$O$_4$ as an acceptor for the removal of H$_2$S at high temperature is presently being investigated by Institute of Gas Technology in Chicago, U.S.A.. However, the regeneration method is reported to be oxidative(16).

2.4. Metal oxides supported by high-area aluminas.

2.4.1. Advantages of using a support.

As can be seen from Table 2.2., metal oxide acceptors are usually applied in the supported form. The main advantages of using a support are:

1. The acceptor has a large surface area and the active component is spread out on this surface. Since gas-solid interaction can only happen at the surface, this results in the most effective use of the active component.

2. The acceptor has more desirable mechanical properties, including attrition resistance, hardness, and compressive strength.

Various modifications of alumina, known as transition aluminas, have good mechanical strength as well as a high surface area and, therefore, find wide use as support material.

2.4.2. Types and thermal properties of high-area aluminas.

The most important aluminas for use as support are γ-Al$_2$O$_3$ and η-Al$_2$O$_3$, which have high surface area and are relatively stable up to 800 °C. Both are very similar in structure and sometimes difficult to distinguish. Their structure is almost identical with that of the spinels discussed in paragraph 2.3.2. As compared with spinel, however, one-ninth of the positions normally occupied by cations are unoccupied (this can be more clearly seen by writing Al$_2$O$_3$ as Al$_{8/3}$O$_4$). These cation vacancies may be distributed in different ways among the tetrahedral and the octahedral holes. According to Pott and Stork(17), the formula of γ-Al$_2$O$_3$ and η-Al$_2$O$_3$ can be written as:

$$\text{Al}_{2/3} + x \square_{1/3} - x \left[ \text{Al}_{2} - x \square_{x} \text{O}_{4} \right]$$

where $0 \leq x \leq 1/3$, $\square$ represents a cation vacancy, and the bracketed term represents octahedral sites. Stone(10) suggested that η-Al$_2$O$_3$ has more tetrahedral Al$^{3+}$ than γ-Al$_2$O$_3$.

When γ- or η-Al$_2$O$_3$ is heated, their surface area remains essentially constant up to 600 °C (the value of this surface area varies with the mode of preparation but is usually between 200 and 350 m$^2$/gm). Above 600 °C the surface area decreases with temperature, but still amounts to about 100 - 140 m$^2$/gm at 800 °C(18,19). Further heating transform γ-Al$_2$O$_3$ into δ-Al$_2$O$_3$ and η-Al$_2$O$_3$ into θ-Al$_2$O$_3$. Gaugain et al.(19) pointed out that the addition of a small amount of a divalent ion such as Mg or Zn to γ- or η-Al$_2$O$_3$, introduced by impregnation, improves the thermal stability and mechanical properties at high temperatures. These divalent ions occupy tetrahedral positions in the alumina lattice.

2.4.3. The forms of metal oxide on the surface of γ- or η-Al$_2$O$_3$.

A metal oxide dispersed on a support may end up in
three different forms(17):
1. it may retain its chemical identity; the carrier acts only as a dispersing agent.
2. it may form a new stoichiometric compound with the support.
3. it may dissolve in the carrier to give a solid solution. Solid solutions are less stable than compounds(20). Thus, if conditions make its formation possible, a compound is the preferred state.

The literature describes γ- and η-Al_2O_3 as supports which exhibit strong interaction with a metal oxide dispersed on their surface. Pott and Stork(17) pointed out that γ- and η-Al_2O_3 readily enter into reaction with many oxides for the following reasons:

a. Since many inorganic oxidic compounds have structures based on densely packed oxygen lattice, compound formation with aluminas generally only involves diffusion of the relatively small cations. The oxygen lattice undergoes but minor rearrangement.

b. Cation diffusion in aluminas is favoured because the structure of the aluminas contains many vacancies.

c. The transition aluminas are thermodynamically metastable and therefore have a stronger tendency to undergo compound formation than a stable phase such as α-Al_2O_3 (the most stable form of alumina).

Selwood et al.(21) studied the formation of manganese oxide on γ-Al_2O_3 by impregnating this support with a solution of Mn(NO_3)_2, followed by drying and calcination in air at 200 °C and 600 °C. They concluded that:
- the layer of manganese oxide in actual contact with the alumina is always subject to the inductive action of the alumina and crystallises as γ-Mn_3O_4 which is isomorphous with the γ-Al_2O_3. The layers not in direct contact with the γ-Al_2O_3 crystallise as α-Mn_3O_4 (600 °C) or β-MnO_2 (200 °C), depending on the calcination temperature.

Lo Jacono et al.(22) established the formation of surface spinel MnAl_2O_4 on γ-Al_2O_3 and η-Al_2O_3 by using hydrogen, instead of air, as the medium of calcination. The calcination temperature was 600 °C and, similar to the experiments done by Selwood et al., the manganese was initially deposited by impregnating the supports with manganese nitrate solution. Further observations of Lo Jacono et al. are:
1. at lower concentrations of manganese (less than 3 to 4 % Mn) all the manganese is in the form of surface spinel MnAl_2O_4.
2. at higher Mn content, any manganese in excess of 3 to 4 % is present as MnO.
3. samples based on γ-Al_2O_3 and those based on η-Al_2O_3 behave similarly.

Lo Jacono and Schiavello(23) observed that Co, Cu, and Ni behave similarly to Mn when deposited on γ- or η-Al_2O_3. Thus, at lower transition metal contents only surface spinels are formed, while at higher concentrations surface spinel and free oxide are present simultaneously. It should be noted that the medium of calcination used by Lo Jacono and Schiavello to obtain the surface spinel of Co, Cu, and Ni was air and not hydrogen. This is quite logical since Co^2+, Cu^2+, and Ni^2+ are unstable in a reducing atmosphere, being reduced to metal. In turn, Mn^2+ is unstable in an oxidizing atmosphere such as air.

It appears probable from the above facts that, provided the conditions are favourable, a surface spinel will be formed on alumina surface as a result of the reaction between a dispersed metal oxide and the alumina support. Furthermore, the structure of the alumina support, which is quite similar to that of spinel, presumably acts as a nucleus favouring the formation of the surface spinel.
2.2.4. Discussion.

The evidence that surface MnAl$_2$O$_4$ can be formed on γ-Al$_2$O$_3$ and that, as shown thermodynamically, the sulfidation of MnAl$_2$O$_4$ is a reversible reaction, provides an indication that the active component of the MnO/γ-Al$_2$O$_3$ acceptor used by Van der Linde/8/ was the surface spinel MnAl$_2$O$_4$. However, one should keep in mind that the bulk thermodynamics of spinels discussed in paragraph 2.3.3. provides not more than a rough guide for predicting the sulfidation behaviour of surface spinels. Differences in properties always exist between bulk compound and surface compound. Pure, high surface area CoAl$_2$O$_4$, for example, does not possess catalytic activity for the oxidation of CO, whereas surface CoAl$_2$O$_4$ does show such an activity/24/.

Examination of the results of Selwood et.al.21) and Lo Jacono et.al.22) presented above leads to the conclusion that one will obtain more manganese in the form of surface spinel than just 3 to 4%w Mn if the dispersion of manganese oxide on the alumina surface is improved. In fact, the steam regenerable acceptor used by Van der Linde/8/ contained about 8%w Mn. He obtained it by repeatedly impregnating γ-Al$_2$O$_3$ with 0.5 molar solution of MnSO$_4$ (up to three times, each impregnation being followed by drying and calcination in H$_2$ stream at 500 - 600 °C). This method of preparation, i.e. multiple impregnation with a dilute solution, is known to give a good dispersion of the active component on the support surface/25,26/). It will be shown in chapter 4 that by this method a steam-regenerable acceptor containing about 8%w manganese can be obtained when impregnating with manganese nitrate solution.

Based on the fact that the sulfidation behaviour of iron aluminate is similar to manganese aluminate (see Figs. 2.4. and 2.5.), it was expected that a steam-regenerable acceptor can also contain iron, in the form of surface FeAl$_2$O$_4$, as the active component. Therefore, beside manganese, iron was also examined in the investigation reported in this thesis. Commercial gamma-alumina was chosen as support material. No attempt was made to test the use of γ-Al$_2$O$_3$ as support material, since the work of Lo Jacono et.al./22/) has shown that γ-Al$_2$O$_3$ and γ-Al$_2$O$_3$ are similar with respect to surface spinel formation.

References.

12. T.J. Gray, "Oxide Spinels", in A.M. Alper, "High Tempera-
CHAPTER 3

EQUIPMENT AND METHODS

3.1. Introduction.

In this chapter, the equipment and experimental techniques used in the work for this thesis are described. The next section contains descriptions of bench-scale experimental units used to study the performance and behaviour of some sulfur removal acceptors based on metal oxides, the experimental procedures, and the method of treatment and/or interpretation of the data obtained. The materials and techniques used to prepare and characterize the acceptors are reported in section 3.3.

3.2. Bench-scale unit.

Two basically similar fixed-bed experimental units were used in this investigation, one being fully automated and the other manually operated. The flow diagram of the automated unit is shown in Fig. 3.1. It consists of gas dosage section [A], reactor section [B], and analysis section [C]. Automatic operation of this unit in carrying out acceptation-regeneration cycles was effected by an Omron sequence controller which actuated solenoid valve 6 in the gas dosage section and solenoid valve system 11 in the reactor section. The flow diagram of the manually operated unit is similar to that in Fig. 3.1., except for the following differences:

- valves 1, 6, and 11 are hand operated valves instead of solenoid valves.
- the unit did not contain gas chromatograph 13 and photionization detector 14.

3.2.1. Gas dosage.

The required gas were supplied from bottles. They
entered the unit via solenoid valves at a pressure of about 0.4 MPa and (except for the \( \text{H}_2\text{S}/\text{N}_2 \) mixture) were passed through purification trains to remove traces of oxygen and water. Each gas then passed a pressure regulator, which reduced its pressure to 0.2 MPa, and a mass flow controller (PFD 112, Precision Flow Devices, Inc.). The metered gas flows were then mixed and sent to reactor section B.

When the gas mixture should contain up to 5 % water vapour, the \( \text{H}_2 \) stream leaving the mass flow controller was passed through water vapour generator 5 by correctly positioning solenoid valve 6. In the generator, the gas flowed through a fixed-bed of \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \) which produces water vapour according to dehydration reaction (1):

\[
\text{FeSO}_4 \cdot 7\text{H}_2\text{O} (s) \rightarrow \text{FeSO}_4 \cdot 4\text{H}_2\text{O} (s) + 3 \text{H}_2\text{O} (g)
\]

The temperature of the iron sulfate bed was kept constant by placing the bed in a thermostat bath. More details about this water vapour generator are given in Appendix A at the end of this chapter.

### 3.2.2. Reactor section

Fixed-bed reactor 7 was a quartz tube, 9 mm in diameter. The acceptor particles (size 0.25 - 0.85 mm) were packed to a height of 50 - 150 mm. The ratio of length and diameter of the bed to the size of the acceptor particle were such that plug flow of the gas through the bed could be assumed (2).

The reactor was immersed in a bed of carborundum particles 8, which acted as a heat sink and source. This carborundum bed was placed in an electrically heated air fluidized sand bed thermostat 9. The reactor temperature was kept constant (range: 300 - 700 °C) by controlling the temperature of the fluid-bed thermostat with an Eurotherm temperature controller. To prevent contact of hydrogen and air in the case of reactor breakage, the carborundum chamber was continuously flushed with nitrogen. Steam needed for the regeneration of the acceptor was generated at the reactor inlet by injecting water from motorized burette 10 through a stainless steel capillary.

Solenoid valves system 11 in the reactor section allowed the feed gas to bypass the reactor for determination of the inlet concentration of \( \text{H}_2\text{S} \).

### 3.2.3. Analysis section

By means of three four-way valves, 12, the gas flow leaving the reactor section could be passed through one
or all of the following analytical instruments:
a) gas chromatograph
b) photoionization detector
c) continuous titration system

The gas chromatograph was equipped with a 1 ml sampling loop and a 1.70 m column filled with Porapak QS 80-100 pretreated thermally at 250 °C for 3 hours. The column temperature was 100 °C and the hydrogen carrier gas flow 30 ml/min. At these conditions N₂, CO₂, H₂S, COS, and H₂O could be separated within 7 minutes. Detection was accomplished by a katharometer maintained at 150 °C, the bridge current being 200 mA. The peak surfaces were electronically integrated, recorded, and printed.

The photoionization detector (HNU System, Inc.) was installed to measure low concentrations of H₂S (less than 200 ppmv) in the reactor effluent during acceptance stage. In this instrument, the gas passed through an ionization chamber irradiated by a 10.2 eV ultraviolet lamp specially selected for H₂S. The radiation was of such strength that only H₂S would be ionized. The extent of ionization was determined by a normal ionization detector (comparable to a flame ionization detector). Thus, a continuous analysis of low concentrations of H₂S could be obtained.

The titration system is based on the well established fact that a cadmium salt solution can remove H₂S completely from a gas phase intimately contacted with it. The H₂S reacts with the cadmium ion producing cadmium sulfide precipitate and hydrogen ion:

\[
\text{H}_2\text{S} + \text{Cd}^{2+} \rightarrow \text{CdS} + 2\text{H}^+ \quad (2)
\]

The H₂S content of the gas can be determined by titrating the H⁺ formed according to reaction (2) with a standard base solution. Accordingly, the gas stream leaving the reactor section entered the baffled titration vessel (see Fig. 3.2.) of continuous titration system; the gas was dispersed by stirring in solution of CdSO₄ (0.1 - 0.3 M) at a pH of 4. The decrease of the solution pH due to reaction (2) was sensed by a combined glass-calomel electrode, which caused a pH controller (Titrator E526, Metrohm AG) to actuate a motor burette filled with a 0.1 M NaOH titrant in order to keep the pH of the solution in the titration vessel at 4. During operation, an analog signal (0 - 1000 mV) proportional to the position of the burette was continuously recorded on a strip chart recorder. This signal was also scanned at a frequency of 0.78 s⁻¹ by a data acquisition interface and stored as raw data in the computer facility of the department.

The titration system was on line during all runs, but not when testing the equipment or calibrating gas flows.

3.2.4. Procedure.

The fluid bed was first set at the desired temperature, usually between 400 and 600 °C. The reactor was filled with the desired amount of acceptor, flushed with nitrogen, and then dipped in the gently fluidizing carborundum in the bed chamber. After tightening the connection of the reactor to the rest of the unit, nitrogen was passed through the reactor. Ten minutes later this was replaced by a stream of ni-
trogen/hydrogen mixture to keep the acceptor under reducing conditions.

One hour after the reactor had been installed, the first acceptation-regeneration cycle could be started. To prevent the decomposition of $H_2S$ to hydrogen and elemental sulfur, at least 7 ml/min $H_2$ ($25^\circ C$) was always included in the stream of gas mixture fed to the reactor. The absorption mixture in the titration vessel was replaced daily with a fresh charge of 125 ml cadmium sulfate solution.

Several deliberate comparison tests with an acceptor containing 8 %w Mn and daily observation indicated that the automated unit and the manual unit performed similarly and produced comparable results, also in terms of acceptor deactivation.

3.2.5. Interpretation of results.

Every acceptation-regeneration cycle of the present study consisted of four steps:

1. Measurement of the molar inlet flow of $H_2S$; to that end, the $H_2S$-containing feed gas was fed directly to the analysis section, bypassing the reactor.
2. Acceptation: the feed gas was switched to pass through the reactor and the $H_2S$ content of the reactor effluent was monitored.
3. Regeneration: the sulfur-loaded acceptor was treated with a steam-containing gas and the amount of $H_2S$ released was monitored.
4. "Drying": the regenerated acceptor was flushed (usually for a period of one hour) with nitrogen/hydrogen mixture.

Before steps 2 and 3 were carried out, the tubing in the reactor and analysis sections was flushed with a dry, $H_2S$-free gas.

A schematic representation of the continuous titration data obtained from a complete cycle is shown in Fig. 3.3. When measuring the feed gas concentration, the cumulative amount of $H_2S$ absorbed in the titrator increases linearly with time, indicating constancy of the $H_2S$ feed rate. The slope of this line, $\tan \alpha$, represents the molar feed rate of $H_2S$. When the stream of $H_2S$ is switched to pass it through the reactor, the effluent from the acceptor bed is initially free of $H_2S$. As time proceeds, however, this effluent stream contains an increasing amount of $H_2S$ and, if the acceptation is carried out long enough, say until $t_m$ minutes, the outlet concentration of $H_2S$ finally reaches the inlet value. The curve ABC in Fig. 3.3 is the cumulative (or integrated) breakthrough curve of the acceptor bed. The slope of this...
curve is proportional to the concentration of \( \text{H}_2\text{S} \) in the reactor effluent.

Although the cadmium salt solution in the titration vessel completely removes even minute amounts of \( \text{H}_2\text{S} \) present in the gas passed through it, under the conditions applied in the present work (i.e. gas flow rates of less than 300 ml/min at 25 °C) the lower sensitivity limit of the whole titration system is about 100 ppmv \( \text{H}_2\text{S} \). Thus, during acceptation, the titration data indicate practically zero cumulative amount of \( \text{H}_2\text{S} \) until point B is reached. At this point, the outlet concentration of \( \text{H}_2\text{S} \) is about 100 ppmv.

Because it is easy to observe in the continuous titration data, the outlet concentration of 100 ppmv \( \text{H}_2\text{S} \) was chosen as the breakthrough concentration (or breakthrough point). Comparison of this value with the various values listed in Table 1.3. indicates that this is low enough for desulfurization of fuel gas in the coal gasification/combined-cycle power plants, supposedly the most important application of high temperature desulfurization.

The breakthrough capacity \( \bar{q}_b \) of the acceptor was calculated from the breakthrough time \( t_b \) and the inlet flow rate of \( \text{H}_2\text{S} \), \( \tan a \), using the formula:

\[
\bar{q}_b = \frac{t_b \cdot \tan a}{w}
\]

where \( w \) is the weight of acceptor in the reactor. It should be understood that the quantities \( t_b \), \( t_c \), and \( t_r \) shown in Fig. 3.3. are "true" values (i.e. they have been corrected for the various dead times of the system). The sulfur load of the acceptor at the end of the acceptation stage \( q_c \) is:

\[
q_c = \frac{t_c \cdot \tan a - U}{w}
\]

where \( U \) is the cumulative amount of \( \text{H}_2\text{S} \) found in the reactor off gas during the cycle. During regeneration, the sulfur released by the acceptor produced the regeneration (or elution) curve DE. The percentage of completion of regeneration is:

\[
% - \text{reg} = \frac{R}{t_c \cdot \tan a - U}
\]

where \( R \) is the amount of sulfur recovered from the acceptor by the regeneration. These calculations were routinely carried out by a computer programme which treated the raw data stored in the computer. In addition, the programme also computed the conversions (or degree of utilization) of the active component of the acceptor (i.e. manganese or iron) at breakthrough and at the end of acceptation stage, and the slope of the cumulative breakthrough as well as elution curve.

3.3. Acceptor preparation and characterization.

3.3.1. Materials

The characteristics of supports used in this study are listed in Table 3.1. Nearly all experiments were carried out with acceptors containing standard \( \gamma\text{-Al}_2\text{O}_3 \) as support. The other carriers were only used in several comparative tests. The aluminas, silica gel, and silica-alumina were supplied by Ketjen Catalyst Department of Akzo Chemie Nederland BV. The pure MgAl\(_2\)O\(_4\) spinel sample was received from De Korte (5) who described its method of preparation.

All solutions used to impregnate the supports were freshly made from analytical grade chemicals and distilled water.

3.3.2. Methods of acceptor preparation.

Most of the acceptors used were prepared via the wet impregnation route outlined in Fig. 3.4. 15 g of support ma-
Table 3.1. Support characteristics.

<table>
<thead>
<tr>
<th>Support</th>
<th>Surface area, $m^2/g$</th>
<th>Pore volume, ml/g</th>
<th>Analytical data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard $\gamma$-$Al_2O_3$</td>
<td>263</td>
<td>0.67</td>
<td>SiO$_2$ 0.76 %w</td>
</tr>
<tr>
<td>(Alumina 001 - 1.5E)</td>
<td></td>
<td></td>
<td>Na$_2$O 0.05 %w</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4$ 1.6 %w</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe 0.02 %w</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cl 0.02 %w</td>
</tr>
<tr>
<td>High purity $\gamma$-$Al_2O_3$</td>
<td>167</td>
<td>0.52</td>
<td>SiO$_2$ 1.31 %w</td>
</tr>
<tr>
<td>(Alumina 000 - 1/10&quot;E)</td>
<td></td>
<td></td>
<td>Na$_2$O 0.24 %w</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4$ 1.4 %w</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fe 0.03 %w</td>
</tr>
<tr>
<td>High porosity $\gamma$-$Al_2O_3$</td>
<td>262</td>
<td>1.09</td>
<td>SiO$_2$ 5.4 %w</td>
</tr>
<tr>
<td>(Alumina 001 - 5P)</td>
<td></td>
<td></td>
<td>Na$_2$O 0.05 %w</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO$_4$ 1.12 %w</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al 0.20 %w</td>
</tr>
<tr>
<td>Silicagel AT23</td>
<td>385</td>
<td>0.90</td>
<td>Na 0.03 %w</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ca 0.09 %w</td>
</tr>
<tr>
<td>Silica-alumina</td>
<td>400</td>
<td>0.56</td>
<td>Al$_2$O$_3$ 13 %w</td>
</tr>
<tr>
<td>(Low alumina grade, LA - 100 - 3P)</td>
<td></td>
<td></td>
<td>Na$_2$O 0.1 %w</td>
</tr>
<tr>
<td>Synthetic MgAl$_2$O$_4$</td>
<td>136</td>
<td>0.4</td>
<td>SO$_4$ 1.0 %w</td>
</tr>
</tbody>
</table>
|                                |                       |                   | Fe 0.03 %w                | 5-6 hr drying
|                                |                       |                   | room temperature drying   |
|                                |                       |                   | drying/precalcination     |
|                                |                       |                   | reductive calcination     |
|                                |                       |                   | acceptor                  |

Fig. 3.4. The wet impregnation method of acceptor preparation.

Material was soaked in 50 ml aqueous solution of the salt of the desired metal for 16-17 hours. After filtration the impregnated support was dried by leaving it on the Buchner funnel with suction for 5-6 hours. When salts of an organic acid were used as impregnant the dried acceptor was precalcined in air, because direct reductive calcination resulted in black acceptors due to carbon deposition. However, as was found late in the investigation, this precalcination step is not fully effective in completely removing carbon from the acceptor (cf. chapter 4, page 61).

When the supported oxide was that of manganese or iron, the acceptor was oxidized to some extent as soon as it
came into contact with air, even at room temperature. In the case of manganese-containing acceptors this phenomenon was readily observed because it was accompanied by a colour change of the acceptors from cream or green (reduced state) to brown (oxidized state).

Two acceptors, $\text{MgAl}_2\text{O}_4$-supported manganese and iron aluminates, were prepared by the dry impregnation route. The $\text{MgAl}_2\text{O}_4$ support was titrated to incipient wetness with a saturated solution of nitrates of aluminum and manganese/iron ($\text{Me : Al} = 1 : 2$, Me = Mn or Fe) and left at room temperature until it appeared dry. Further drying and reduction of this acceptor was done in the same way as the acceptors prepared by wet impregnation (see Fig. 3.4.).

A sample of $\text{MnAl}_2\text{O}_4$ spinel was prepared as follows. A mixture of $\text{Mn(NO}_3\text{)}_2\cdot 4\text{H}_2\text{O}$ and $\text{Al(NO}_3\text{)}_3\cdot 9\text{H}_2\text{O}$ (molar ratio 1 : 2) was heated slowly to 300 °C in a nitrogen atmosphere. During this heating the mixture first melted and then decomposed. After evolution of nitrogen oxides was complete, the black solid residue obtained was heated under a stream of $\text{H}_2$ to 1000 °C and kept at this temperature for about 7 hours. The structure of the resulting spinel was determined by X-ray diffraction.

### 3.3.3. Analysis and characterization of acceptors

Six analytical techniques were used to characterize acceptors: atomic absorption spectroscopy, X-ray diffraction, diffuse reflectance spectroscopy, Mössbauer spectroscopy, Electron Spectroscopy for Chemical Analysis (ESCA), and surface area measurements.

The active metal content of the acceptors was determined by atomic absorption spectroscopy (AAS). For this purpose, 200 mg acceptor sample was dissolved in 15 ml aqua regia at 80 °C and then diluted with water to a concentration range suitable for the determination of the desired metal.

X-ray diffraction was applied to determine the structure of the acceptors, using the Guinier-de Wolff method with CuKa radiation. One acceptor sample was heated to 600 °C under a stream of 5% v $\text{H}_2$ in nitrogen and kept at this temperature for about 15 hours. The diffraction pattern of this sample was recorded by a Guinier-Lenne camera. The radiation used was also CuKa.

Diffuse reflectance spectroscopy was used to determine the site occupied by Mn$^{2+}$ ion in manganese-based acceptors. The instrument used to obtain the spectra was a Beckman DK-2 spectrophotometer. The standard white material used was $\text{BaSO}_4$. Because the sample should be in its reduced state during measurement, care was taken to avoid contact with air, which would result in its immediate oxidation. To that end, the special sample holder of Fig. 3.5 was constructed. This sample holder, which fits the sample chamber of the Beckman DK-2 spectrophotometer, allows the acceptor sample to be reduced and then isolated from air for the measurement.
measurement of its reflectance spectrum. The sample was reduced at 500°C for 1.5 hours. During this treatment, a \( \text{H}_2 \) stream was passed through the sample. Subsequently the quartz part of the cell was dipped into a Muller oven while the pyrex part was kept cool by a stream of cold air.

The BET technique using \( \text{N}_2 \) as adsorbate was applied to measure the surface area of the acceptors. Prior to measurement, the sample was evacuated down to 1 \( \times \) 10\(^{-5} \) mmHg and heated up to 400°C. Electron Spectroscopy for Chemical Analysis (ESCA) and Mössbauer spectroscopy were used to measure, respectively, the surface chemical composition of the acceptors and the valence of iron in the iron-based acceptors.

References.

APPENDIX A

Since the iron sulfate water vapour generator mentioned in section 3.2.1. is an accurate system for producing a gas stream containing low, constant concentrations of water vapour (which is usually difficult in laboratory work), some details about the generator are given here.

The dew point of the gas leaving the iron sulfate bed is related to bath temperature by a linear relation (1):

\[
T_d = 1.134 T_b - 11.6
\]

where:
- \( T_d \) = dew point of the outgoing gas, °C.
- \( T_b \) = bath temperature, °C (10 - 50 °C).

The standard error of each coefficient in eq. (A1) is 0.6 % (/). Thus, the volume fraction of water vapour in the outgoing gas is:

\[
y = \frac{P_{H_2O}}{P_{tot}}
\]

in which \( P_{H_2O} \) is the vapour pressure of water at \( T_d \), \( P_{tot} \) is the total pressure at the end of the bed. If the volumetric flow rate \( \phi_v \) of the dry gas passed through the iron sulfate bed is known, the volumetric flow rate \( \phi_{vw} \) of the water vapour

\[
\phi_{vw} = \frac{\gamma \phi_v}{1 - \gamma \phi_v}
\]

in which \( \gamma \) is the relative humidity of the outgoing gas.

The design of the iron sulfate bed used in this work follows that of Parkinson and Day (/) who recently invented and developed this technique. The diameter of the bed is 33 mm.
and the gas residence time is 70 s. During the calibration
tests done in this work, the constancy of the humidity of the
outgoing gas was established by monitoring its dew point with
a continuous dew point meter. A few gravimetric measurements
of the water vapour content of the gas leaving the bed (by
absorbing the water vapour with magnesium perchlorate and
weighing) confirmed the result of Parkinson and Day (1) that
the overall accuracy of this technique (including the accu­
cracy of the gas flow) is 2.5 %. Depletion tests indicated
that the iron sulfate should be replaced by a fresh charge
when half of the bed has been converted to FeSO$_4$.4H$_2$O, which
can be seen from the white colour of the tetrahydrate. If
higher conversions are allowed the water vapour content of
the bed effluent is no longer constant. The FeSO$_4$.7H$_2$O used
in this work was of analytical grade.

A water vapour generator based on this technique
and Parkinson and Day's design has been introduced on the
market recently by Analytical Development Corp.

Reference.

CHAPTER 4
ACCEPTOR PERFORMANCE IN RELATION TO ITS COMPOSITION AND
STRUCTURE

4.1. Introduction

It has pointed out in chapter 1 that the objectives
of the present work are, among others,
- to study the relation between the method of preparation and
the properties of MnO on γ-Al$_2$O$_3$ acceptors, especially the
desulfurization and steam-regeneration performance.
- to investigate whether other metal oxides can behave like
manganese oxide when supported on γ-Al$_2$O$_3$.
- to test and compare the desulfurization and regeneration
performance of various acceptors and to select the best in
terms of its sulfur removal capacity and regenerability.

This chapter deals with these objectives. It presents and dis­
cusses the results of comparative tests on the desulfurization
and regeneration behaviour of a number of acceptors containing
manganese or other transition metal oxides, as well as the re­
lation between acceptor behaviour, composition, structure, and
method of preparation.

4.2. Desulfurization-regeneration test.

4.2.1. Experimental.

4.2.1.1. Acceptors.

The acceptors subjected to the comparative test are
listed in Table 4.1. With the exception of acceptor # 7
(MnAl$_2$O$_4$), they were prepared via the wet impregnation tech­
nique described in section 3.3.2.; therefore only preparation
conditions specific to each acceptor are shown in the table.
The last column, which indicates whether in an actual process
cycle an acceptor can be considered "technically regenerable"
Table 4.1. Characteristics of acceptors subjected to comparative desulfurization-regeneration tests.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Support</th>
<th>Me</th>
<th>%w</th>
<th>Colour</th>
<th>Preparation conditions</th>
<th>Technical regenerability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>st. Al₂O₃</td>
<td>Mn</td>
<td>7.9</td>
<td>green</td>
<td>1 x 2.0 N Y</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>ditto</td>
<td>Mn</td>
<td>8.0</td>
<td>cream</td>
<td>4 x 0.5 N Y</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>ditto</td>
<td>Mn</td>
<td>10.1</td>
<td>pale green</td>
<td>4 x 0.7 N N</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>ditto</td>
<td>Mn</td>
<td>7.2</td>
<td>cream</td>
<td>3 x 0.5 S Y</td>
<td>Yes</td>
</tr>
<tr>
<td>5</td>
<td>ditto</td>
<td>Mn</td>
<td>7.6</td>
<td>cream</td>
<td>1 x 2.0 A Y</td>
<td>Yes</td>
</tr>
<tr>
<td>6</td>
<td>ditto</td>
<td>Mn</td>
<td>13.0</td>
<td>cream</td>
<td>1 x 4.0 N Y</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td>MnAl₂O₄</td>
<td>Mn</td>
<td>27.6</td>
<td>cream</td>
<td>* N Y</td>
<td>Yes</td>
</tr>
<tr>
<td>8</td>
<td>SiO₂</td>
<td>Mn</td>
<td>8.0</td>
<td>white</td>
<td>1 x 1.5 A Y</td>
<td>No</td>
</tr>
<tr>
<td>9</td>
<td>SiO₂</td>
<td>Mn</td>
<td>6.9</td>
<td>green</td>
<td>1 x 1.5 N Y</td>
<td>No</td>
</tr>
<tr>
<td>10</td>
<td>SiO₂, Al₂O₃</td>
<td>Mn</td>
<td>4.9</td>
<td>white</td>
<td>1 x 0.8 A Y</td>
<td>No</td>
</tr>
<tr>
<td>11</td>
<td>st. Al₂O₃</td>
<td>Mn</td>
<td>6.1</td>
<td>cream</td>
<td>1 x 1.5 A Y</td>
<td>Yes</td>
</tr>
<tr>
<td>12</td>
<td>ditto</td>
<td>Mn</td>
<td>4.4</td>
<td>cream</td>
<td>1 x 1.0 A Y</td>
<td>Yes</td>
</tr>
<tr>
<td>13</td>
<td>ditto</td>
<td>Mn</td>
<td>2.7</td>
<td>cream</td>
<td>1 x 0.5 A Y</td>
<td>Yes</td>
</tr>
<tr>
<td>14</td>
<td>ditto</td>
<td>Mn</td>
<td>12.2</td>
<td>pale green</td>
<td>2 x 1.5 A N</td>
<td>No</td>
</tr>
<tr>
<td>15</td>
<td>po. Al₂O₃</td>
<td>Mn</td>
<td>8.7</td>
<td>cream</td>
<td>1 x 1.5 A Y</td>
<td>Yes</td>
</tr>
<tr>
<td>16</td>
<td>ditto</td>
<td>Mn</td>
<td>10.4</td>
<td>cream</td>
<td>1 x 2.0 A Y</td>
<td>Yes</td>
</tr>
<tr>
<td>17</td>
<td>pu. Al₂O₃</td>
<td>Mn</td>
<td>5.1</td>
<td>cream</td>
<td>1 x 1.2 A N</td>
<td>No</td>
</tr>
<tr>
<td>18</td>
<td>ditto</td>
<td>Mn</td>
<td>12.3</td>
<td>green</td>
<td>1 x 2.0 A Y</td>
<td>Yes</td>
</tr>
<tr>
<td>19</td>
<td>si. Al₂O₃</td>
<td>Mn</td>
<td>7.2</td>
<td>cream</td>
<td>1 x 2.0 A Y</td>
<td>Yes</td>
</tr>
<tr>
<td>20</td>
<td>st. Al₂O₃</td>
<td>Zn</td>
<td>8.7</td>
<td>white</td>
<td>1 x 1.2 A Y</td>
<td>Yes</td>
</tr>
<tr>
<td>21</td>
<td>ditto</td>
<td>Ni</td>
<td>4.2</td>
<td>turquoise</td>
<td>1 x 0.5 A Y</td>
<td>No</td>
</tr>
<tr>
<td>22</td>
<td>ditto</td>
<td>Co</td>
<td>3.2</td>
<td>deep blue</td>
<td>1 x 0.5 A Y</td>
<td>Yes</td>
</tr>
<tr>
<td>23</td>
<td>ditto</td>
<td>Fe</td>
<td>4.7</td>
<td>grey-green</td>
<td>1 x 1.0 0 Y</td>
<td>Yes</td>
</tr>
<tr>
<td>24</td>
<td>ditto</td>
<td>Fe</td>
<td>6.3</td>
<td>grey-green</td>
<td>2 x 1.0 0 Y</td>
<td>Yes</td>
</tr>
</tbody>
</table>

\*st = standard, po = high porosity, pu = high purity, si = high silica. For support characteristics see Table 3.1.  
†Active metal. The colour of Mn-acceptors is only observable in reduced condition.  
‡Code : number of impregnations x molarity of solution, followed by the type of salt used (Acetate, Nitrate, S= sulfate, O=ammonium iron(III) oxalate). For further detail see Fig. 3.4. The atmosphere of calcination for acceptors containing Zn, Ni, and Co was air instead of hydrogen.  
§This acceptor was reductively calcined at 1000 C for 1 hr.  
¶See section 3.3.2. for the procedure of preparation.

or not, is included to provide a complete overview of acceptor characteristics; actually it is one of the conclusions drawn from the results of the test to be described.

Acceptors #1 to 10 were used to study the effect of preparation methods on the behaviour of various manganese-containing sorbents, acceptors #11 to 13 to investigate the nature of Al₂O₃ support and the general effect of the impregnated manganese oxide, and acceptors #20 to 24 to investigate the desulfurization-regeneration performance of other transition metal oxides.

4.2.1.2. Test procedure.

The H₂S acceptance-regeneration performance of the acceptor was tested at 600 °C in the manually-operated fixed bed bench-scale unit (cf. section 3.2.). In each test 3 g acceptor of size 0.4 - 0.6 mm was used. During acceptance, a gas mixture of 1.2 % H₂S, 11 % H₂, and 87.8 % N₂ was passed through the acceptor bed at a flow rate of 100 Nml/min. Seven minutes after the concentration of H₂S in the bed effluent had reached about 100 ppm the acceptance was stopped. The breakthrough capacity of the acceptor, Qᵇ, (cf. section 3.2.5.), and the breakthrough conversion of the transition metal, αₑ,b, were the principal data gathered.

The sulfur loaded acceptor was then regenerated with a gas stream consisting of steam and nitrogen + hydrogen (H₂ : N₂ = 8 : 1). This regeneration was divided into three stages:
- 13 min with a steam flow rate of 15.7 Nml/min (steam content of regenerating gas = 17 %)
- 13 min with a steam flow rate of 313 Nml/min (steam content = 78 %)

H/ml/min = normal milliliter per minute, i.e. the flow rate at 25 °C and 100 kPa.
- "drying" under the \( \text{N}_2 + \text{H}_2 \) stream until \( \text{H}_2\text{S} \) could no longer be detected by the titration unit (usually within an hour). The degree of completion of regeneration at the end of this stage, \( \%\text{-reg.} \), was then recorded.

The total amount of steam injected in the regeneration was much larger (50 - 200 x) than the total amount of sulfur in the acceptor. Thus, it is reasonable to consider an acceptor which is not completely regenerated by this procedure as being "technically irregenerable".

In the test, acceptors #7, 8, and 10 were found to have zero breakthrough capacity. Therefore, an alternative procedure to test the regenerability of these acceptors was adopted. The acceptation stage was prolonged to sulfide the acceptor until it contained 1 %w sulfur. It was then regenerated using the above procedure.

### 4.2.2. Results and discussion.

#### 4.2.2.1. Relation between preparation method and acceptor behaviour.

The results of the test on acceptors #1 to 10 are presented in Table 4.2. It shows that acceptor #1, prepared via a single impregnation of \( \gamma\text{-Al}_2\text{O}_3 \) with a concentrated manganese nitrate solution, is irregenerable. Calcination at higher temperatures can induce regenerability to this type of sorbent but at the cost of a marked loss in desulfurization capacity, as exemplified by the performance of acceptor #6. The latter was calcined at 1000 °C, a temperature at which even a macroscopic mixture of MnO and \( \gamma\text{-Al}_2\text{O}_3 \) reacts sufficiently rapidly to form bulk MnAl\(_2\)O\(_4\) spinel(\(^{1/1}\)).

By contrast, the technique of repeated impregnation with a dilute solution can produce regenerable acceptors having moderate sulfur removal capacities. A comparison of the performance of acceptors #2 and 3, however, indicates that even if an acceptor is prepared using a suitable technique, it will be regenerable only if its manganese content is not higher than, say, 9 %w. More data and discussion on this latter topic will be presented in paragraph 4.2.2.3.

### Table 4.2. Desulfurization capacity and steam-regenerability of various acceptor containing manganese.

| Acceptor | Support | Impregnation method | \( \%\text{w-Mn} \) | \( \%\text{w-S} \) | \( \%\text{Mn},b \) | \%-reg.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \gamma\text{-Al}_2\text{O}_3 )</td>
<td>1 x 2.0</td>
<td>N</td>
<td>7.9</td>
<td>3.8</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>ditto</td>
<td>4 x 0.5</td>
<td>N</td>
<td>8.0</td>
<td>1.5</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>ditto</td>
<td>4 x 0.7</td>
<td>N</td>
<td>10.1</td>
<td>3.0</td>
<td>51</td>
</tr>
<tr>
<td>4</td>
<td>ditto</td>
<td>3 x 0.5</td>
<td>S</td>
<td>7.2</td>
<td>1.0</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>ditto</td>
<td>1 x 2.0</td>
<td>A</td>
<td>7.6</td>
<td>1.6</td>
<td>34</td>
</tr>
<tr>
<td>6</td>
<td>ditto</td>
<td>1 x 4.0</td>
<td>Mn(^2)</td>
<td>13.0</td>
<td>0.5</td>
<td>7</td>
</tr>
<tr>
<td>7</td>
<td>MnAl(_2)O(_4)</td>
<td>-</td>
<td>27.6</td>
<td>0</td>
<td>0</td>
<td>100(^{\dagger})</td>
</tr>
<tr>
<td>8</td>
<td>( \text{SiO}_2 )</td>
<td>1 x 1.5</td>
<td>A</td>
<td>8.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>( \text{SiO}_2 )</td>
<td>1 x 1.5</td>
<td>N</td>
<td>6.9</td>
<td>2.9</td>
<td>73</td>
</tr>
<tr>
<td>10</td>
<td>( \text{SiO}_2\cdot\text{Al}_2\text{O}_3 )</td>
<td>1 x 0.8</td>
<td>A</td>
<td>4.9</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^{\dagger}\)see the footnote of Table 4.1.

\(^{\dagger}\)asductively calcined at 1000 °C for 1 hr.

Repeated impregnation using dilute manganese sulfate solutions was used extensively by Van der Linde\(^{2}\) to produce regenerable sulfur removal acceptors containing up to 8 %w-Mn; acceptor #4 is an example. Note that Van der Linde found that single impregnations with concentrated manganese sulfate solutions produced acceptors having low reactivities and capacities.

Although it is a useful technique for preparing steam-regenerable acceptors, the repeated impregnation method is time consuming and costly. In this connection, the performance of acceptor #5 shows that the use of manganese acetate is advantageous : a steam-regenerable acceptor can be obtained by a single impregnation with a concentrated solution. Consequently, acetate solutions were used to prepare most of the
acceptors studied in this work. The extreme instability of ferrous acetate solution, however, prevented it to be used conveniently to prepare similar iron-containing acceptors. Ammonium iron(III) oxalate solutions gave satisfactory results and were used instead.

It has been stated in section 2.4.3. that data from the literature\(^{3,4}\) indicate acceptors prepared by impregnating \(\gamma\)-Al\(_2\)O\(_3\) with a concentrated solution of manganese nitrate to exhibit a poor degree of dispersion. In such acceptors all the manganese in excess of 4 \(\text{wt\%}\) exists as clusters of MnO. Because MnO reacts irreversibly with H\(_2\)S, as has been shown thermodynamically in section 2.3.3. and proved experimentally by Van der Linde\(^{2}\), it follows that MnO causes this type of sorbent to be insufficiently regenerable. It explains why acceptor \#1, derived from a concentrated manganese nitrate solution, cannot be regenerated completely.

Several investigators\(^{2,5,6}\) have reported that the technique of repeated impregnation with dilute solutions will result in a fine dispersion of active component on the surface of the support. Consequently, acceptors \#2, 3, and 4 may be considered to consist of finely dispersed MnO on the surface of \(\gamma\)-Al\(_2\)O\(_3\). An explanation of the fact that these acceptors are relatively easy to regenerate has been presented in section 2.4.3.: this fact was ascribed to the formation of surface MnAl\(_2\)O\(_4\) spinel as a result of the reaction of the finely dispersed MnO and \(\gamma\)-Al\(_2\)O\(_3\). Two observations presented in sections 4.1. and 4.2. respectively, provide a strong indication that this proposition is a sound one:

- The colour of the regenerable acceptors is similar to that of MnAl\(_2\)O\(_4\) (indicating a similar environment around the divalent manganese ion), and
- MnAl\(_2\)O\(_4\) itself reacts reversibly with H\(_2\)S.

As can be seen from the data in Table 4.2., however, bulk MnAl\(_2\)O\(_4\) has a lower reactivity towards H\(_2\)S than surface spinel (i.e. both are regenerable but surface spinel has a breakthrough capacity whereas bulk spinel does not). This might be due to the following factors:

- The MnAl\(_2\)O\(_4\) sample has a relatively low surface area. This is inferred from the observation that the bulk density of the MnAl\(_2\)O\(_4\) sample was about four times that of \(\gamma\)-Al\(_2\)O\(_3\) of similar particle size.
- The structure of bulk MnAl\(_2\)O\(_4\) is more ordered than that of surface MnAl\(_2\)O\(_4\). This is because the latter is, firstly, a surface compound and, secondly, formed on \(\gamma\)-Al\(_2\)O\(_3\), which is a defective spinel.

Of these two factors, the second one was judged to be more probable, because an acceptor deactivation study (see section 5.2. and Fig. 5.4.) showed that the main cause of acceptor deactivation is the recrystallization of the surface spinel to form a bulk-aluminate-like structure, whereas the acceptor itself still has a high surface area.

Since the acceptor derived from impregnation of \(\gamma\)-Al\(_2\)O\(_3\) with a manganese acetate solution is easily regenerable, it follows that impregnation of \(\gamma\)-Al\(_2\)O\(_3\) with manganese acetate solution also results in a fine dispersion of MnO which then reacts with the support to yield surface MnAl\(_2\)O\(_4\) spinel. This conclusion is strengthened further by the results presented in section 4.3. dealing with acceptor characterization.

Performance data of acceptors using silica or silica-alumina as support (see Table 4.2.) show that these are technically irregenerable. There is, however, a significant difference in reactivity between silica-supported acceptors derived from nitrate and from acetate. To explain this difference in behaviour, one can assume that impregnation with a manganese nitrate solution, also in the case of silica, results in clusters of MnO on the surface and that impregnation with manganese acetate again produces fine dispersion of MnO. As silica and silica-alumina are acidic supports\(^{7}\) and since MnO is a really basic oxide\(^{8}\), it is to be expected that these supports reduce the reactivity of MnO towards H\(_2\)S. The extent of this reduction is small for acceptor \#9, which contains free MnO, and large for acceptors \#8 and \#10, to the extent that the latter two acceptors have a negligible breakthrough capacity.
4.2.2.2. The effect of manganese content on the capacity of regenerable acceptors.

Table 4.3 presents the test results on acceptors \# 5 and 11 to 13, all of which were prepared by impregnation of standard γ-Al₂O₃ with manganese acetate solutions of different concentrations. As was expected, the lower the manganese content the lower the breakthrough capacity of the acceptor. Interestingly, however, the breakthrough conversion of manganese is higher as the manganese content is lower. This may indicate that an acceptor with a lower manganese content is more reactive towards H₂S. A more detailed explanation of this observation can be found in chapter 6.

4.2.2.3. Influence of the nature of the alumina.

Table 4.4 summarizes the results of tests on various acceptors using several types of γ-Al₂O₃ as supports. In general, no significant differences in behaviour were found between acceptors prepared with different types of γ-Al₂O₃. The results listed, however, strengthen the supposition of paragraph 4.2.2.1. that there exists a certain maximum content of manganese above which the acceptor cannot be regenerated completely. From the performance data of acceptors \# 15 and 16, which use high porosity γ-Al₂O₃ (SBET = 260 m²/g) as support, this upper limit of manganese content is estimated to be between 3.3 and 4.0 \%w-Mn per 100 m² support surface. In this connection, the results obtained by Friedman et.al.9 from an extensive study on the interaction of cupric ions with γ-Al₂O₃ supports are of interest. These authors concluded that a number of transition γ-aluminas appear to have a similar threshold loading for the appearance of crystalline cupric oxide of about 4 \%w-Cu/100 m² support surface. If this figure for Cu is converted to that for Mn by simply using the atomic mass ratio (55/63.5), the result is 3.5 \%w-Mn/100 m², a value in agreement with the threshold loading of manganese found in the present work.

If it is assumed that the deposition of manganese on the surface of alumina occurs via an exchange reaction:

\[
\text{Mn}^{2+} + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Mn}^{4+} + 2\text{H}^+ \quad (1)
\]
one can make a rough estimate of the threshold loading of manganese from the knowledge of the total number of hydroxyl groups which completely covers the alumina surface. It is known\(^ {10,11}\) that on a completely covered surface each hydroxyl group occupies \(8 \times 10^{-20}\) \(\text{m}^2\). Thus, there are \(12.5 \times 10^{-20}\) \(\text{OH}\) groups per 100 \(\text{m}^2\) of completely covered surface. The results of Peri's classical simulation work\(^ {12}\) indicate that only two-thirds of these hydroxyl groups can be removed (by heating) without disturbing local order (i.e. causing defect formation). If it is analogously assumed that only two-thirds of the hydrogen atoms of the hydroxyl groups can be replaced by reaction (1) without causing surface reorganization, then the threshold loading of manganese is \(0.5 \times (2/3) \times 12.5 \times 10^{-20}\) \(\text{Mn}\) ions per 100 \(\text{m}^2\) or \(3.5 \text{wt-Mn}\) per 100 \(\text{m}^2\) of support surface, a value which nicely matches the experimental one given above.

It should be emphasized that the model is somewhat speculative in nature in that it involves the above assumption.

4.2.2.4. The behaviour of acceptors based on other transition metals.

The performance of various acceptors containing different active metals is compared in Table 4.5. The regenerability of acceptors containing Mn and Fe and the irregenerability of Ni-containing acceptor are in agreement with the prediction based on the bulk thermodynamic properties of the corresponding aluminate spinels as discussed in section 2.3.3.

Zinc and cobalt behave like manganese and iron in the sense that they also form regenerable acceptors. Strohmeier and Hercules\(^ {13}\) recently reported that surface \(\text{ZnAl}_2\text{O}_4\) spinel has a low reactivity towards sulfidation. Anderson et al.\(^ {14}\) reported that the breakthrough conversion of zinc in their acceptor (75.9 % \(\text{ZnAl}_2\text{O}_4\), 24.1 % \(\text{Al}_2\text{O}_3\)) is about 15 % when tested at 760 °C. The performance of the zinc-based acceptor studied in the present work (i.e. acceptor # 20) is in general agreement with these literature data.

Comparison of the performance of the regenerable acceptors listed in Table 4.5. leads to the conclusion that acceptors based on manganese or iron are superior to those based on zinc and cobalt. Zinc-based acceptors are rather unreactive towards \(\text{H}_2\text{S}\) and the cobalt-based acceptor is undoubtedly more expensive than those based on manganese or iron; it did not offer any compensation, e.g. in the form of a much higher capacity. Consequently, only acceptors based on manganese and iron were studied in more detail in the present work.

4.3. Acceptor characterization.

4.3.1. General.

In paragraph 4.2.2.1., variations in the degree of dispersion of \(\text{MnO}\) have been postulated to explain the differences in behaviour of \(\text{MnO}\) on \(\gamma\)-\(\text{Al}_2\text{O}_3\) acceptors containing less than 9 %wt-Mn. Irregenerable acceptors are described as containing poorly dispersed clusters of \(\text{MnO}\) whereas the regenerable ones are considered to contain finely dispersed \(\text{Mn}\) in the form of the reaction product with the \(\gamma\)-\(\text{Al}_2\text{O}_3\), i.e. a surface \(\text{MnAl}_2\text{O}_4\) spinel. In order to confirm this proposition, se-
veral MnO on γ-Al₂O₃ acceptors were characterized by X-ray diffraction analysis and diffuse reflectance spectroscopy. Furthermore, a Mössbauer spectroscopic study of regenerable acceptors containing iron was carried out to gain an understanding of the behaviour of iron in such a material. Results are reported below.

4.3.2. X-ray diffraction analysis.

The X-ray diffraction (XRD) patterns of fresh manganese-containing acceptors are shown in Fig. 4.1 together with the XRD pattern of the γ-Al₂O₃ support. The latter gives broad, diffuse diffraction lines (Fig. 4.1.B) indicating poor crystallinity. The XRD patterns of regenerable acceptors (Fig. 4.1.C and D) are virtually identical to the γ-Al₂O₃ pattern. This is interpreted as an indication that the manganese in such acceptors is too highly dispersed to cause any noticeable change in the alumina structure. On the other hand, the XRD pattern of an irregenerable acceptor (Fig. 4.1.E) shows several sharp diffraction lines in addition to the diffuse pattern. They were identified as the characteristic diffraction lines of MnO. This confirms the supposition that the irregenerable acceptor contains poorly dispersed clusters of manganese monoxide (MnO).

In an attempt to characterize the property of the acceptor at process conditions, an X-ray diffraction analysis was also carried out on acceptor # 5 at 600 °C under a stream of 5 % H₂ in nitrogen. No change in the XRD pattern, as compared to that of Fig. 4.1.D, was observed. Therefore, it was concluded that the XRD patterns obtained at room temperature (and in air) represent the true character of the acceptor under process conditions.

4.3.3. Diffuse reflectance spectroscopy.

Diffuse reflectance (DR) spectra of a number of acceptors were obtained using a Beckman DK2 spectrophotometer. The sample pretreatment for this measurement has been described in section 3.3.3.

The DR spectra of several acceptor samples are shown in Fig. 4.2 together with the spectra of MnO (octahedral Mn²⁺), MnAl₂O₄ (tetrahedral Mn²⁺), and γ-Al₂O₃. The spectrum of γ-Al₂O₃ is almost flat and does not contain any noticeable peak. This means that the peaks appearing in the spectra of acceptor samples are attributable to manganese compounds.

The of MnO shows a large absorption peak with a maximum at about 620 nm. This peak is also present in the spectra of acceptors # 1 and 3 which are irregenerable but absent in the spectra of regenerable acceptors (# 2 and 4). Because the result of X-ray diffraction analysis presented in the preceding section shows that acceptors # 2 and 4 do not contain MnO and that acceptor # 1 does contain this oxide, it is reasonable to consider this peak as the characteristic peak of MnO (or octahedral Mn²⁺). This is in line with the observation that acceptor # 3 (10.1 %w-Mn) has a smaller "MnO peak" than acceptor # 1 (7.9 %w-Mn), i.e. the former contain less free MnO than the latter. Accordingly, acceptor # 3 should be easier
to regenerate; inspection of performance data listed in Table 4.2. indicates that this is so. This points to the conclusion that the relative size of the absorption peak with a maximum at 620 nm is a measure of acceptor regenerability: the smaller the peak, the easier the regeneration.

Fresh regenerable acceptors made by repeated impregnation with different salts seem to show a slight variation in surface composition (or structure). This is exemplified by the slightly different spectra of acceptors #2 and 4; the former is derived from nitrate and the latter from sulfate. Their use in an acceptation-regeneration process tends to smooth this variation: as shown in Fig. 4.3., the DR spectra of acceptors used in 5 acceptation-regeneration cycles have become completely similar.

The DR spectra of regenerable acceptors derived from acetates show a similar absence of the "MnO peak"; Fig. 4.4(c) gives an example of them. It was observed, however, that this type of acceptor gives considerably less reflectance than acceptors derived from nitrate or sulfate (this observation was made by comparing the absolute reflectance values of the spectra produced). Because it was suspected that this was due to traces of carbon not completely removed by the reductive calcination procedure, several samples of an acetate-derived acceptor were calcined in air at 600 °C for 16 hours. The acceptation-regeneration performance of the acceptors was not affected by this treatment but their reflectance was improved.
considerably. Moreover, the DR spectra of the acceptors so treated almost completely resemble that of MnAl$_2$O$_4$ and, therefore, provide a strong indication that the active component of regenerable acceptors, at least those derived from acetate, is surface MnAl$_2$O$_4$ spinel (or tetrahedral Mn$^{2+}$). Fig. 4.4(b) gives an example of the DR spectra of acetate-derived acceptors that have been treated in the manner described.

4.3.4. Mössbauer spectroscopy.

4.3.4.1. Introduction.

In contrast to the preceding paragraphs, this one does not deal with manganese-containing acceptors but with those based on iron. The reason is that manganese is, unfortunately, not a Mössbauer-active element, in contrast to iron. The iron-containing acceptors studied, however, show desulfurization-regeneration behaviour comparable to a manganese containing acceptor with a similar metal content. Acceptation-regeneration experiments on these Fe-containing acceptors are discussed in the next chapter.

4.3.4.2. Experimental.

Mössbauer spectroscopy was used to study the behaviour of iron during the various stages of preparation of a regenerable acceptor containing 3.6 wt.-Fe. It was prepared via impregnation of standard γ-Al$_2$O$_3$ with an 0.5 M solution of ferrous sulfate. In the study, uncalcined sample of dry, impregnated γ-Al$_2$O$_3$ was placed in a reactor fitted to the Mössbauer spectrometer, reductively calcined and, after cooling to room temperature, exposed to air. The Mössbauer spectra were taken from the sample before and after the reduction as well as after exposure to air. The reduction was accomplished at 600 °C for about 6 hours using a flow of 150 nml/min hydrogen, humidified by passing it through a water-filled washing-flask. The reactor-spectrometer system has been described in detail by Niemantsverdriet (15). All spectra were obtained using a constant acceleration spectrometer with a 57-Co in Rh source at room temperature. The spectra were not corrected for the varying distance between source and detector. Hence, the curved background in the spectra to be presented is of instrumental origin.

In addition, Mössbauer spectra were also taken from a number of acceptors prepared by impregnation of various aluminas with a 1.0 M solution of ammonium iron(III) oxalate.

4.3.4.3. Method of interpretation.

To obtain the Mössbauer parameters (isomer shift, quadrupole splitting, line width, and spectral area), each spectrum was modelled by a combination of subspectra consisting of Lorentzian-shaped lines and a parabola accounting the curved background. The parameters and the coefficients of the parabola were then determined by fitting the model to the spectrum using an iterative non-linear minimization routine. In the case of spectral doublets, the line widths and the absorption areas of the two peaks were considered to be equal. Isomer shifts (I.S.) are reported relative to the NBS standard sodium nitroprusside (SNP) at room temperature.

4.3.4.4. Results and discussion.

The spectra of the uncalcined, reduced, and air-exposed forms of the sulfate-derived acceptor are shown in Fig. 4.5. The spectrum of the uncalcined material only shows an electric quadrupole doublet of a Fe$^{3+}$ compound; there is no indication of the presence of Fe$^{2+}$. Reduction with humid H$_2$ drastically changes this doublet. It follows from the values of isomer shift (I.S.) as well as quadrupole splitting.

The results presented were obtained in cooperation with Dr. A.M. van den Kraan, Intenuniversity Reactor Institute, Delft, who also contributed to the interpretation of the data. This substantial contribution is gratefully acknowledged.
Table 4.6. The isomer shift (I.S.), quadrupole splitting (Q.S.) and spectral contribution corresponding to the spectra in Fig. 4.5.

<table>
<thead>
<tr>
<th>Sample form</th>
<th>I.S. Fe$^{3+}$ (mm/s)</th>
<th>Q.S. Fe$^{3+}$ (mm/s)</th>
<th>%</th>
<th>I.S. Fe$^{2+}$ (mm/s)</th>
<th>Q.S. Fe$^{2+}$ (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncalkined</td>
<td>0.64</td>
<td>0.75</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
| reduced     | -                     | -                     | 0  | 1.39                  | 2.25                  | 60
| air exposed | 0.62                  | 0.94                  | 70  | 1.24                  | 1.97                  | 30

Fig. 4.5. Mössbauer spectra of a regenerable acceptor during the various stages of its preparation.

In order to get some idea about the dispersion of the iron (in the trivalent as well as the divalent state) on the alumina support, measurements were done on the air-exposed sample at 295, 77, and 4.2 K. The spectra obtained are shown in Fig. 4.6. and the corresponding Mössbauer parameters given in Table 4.7. Although the shape of the spectra remain the same, a diffuse, broadened background superimposed upon the Fe$^{2+}$ and Fe$^{3+}$ quadrupole splittings was observed at 4.2 K (see Fig. 4.6.). This broadened background was neglected in the computer analysis of the spectrum to yield the parameters in Table 4.7.

It follows from Table 4.7. that the ratio of spectral contributions of Fe$^{2+}$ and Fe$^{3+}$ is almost constant with temperature. The appearance of the diffuse broadened background instead of a well resolved sextuplet (which may still be broadened due to a distribution of particle size) indicates that the iron ions are highly dispersed on the alumina support. Furthermore, the spectrum of the reduced sample, which shows an asymmetrical quadrupole splitting, was found to be identical with the spectrum of coal slags after gasification. It is likely that the asymmetry of the doublet is due to the occurrence of different environments of Fe$^{2+}$, such as is found in amorphous iron silicates. The indication that the system contains highly dispersed iron ions and the similarity of its spectra with those of coal slags may mean that the iron ions are built-in into the alumina support. However, in contrast to the slags samples, the iron ions are so near to the surface that they can react with hydrogen and oxygen, as follows from Fig. 4.5.
The observed behaviour of iron in the acceptor can be explained by assuming that the iron is present in the reduced sample in the form of surface FeAl\textsubscript{2}O\textsubscript{4} spinel. The grey green colour of the reduced acceptor is an additional observation that support this assumption. Moreover, this also explains why the iron ions built-in into the alumina support can still be reached by reactants such as H\textsubscript{2} or O\textsubscript{2}. It is likely that the thermodynamic properties of surface spinel do not differ appreciably from those of bulk FeAl\textsubscript{2}O\textsubscript{4} spinel. Using thermodynamic data for the bulk spinel tabulated in the literature\cite{18} it is found that the reaction:

\begin{equation}
\text{FeAl}_{2}\text{O}_4(s) + \text{H}_2(g) = \text{Fe}(s) + \gamma\text{Al}_{2}\text{O}_3(s) + \text{H}_2\text{O}(g) \tag{2}
\end{equation}

has \(\Delta G^o\) values of +68 to +48 kJ/mol at 25 to 800 °C. Thus, reduction of FeAl\textsubscript{2}O\textsubscript{4} to metallic iron is impossible. This is in line with the observation from the Mössbauer spectrum that at a reduction temperature of 600 °C the iron stays in the divalent state and cannot be reduced to metal.

Thermodynamic calculation also shows that the reaction:

\begin{equation}
4(\text{s}) + \frac{1}{6}\text{O}_2(g) = \frac{1}{3}\text{Fe}_{3}\text{O}_4(s) + \gamma\text{Al}_{2}\text{O}_3(s) \tag{3}
\end{equation}

has \(\Delta G^o\) values of -40 to -16 kJ/mol at 25 to 900 °C, which indicates that even bulk FeAl\textsubscript{2}O\textsubscript{4} is thermodynamically unstable in air. The tendency of the surface spinel to oxidize in air must be quite high because of its highly dispersed nature. This is the explanation of the observation that the reduced sample is oxidized on exposure to air. The results further show that the percentage ratio of divalent to trivalent iron in the air exposed sample (Table 4.6.) agrees nicely with that in FeO\textsubscript{3} (Fe\textsuperscript{2+}Fe\textsuperscript{3+}O\textsubscript{4}). Thus, it can be concluded that the assumption of surface spinel formation provides a rational explanation for the behaviour of regenerable acceptors containing iron.

Finally, Fig. 4.7. presents the spectra of various iron-based acceptors prepared by impregnation of aluminas with...
Fig. 4.7. Mössbauer spectra of air-exposed samples of iron on various \( \gamma\)-Al\(_2\)O\(_3\).

- a. 4.7 \( \% \) Fe on standard \( \gamma\)-Al\(_2\)O\(_3\) (acceptor # 23)
- b. 4.5 \( \% \) Fe on high purity \( \gamma\)-Al\(_2\)O\(_3\)
- c. 6.2 \( \% \) Fe on high porosity \( \gamma\)-Al\(_2\)O\(_3\)
- d. 6.7 \( \% \) Fe on high silica \( \gamma\)-Al\(_2\)O\(_3\)
- e. 5.9 \( \% \) Fe on high silica \( \gamma\)-Al\(_2\)O\(_3\)

1.0 M solution of ammonium iron(III) oxalate. The spectra were taken from air-exposed samples. The corresponding Mössbauer parameters are given in Table 4.8. It follows from the similarity of the spectra in Fig. 4.7. and the Mössbauer parameters in Table 4.8. that the type of \( \gamma\)-Al\(_2\)O\(_3\) used as support does not have a significant influence on the behaviour of the dispersed iron, provided that the acceptors are prepared in a similar manner. Furthermore, comparison of the spectra in Fig. 4.7. with that of an air-exposed sample in Fig. 4.5. indicates that only minor differences in behaviour exist between the sulfate-derived and the oxalate-derived acceptors studied here.

4.4. Conclusions.

Based on the experimental results and the discussion presented in the foregoing sections, the following conclusions are drawn:

### Table 4.8. Mössbauer parameters derived from the spectra of Fig. 4.7.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>I.S. Fe(^{3+})</th>
<th>Q.S. Fe(^{3+})</th>
<th>%</th>
<th>I.S. Fe(^{2+})</th>
<th>Q.S. Fe(^{2+})</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7 ( % ) Fe on standard ( \gamma)-Al(_2)O(_3)</td>
<td>0.59</td>
<td>0.98</td>
<td>58</td>
<td>1.22</td>
<td>1.89</td>
<td>42</td>
</tr>
<tr>
<td>4.5 ( % ) Fe on high purity ( \gamma)-Al(_2)O(_3)</td>
<td>0.58</td>
<td>0.94</td>
<td>40</td>
<td>1.23</td>
<td>1.80</td>
<td>60</td>
</tr>
<tr>
<td>6.2 ( % ) Fe on high porosity ( \gamma)-Al(_2)O(_3)</td>
<td>0.62</td>
<td>1.03</td>
<td>46</td>
<td>1.22</td>
<td>1.85</td>
<td>54</td>
</tr>
<tr>
<td>6.7 ( % ) Fe on high silica ( \gamma)-Al(_2)O(_3)</td>
<td>0.62</td>
<td>1.03</td>
<td>60</td>
<td>1.24</td>
<td>2.00</td>
<td>40</td>
</tr>
<tr>
<td>5.9 ( % ) Fe on high silica ( \gamma)-Al(_2)O(_3)</td>
<td>0.62</td>
<td>0.98</td>
<td>62</td>
<td>1.22</td>
<td>2.02</td>
<td>38</td>
</tr>
</tbody>
</table>
1. There are two types of manganese oxide on γ-Al₂O₃ acceptors. The first consists of clusters of MnO on the surface of the support, whereas the second is composed of finely dispersed MnO which interacts strongly with the γ-Al₂O₃, forming surface MnAlO₂₄ spinel.

2. Of these two types of manganese-based acceptors only the second type, i.e. acceptors containing highly dispersed manganese, can be used as an acceptor in cyclic steam-regenerative, high temperature removal of H₂S. An efficient way to prepare this acceptor is by wet impregnation of γ-Al₂O₃ with a concentrated solution of manganese acetate.

3. The surface of γ-Al₂O₃ appears to have a maximum capacity of about 3.5 wt-Mn/100 m² to accommodate the manganese in the form of surface MnAlO₂₄ spinel.

4. Zinc, iron, and cobalt behave similarly to manganese in the sense that they also form steam-regenerable acceptors when dispersed on γ-Al₂O₃. However, only iron shows comparable performance to manganese and therefore merits of further investigation.

5. Visual observation, desulfurization-regeneration tests and Mössbauer spectroscopy provide sufficient indication that the iron in a steam-regenerable acceptor is bound by the γ-Al₂O₃ as surface FeAlO₂₄, similar to manganese-containing acceptors.

6. No significant differences in the behaviour of manganese or iron containing acceptors were found to result from the use of different types of γ-Al₂O₃. Supports with high surface area are preferred (cf. conclusion 3).

References.


CHAPTER 5
THE INFLUENCE OF PROCESS VARIABLES ON ACCEPTOR PERFORMANCE

5.1. Introduction.

This chapter presents and discusses the results of a study on the influence of the most important process variables, such as temperature and feed gas composition, on the sulfur breakthrough capacity of the acceptors. The investigation was carried out on steam-regenerable acceptors applied in the fixed-bed experimental unit described in chapter 3. General information concerning the condition under which the data were obtained are given in section 5.2. The presentation of the experimental results themselves begins in section 5.3, dealing with acceptor deactivation. The effect of various process variables on the performance of stable acceptors is then discussed in sections 5.4 to 5.8. Finally, section 5.9 summarizes the main points of this chapter.

5.2. Experimental.

The experimental procedure of the cyclic regenerative process and the associated method of data interpretation has been described in sections 3.2.4 and 3.2.5. Unless otherwise noted at appropriate places in this chapter, the experimental conditions are as follows:

- The reactor contained 3 g acceptor of 0.33 mm mean particle size (0.25 - 0.42 mm sieve fraction). The length of the reactor bed corresponding to this amount of acceptor was usually about 65 mm. As has been stated in chapter 3, the reactor diameter was 9 mm.
- The feed rate during acceptation was 100 ml/min (25 °C), consisting of 1 %v H₂S, 10 %v H₂, and 89 %v N₂. When the feed had to contain other gaseous components (e.g. H₂O, CO), the flow of N₂ was reduced to keep the total flow rate constant.
- The regenerating gas consisted of 35 % H₂O, 58 % N₂, and 7 % H₂; it was fed at a rate of 150 ml/min. The regeneration was carried out until the titration unit downstream of the acceptor bed did not detect any more sulfur.

5.3. Acceptor deactivation.

When fresh acceptor were applied in the cyclic regenerative process investigated, stable performance could only be obtained after an initial period of deactivation. During this period, the sulfur removal capacity of the acceptor decreases with time. As shown in Fig. 5.1, the deactivation process practically ceased after 4 - 5 days at 600 °C. Beyond this period the acceptor exhibited a stable performance with breakthrough capacity somewhat less than 50 % of the initial value. After being applied for about three months in the cyclic process, the breakthrough capacity of the manganese- and iron-containing acceptors of Fig. 5.1 was about 0.75 and 0.45 %w-S, respectively. The acceptor based on manganese was somewhat more stable than that based on iron. Note that during this three-month period the manganese- and iron-containing acceptors at 600 °C.

![Fig. 5.1. Deactivation of manganese- and iron-containing acceptors at 600 °C.](image-url)
iron-containing acceptors were subjected to some 260 and 150 cycles, respectively.

Further experiments and/or observations on the deactivation are as follows:

1. The deactivation was not caused by accumulation of unregenerated sulfur on the acceptor because a sulfur balance made on every cycle indicated complete regeneration (accuracy ± 3%), i.e. no unregenerated sulfur.

2. At 400 °C, the deactivation was negligibly slow. At this temperature, the breakthrough capacity of the fresh manganese-containing acceptor (from the same batch as the acceptor in Fig. 5.1.) decreased from 0.95 %w-S in the first cycle to 0.90 %w-S in the 51st cycle (about 3 weeks operation).

3. The deactivation at 600 °C could be imitated by simply keeping the acceptor under H₂-stream at 600 °C for about a week. When samples of fresh manganese-containing acceptor (again from the same batch as the acceptor in Fig. 5.1.) were treated in this way and subsequently subjected to a one-week test in the cyclic process, they showed a virtually constant breakthrough capacity of about 0.85 %w-S (cf. Fig. 5.1.)

From these observations it can be concluded that the principal process variable causing the deactivation is temperature.

Mechanism of deactivation. There are two conceptually probable mechanisms of the above deactivation:

a. Diffusion of the active component (Mn or Fe) into the bulk of the γ-Al₂O₃ support, making it less readily available for sulfur capture.

b. (Re)crystallization of the surface spinel and/or the γ-Al₂O₃ support forming clusters which are less reactive towards H₂S.

It has been pointed out in section 2.4.3. that cation diffusion in γ-Al₂O₃ is favoured because the structure of alumina contains many vacancies. If these vacancies are filled the diffusion will be prevented (or, at least, retarded).

Thus, one way to test if the diffusion of the active component is the main cause of acceptor deactivation is to replace γ-Al₂O₃ with a support having similar structure (i.e. spinel) but containing no or very few cation vacancies. Based on this consideration, the performance of fresh MgAl₂O₄-supported MnAl₂O₄ and FeAl₂O₄ acceptors was examined. The results are shown in Fig. 5.2, together with data on a MnO on γ-Al₂O₃ acceptor containing a comparable amount of Mn.

It is clear from Fig. 5.2 that the deactivation trends of MgAl₂O₄- and γ-Al₂O₃-supported acceptors are similar. These results suggest that diffusion of an active component into the bulk of the support is not the (main) mechanism of deactivation because, if it were, the deactivation of the acceptor using MgAl₂O₄ as support should be far slower than that of acceptors based on γ-Al₂O₃.

![Fig. 5.2. Deactivation of manganese- and iron-containing acceptors at 600 °C.](image-url)
To verify the supposition that recrystallization of the surface spinel and/or the γ-Al₂O₃ support is responsible for the deactivation of the acceptors, the fresh and the deactivated forms of the acceptors of Fig. 5.1 were subjected to three measurements:

- BET surface area
- surface composition by Electron Spectroscopy for Chemical Analysis (ESCA)
- X-ray diffraction

The results of surface area measurements are shown in Table 5.1.

**Table 5.1. BET surface area of fresh and deactivated acceptors.**

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Surface area, m²/g.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
</tr>
<tr>
<td>8.1 %w-Mn on γ-Al₂O₃</td>
<td>224</td>
</tr>
<tr>
<td>4.5 %w-Fe on γ-Al₂O₃</td>
<td>237</td>
</tr>
</tbody>
</table>

The surface area of the deactivated acceptors is about 60% of that of the fresh ones. This suggests that the decrease of the surface area may be the cause of the deactivation of the acceptor, the more so because the percentage decrease in acceptor capacity is of the same order of magnitude as the decrease of the surface area.

The ESCA spectra of fresh and deactivated manganese containing acceptors were quite similar, also with regard to the dimensions of manganese and aluminum peaks. This indicates that the surface composition of the acceptors remains unchanged during deactivation. It also strengthens the conclusion that diffusion of Mn into the bulk of the support is not the cause of deactivation. In that case, ESCA measurement would have shown the surface of the deactivated acceptor to contain less manganese than that of the fresh one. No ESCA measurements were done on iron-containing acceptors because these were expected to behave similarly.

The X-ray diffraction patterns of the fresh and the deactivated acceptors are shown in Fig. 5.3. The diffraction bands of the deactivated acceptors (Fig. 5.3b. and d) are more intense than those of fresh acceptors. This can be more clearly observed in Fig. 5.4, where the diffractograms of Mn-acceptors are compared with that of MnAl₂O₄. The peaks in the diffractogram of the deactivated acceptor are sharper than those of the fresh one; the growth of the peak around 2θ = 60° is very obvious. Furthermore, the center of the peaks of the deactivated acceptor have slightly shifted to a smaller diffraction angle relative to those of the fresh one and the diffractogram of the former resembles that of MnAl₂O₄. These facts all point to the recrystallization of surface spinel to form a bulk-aluminate-like structure.

**Fig. 5.3. X-ray diffraction patterns of fresh and deactivated acceptors.**
- a. 8.1 %w-Mn on γ-Al₂O₃ (fresh)
- b. 8.1 %w-Mn on γ-Al₂O₃ (deactivated)
- c. 4.5 %w-Fe on γ-Al₂O₃ (fresh)
- d. 4.5 %w-Fe on γ-Al₂O₃ (deactivated)
The above results of surface area measurements, ESCA, and X-ray diffraction are not in conflict with each other, for recrystallization of the surface spinel may not change the surface composition but can cause a decrease in surface area. Thus it can be concluded that the deactivation (i.e., the decrease in breakthrough capacity) of the acceptor is, at least partly, due to the recrystallization of the surface spinel.

5.4. Influence of temperature on acceptor capacity.

In this and in subsequent sections the results of an acceptor performance study at various process conditions will be presented. All the data of this part of the study were obtained with stable acceptors, i.e., acceptors which have passed the period of rapid deactivation at 600 °C.

The breakthrough capacity of some acceptors at various temperatures are shown in Fig. 5.5. Raising the temperature from 400 to 600 °C increases the capacity by a factor of two in the case of manganese-containing acceptors and three-fold in the case of iron-containing acceptor. The capacities of the acceptors containing 3.6 and 4.5 %w Fe are the same. This was taken to be an indication that the active ingredient of the acceptor containing a lower percentage of active metal is more reactive towards H₂S. A similar observation on manganese-based acceptors was presented in paragraph 4.2.2.2.

The explanation of the positive influence of temperature on the breakthrough capacity may be based on kinetics as well as on equilibrium consideration:

- **Kinetic consideration**: The rate coefficients of the intrinsic chemical reaction(s) and mass transport processes involved in the transfer of H₂S from the gas to the reactive sites on the acceptor will, as a rule, become larger at higher temperature. Thus, raising the temperature increases the rate of H₂S capture.

- **Equilibrium consideration**: The thermodynamics of bulk spinels (cf. section 2.3.3.) show that sulfidation becomes more...
favourable at higher temperature. As it is likely that the behaviour of the surface spinel will be similar to that of the bulk material, the equilibrium capacity for \( \text{H}_2\text{S} \) of the surface spinel (i.e. acceptor) can be expected to increase with temperature.

5.5. Dependence of acceptor capacity on \( \text{H}_2\text{S} \) concentration.

Performance data of manganese- and iron-containing acceptors in treating feed gases of different \( \text{H}_2\text{S} \) concentrations are shown in Fig. 5.6. Except in the case of iron-based acceptor at 400 °C, acceptor capacity becomes somewhat lower as the \( \text{H}_2\text{S} \) concentration of the treated gas increases. In other words, the capacity has a weakly negative dependence on \( \text{H}_2\text{S} \) concentration in the feed.

It is important to realize that the investigation was carried out under the conditions of constant total feed rate and constant amount of acceptor in the reactor (cf. section 5.2.). Thus, the results shown in Fig. 5.6. also imply that the breakthrough time decreases strongly with \( \text{H}_2\text{S} \) concentration of the feed; doubling the feed concentration will reduce the breakthrough time by a factor larger than two. Modelling studies (cf. chapter 6) indicate that the breakthrough capacity is the net effect of two types of \( \text{H}_2\text{S} \)-consuming processes occurring in the acceptor bed. The first is a fast, instantaneously equilibrating reaction; its contribution to breakthrough capacity is, of course, independent of breakthrough time. The second is a slow process. The weakly negative dependence of breakthrough capacity on feed concentration is due to the decreased contribution of this processes to the breakthrough capacity because, as the breakthrough time becomes shorter, it has less chance (time) to proceed.

5.6. Influence of water content of feed gas.

The importance of examining the influence of water (vapour) on acceptor capacity becomes obvious if one recalls that:
- most industrial gaseous streams to be desulfurized contain some water.
- water (i.e. steam) is the regenerating agent of the acceptor studied here.

The dependence of acceptor capacity on the water content of the feed is shown in Figs. 5.7. to 5.9.. To make the interpretation easier, the capacity is expressed by a relative scale, using the breakthrough capacity at zero water content as a reference. As can be seen from the figures, water strongly decreases acceptor capacity. Its influence is strongest in the relatively dilute region; the presence of 1 %v of water in the feed reduces the acceptor capacity by about 30 - 40 %; at 2 %v water content the capacity reduction is about 40 - 50 %.
Gas chromatographic analysis of the reactor effluent indicated a net production of water during H$_2$S acceptation; roughly one mole of H$_2$O being released by the acceptor for each mole of H$_2$S captured. This phenomenon was also observed when the acceptation was carried out with a water-free feed gas and a dry acceptor, i.e. experiments in which gas chromatographic analysis of the bed effluent indicated the absence of water prior to feeding H$_2$S containing gas to the reactor.

From the above results, it is concluded that the main mechanism of the acceptation and/or regeneration process is a reversible H$_2$S-H$_2$O exchange reaction between the acceptor and the gas phase. The simplest conceivable representation of this exchange reaction is:

$$H_2S(g) + MeO/\gamma-Al_2O_3(s) \rightleftharpoons MeS/\gamma-Al_2O_3(s) + H_2O(g)$$

\(Me = Mn, Fe\)
The fact that water strongly reduces the acceptor capacity indicates that the values of the equilibrium constant of this exchange reaction are approximately unity in the temperature range investigated. In agreement with the point of view maintained so far, this result also indicates that it is better to describe the active component of the acceptor as a surface spinel than as a dispersed pure oxide because the sulfidation equilibrium constant of the spinel is around unity whereas that of pure oxide is greater than 100 (cf. section 2.3.3.).

5.7. Influence of hydrogen and carbon oxides.

It has been pointed out in the previous chapters that the largest potential application of high temperature desulfurization is in the field of processing of coal gasification products. As carbon oxides and hydrogen are the key components of these gases, it is obvious that knowledge of their influence on acceptor capacity is required.

In section 3.2.4., it has been pointed out that the feed gas used in the present work invariably contained 7% v H$_2$ or more. This was done because, at lower hydrogen contents, noticeable decomposition of H$_2$S to sulfur and hydrogen may occur. Further experiments using feeds consisting of H$_2$S, N$_2$, and 7-90% v H$_2$ showed that in this concentration range hydrogen did not have a direct influence on the sulfur breakthrough capacity of the acceptor.

The influence of carbon oxides on the performance of the acceptor is shown in Fig. 5.10. The range of carbon oxides content examined reflects those usually found in coal gasifier effluents (cf. Table 1.1.). The presence of carbon monoxide in the feed gas produced a favourable effect, i.e. it increases acceptor capacity. This positive influence was, however, only observed at higher temperatures. At or below 400°C in the case of acceptors based on iron, and at or below 500°C in the case of manganese-containing acceptors, no improvement in performance due to the presence of carbon monoxide was found.

An obvious explanation for the positive effect of carbon monoxide on acceptor performance is that this compound consumes the water produced by the acceptation process via the well-known shift reaction:

$$\text{CO}(g) + \frac{1}{2}\text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$$
The disappearance of water increases the driving force of the \( \text{H}_2\text{S} \) acceptation; accordingly, the acceptor captures more sulfur. This is reflected in the observed increase of acceptor capacity.

The formation of \( \text{CO}_2 \) by the shift reaction was verified by gas chromatographic analysis. Measurements of the composition of gases leaving the manganese-based acceptor bed at 600 °C indicated that the shift reaction almost reached equilibrium. The equilibrium constant calculated from the experimental results is 2.3, which is very close to the literature value of 2.65 (at 600 °C) (1).

Based on the fact that \( \text{CO}_2 \) increases acceptor capacity by consuming water via the shift reaction, it is easy to predict that \( \text{CO}_2 \) will act in the reverse way, i.e. it decreases the acceptor capacity. Also, the higher the hydrogen content the more negative the influence of \( \text{CO}_2 \) on acceptor performance. Some tests with an iron-based acceptor verified that such is indeed the case (cf. Fig. 5.10).

The results of the previous section show that the presence of water in the feed gas strongly decreases acceptor capacity whereas those of this section show that carbon monoxide increases acceptor capacity by removing the water produced by the acceptation reaction. Results of experiments carried out to examine acceptor performance when the feed gas simultaneously contains \( \text{H}_2\text{O} \) and \( \text{CO} \) are shown in Fig. 5.11.

It follows from this figure that the adverse effect caused by a small amount of water normally present in most industrial gaseous streams can be eliminated, or at least minimized, if the gas contains a substantial amount of \( \text{CO} \). This increases the potential usefulness of the acceptor for high temperature desulfurization of coal gasifier effluent, because the gas produced by modern gasification processes usually contains a small amount of water but substantial amounts of carbon monoxide (2). (See also Table 1.1.)

The widely accepted mechanism of shift reaction on chromia-promoted iron oxide catalyst (high temperature shift catalyst (3,4)) is:

\[
\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3 \text{FeO} + \text{CO}_2
\]

\[
3 \text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2
\]

The applicability of this mechanism to the iron-containing acceptor studied here is questionable as it requires the presence of \( \text{Fe}_3\text{O}_4 \), in which two-thirds of the iron is in a valence state of three, whereas Mössbauer spectroscopy (cf. section 4.3.) show that the acceptor kept in a humid hydrogen contains only \( \text{Fe}^{2+} \). A similar mechanism is even more unlikely in the case of manganese, which is not a shift catalyst (5).

A possible mechanistic explanation of the shift reaction on the acceptors is through the formation and decomposition of surface formate complex:

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{HCOOH(ads)} \rightarrow \text{CO}_2 + \text{H}_2
\]

This mechanism was proposed some twelve years ago by Van Herwijnen (6) to explain the shift reaction on a copper/zinc oxide catalyst. Recently, Amenomiya (7-9) found that \( \gamma\text{-Al}_2\text{O}_3 \)
catalyses the CO-shift reaction at 400-600 °C and, using in-situ infra red spectroscopy, showed that the reaction proceeds via the formation and decomposition of surface formate complex given above. He also pointed out that the reaction is too slow at 400 °C and that at the temperature range studied, the rate determining step of the reaction is the decomposition of the formate complex. As γ-Al₂O₃ is the support of the acceptors of the present work, it is clear that this mechanism may explain the shift reaction on the acceptors.

5.8. Application.

It follows from the results presented in the foregoing sections that, if the acceptor studied here is used to desulfurize coal gasifier effluents, it is better to operate the purification unit at the higher end of the temperature range examined, i.e. 600 °C. The advantages gained from operation at this level of temperature are:

- the required cooling and reheating system, e.g. when the purified gas is to be burnt in a combined cycle unit, will be simpler and the overall thermal efficiency of the plant will be higher.
- acceptor capacity is higher because, firstly, the temperature is high and, secondly, the negative influence of water vapor will be more than compensated by the presence of a substantial amount of carbon monoxide. This will result in either a smaller reactor or a longer cycle time.

On the other hand, for applications in petrochemical or petroleum refining industries, it is better to use the acceptor at 400 °C. This will have the advantages that side reactions, such as hydrocarbon cracking, are less likely to occur and that fresh acceptors can be used without prior deactivation. Moreover, in these industries, most processes in which desulfurization with solid acceptors may be applied do not operate at temperatures above 500 °C. The gas to be desulfurizes should contain no more than a trace amount of water if the capacity of the acceptor is to be reasonably high.

5.9. Summary.

The results presented in this chapter show that when fresh acceptors are applied to desulfurize gases in a cyclic process, stable performance is obtained after an initial period of deactivation. The deactivation is affected only by operating temperature, being negligibly slow at 400 °C and becoming faster as the temperature is higher. The main cause of deactivation presumably is recrystallization of surface spinel resulting in a decrease of reactivity and/or loss of surface area.

The breakthrough capacity of the acceptor doubles when the temperature is increased from 400 to 600 °C. This improvement in capacity is not only due to more favourable kinetics but also to the shifting of equilibrium position towards a more favourable one. Acceptor capacity is only slightly affected by H₂S concentration, being somewhat lower at higher concentrations. On the other hand, the capacity of the acceptor is adversely affected by the presence of water vapor in the feed gas, which is a logical consequence of the fact that the acceptor is regenerable with steam. This negative influence of water can, however, be compensated if the feed gas contains carbon monoxide, because the latter consumes water via the well-known shift reaction.

References.

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CHAPTER 6

MODELLING

6.1. Introduction.

In contrast to chapters 4 and 5, which deal with breakthrough capacities, structure and composition of the acceptors, this chapter considers the breakthrough curves. Specifically, it presents the results of preliminary work aimed at a quantitative description of breakthrough behaviour of the acceptor and an attempt to extract appropriate process parameters. Due to its preliminary nature, the work considers only manganese-containing acceptors in the acceptation phase of the process. The study of the regeneration stage and the qualitatively similar behaviour of iron-containing acceptors should be subjects of subsequent work.

In section 6.2., various phenomena occurring during the acceptation of $\text{H}_2\text{S}$ are derived from the features of the breakthrough and elution curves of $\text{H}_2\text{S}$ and $\text{H}_2\text{O}$, respectively. Section 6.3. deals with some fundamental aspects of fixed-bed sorption theory which forms the basis of the modelling study. A simple model is then proposed in section 6.4. to describe the breakthrough behaviour of the acceptor under certain conditions. In section 6.5., a more general, unavoidably rather complicated model is formulated. The capability of this model is demonstrated through comparisons of simulation and experimental results. The difficulties of solving the model equations and in estimating the parameters are also discussed. Section 6.6. shows how the presence of carbon monoxide in the feed gas affects the composition of the reactor effluent. The chapter ends with section 6.7. which contains suggestions for subsequent modelling studies.

The conditions under which breakthrough/elution curves were obtained during routine acceptation-regeneration are described in section 3.2. dealing with the general experiment-
6.2. Experimental breakthrough and elution curves.

6.2.1. Acceptation stage.

Typical breakthrough and elution curves of, respectively, H$_2$S and H$_2$O obtained during acceptation are shown in Fig. 6.1. Prior to breakthrough time $t_b$, the reactor effluent contained very low, almost constant concentrations of H$_2$S, amounting to about 20 ppmv at 400 °C and 10 ppmv at 600 °C. When the feed gas concentration was raised to about 3 %v H$_2$O, these became 60 and 40 ppm, respectively. As the lowest feed concentration used in this work was 0.5 %v H$_2$S (5000 ppmv), this means that at least 99 % of the H$_2$S in the feed gas was removed by the acceptor. At breakthrough the concentration of H$_2$S in the reactor off-gas suddenly rose to 10-30 % of its inlet value. Thereafter, it increased at a much slower rate, resulting in breakthrough curves of the type shown in the figure. These observations apply to both fresh and deactivated acceptors. In other words, acceptor deactivation did not influence the shape of the breakthrough curves; it only caused the breakthrough time $t_b$ to become shorter.

The acceptor was found to release water in the acceptation stage. As can be seen from Fig. 6.1., the area below the water elution curve, which is a measure of the total amount of water eluted, is comparable to the area between the horizontal line (C/$C_{H_2S,0}$ = 1 and the H$_2$S breakthrough curve, i.e. a measure of the total amount of H$_2$S removed. This was interpreted as an indication that the principal reaction occurring in the reactor during the acceptation stage is an equimolar hydrogen sulfide-water exchange between the gas and the solid phase. As has been stated in section 5.6., the simplest conceivable representation of this exchange reaction is

$$H_2S(g) + MnO/γ-Al_2O_3(s) \rightarrow MnS/γ-Al_2O_3(s) + H_2O(g) \quad (1)$$

If this process is the only one occurring in the reactor, then it follows from the stoichiometry that:

$$C_{H_2S,0} + C_{H_2O,0} = C_{H_2S,\text{out}} + C_{H_2O,\text{out}}$$

or in the case of dry feed gas ($C_{H_2O,0} = 0$),

![Fig. 6.1. Typical breakthrough (elution) curves of H$_2$S (H$_2$O). The symbols of $C_{H_2S,0}$ and $C_{H_2O,0}$ denote the concentration of hydrogen sulfide and water in the feed, respectively.](image)
The desorption results in the appearance of water in the reactor effluent. The fact that the water concentration rises to values higher than the inlet concentration of \( \text{H}_2\text{S} \) strongly supports the supposition that the desorption occurs via the two mechanisms indicated above. If water is to desorb freely, i.e., without the displacement effect due to \( \text{H}_2\text{S} \) adsorption, then it should follow from a heuristic reasoning that, if the feed gas is dry, the concentration of water in the reactor effluent will never be higher than the inlet concentration of \( \text{H}_2\text{S} \).

Another feature of the curve shown in Fig. 6.1. is of importance in the development of phenomenological models of acceptation. Even at times sufficiently long after the breakthrough point \( (\tau_b) \), the concentrations of \( \text{H}_2\text{S} \) and \( \text{H}_2\text{O} \) in the reactor effluent have not yet reached their inlet values. As the experimental data show, the approach to these end concentrations is remarkably slow. Two different interpretations are:

1. The acceptor surface contains only one type of oxygen-sulfur exchange site, the final exhaustion of which proceeds much more slowly than the initial reaction.
2. There exist two types of oxygen-sulfur exchange site, one of which is much more reactive than the other.

The former interpretation is used in section 6.4., the latter in section 6.5.

6.2.2. Regeneration.

Two mechanisms of \( \text{H}_2\text{S} \) removal from the gas phase by the acceptor have been postulated in the above discussion: exchange reaction and adsorption. Because the regeneration of chemically reacted sulfur requires a specific regenerant (i.e., steam) whereas that of adsorbed \( \text{H}_2\text{S} \) does not, it is clear that the elution curves of both types of sulfur can be obtained separately by first flushing the saturated acceptor bed with a dry inert gas (e.g., \( \text{N}_2 + \text{H}_2 \)) to elute the adsorbed \( \text{H}_2\text{S} \), and subsequently treating the bed with a steam-containing gaseous stream to regenerate the chemically bound sulfur. Fig. 6.2.
The desorption of the rest of the \( \text{H}_2\text{S} \) is difficult.

The area below the elution curve in Fig. 6.2b. is much larger than that in Fig. 6.2a., indicating that the total amount of sulfur bound chemically is appreciably larger than the total amount of sulfur adsorbed. This strengthens the assumption made earlier that sulfur-oxygen exchange reaction(s) is (are) the principal process occurring during acceptance (and thus also during regeneration).

6.2.3. Influence of physical transport processes.

The breakthrough and elution curves shown in Figs. 6.1. and 6.2., and also those presented in sections 6.4. and 6.5., were obtained from experiments using a total feed rate of about 100 ml/min (STP) and acceptor particle sizes between 0.25 and 0.42 mm (average size 0.33 mm). Some experiments carried out at 600 °C using acceptors with particle sizes of 0.60 - 0.85 mm (average size 0.72 mm) showed that neither the form of the breakthrough and elution curves nor the breakthrough capacity of the acceptor were influenced by the particle size. This result was interpreted as an indication that the global rates of acceptance and regeneration were not limited by pore diffusion. This conclusion is based on the expectation that, if pore diffusion is the limiting step, the breakthrough capacity will be significantly influenced by particle size, larger particle having smaller capacity.

The area below the elution curve in Fig. 6.2b. is much larger than that in Fig. 6.2a., indicating that the total amount of sulfur bound chemically is appreciably larger than the total amount of sulfur adsorbed. This strengthens the assumption made earlier that sulfur-oxygen exchange reaction(s) is (are) the principal process occurring during acceptance (and thus also during regeneration).

Further experiments using beds of different length (5 - 15 cm) and total flow rates up to 300 ml/min showed the absence of influence of these physical variables on the acceptance-regeneration processes. Based on these results and the rule of thumb that pore diffusion is usually slower than external mass transfer(1,2), it was concluded that the experimental data obtained were free of mass transfer limitations.

6.3. Fundamentals of isothermal fixed-bed sorption theory.

The theory of fixed-bed sorption processes has been reviewed recently by Rodrigues(3-5) and others(6,7); for de-
tailed information the reader is referred to these authors. This section will only treat those aspects of the theory which are of decisive importance to the modelling study in sections 6.4. and 6.5..

6.3.1. Continuity equations.

For a radially uniform cylindrical fixed-bed sorber, the flux $N_i$ of the $i$-th sorbable component in axial direction is the sum of a bulk convective term and an axial dispersion term:

$$N_i = v C_i + D_a \frac{\partial C_i}{\partial z} \tag{4}$$

where $v$ is the interstitial gas velocity ($m/s$), $D_a$ the axial dispersion coefficient ($m^2/s$), $C_i$ the concentration of the $i$-th sorbable component ($mol/m^3$), and $z$ the axial distance from the inlet of the bed ($m$). A mass balance of the $i$-th sorbable component over a volume element $dV = A_d dz$, where $A_d$ is the cross-sectional area of the bed ($m^2$), gives:

$$\left. \epsilon \frac{\partial N_i}{\partial z} \right|_z = \left. \epsilon \frac{\partial N_i}{\partial z} \right|_{z + dz} + 2 C_i \frac{\partial c}{\partial t} \Delta z + 3 \frac{\partial q_i}{\partial t} \Delta z \tag{5}$$

where $c$ is the void fraction of the bed (dimensionless), $t$ time ($s$), and $q_i$ the concentration of the $i$-th component in the solid phase ($mol/m^3$ of bed); $q_i = \rho_i \cdot q_i$, where $\rho_i$ is the bulk density of the acceptor ($kg/m^3$) and $q_i$ the amount of $i$-th component adsorbed per unit mass of acceptor ($mol/kg$). By taking the limit as $\Delta z \to 0$ and assuming that $v$ and $D_a$ are constants, the above equation yields:

$$\frac{\partial C_i}{\partial t} + \frac{1}{c} \frac{\partial q_i}{\partial t} + v \frac{\partial C_i}{\partial z} = D_a \frac{\partial^2 C_i}{\partial z^2} \tag{6}$$

When $D_a = 0$ (no axial dispersion, that is, plug flow), eq.(6) reduces to:

$$\frac{\partial C_i}{\partial t} + \frac{1}{c} \frac{\partial q_i}{\partial t} + v \frac{\partial C_i}{\partial z} = 0 \tag{7}$$

A separate mass balance for the solid phase gives:

$$\frac{\partial q_i}{\partial t} = \frac{R_i}{\rho_i} \tag{8}$$

Conceptually, given an expression of $R_i$ in terms of $C_i$, $q_i$, and probably also $t$ and $z$, eq.(5) or eq.(6) can be solved to yield $C_i$ as a function of $t$ and $z$. Depending on the initial conditions imposed, the values of $C_i(t, z)|_{z=L}$, where $L$ is the length of the acceptor bed, represent the breakthrough or elution curve of the $i$-th component.

6.3.2. Rate of sorption.

Consider the simple reversible exchange reaction:

$$A(g) + MeB(s) = MeA(s) + B(g) \tag{9}$$

Reaction (1) conforms to this "generalized notations" ($A =$ sulfur, $Me =$ manganese, $B =$ oxygen). It is reasonable to assume that the intrinsic rate $-r_A$ of this reaction is:

$$-r_A = k_1 C_A (Q - q_A) - \frac{k_1}{K} C_B q_A \tag{10}$$

where $k_1$ is the forward rate constant ($m^3.mol^{-1}.s^{-1}$), $Q$ the stoichiometric capacity of the acceptor ($mol/m^3$ of bed), and $K$ the equilibrium constant (dimensionless):

$$K = \frac{C_B,eq q_A,eq}{C_A,eq (Q - q_A,eq)} \tag{11}$$

Here the subscript "eq" means "at equilibrium". The $C_B$'s in eqs. (9) and (10) are related to the $C_A$'s through the stoichiometry:
\[
C_B = C_{A_0} + C_{B_0} - C_A
\]  
\(11\)

in which \(C_{A_0}\) and \(C_{B_0}\) are the initial (or inlet) concentration of A and B, respectively.

If the sorption process is kinetically controlled, the global rate of sorption can be assumed to be equal to the intrinsic rate of the reaction. Thus,

\[
\frac{dA}{dt} = k_1 C_0 (Q - q_A) - \frac{k_1 C_B}{K} q_A
\]  
\(12\)

If, in addition, the reaction is fast (i.e. the forward reaction rate constant \(k_1\) is large) the process can be assumed to reach equilibrium instantaneously everywhere in the sorbent bed (cf. eq.(10)). In this case, the expression for the global rate of sorption takes the form:

\[
\frac{\Delta C}{\Delta t} = \left( \frac{q_{A_{eq}}}{3c_{A_{eq}}} \right) \frac{3c_A}{3t} \frac{c_{A_{eq}}}{c_A}
\]  
\(13\)

Physically, \(\frac{q_{A_{eq}}}{3c_{A_{eq}}}\) is the rate of change of equilibrium concentration of the solid phase with respect to the gas phase concentration. Geometrically, it is the slope of the isotherm, the expression of which can be derived from eq.(10). The analysis of the performance of a fixed-bed sorbent based on eq.(6), the plug flow continuity equation, coupled with the assumption that local equilibrium is established instantaneously at every point within the bed is called the local equilibrium theory of fixed-bed sorption. The remarkable usefulness of this theory stems from the fact that the form of the isotherm determines the basic form of the breakthrough/elution curve. Kinetic and physical transport effects merely cause the curve to become somewhat more diffuse. A prediction from the equilibrium theory can be refined by corrections for non-equilibrium effects, whereas a complex isotherm will produce basically new effects that cannot be accounted for by corrections or minor modifications(8). The modelling studies presented in sections 6.4. and 6.5. are, therefore, primarily based on the equilibrium theory.

6.3.3. Prediction of breakthrough/elution curves on the basis of equilibrium theory.

In this paragraph, the application of equilibrium theory to reaction (8) with equilibrium relation (10) will be presented in some detail, the objective being the following:

- to obtain a simple illustration of the rationale behind the solution of the more complicated model treated in sections 6.4. and 6.5.;
- to examine the validity of reaction (8), a major building block of the model postulated in section 6.5., by considering the breakthrough/elution curve resulting from it.

Isotherm. Substitution of eq.(11) into eq.(10) gives:

\[
K = \frac{(C_{A_0} + C_{B_0} - C_A)q_A}{C_A (Q - q_A)}
\]  
\(14\)

The subscript "eq" was left out of eq.(14) because this will not cause any ambiguity when dealing with equilibrium situations only. It is further assumed that the inlet concentration of B (i.e. water) is zero; \(C_{B_0} = 0\). By introducing dimensionless quantities,

\[
x = \frac{c_A}{C_{A_0}} \quad \text{and} \quad y = \frac{q_A}{Q}
\]  
\(15\)

eq.(14) can be written as:

\[
K = \frac{y(1 - x)}{x(1 - y)}
\]

which, when solved for \(y\), gives the isotherm equation:

\[
y = \frac{Kx}{1 + (K - 1)x}
\]  
\(16\)

Plots of this isotherm are shown in Fig. 6.3. for several values of \(K\). The plot is linear if \(K = 1\), convex when \(K > 1\), and concave if \(K < 1\). The slope \((dy/dx)\) of the isotherm is:

\[
\frac{dy}{dx} = \left(1 + (K - 1)x\right)^2
\]  
\(17\)
Initial conditions. The acceptation experiments of the present work were started by switching at $t = 0$ to a feed stream containing a constant $H_2S$ concentration, $C_A$, to pass through a completely regenerated acceptor bed ($q_A = 0$). This means that the initial condition is:

$$
\begin{align*}
\text{at } z = 0, & \quad C_A = \begin{cases} 0 & t < 0 \\ C_{A_0} & t > 0 \end{cases} \\
\text{or, in dimensionless form:} & \quad x = \begin{cases} 0 & \theta < 0 \\ 1 & \theta > 0 \end{cases}
\end{align*}
$$

where:

$$
\zeta = \frac{z}{L} ; \quad \theta = \frac{t}{L \alpha} ; \quad \alpha = \frac{V}{n L} C_{A_0}
$$

Here $L$ denotes the length of the acceptor bed (m), $\zeta$ is the dimensionless distance, $\theta$ the dimensionless time, and $\alpha$ the dimensionless stoichiometric capacity of the acceptor; the other quantities are as defined previously. Initial condition (18) implies that a step change of dimensionless concentration from 0 to 1 is applied (see sketch) at time zero ($\theta = 0$).

Breakthrough curves. From eqs. (6), (7), and (13) it follows that:

$$
\frac{\partial C_A}{\partial t} + \frac{1}{C_A} \left( \frac{\partial q_A}{\partial t} \right) \frac{\partial C_A}{\partial x} + \nu \frac{\partial C_A}{\partial \nu} = 0
$$

which, in terms of the dimensionless quantities $x$, $y$, $\theta$, $\zeta$, and $\alpha$ defined in (15a,b) and (19a,b,c) can be rewritten as:

$$
\left[ \frac{1}{\alpha} + y'(x) \right] \frac{\partial x}{\partial \nu} + \frac{\partial x}{\partial \zeta} = 0
$$

or:

$$
\frac{\partial x}{\partial \nu} - \frac{\partial x}{\partial \zeta} = \frac{1}{\alpha} + y'(x) \quad (20)
$$

Now, from differential calculus (9):

$$
\frac{dx}{d\nu} = \frac{\partial x}{\partial \nu} + \frac{\partial x}{\partial \zeta} \frac{d\zeta}{d\nu} \quad (21)
$$

When $dx = 0$ (that is, $x = \text{constant}$),

$$
\frac{d\zeta}{d\theta} = \frac{\partial x}{\partial \zeta} \quad (22)
$$

It follows from (20) and (22) that:

$$
\frac{d\zeta}{d\theta} = \frac{1}{\alpha} + y'(x) \quad (23)
$$

This relation is still general, i.e. it is still independent of the specific initial conditions and the isotherm. The initial conditions are required in the evaluation of the definite
integral which follows from (23):

\[
\int_0^x \frac{\theta \, d\theta}{\zeta} = \left[ \frac{1}{a} + y'(x) \right] \frac{\zeta}{0}
\]

where \( \theta_{x, \zeta=0} \) denotes the time \( \theta \) at which concentration \( x \) passes the inlet of the bed. As initial conditions (18) imply that \( \theta_{x, \zeta=0} = 0 \), integration straightforwardly results in:

\[
\theta = \left[ \frac{1}{a} + y'(x) \right] \zeta
\]

For exchange reaction (8), eq. (17) can be substituted for \( y'(x) \) in (25) to give, after rearrangement:

\[
x = \frac{\sqrt{K\zeta} - 1}{\{a - \frac{1}{a}\} a - 1}
\]

The equation of the breakthrough curve is obtained by setting \( \zeta = 1 \) (reactor outlet). Thus,

\[
x = \frac{\sqrt{K - 1}}{\{a - \frac{1}{a}\} a - 1}
\]

Plots of breakthrough curves for several values of \( K \) are shown in Fig. 6.4. In most cases, also in the present work, the value of the stoichiometric capacity is large \( (a > 1000) \). This means that in the region of practical interest, i.e. \( (0 \leq \frac{1}{a}) \) around unity, \( (0 - \frac{1}{a}) = 0 \).

As can be seen from Fig. 6.4a., for \( K < 1 \) (concave isotherms) the breakthrough curve takes the form of a dispersive front. The front steepens with increasing value of the equilibrium constant and when \( K \) is equal to unity (linear isotherm) it becomes a step change. The latter is the "best" form of breakthrough curve one can expect, because it means that no leakage of component A occurs before the acceptor is completely exhausted.
drawn so as to make the two areas I and II equal. This is required by a mass balance consideration since area \((I + III)\) is a measure of the total amount of component A retained by the acceptor bed.

As has been discussed in section 6.2., experimental evidence shows that the principal process occurring in the acceptance/regeneration stage of the present investigation is an oxygen-sulfur exchange reaction. This suggests that a model based solely on a suitable exchange reaction scheme might be able to give at least a fair description of the experimental results. As a start of an attempt to find such a model, the suitability of scheme (8) with \(K < 1\) was examined. It was, however, found not to apply. This was checked by plotting \(x\) against \(\theta = \frac{1}{Q}\), according to eq. (26) such a plot should be a straight line. However, two broken lines were invariably obtained when the experimental breakthrough data were plotted in the manner specified. Moreover, a qualitative comparison of the step front of Fig. 6.4., which should be obtained if \(K > 1\), and the experimental \(H_2S\)-breakthrough curves in Fig. 6.1. directly reveals the unsuitability of exchange reaction (8) as a candidate model.

6.4. Model based on an alternative exchange reaction.

6.4.1. Basis of model.

An oxygen-sulfur exchange reaction with a different stoichiometry, viz.:

\[
H_2S(g) + 2 \text{MnO}(s) \rightleftharpoons \text{Mn}_2\text{O}_3(s) + H_2O(g) \quad (27)
\]

or, more generally written:

\[
A(g) + 2S(s) \rightleftharpoons p(s) + B(g) \quad (28)
\]

was then examined as a basis for the sorption model in the fixed-bed reactor. The primary assumptions for this model are as follows:

- the acceptor bed is isothermal
- plug flow in the bed
- the reaction is so fast that instantaneous equilibrium between gas and acceptor is established everywhere in the bed.

Stoichiometry and the equilibrium assumption leads to the relations:

\[
C_B = C_{A,o} + C_{B,o} - C_A
\]

and

\[
K = \frac{q_A(C_{A,o} + C_{B,o} - C_A)}{C_A Q - q_A} \quad (29)
\]

where \(K\) is the equilibrium constant, \(q\) the stoichiometric capacity, and \(q_A\) the concentration in the solid phase. The isotherm of reaction (27) can assume the form shown in Fig. 6.5a. (see also Fig. 6.6.); it contains a convex as well as a concave part. As a consequence, the breakthrough curve corresponding to the complex isotherm of Fig. 6.5a. is composed of a step change in the concentration followed by a dispersive front (see Fig. 6.5b.). The intersection between the two parts of the breakthrough curve is determined by the composition corresponding to abscissa \(x\) of the tangency point between the isotherm and a straight line through the origin \((0,10)\).

Exchange reaction (27) implies that two moles of manganese are required in order to capture one mole of sulfur.
This postulate is based on the observation that the breakthrough conversion of the manganese or the iron in the acceptor, which was routinely calculated in every cycle and based on a sulfur to active metal ratio of unity, was always relatively low, i.e., in general < 40%, as follows from the breakthrough conversions of steam-regenerable acceptors in tables 4.2 to 4.5 in chapter 4. Moreover, prolonged acceptation experiments, i.e., experiments carried out until the concentration of \( \text{H}_2\text{S} \) in the reactor effluent became equal to that of the feed, showed that the ultimate conversion of the active metal was about 50%.

The aforementioned observation seems to hold not only for the acceptors studied in the present work, Parera et al. recently investigated the adsorption isotherm of \( \text{H}_2\text{S} \) on Pt on \( \text{Al}_2\text{O}_3 \) catalysts at 500 °C. From their results they concluded that, whereas the known sulphide of platinum (PtS) has a Pt/S ratio of 1:1, the total amount of sulfur chemisorbed by the catalysts correspond to a Pt/S ratio of 2:1.

6.4.2. Isotherm.

In terms of the dimensionless variables \( x \) and \( y \) defined in (15), the equilibrium expression (29) is

\[
y = \frac{y(1 + y - x)}{4Q(1 - y)^k x}
\]

where \( y = \frac{C_{\text{B},\text{S}}}{C_{\text{A},\text{O}}} \). Solving eq. (30) for \( y \) results in the isotherm equation:

\[
y = \frac{1}{b} \left\{ \frac{b + 2p}{(b + p)(1 - y)} - \sqrt{4p(b + p)} \right\}
\]

where \( b = 16.12Q \) and \( p = \frac{1 + y}{x} - 1 \). As can be seen in Fig 6.6, the isotherm may be concave, convex, or even complex (convex in the lower region of \( x \) but becomes concave as \( x \) approaches unity), depending on the values of parameters \( b \) and \( y \). More precisely, for \( b \leq 2 \) the isotherm is wholly concave, independent of the value of \( y \). If \( b > 2 \), the isotherm is complex when \( y \) is relatively small (\( y < 1/[b - 2] \)); at higher values of \( y \) it becomes convex throughout.

The equation of the isotherm's slope can be derived from (31). It is:

\[
y'(x) = \frac{dx}{dy} = \frac{(p + 1)^2}{b(1 + y)} \left\{ \frac{b + p}{p} + \frac{\sqrt{b + p}}{b + p} - 2 \right\}
\]

This expression of \( y'(x) \), and eq. (31) for \( y(x) \), can be used to find abscissa \( x' \) of tangency point between the isotherm and a straight line through the origin, that is by solving condition equation \( y(x') = x'y'(x') \). The result is:

\[
x' = \left( \frac{1 + y}{b} \right) \frac{b - 2}{b - 1}
\]

The condition \( b > 2 \) and \( y < 1/(b - 2) \), which was mentioned above as determining the range of condition in which the isotherm is complex, was actually derived from this analytical
expression of $x^*$. The other important characteristics of the isotherm are:

$$y_{x=1} = \frac{1}{b} \left( b + 2\gamma - \sqrt{4\gamma(b + \gamma)} \right) \quad (34)$$

$$y'(x^*) = \frac{b - 1}{b(1 + \gamma)} \quad (35)$$

$$y'(0) = -\frac{b}{4(1 + \gamma)} \quad (36)$$

The last equation was obtained by applying L'Hospital's rule to evaluate $(32)$ at $x = 0$.

6.4.3. Breakthrough curve.

When the isotherm is complex, i.e. $0 < x^* < 1$, the breakthrough curve consists of a discontinuity followed by a dispersive front (cf. Fig. 6.5.). The equation of the shock line is:

$$\left( \frac{\theta - \frac{1}{a}}{\gamma} \right) = y'(x) = \frac{b - 1}{b(1 + \gamma)} \quad (37)$$

whereas the equation of the dispersive front can be obtained by substituting eq. $(32)$ into eq. $(25)$ and setting $\zeta = 1$. The result is:

$$\left( \frac{\theta - \frac{1}{a}}{\gamma} \right) = \left( \frac{p + 1}{b(1 + \gamma)} \right)^2 \sqrt{\frac{b + p}{p}} + \frac{\sqrt{b + p} - 2}{p} \quad (38)$$

Thus, a complete description of the breakthrough curve is:

$$x = \begin{cases} 0 & \left( \frac{\theta - \frac{1}{a}}{\gamma} \right) \leq \frac{b - 1}{b(1 + \gamma)} \\ x \text{ given by eq. (38)} & \left( \frac{\theta - \frac{1}{a}}{\gamma} \right) > \frac{b - 1}{b(1 + \gamma)} \end{cases} \quad (39)$$

As eq. $(38)$ cannot be inverted to yield an explicit expression of $x$ as a function of $\left( \frac{\theta - \frac{1}{a}}{\gamma} \right)$, the values of $x$ at predetermined values of time should be found by solving eq. $(38)$ numerically, e.g. by bisection and/or secant method/12).

6.4.4. Parameter estimation.

The model equations presented above contain two free parameters $K$ and $Q$, hidden in two dimensionless quantities $a$ ($= Q/[e C A_i O]$) and $b$ ($= 16KQ$). The fitting of theoretical to experimental breakthrough curves and estimation of the best values of equilibrium constant $K$ and acceptor capacity $Q$ was done using subroutine ZKSSQ of the International Mathematical and Statistical Library/13), which implements a finite difference version of the Levenberg-Marquardt nonlinear regression method/14). The results are summarized in Figs. 6.7. to 6.11. and Tables 6.2. and 6.3.. The experimental conditions associated with the data presented in Figs. 6.7. to 6.11. are listed in Table 6.1..

The model gives an excellent fit for the breakthrough data obtained with dry feeds and at temperatures up to $550^\circ$C (Figs. 6.7. and 6.8.). At $600^\circ$C, the fit is rather poor, see Fig. 6.9.. This indicates the presence of another process, presumably a slow, kinetically controlled exchange reaction, which becomes important at higher temperatures (i.e. above...
Table 6.1. Experimental conditions associated with the data in Figs. 6.7 to 6.11.

<table>
<thead>
<tr>
<th>Fig. 6.7</th>
<th>Fig. 6.8</th>
<th>Fig. 6.9</th>
<th>Fig. 6.10</th>
<th>Fig. 6.11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn content of acceptor, %w.</td>
<td>8.1</td>
<td>8.1</td>
<td>8.1</td>
<td>8.1</td>
</tr>
<tr>
<td>Acceptor state</td>
<td>stable</td>
<td>stable</td>
<td>stable</td>
<td>fresh</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>450</td>
<td>550</td>
<td>600</td>
<td>400</td>
</tr>
<tr>
<td>Residence time, L/v, s.</td>
<td>0.410</td>
<td>0.383</td>
<td>0.324</td>
<td>0.439</td>
</tr>
<tr>
<td>$C_{H_2S,O}$, mol/m$^3$</td>
<td>0.1574</td>
<td>0.1259</td>
<td>0.1262</td>
<td>0.1553</td>
</tr>
<tr>
<td>Accepter bulk density, $\rho_b$, kg/m$^3$</td>
<td>700</td>
<td>700</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>Bed void fraction, $\epsilon$</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

$^a$stable = deactivated, fresh = undeactivated
$^b$assumed value

Fig. 6.7. Comparison of theoretical breakthrough curve with experimental data obtained with a stable acceptor (8.1% Mn) at 450 °C.

O experimental data

— curve of best fit:

$Q = 175.6$ mol/m$^3$ ($a = 2790$)

$K = 7.114 \times 10^{-4}$ m$^3$/mol ($b = 1.999$)

Fig. 6.8. Comparison of theoretical breakthrough curve with experimental data obtained with a stable acceptor (8.1% Mn) at 550 °C.

O experimental data

— curve of best fit:

$Q = 246.6$ mol/m$^3$ ($a = 4897$)

$K = 5.023 \times 10^{-4}$ m$^3$/mol ($b = 1.982$)

Fig. 6.9. Comparison of theoretical breakthrough curve with experimental data obtained with a stable acceptor (8.1% Mn) at 600 °C.

O experimental data

— curve of best fit:

$Q = 268.5$ mol/m$^3$ ($a = 5361$)

$K = 4.621 \times 10^{-4}$ m$^3$/mol ($b = 1.985$)
Moreover, as has been shown in section 6.2., even at low temperatures adsorption of $H_2S$ and $H_2O$ actually occurs. In summary, these findings imply that both the parameters $K$ and $Q$ of the model are, in fact, lumped parameters containing the various basic parameters of the phenomena occurring during the acceptation process.

The values of equilibrium constant $K$ and the stoichiometric capacity $Q$ of the acceptor obtained from the fits at various temperatures are listed in Table 6.2. If exchange reaction (28) is a true representation of the acceptation process, then the value of stoichiometric capacity $Q$ should logically be independent of temperature. The fact that the values of $Q$ in Table 6.2. vary with temperature reflects the semi empirical (or lumped-parameter) nature of the model. Thus, the temperature variation of the values of $K$ and $Q$ listed in the table should not be interpreted in an exact, physically meaningful manner. Rather, each pair of values should be considered as model parameters useful for predicting the acceptation performance under the specified conditions.

Table 6.2. Parameters of exchange reaction (27) for a stable acceptor containing 8.1 % w-Mn.

<table>
<thead>
<tr>
<th>$T$ ($^\circ$C)</th>
<th>$K$ ($10^{-4}$ m$^3$/mol)</th>
<th>$Q$ (mol/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4.2</td>
<td>180</td>
</tr>
<tr>
<td>450</td>
<td>7.1</td>
<td>176</td>
</tr>
<tr>
<td>500</td>
<td>5.5</td>
<td>202</td>
</tr>
<tr>
<td>550</td>
<td>5.0</td>
<td>247</td>
</tr>
<tr>
<td>600</td>
<td>4.6</td>
<td>269</td>
</tr>
</tbody>
</table>

Influence of the manganese content of the acceptor. The model was also found to fit excellently the breakthrough data obtained using fresh acceptors at 400 $^\circ$C and water-free feeds. This is illustrated in Fig. 6.10. The values of $K$ and $Q$

![Figure 6.10. Comparison of theoretical breakthrough curve with experimental data obtained with a fresh acceptor (8.1 %-Mn) at 400 $^\circ$C.

- Experimental data
- Curve of best fit:
  $Q = 489.6$ mol/m$^3$ ($\alpha = 7880$)
  $K = 2.695 \times 10^{-4}$ m$^3$/mol ($b = 2.11$)

Table 6.3. Parameters of exchange reaction (27) for fresh acceptors at 400 $^\circ$C.

<table>
<thead>
<tr>
<th>Mn-content of acceptor, %w.</th>
<th>$Q_{theor.}$ (mol/m$^3$)</th>
<th>$Q_{exp.}$ (mol/m$^3$)</th>
<th>$K$ ($10^{-4}$ m$^3$/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>515</td>
<td>490</td>
<td>2.7</td>
</tr>
<tr>
<td>6.1</td>
<td>388</td>
<td>360</td>
<td>3.5</td>
</tr>
<tr>
<td>4.4</td>
<td>261</td>
<td>242</td>
<td>4.3</td>
</tr>
<tr>
<td>2.7</td>
<td>172</td>
<td>163</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Corresponding to fresh acceptors of different manganese content are listed in Table 6.3. The parameter values given in this table (and also in Table 6.2.) are the rounded form of the values obtained by the computer (cf. Figs. 6.7. to 6.10.). Simulation tests indicated that the rounding is permissible as
an additional high-temperature exchange reaction which proceeds much more slowly than the main exchange reaction postulated in the model.

6.5. Model based on sorption and exchange reaction.

6.5.1. Basic postulates and equations.

Based on the qualitative interpretation of the form of breakthrough/elution curves of $H_2S/H_2O$, it was proposed in section 6.2. that the following processes probably occur during acceptation and regeneration:

1. A fast oxygen-sulfur exchange reaction (the principal process)
2. A slow oxygen-sulfur exchange reaction
3. Adsorption/desorption of $H_2S$ as well as $H_2O$

Furthermore, it has been stressed in the previous section that if a model is intended to have a broader range of validity, it should not only be based on the fast exchange reaction, but also take the sorption and the slow reaction into account. Therefore, following these proposals, the present model assumes that during acceptation and regeneration three mechanisms apply:

(A = $H_2S$ or S, $B = H_2O$ or O)

1. A fast exchange reaction,

$$A(g) + S_1B(s) = \frac{K_A}{C_A} S_1A(s) + B(g) \quad (42)$$

$$r_A = k_r \left[ \frac{C_A}{(Q_1 - q_1) - \frac{C_B q_1}{K}} \right] \quad (43)$$

2. A slow exchange reaction in the solid phase,

$$S_1A(s) + S_2B(s) = \frac{K_s}{q_1} S_2A(s) + S_1B(s) \quad (44)$$

$$r_{S_2B} = k_s \left[ q_3(Q_2 - q_2) - q_2(Q_1 - q_1) \right] \quad (45)$$

The equilibrium constant of this reaction is simply assumed to be unity. Note that the terms "fast" and "slow" mean that $k_r$ is supposed to be much larger than $k_s$.

3. Competitive, Langmuirian adsorption of A and B,

$$A(g) + S_3(s) = \frac{K_A}{C_A} S_3A(s) \quad (46)$$

$$C_A \left( Q_3 - q_{3A} - q_{3B} \right) - q_{3A} \quad (47)$$

$$B(g) + S_3(s) = \frac{K_B}{C_B} S_3B(s) \quad (47)$$

$$C_B \left( Q_3 - q_{3A} - q_{3B} \right) - q_{3B} \quad (47)$$

These are assumed to reach equilibrium instantaneously; this equilibrium is described by:

$$K_A = \left( Q_3 - q_{3A} - q_{3B} \right) C_A \quad (48)$$

$$K_B = \left( Q_3 - q_{3A} - q_{3B} \right) C_B \quad (48)$$

or, when solved for $q_{3A}$ and $q_{3B}$:

$$q_{3A} = \frac{K_A C_A}{1 + K_A C_A + K_B C_B} Q_3 \quad (49)$$

$$q_{3B} = \frac{K_B C_B}{1 + K_A C_A + K_B C_B} Q_3 \quad (50)$$

Due to the presence of "non exchange" sorptions (46) and (47), the concentrations of A and B at any point in the reactor are not connected by a fixed relation such as:

$$C_{A,0} + C_{B,0} = C_A + C_B$$

This means that $C_A$ and $C_B$ must be considered independent of each other and, consequently, a separate mass balance must be written for each of them. From eq.(6) it follows that these are:

...
Thus,\[\frac{\frac{C_A}{\Delta t}}{=0} + \frac{1}{\epsilon} \frac{\frac{q_A}{\Delta t}}{+ v \frac{\frac{C_A}{\Delta x}}{=0}}\] \[\frac{\frac{C_B}{\Delta t}}{=0} + \frac{1}{\epsilon} \frac{\frac{q_B}{\Delta t}}{+ v \frac{\frac{C_B}{\Delta x}}{=0}}\]

where \(q_A = q_1 + q_2 + q_{3A}\) and \(q_B = (Q_1 - q_1) + (Q_2 - q_2) + q_{3B}\).

Thus,\[\frac{\frac{q_A}{\Delta t}}{= k_r \left[ C_A(Q_1 - q_1) - \frac{C_A q_1}{K} \right] + \left( \frac{\frac{q_{3A}}{\Delta t}}{+ \frac{\frac{C_A}{\Delta x}}{=0}} \right) \frac{\frac{C_A}{\Delta x}}{=0}}{\left( q_1 + q_2 \right) \frac{\frac{q_B}{\Delta t}}{=0} + \frac{\frac{q_{3B}}{\Delta t}}{=0} \frac{\frac{C_B}{\Delta x}}{=0}}\]

\[\frac{\frac{q_B}{\Delta t}}{= k_r \left[ C_A(Q_1 - q_1) - \frac{C_A q_1}{K} \right] + \left( \frac{\frac{q_{3B}}{\Delta t}}{+ \frac{\frac{C_B}{\Delta x}}{=0}} \right) \frac{\frac{C_B}{\Delta x}}{=0}}{\left( q_1 + q_2 \right) \frac{\frac{q_A}{\Delta t}}{=0} + \frac{\frac{q_{3A}}{\Delta t}}{=0} \frac{\frac{C_A}{\Delta x}}{=0}}\]

where \(q_{3A}\) and \(q_{3B}\) are given by (50) and (51), respectively.

In order to make the (numerical) solution easier and safer (preventing computer overflow and/or underflow) and also to simplify the interpretation of results of calculation, the following dimensionless quantities are introduced:

\[\zeta = \frac{x}{L} ; \quad x_A = \frac{C_A}{C_0} ; \quad x_B = \frac{C_B}{C_0} ; \quad y_1 = \frac{q_1}{Q_1} ; \quad y_2 = \frac{q_2}{Q_2} ; \quad y_{3A} = \frac{q_{3A}}{Q_3} ; \quad y_{3B} = \frac{q_{3B}}{Q_3} ; \quad \lambda_1 = \frac{Q_1}{Q_0} ; \quad \lambda_2 = \frac{Q_2}{Q_0} ; \quad \lambda_3 = \frac{Q_3}{Q_0} ; \quad a_0 = \frac{q_0}{C_0} ; \quad \theta_0 = \frac{q_0}{C_0 L} ; \quad \kappa_1 = k_r C_A a_0 L / \nu ; \quad \kappa_2 = k_r C_A a_0 \lambda L / \nu\]

(54a-54n)

Some of these quantities (e.g. \(\zeta\)) have already been defined previously (see also List of Symbols at the end of the thesis). \(C_0\) and \(Q_0\) represent a reference concentration and a reference capacity, respectively. The value of \(C_0\) was chosen to correspond to a gas concentration of 1% and \(Q_0\) was assigned a value of 0.2 mol/kg acceptor (or 140 mol/m² reactor). Eqs. (52) and (53) were then written in terms of these dimensionless quantities and rearranged. The results are, partially in matrix-vector notations, as follows:

\[\frac{\frac{q_A}{\Delta t}}{= M^{-1} u} \quad \frac{\frac{q_B}{\Delta t}}{= M^{-1} \left( \frac{3x_A}{3t} - \lambda_1 F_1 \right) \frac{\frac{q_{3A}}{\Delta t}}{= M^{-1} \frac{3y_{3A}}{3t}} \frac{\frac{q_{3B}}{\Delta t}}{= M^{-1} \frac{3y_{3B}}{3t}} \frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0} \frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0} \frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0}}{\frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0} \frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0} \frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0}}\]

where:

\[\dot{x} = \left( \begin{array}{c} x_A \\ x_B \end{array} \right) ; \quad \dot{u} = \left( \begin{array}{c} -\frac{3x_A}{3t} - \lambda_1 F_1 \\ -\frac{3y_{3A}}{3t} \end{array} \right) \frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0} \frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0} \frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0}}{\frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0} \frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0} \frac{\frac{C_A}{\Delta x}}{=0} \frac{\frac{C_B}{\Delta x}}{=0}}\]

\[F_1 = \kappa_1 \left[ x_A (1 - y_1) - \frac{x_B y_1}{K} \right] ; \quad F_2 = \kappa_2 \left[ y_1 (1 - y_2) - (1 - y_1) y_2 \right] \]

When the acceptation is started by passing a dry feed containing 1% \(H_2O\) through a fully regenerated bed, the initial conditions of the above equations are:

\[\begin{array}{l}
\dot{x}_A = 0 \quad \text{at} \quad \theta_0 < 0 , \quad 0 \leq \zeta \leq 1 \\
\dot{x}_B = 0 \quad \text{at} \quad \theta_0 > 0 , \quad \zeta = 0 \\
\dot{x}_A = 0 \quad \text{at} \quad \zeta = 0 \quad \text{for all} \quad \theta_0 \\
\end{array}\]

(58a)

\[\begin{array}{l}
\dot{x}_B = 0 \quad \text{at} \quad 0 \leq \zeta \leq 1 \quad \text{for} \quad \theta_0 < 0 \\
\end{array}\]

(58b)
Considerable difficulties were encountered when attempting to solve eqs. (55) to (57) numerically. The sources of difficulties are the following two interrelated factors:

1. From a mathematical point of view, equations (55) to (57) consist of a pair of nonlinear hyperbolic partial differential equations (PDE's) containing a source term $F$, which, in turn, is affected by the two relatively simple PDE's (56) and (57).

The solutions were expected to possess large gradients (i.e. steep fronts) when simulating the experimental results (breakthrough and elution curves of $H_2S/H_2O$).

The present state of the art of numerical solution of hyperbolic PDE's is far behind those of other classes of PDE's (i.e. elliptic and parabolic). It is directly indicative of this situation that neither the NAG$^6$ nor the IMSL$^6$, the routines of which reside in almost every large computing center throughout the world, has a single routine to solve hyperbolic PDE's.

The trouble of numerically solving hyperbolic PDE's is in discretizing the spatial derivative (i.e. $\partial x / \partial \xi$). The simplest stable scheme applicable to eq. (55) is the first order backward difference:

$$\frac{\partial x}{\partial \xi} = \frac{x_{j+1} - x_j}{\xi_j - \xi_{j-1}} \quad j = 1, \ldots, N \quad (59)$$

The drawback of this scheme is that it introduces much dispersion into the solution. In other words, the solution tends to be much more dispersive than it ought to be, unless a large number of grid points is chosen ($N$ is large and, consequently, the computation time is long). This is particularly true when the solution is expected to exhibit steep fronts. The use of higher order schemes, such as those containing central differences$^{(15)}$, can reduce the dispersion as well as the required number of grid points. However, they are not recommended because they possess an even more dangerous property than the above first order scheme: the use of conventional higher order schemes produces physically unrealistic oscillations behind and ahead of the (steep) fronts. A number of newly proposed schemes$^{(16-19)}$, either truly novel ones or modification of older schemes, are able to produce oscillation-free solutions. However, they are either difficult to implement or still subject to overly restrictive stability limitations.

Based on the above considerations, the backward difference scheme (59) was applied in the present work. The axial distance along the reactor was divided into $N$ equal intervals ($N+1$ grid points); because the value of $\xi$ ranges from zero to unity, the length of each interval ($\xi_j - \xi_{j-1}$) is just 1/N. This approach converts eqs. (55) to (57) into the following set of $4N$ ordinary differential equations ($j = 1, \ldots, N$):

\[
\begin{align*}
\frac{dx_{A,j}}{d\theta_o} &= a_1 \left[ \frac{N(x_{A,j} - x_{A,j-1}) + \lambda_1 F_{1,j}}{a_2} \right] \\
&\quad + a_2 \left[ \frac{N(x_{A,j} - x_{A,j-1}) - \lambda_1 F_{1,j}}{a_2} \right] \\
\frac{dx_{B,j}}{d\theta_o} &= a_1 \left[ \frac{N(x_{B,j} - x_{B,j-1}) + \lambda_1 F_{1,j}}{a_2} \right] \\
&\quad - a_2 \left[ \frac{N(x_{B,j} - x_{B,j-1}) - \lambda_1 F_{1,j}}{a_2} \right] \\
\frac{dy_{1,j}}{d\theta_o} &= F_{1,j} - \frac{\lambda_1}{\lambda_2} F_{2,j} \\
\frac{dy_{2,j}}{d\theta_o} &= F_{2,j} \quad (60a, 60b, 60c, 60d)
\end{align*}
\]

where:

$$a_1 = \frac{1}{\theta_o} + \lambda_3 \left( \frac{3y_{A,j}}{x_{A,j}} \right) \quad a_2 = \lambda_3 \left( \frac{3y_{B,j}}{x_{B,j}} \right)$$

\footnote{Numerical Algorithm Group} \footnote{International Mathematical and Statistical Library}
\[ a_3 = \lambda_3 \left( \frac{3y_{3B}}{2x_A} \right)_j + \frac{1}{\sigma_0 + \lambda_3 \left( \frac{3y_{3B}}{2x_B} \right)_j} \]

\[ \Lambda = a_1^2 - a_2^2 \]

\[ F_{1,j} = k_1 \left( \frac{y_{1,j} - y_{2,j}}{K} \right) \]

\[ F_{2,j} = k_2 \left( y_{1,j} - y_{2,j} \right) \]

The four partial derivatives \( \frac{3y_3}{3x} \) were obtained from the dimensionless forms of (50) and (51):

\[ \frac{3y_{3A}}{3x_A} = \frac{K_a (1 + K_b x_{B,j})}{G_j} \]

\[ \frac{3y_{3B}}{3x_B} = \frac{-K_b (1 + K_a x_{A,j})}{G_j} \]

where \( G_j = (1 + K_a x_{A,j} + K_b x_{B,j})^2 \); \( K_a = K_{A_0}; K_b = K_{B_0} \).

It is worthy of note that this approach, i.e., converting hyperbolic PDE's describing time-dependent phenomena in tubular equipment into a set of N ordinary differential equations (ODE's) using first order backward difference spatial discretization, is equivalent to representing the apparatus with N stirred tanks in series, which is a widely known approximation of tubular reactors in the chemical engineering literature.

To obtain the theoretical breakthrough and elution curves of \( H_2O \) and \( H_2S \) adsorption, respectively, the system of ODE's (60) should be solved numerically. As during this solution process the behaviour of the ODE's (60) might change from stiff to nonstiff and vice-versa, the integrations were carried out by a program which switched automatically between stiff and nonstiff routines. The stiff integrator implemented an embedded Rosenbrock formula of order 4(3) due to Shampine(20) whereas the nonstiff one used an embedded Runge-Kutta formula of order 5(4) due to Fehlberg[21]. The structure of the program, methods of switching, stiffness detection, step size adjustment, etc. followed the guidelines given by Shampine(20) and Shampine and Watts[22]. The correctness of the program was verified using test problems available in the literature[20,23].

Preliminary simulations using simple models showed that a value of \( N = 30 \) (tanks or spatial intervals) was sufficient to produce reasonably accurate approximations. This value was then used to produce the simulation results reported in paragraph 6.5.4.

6.5.3 Parameters of \( H_2O \) and \( H_2S \) adsorption.

6.5.3.1 Introduction.

The model equations given above contain, among others, the sorption parameters of water and hydrogen sulfide. These parameters were estimated from data on \( H_2O \) adsorption and \( H_2S \) desorption, respectively. The results are presented below.

6.5.3.2 Water adsorption.

The measurement of breakthrough behaviour of water on the acceptor was complicated by the apparent adsorption of the vapour on the tubings in the reactor section, despite the fact that the latter were always kept at 80 °C by using heating tapes. Thus, when a stream of gas with a predetermined water content was passed through the bypass line of the reactor section (cf. Fig. 3.1.) the water concentration, as detected by the gas chromatograph in the analysis section, did not immediately reach its set point. A similar result was obtained when the gas was passed through the reactor filled with inert non porous material (0.25 - 0.42 mm quartz particles); see
Fig. 6.12. Breakthrough (a) and elution (b) curves of water on a fixed-bed of quartz particles. The tails of these curves are due to, respectively, adsorption and desorption on/from the tubings. T = 400 °C, C_{H_2O,o} = 1.7 %v., \theta_o = 3000.

Fig. 6.12a. On replacing the wet gas by a dry stream, desorption of water from the tubings occurred, as indicated by the tail in the curve of Fig. 6.12b.

A typical plot of the variation of the water concentration in the reactor effluent during the measurements of water adsorption on the acceptor is shown in Fig. 6.13. The relatively large (but decreasing !) water concentration prior to breakthrough point (\theta_o = 0.72) was understood to have resulted from the desorption of water adsorbed on the tubing during measurement of inlet concentration. Conversely, the fact that water concentration after the breakthrough point did not immediately reach the inlet concentration (x_{B} = 0.75) was interpreted as having been caused by readsoption of water on the tubing. The solid line drawn in the figure is the breakthrough curve of water as expected from equilibrium theory.

Table 6.4. lists the experimental breakthrough capacity at 400 and 600 °C as a function of the inlet concentration of water. From these data, the parameters K and Q of water adsorption were estimated to be:

- 400 °C: Q = 140 mol/m³ K = 14.74 m³/mol
- 600 °C: Q = 168 mol/m³ K = 12.36 m³/mol

The breakthrough capacities calculated using these values of parameters, shown in the last column of Table 6.4., are in good agreement with the experimentally measured ones. The difference in the values of Q at 400 °C and 600 °C is probably due to the difference in "degree of dryness" of the
Table 6.4. Water-breakthrough capacities of an 8 %w-Mn on γ-Al₂O₃ acceptor.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Inlet conc. of H₂O, %v</th>
<th>Breakthrough capacity, mol/m²</th>
<th>exp.</th>
<th>calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>1.21</td>
<td>84</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>2.26</td>
<td>126</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>3.17</td>
<td>133</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>0.75</td>
<td>105</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>1.36</td>
<td>112</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>2.29</td>
<td>133</td>
<td>134</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>3.31</td>
<td>147</td>
<td>143</td>
<td></td>
</tr>
</tbody>
</table>

acceptor at these two temperatures (i.e. at 600 °C the dry acceptor contains less hydroxyl groups and, therefore, can capture more water than at 400 °C).

When the values of the equilibrium constant obtained above are substituted into the Van't Hoff equation:

\[
\ln \left( \frac{K_2}{K_1} \right) = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \frac{\Delta H^\circ}{R}
\]

an estimate of \(\Delta H^\circ = -4.3 \text{ kJ/mol}\) is obtained. This is small compared to that normally found for chemical reactions.

6.5.3.3. \(\text{H}_2\text{S}\) adsorption.

The adsorption of \(\text{H}_2\text{S}\) by the tubing was found to be negligible, in contrast to that of \(\text{H}_2\text{O}\). Thus, the concentration of \(\text{H}_2\text{S}\) in the reactor effluent, as detected by the titrator and/or gas chromatograph in the analysis section, is the real concentration of \(\text{H}_2\text{S}\) released by the acceptor.

The equilibrium constant \((K^\circ)^{\text{H}_2\text{S}}\) of \(\text{H}_2\text{S}\) adsorption could be estimated by measuring the amount of \(\text{H}_2\text{S}\) desorbed when a completely sulfur-saturated acceptor was flushed by an inert stream \((88 \% \text{ H}_2 + 12 \% \text{ N}_2\)). To that end, the acceptor was treated with a gaseous stream containing a constant concentration of \(\text{H}_2\text{S}\) until the effluent composition became equal to that of the feed. This could be achieved by leaving the acceptor under the gas stream overnight. Thereafter, it was flushed by inert and the amount of \(\text{H}_2\text{S}\) eluted was measured.

Another important result of this experiment is the ultimate (total sulfur) capacity of the acceptor, which was obtained by further treatment of the acceptor with a steam-containing gas to regenerate all the chemically bound sulfur. The ultimate capacity is the total sulfur released in both inert flush and steam-regeneration.

The results of the experiments are summarized in Table 6.5. (see Fig. 6.2. for the elution curve of \(\text{H}_2\text{S}\)). As has been stated previously, the ultimate capacity of the acceptor corresponds to a sulfur-to-manganese ratio of about 1 : 2. The deviation from the ratio 1 : 1 in the known compound MnS

Table 6.5. Total sulfur capacity of an 8.0 %w-Mn on γ-Al₂O₃ acceptor and amount of \(\text{H}_2\text{S}\) desorbed by inert flush.

<table>
<thead>
<tr>
<th>Inlet conc. of (\text{H}_2\text{S})</th>
<th>Total sulfur capacity accepted, mol/m³</th>
<th>Nol of (\text{H}_2\text{S}) desorbed by inert flush, mol/m³</th>
<th>S/Mn of acceptor measured</th>
<th>calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.93</td>
<td>489</td>
<td>0.48</td>
<td>36</td>
</tr>
<tr>
<td>400</td>
<td>1.60</td>
<td>458</td>
<td>0.45</td>
<td>36</td>
</tr>
<tr>
<td>400</td>
<td>2.24</td>
<td>468</td>
<td>0.46</td>
<td>50</td>
</tr>
<tr>
<td>600</td>
<td>1.03</td>
<td>462</td>
<td>0.45</td>
<td>31</td>
</tr>
<tr>
<td>600</td>
<td>1.52</td>
<td>570</td>
<td>0.45</td>
<td>34</td>
</tr>
<tr>
<td>600</td>
<td>1.96</td>
<td>529</td>
<td>0.52</td>
<td>52</td>
</tr>
</tbody>
</table>
presumably reflects the fact that the manganese is bound by the alumina support.

Analogous to the case of $H_2O$, the relation between the amount of adsorbed sulfur $q_{3A,b}$ and gas phase concentration $x_{A,o}$ is:

$$q_{3A,b} = \frac{k_c c x_{A,o}}{1 + k_c c x_{A,o}} q_3$$  \hspace{1cm} (63)

From the data in Table 6.5 and using the value of $q_3$ obtained in the previous paragraph, the equilibrium constant was estimated to be:

- $400^\circ C$: $K_A = 1.38 \text{ m}^3/\text{mol}$
- $600^\circ C$: $K_A = 1.36 \text{ m}^3/\text{mol}$

### 6.5.4. Verification of model.

Apart from the known adsorption parameters $K_A$, $K_B$, and $Q_2$, the model equations contain five other parameters $K$, $k_1$, $k_2$, $Q_1$ and $Q_2$ which relate to the exchange reactions. To obtain rough estimates of these remaining parameters, simulation runs were carried out, guided by a statistical method of parameter screening (Placket-Burman design\(^{24,25}\)). This effort resulted in the set of parameter values listed in Table 6.6. The breakthrough (elution) curves calculated using these parameter values are compared to experimental data in Figs. 6.14a. to 6.14e. As the figures show, the simulated curves are in satisfactory agreement with the experimental results. The observed discrepancies in the case of the water elution curves may be attributed to the low quality of the experimental data: as has been pointed out previously, the bed sorption data are obscured by adsorption of water vapour on the tubing in the reactor section of the experimental unit. Thus, noting this fact and recognizing that the parameter values in Table 6.5. are only rough estimates, it is concluded that the model correctly describes the experimental results in a relatively wide range of conditions.

### Table 6.6. Estimated values of parameters of sorption-reaction model (42) to (51).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>400 $^\circ C$</th>
<th>600 $^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$, dimensionless</td>
<td>4.7</td>
<td>3.6</td>
</tr>
<tr>
<td>$k_1$, $\text{m}^3/\text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>$Q_1$, mol.m$^{-3}$</td>
<td>160</td>
<td>209</td>
</tr>
<tr>
<td>$k_2$, $\text{m}^3/\text{mol}^{-1} \cdot \text{s}^{-1}$</td>
<td>$10^{-3}$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>$Q_2$, mol.m$^{-3}$</td>
<td>140</td>
<td>210</td>
</tr>
<tr>
<td>$K_A$, $\text{m}^3/\text{mol}^{-1}$</td>
<td>1.38</td>
<td>1.36</td>
</tr>
<tr>
<td>$K_B$, $\text{m}^3/\text{mol}^{-1}$</td>
<td>14.74</td>
<td>12.36</td>
</tr>
<tr>
<td>$Q_3$, mol.m$^{-3}$</td>
<td>140</td>
<td>168</td>
</tr>
</tbody>
</table>

### Fig. 6.14. Comparisons of simulated and experimental breakthrough (elution) curves of $H_2S$ ($H_2O$) at various conditions.

**Acceptor**: deactivated 8.0 %w-Mn on $\gamma$-Al$_2$O$_3$. 

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Resubmitted
Fig. 6.14. (contd.)
The outcome of the simulation work presented here suggests that the model must be fitted directly to the experimental data using a formal (non-linear) regression technique in order to obtain accurate and completely interpretable parameter values. The rough estimates listed in Table 6.6 can, perhaps, be used as initial values to start the iteration of the regression routine. This was, however, not done in the present work for the following reasons:
- as noted above, the quality of the water elution data is not yet satisfactory and, consequently, does not allow accurate estimation of parameter values.
- the fitting would take an unacceptably long computer time, because each iteration in such an activity would require integration of 120 ordinary differential equations (60a-d). Observations made during the above simulation study show that every integration of the ODE's to produce a complete breakthrough/elution curve took 2 - 3 minutes computation time on the Amdahl computer of the University's Computing Center. Moreover, no matter how accurate the integration is carried out, the result can at most a fair approximation to the exact solution of the model equations, because the 120 ODE's (60a-d) arise from discretization of the four basic PDE's of the model, eqs. (55) to (57), using a first order scheme at a moderate number of grid points (i.e. 30). This point will be discussed further in section 6.7, where some suggestions for subsequent modelling studies will be made.

The model equations and the parameter values listed in Table 6.6. can also be used to simulate the concentrations in the reactor effluent during regeneration of a sulfur-saturated bed, provided that the concentration profile of the acceptor bed at the start of the process is known. Fig. 6.15. shows breakthrough (elution) curves of H$_2$O and H$_2$S resulting from the regeneration of a completely saturated bed with a gas containing 3.5 \% H$_2$O. The H$_2$S-free regenerant contains 3.5 \% H$_2$O.

Fig. 6.15. Simulated breakthrough (elution) curve of H$_2$O (B) and H$_2$S (A) during regeneration of a completely sulfur-saturated acceptor bed. The gas used to saturate the bed contains 1 \% H$_2$S and 0 \% H$_2$O.

6.5.5. Conclusions.

The material presented in this section shows that it is possible to describe the dynamics of H$_2$S acceptance on the acceptor by a model based on:
- two oxygen-sulfur exchange reactions proceeding at very significantly different rates, and
- competitive adsorption of H$_2$S and H$_2$O.

A simulation study shows that the model predictions agree satisfactorily with the experimental results, though accurate estimates of model parameters were not obtained. Some difficulties encountered in solving model equations as well as estimating model parameters have also been discussed.

When the feed gas to be desulfurized contains carbon monoxide, marked changes occurred in the reactor effluent composition during acceptation, as compared to the results obtained with feeds free of carbon oxides. These changes are the appearance of CO\textsubscript{2} and COS, see Fig. 6.16. Carbon dioxide is produced by the shift conversion of CO with water which is either generated by the acceptation reaction or already present in the feed:

\[ \text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \]  

(64)

Carbonyl sulfide was probably formed by reaction of CO with H\textsubscript{2}S:

\[ \text{CO(g)} + \text{H}_2\text{S(g)} \rightleftharpoons \text{COS(g)} + \text{H}_2(g) \]  

(65)

Fortunately, COS was only observed in the reactor effluent after breakthrough, which implies that the oxide acceptor effectively removed sulfur in the form of both H\textsubscript{2}S and COS. Case et al. (26) reported that reaction (65) rapidly attains equilibrium. According to Kohl and Riesenfeld (27), the equilibrium constant

\[ K = \frac{[\text{H}_2][\text{COS}]}{[\text{H}_2\text{S}][\text{CO}]} \]

is about 0.054 at 600 °C. The values calculated from the data in Fig. 6.16. (K = 0.06) is close to this. Thus, reaction (65) can be assumed to be in equilibrium. As has been pointed out in section 5.7. and can be verified from the data in Fig. 6.16., the CO shift conversion, reaction (64), also attained equilibrium.

Another important effect resulting from the presence of CO in the feed is the decrease in the acceptor's capacity to adsorb water. As has been discussed in section 6.2., water produced by the acceptation reactions is adsorbed by certain

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**Fig. 6.16. Dynamic variation of reactor effluent composition when the desulfurization feed contains carbon monoxide.**

- **Temperature**: 600 °C
- **Gas residence time, L/v**: 1 s
- **Feed composition**:
  - H\textsubscript{2}: 32.3
  - H\textsubscript{2}S: 1.1
  - H\textsubscript{2}O: 2.05
  - CO\textsubscript{2}: 0
  - COS: 0
  - N\textsubscript{2}: balance
sites on the acceptor surface, with the result that no water was found in the reactor effluent initially during acceptation operation when using relatively dry feed gas. When the dry feed contains CO, however, water appeared in the reactor effluent immediately after the start of the acceptation, although its concentration was low because it has partially been converted to CO₂ by the shift reaction. This observation may indicate that CO was adsorbed on the same sites as water, thus diminishing the capacity of the acceptor for water adsorption. This is in line with the proposed mechanism of the shift conversion via the formation of formate complex (cf. section 5.5.1); the formation of the complex is probably preceded by adsorption of both CO and H₂O on the acceptor surface. In addition, the relatively bulky formate complex may hinder further adsorption of H₂O and, consequently, result in an apparent decrease of acceptor capacity for water adsorption.

In the present work, an attempt has also been made to include the influence of CO in the sorption-reaction model of section 6.5. The rate of the shift conversion was assumed to be:

\[ r_{CO_2} = k_1(CO \cdot H_2O - CO_2 \cdot H_2O / K_1) \]  

(66)

The rate of reaction (65) was supposed to follow an expression analogous to (66). In order to be consistent with the fact that either of the above reactions rapidly attains equilibrium, the rate constants were assigned a relatively large value (0.04 m³ mol⁻¹ s⁻¹). By inclusion of these two reactions, the basic PDE's of the model increased from 4 to 6 and the number of ODE's to be integrated grew from 120 to 180. Simulation calculations resulted in a qualitatively correct variation of CO₂ concentration. The predicted elution curves of CO₂ and H₂O were, however, far from reality: the model predicted that both H₂O and CO₂ would appear in the reactor effluent after the acceptation has proceeded for some time. This incorrect result was obtained because the fact that the presence of CO decreased the amount of water adsorbed was not taken into account. Thus, the water produced in the beginning of the acceptation was implicitly assumed to be adsorbed quantitatively, resulting in a zero concentration in the gas phase and, consequently, a zero value of the rate expression (66).

It is therefore suggested that subsequent modelling studies to explain the fate of CO should take the influence of CO on water adsorption into account.

6.7. Concluding remarks and some suggestions for further modelling studies.

In this chapter, the results of preliminary attempts to describe the dynamic process of H₂S acceptation quantitatively on a MnO/γ-Al₂O₃ acceptor have been presented. A simple model based on an exchange reaction was formulated in section 6.4. and shown to be a useful approximation to acceptor behaviour in the temperature range investigated, provided that the feed gas to be desulfurized is dry. The failure of the model to predict the behaviour of an acceptor treating wet feeds was ascribed to the fact that it neglects the phenomena of H₂O and H₂S adsorption on the acceptor. A more general model which takes sorption into account was developed in section 6.5. Through comparison of simulation calculations and experimental results the model was demonstrated to be valid under a wide range of conditions. Accurate estimates of model parameters could, however, not yet be obtained owing to the presence of some obstacles. As was noted in paragraph 6.5.4., these obstacles are partly experimental in nature - the low quality of water elution data due to the disturbing effect of adsorption on the tubing - and partly computational, viz. the inefficiency and inaccuracy of numerical solutions of equations of the type contained in the model.

To obtain accurate estimates of the model parameters, it is suggested that the interaction of the acceptor with H₂S, H₂O, and CO should be studied using a thermobalance, preferably coupled with a gas chromatograph. This technique has the obvious advantage of allowing a direct and accurate measurement of accumulation (depletion) of a component on (from) the acceptor. Thus, reliable data can be gathered on adsorption.
rates and isotherms, total sulfur capacity of acceptor, equilibrium positions and rates of the exchange reactions etc., provided that mass transfer limitations can be avoided. From these data, accurate values of model parameters may be extracted in a relatively straightforward manner. It is expected that these parameter values can be used with confidence to simulate the behaviour of fixed acceptor beds during acceptance as well as regeneration.

The simulation results of the present work were obtained by representing the fixed-bed sorber as 30 tanks in series (or, in a mathematical sense, through spatial discretization of the PDE's describing the fixed-bed conservation equations using first order backward difference and 31 grid points). As has been pointed out in paragraph 6.5.4., the results are, at most, moderately accurate. If solutions of better quality are required, something should be done to improve the numerical method used.

Recent developments in the field of numerical analysis show that the accuracy of numerical solutions of time-dependent partial differential equations can be remarkably improved if the grid points are neither equally-spaced nor fixed (time-independent). This means that as the (numerical) solution evolves, the algorithm should adapt the grid points to the nature of the solution, placing a rather closely-spaced grid points in the region of rapid change (e.g. in a steep front). These techniques, called dynamically-adaptive grid methods (28), have been and are still being studied actively by numerical analysts since the end of the last decade (29, 30). At the time of writing, good methods are becoming available in the literature. Of particular promise is the moving finite element method (31) which yields excellent resolution of steep fronts and discontinuities. Unfortunately, this method is very complex and difficult to implement.

Recently, Madsen (32) proposed an adaptive grid implementation of first order backward difference (that is a "variable volume tanks in series" model). The method is relatively simple to comprehend, yet it results in a remarkably improved solution compared to the conventional tanks-in-series model. It is estimated that with this technique solutions of good accuracy can already be obtained using 15 - 20 tanks instead of 30 adopted in the present work, which implies a useful reduction in computation time. Therefore, it is proposed that subsequent simulation studies should try this technique.

Finally, it is also recommended that a further thermobalance and simulation study should include not only MnO on γ-Al₂O₃ but also iron-containing acceptor.

References.

CHAPTER 7

EVALUATION

7.1. Introduction.

In previous chapters the influence of preparation methods and process conditions on the sulfur removal capacity, steam-regenerability, and breakthrough behaviour of the acceptors were discussed. In this chapter, simplified schemes of fixed- and fluidized-bed high-temperature desulfurization processes will be presented together with a discussion on potential advantages and problems which result from applying the steam-regenerable acceptors of the present work in these operation modes. The proposed processes will also be compared to those described in the literature.

7.2 Fixed bed process.

7.2.1. Description.

A simplified flowsheet of a fixed-bed high-temperature desulfurization processes based on steam-regenerable acceptors of the present study is shown in Fig. 7.1. The conditions shown in this figure are based on the assumption that the unit is an integral part of a coal gasification combined cycle power plant utilizing a high-pressure second-generation gasifier (e.g. Shell-Koppers, Texaco). The heart of the unit is a fixed-bed desulfurizer-regenerator system R1-R2 which is operated in a swing mode. In Fig. 7.1. only two absorption vessels are shown, one in the desulfurization/acceptation phase (R1) the other in the regeneration phase (R2). In practice, more than two vessels will be required (see next paragraph).

The term absorption/absorber is chosen here although the process itself involves adsorption on the surface of the acceptor.

Depending on the type of coal and gasifier used, the feed gas entering the desulfurization unit may contain 0.4 - 1.4 % v H₂S and trace amounts of organic sulfur compounds (see section 1.1. and Table 1.2.). The gas is passed through a freshly regenerated acceptor bed in vessel R1 where its H₂S content is reduced to 10 - 40 ppm (cf. section 6.2.). As discussed in section 6.6., COS is also removed. Thus the clean gas leaving the bottom of the absorber can be sent directly to the combined cycle unit because its sulfur content is low enough. However, when the gas is to be used in a fuel cell or for catalytic synthesis, a zinc oxide guard bed should be installed downstream of the absorber system to carry out the final stage of purification, i.e. from 10 - 40 ppm to less than 1 ppm H₂S.

When the concentration of H₂S in the clean gas
reaches breakthrough (< 500 ppm for combined cycle application), the regeneration of the acceptor bed in vessel R2 must be complete. At this time, the valve system is switched to interchange the roles of vessel R1 and R2; the former becomes the regenerator, the latter the absorber/desulfurizer. The regeneration of the sulfur-saturated bed is carried out at a temperature and a pressure similar to those in the desulfurizer. Results of a preliminary experimental and simulation study of the regeneration phase (cf. sections 6.2 and 6.5.) indicate that it is possible to obtain a regenerator off-gas containing 10 - 50 vol % H2S. To concentrate the H2S, the pressure and the temperature of the regenerator off-gas are reduced to about 0.2 MPa and 50 °C, respectively, by passing it through heat recovery system HR (waste-heat boiler/condenser/cooler). The H2S is then separated from water in gas-liquid separator SP and sent to a Claus unit. Note that the end values of temperature and pressure reduction mentioned here are actually determined by the operating pressure of the Claus unit and the maximum acceptable level of water vapour in the catalytic reactors of that unit, which are about 0.15 MPa and 25-30 °C, respectively [1, 2].

The water leaving the bottom of separator SP will dissolve some H2S and probably also contains some sulfur particles produced by gas-phase decomposition of hydrogen sulfide. The dissolved H2S is removed by contacting the water stream with the feed air to the Claus unit in stripper ST. If the level of sulfur entrainment by the water stream is too high, a filter should be installed upstream of pump P.

To minimize pressure drop, industrial-scale fixed bed absorbers will require relatively large acceptor particles, typically 2.5 to 10 mm in size (extrudates or pellets). As this is 10-30 times larger than the size of the acceptor in the present work, the performance of a real fixed-bed may be expected to differ from that of the mini fixed-bed studied here, because in the former the process rate may be limited by pore diffusion. Moreover, the high operating pressure of industrial processes may also result in a different acceptor behaviour. Further experiments are needed to verify that acceptor performance/behaviour under these industrial conditions are acceptable.

7.2.2. Comparison with other processes.

As has been discussed in paragraphs 2.2.3. and 2.2.4., most hot gas desulfurization processes produce SO2 as a regeneration product, the conversion of which to sulfur in a Claus plant requires reducing agents (e.g. H2, CO). In a coal gasification combined cycle plant, the consumption of process gas by this reduction represents a loss of approximately 1.5 percentage-point in the overall thermal efficiency of the plant (i.e. coal to electricity), after adjustment for heat recovery [3]. The process proposed here has a sizable advantage in that its regeneration product is H2S, which can be converted to sulfur by oxidation with air. Thus, it eliminates the costly consumption of process gas in the Claus unit and, consequently, leads to a potential improvement in the thermal efficiency of the whole plant.

The above potential advantage of the present process results from the feasibility of regenerating the acceptor with steam. This regeneration method also brings two other advantages to the process:

1. It follows from the thermodynamic calculation in paragraph 2.3.3. that the regeneration, which is exactly the reverse of the acceptation process, involves small heat effects. This means that the process temperature can be easily controlled to maintain isothermality. Moreover, as experiments showed, both the acceptation and regeneration stages can be carried out at the same temperature and pressure. In the case of processes using oxidative regeneration and yielding SO2 as product (cf. Table 2.2.), satisfactory operation can be attained only by applying an excessively tight temperature control [3] (e.g. by adding a large amount of diluent to the regenerator feed-air or by using costly externally cooled multitubular reactor vessels) because the oxidation reactions are highly exothermic (see paragraph 2.2.3.).
2. Because the regeneration is non-oxidative, i.e. with steam, no oxidation of the active component of the acceptor (i.e. manganese or iron) occurs. As a result, there is no consumption of process gas for acceptor reduction during the acceptation phase. This is not the case in the MERC iron oxide process, for example, where the iron oxidized by air during regeneration is reduced by H₂/CO in the acceptation. The latter phenomenon may even have a more adverse effect than the 1 or 2 % loss of process gas: an extensive reduction of the iron oxide at the start of the desulfurization phase may cause the heating value of the fuel to drop temporarily to a level that impairs the performance of the combined cycle unit [J].

The steam-regenerability of the acceptor causes the proposed process to be sensitive to humidity of the feed gas. Thus, whereas the MERC process can satisfactorily desulfurize gases containing up to 6-20 % water vapor [J,1], the present process is applicable only to relatively dry feeds. Gaseous stream with a H₂O content of 4-5 % can be handled provided that they also contain a substantial amount of carbon monoxide which can remove water via a shift reaction (see section 5.7.). Fortunately, product gases of modern, high-temperature high pressure gasifiers usually fulfill this requirement, see e.g. Table 1.1. In addition, recent surveys [J,4] show that the gases may contain a few percent by volume of light hydrocarbons (principally methane). Although it is expected that these will not adversely affect acceptor performance, experiments to examine their influence still have to be performed. Also, for applications of the proposed process in the petroleum industries, tests should be carried out to determine whether or not higher hydrocarbons (C > 2) will crack on the acceptor, for this may result in either deterioration of acceptor due to coke deposition or undesirable change in the quality of the treated product. In this connection, an observation of Lankhuizen [5] is quite promising: he found no coke formation occurs when a stream of gaseous hydrocarbons is passed through a bed of manganese oxide on alumina at temperature of up to 600 °C.

Another weakness of the process is the relatively low sulfur-removal capacity of the acceptor. An acceptor containing 8 %w-Mn on γ-Al₂O₃ has a capacity of about 1 %w-S at 600 °C. In contrast, the MERC acceptor (25 % Fe₂O₃, 75 % SiO₂) has a capacity of 8-10 %w-S [J]. To obtain a clear picture about the implications of these capacities in practice, consider a 1000 MW coal gasification combined cycle plant burning about 500 ton/hr Illinois No. 5 coal containing 4 %w sulfur (moisture- and ash-free basis, 90 % of the sulfur appears in the gasifier product). Evaluation studies done by several institutions [J,6] indicate that, in order to ensure a smooth desulfurization-regeneration cycle and a continuous, uninterrupted feed to the Claus unit, the MERC fixed-bed process will require 16 vessels, each holding approximately 90 tons of sorbent; the acceptation as well as the regeneration phase take about 4 hr. If the present process is applied using the same amount of acceptor and number of beds, the duration of acceptation/regeneration phase will be rather short, viz. about 24 minutes. In addition, the vessels should be twice as large, because the bulk density of the present acceptor (= 700 kg/m³) is approximately half of that of the MERC sorbent (= 1500 kg/m³). Further calculations indicated that when the acceptation phase is terminated, the process gas hold-up in the bed is relatively large, i.e. amounting to 1-4 % of the clean gas produced.

It follows from the above facts that an acceptor capacity of 1 %w-S is rather low for application in a fixed-bed swing process. Research is, therefore, still needed to find steam-regenerable acceptors having a significantly higher capacity than that of the present study. To that end there are two lines of investigation which can be pursued:

1. As discussed in section 5.3., the capacity of an 8 %w-Mn on γ-Al₂O₃ acceptor is initially about 2 %w-S, but it deactivates due to sintering and reaches a stable capacity of

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roughly 1 \% w-S. If the deactivation can be prevented, one may obtain an acceptor having a capacity of about 2 \% w-S. In this context, the work of Lo Jacono et al. (7) is of interest. They observed that addition of a small amount of foreign ions such as Ga$^{3+}$ or Ce$^{4+}$ influences the behaviour of the acceptor (i.e. surface spinel). Moreover, it may be possible to raise the manganese content of the acceptor up to about 9.5 \% w (cf. paragraph 4.2.2.3.).

2. A steam-regenerable acceptor having a high manganese (or iron) content can, perhaps, be obtained via preparation methods different from that used here (i.e. wet impregnation of \(\gamma\)-Al$_2$O$_3\)). Examples are coprecipitation and cocrystallization methods (8). However, the formation of a true aluminate spinel should apparently be avoided according to results of the present work, which indicate that this substance may have a low reactivity (cf. paragraph 4.2.2.1. and section 5.3.).

7.3. Fluidized-bed process.

As discussed above, due to the relatively low sulfur removal capacity, the application of the acceptor in a fixed bed system presents problems such as short cycle time (i.e. frequent regeneration) and relatively large fuel-gas hold-up. These difficulties can in principle be avoided by applying the acceptor in a fluidized-bed system. Fig. 7.2. shows the desulfurizer-regenerator section of this purification plant schematically. The other part of the plant are similar to those in Fig. 7.1.

Because a fluidized-bed system operates continuously, it eliminates the disadvantageous process gas hold-up featured by the fixed-bed swing process which, at best, can operate only in a quasi-continuous manner. 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 relatively low capacity of the acceptor is not much of a problem because large circulation rates of solid between the desulfurizer and the regenerator are possible. Also, due to its continuous operation, it ensures a feed of constant composition to the Claus unit. This is difficult to achieve with a fixed-bed system, where the \(H_2S\) concentration in the regenerator off-gas usually declines as the recuperation of the acceptor approaches completion.

Process rate limitation by pore-diffusion is less likely to be encountered in a fluidized-bed system because it employs small acceptor particles, typically between 10 \(\mu\)m and 1 mm. The sulfur removal efficiency of this system, however, may be lower than that of a fixed-bed system because of extensive mixing and the bypassing of acceptor particles by bubbles; to some extent this can be circumvented by using an internally staged bed.

In order to judge the suitability of the acceptor to be used in a fluidized-bed system, much work remains to be done. Tests should be carried out to produce acceptor parti-
cles having a satisfactory resistance towards attrition and agglomeration. A poor attrition resistance will result in an excessive loss of acceptor as fines and, thereby, a high make up requirement, whereas agglomeration of acceptor particles would lead to a poor fluidization. Furthermore, experimental as well as simulation work should be conducted to evaluate the acceptation and regeneration performance of the acceptor in such a system.

7.4. Conclusions.

The material presented in the foregoing sections shows that high-temperature desulfurization processes based on a steam regenerable acceptor can have a number of important advantages compared to existing ones. To improve the feasibility of these processes, further studies are required to produce acceptors having a capacity significantly higher than 1 %w-S at 600 °C. In addition, experiments are still needed to examine the influence of a high operating pressure and the presence of hydrocarbons in the feed on the performance and/or behaviour of the acceptor.

For acceptors having relatively low capacities, it may be more advantageous to apply the acceptors in a fluidized-bed system. Evaluation of acceptor suitability for this operation mode is, therefore, recommended. As suggested in section 6.7., thermobalance experiments are required to provide good estimates of process parameters. These can then be used to evaluate fixed- as well as fluidized-bed behaviour of acceptor during acceptation-regeneration cycles.

References.

8. P. Courty and C. Marcilly in ibid, pp 119-145.
LIST OF SYMBOLS

- $a_i$: activity of the $i$-th component
- $b$: dimensionless parameter (eq. (31) of chapter 6)
- $C_i$: concentration of the $i$-th component in the gas phase \( \text{mol} \cdot m^{-3} \)
- $D_a$: axial dispersion coefficient \( m^2 \cdot s^{-1} \)
- $H$: enthalpy \( J \cdot mol^{-1} \)
- $I.S.$: isomer shift \( \text{mmol}^{-1} \)
- $k$: forward reaction rate constant \( 3 \text{mol}^{-1} \cdot s^{-1} \)
- $K$: equilibrium constant (may or may not have a dimension, depending on its specific definition)
- $L$: length of acceptor bed \( m \)
- $N_i$: flux of the $i$-th component \( \text{mol} \cdot m^{-2} \cdot s^{-1} \)
- $P_i$: partial pressure of the $i$-th component (eq. (5) of chapter 2) \( Pa \)
- $P$: dimensionless variable (eq. (31) of chapter 6) \( Pa \)
- $q_i$: concentration of the $i$-th component in the solid phase \( \text{mol} \cdot m^{-3} \)
- $Q$: stoichiometric capacity of the solid phase \( \text{mol} \cdot m^{-3} \)
- $q_b$: breakthrough capacity of acceptor \( \text{mol} \cdot s^{-3} \text{ or mol/kg} \)
- $q_c$: sulfur load of the acceptor at the end of the acceptation stage \( \text{mol/kg} \)
- $Q.S.$: quadrupole splitting \( \text{mm/s} \)
- $-r_i$: intrinsic reaction rate of the $i$-th component \( \text{mol} \cdot m^{-3} \cdot s^{-1} \)
- $R$: total amount of sulfur recovered from the acceptor in the regeneration stage \( \text{mol} \)
- $R_i$: global rate of sorption of the $i$-th component \( \text{mol} \cdot m^{-3} \cdot s^{-1} \)
- $t$: time \( s \)
- $t_b$: breakthrough time
- $t_c$: total acceptation time \( s \)
- $t_R$: total regeneration time \( s \)
- $T$: temperature \( ^\circ \text{C or K} \)
- $u$: cumulative amount of $H_2S$ found in the reactor effluent during the acceptation stage \( \text{mol} \)
- $v$: interstitial velocity of gas through acceptor bed \( m/s \)
- $w$: weight of acceptor in the reactor \( g \text{ or kg} \)
- $x$: stoichiometric factor (eqs. (2) and (3) of chapter 2)
- $x$: dimensionless gas phase concentration \( = C/C_0 \)
- $y$: stoichiometric factor (eqs. (2) and (3) of chapter 2)
- $y$: dimensionless solid phase concentration \( = q/q_b \)
- $z$: axial distance from reactor inlet \( m \)
- $\alpha$: degree of completion of regeneration \( \% \)
- $\alpha$: angle of $H_2S$ titration curve (paragraph 3.2.5.)
- $\alpha$: dimensionless stoichiometric capacity of acceptor \( = Q/(C_0) \)
- $\alpha$: modification of alumina
- $\alpha$: ratio of inlet concentration \( = C/H_2O/C_2H_2S \)
- $\alpha$: modification of alumina
- $\alpha$: void fraction of acceptor bed
- $\alpha$: dimensionless axial distance \( = z/L \)
- $\alpha$: modification of alumina
- $\alpha$: modification of alumina
dimensionless time (eqs. (19) and (54) of chapter 6)

$k$

dimensionless rate constant (eq. (54) of chapter 6)

$\lambda$

capacity ratio (eq. (54) of chapter 6)

$\rho_b$

bulk density of acceptor kg/m$^3$

$\Phi$

cross sectional area of acceptor bed m$^2$

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1. Older references sometimes present a more correct treatment of a problem than a relatively recent one, as is illustrated by the derivation of the equation of breakthrough curve for fixed-bed sorption processes controlled by an irreversible surface reaction in:

H.N. Chu and T.J. Houser, *J. Catal.* 3 368 (1964)


2. The parameter values used to produce a computer solution of a mathematical model should be reported without any rounding, unless it has been checked a priori that the rounding will not lead to a significant change in the solution.


3. The defect at the front side of chromatographic peak in a system involving the BET isotherm does not correspond to the B point but to the tangency point between the isotherm and a straight line through the origin.


4. The "continuously fed batch reactor" (CFBR) recently proposed as an experimental tool for kinetic studies is less attractive than conventional batch or CSTR method, because
the condition for a valid measurement in the CFBR is more
difficult to achieve.


5. Ruth et al. concluded that the reduction of manganese
oxides by hydrogen is controlled by diffusion at lower tem­
perature and by chemical reaction at higher temperature. If
their experimental data are analyzed correctly, the usual
conclusion - i.e. that chemical reaction is the controlling
step at lower temperature - is obtained.

V. Ruth, S. Ali, and V. B. Tare, Z. Phys. Chem. (Leipzig)
260(3) 517 (1979)

O. Levenspiel, "Chemical Reaction Engineering", 2nd. ed.,
John Wiley & Sons, New York, 1972, chapter 12

T. J. W. de Bruijn, T. H. Soerawidjaja, W. A. de Jong, and

6. The Runge-Kutta-Gill method is unsuitable for solving stiff
systems of ordinary differential equations (ODE's). There­
fore, a fair way of demonstrating the power of a new method
for stiff ODE's is by comparing its efficiency with that of
existing method(s) for stiff ODE's and not with that of
Runge-Kutta-Gill's.


7. The steam-regenerability of a MnO/γ-Al₂O₃ acceptor for H₂S
removal is caused by the interaction of the MnO and the
γ-Al₂O₃ support to form surface MnAl₂O₄ spinel.

This thesis, chapter 4

8. The warning :

Roken bedreigt de gezondheid. De Minister van Volksge­
zondheid en Milieuhygiëne. Nicotine x mg, teer y mg.

which can be found on every package of cigarette and shag,
should also be printed on cigar boxes.

9. For cooperation projects in developing countries to be
more effective, the sending of a larger proportion of ex­
perienced persons to these countries is a far better mean
than a mere increase in the number of "experts".

Delft, 13 juni 1986

T. H. Soerawidjaja