STEAM-REGENERATIVE REMOVAL OF H<sub>2</sub>S AT HIGH TEMPERATURES USING METAL OXIDE ON ALUMINA ACCEPTORS

# STEAM-REGENERATIVE REMOVAL OF H<sub>2</sub>S AT HIGH TEMPERATURES USING METAL OXIDE ON ALUMINA ACCEPTORS

# Proefschrift

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Kepada: Éndang, Aakh, dan Adi

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SUMMARY

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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 apppropriately dispersed on a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support is used as a H<sub>2</sub>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<sub>2</sub>O<sub>4</sub> or FeAl<sub>2</sub>O<sub>4</sub> 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<sub>2</sub>O<sub>3</sub> with a concentrated manganese acetate solution. When the nitrate salt of manganese is used, repeated impregnation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with dilute solutions must be applied to produce steam-regenerable acceptors with sufficiently high manganese content (8 %w). On the other hand, a single impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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  $\gamma\text{-Al}_{3}\text{O}_{3}.$ 

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  $\gamma-\lambda l_2O_3$ .

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 %w Mn is roughly 1 %w sulfur at  $600^{\circ}$ C. The rate of deactivation depends only on the operating temperature; it is negligibly slow at  $400^{\circ}$ 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  $600^{\circ}$ C. This improvement is not only due to more favourable kinetics but also to a more favourable equilibrium. Acceptor capacity is only slightly affected by the H<sub>2</sub>S 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 acceptation of  $H_2S$  is a rapid equimolar sulfur-oxygen exchange between the gas and the solid phase to produce  $H_2O$ . 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  $\rm H_2O$  as well as  $\rm H_2S$  are adsorbed by the acceptor. These facts are used to formulate a simple description of the overall process of  $\rm H_2S$  acceptation, i.e. a reversible sulfuroxygen 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  $\rm H_2O$  and  $\rm H_2S$  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 %w S at 600  $^{\circ}$ C.

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SAMENVATTING

De regeneratieve verwijdering van H<sub>2</sub>S 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 metaaloxyde 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 ijzeroxyde op y-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 MnAl\_0, of FeAl\_0, 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 efficiënste manier om door stoom regenereerbare mangaan houdende acceptoren te maken blijkt natte impregnatie van  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> met een geconcentreerde mangaanacetaat oplossing te zijn. Bij gebruik van het ntraatzout van mangaan is herhaalde impregnatie met een verdunde oplossing noodzakelijk om tot door stoom regenereerbare acceptoren te komen met een redelijk mangaangehalte (8 gew%). 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> aangepast wordt.

Karakterisering van de acceptoren met behulp van röntgendiffractie, reflectiespectroscopie en Mössbauer spectroscopie sreunen 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 oxyde op de alumina drager bestaat. Het gebruik van verschillende typen  $\gamma-Al_2O_3$  heeft niet geleid tot significante verschillen in het gedrag van de verkregen acceptoren.

Bij toepassing van verse 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 gew% mangaan bedraagt bij 600 °C ongeveer 1 gew% zwavel. De snelheid waarmee deactivering optreedt is alleen afhankelijk van de temperatuur; bij 400 °C is deze verwaarloosbaar en neemt langzaam toe met de temperatuur. De belangrijkste oorzaak is waarschijnlijk herkristallisatie van oppervlakte spinel die resulteert in verlies van activiteit en/of katalytisch oppervlak.

Bij verhogen van de temperatuur van 400 naar 600  $^{\circ}$ C verdubbelt de doorbraak capaciteit van de acceptor. Deze toename wordt niet alleen veroorzaakt door snellere reacties maar ook door een gunstiger ligging van het evenwicht. De capaciteit wordt slechts in geringe mate beinvloedt door de H<sub>2</sub>S concentratie en is wat lager bij hogere concentraties. Anderzijds wordt de capaciteit van de acceptor ongunstig beinvloedt door waterdamp in de voeding; een logisch gevolg van het feit dat de acceptor met stoom geregenereerd kan worden. Deze negatieve invloed van water vermindert aanzienlijk als de voeding koolmonoxyde bevat omdat daarmee de bekende shiftreactie optreedt.

Tijdens de acceptatie van H<sub>2</sub>S is de voornamste reactie een snelle equimolaire uitwisseling tussen gas en vaste stof van zwavel met zuurstof onder vorming van H<sub>2</sub>O. Tijdens regeneratie vindt de omgekeerde reactie plaats. In een geheel

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beladen acceptor bedraagt de molaire verhouding van zwavel tot mangaan ongeveer 1 op 2. Naast uitwisseling vindt ook adsorptie van relatief kleine hoeveelheden H<sub>2</sub>S en H<sub>2</sub>O plaats. Een eenvoudig model voor de H<sub>2</sub>S 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  $\rm H_2O$  en H\_S. 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 ontzwavelingsprocessen die bij hoge temperatuur werken en gebaseerd zijn op door stoom regenereerbare acceptoren een aantal belangrijke voordelen kunnen hebben in vergelijking met de bestaande processen. Teneinde de toepassingsmogelijkheden te vergroten is nader 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  $\mathrm{H}_2\mathrm{S}$  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  $^{\circ}$ 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/m<sup>3</sup>, 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  $H_2S$  with lesser portions of COS, CS<sub>2</sub>, 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  $H_2S$ , 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(1) indicates that the  $H_2S$  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.

		and the second second second
Gasifying medium :	steam + 0 <sub>2</sub>	steam + air
		A Darry Stranger
co	62.2 %v	22.7 %v
н <sub>2</sub>	28.0	8.3
СНа	0.1	
H <sub>2</sub> O	2.7	4.6
co,	2.4	4.9
H <sub>2</sub> S	0.9	0.4
Traces (COS,HCN,NH <sub>3</sub> ,NO)	0.2	0.1
N <sub>2</sub> , Ar	3.5	59.0
	100.0	100.0
Heating value, MJ/Nm <sup>3</sup>	11.8	4.1
Temperature, <sup>°</sup> C	1400	1400
Pressure, MPa	2	2

Data of reference (2)

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

Gasificatio	on process :	Lurgi	Synthane	MERC
Sulfur as :	H <sub>2</sub> S	95.0	94.9	91.5
	cos	2.4	2.6	6.5
	CS <sub>2</sub>	0.3	0.2	0.7
	Mercaptans	2.0	0.8	0.5
	Thiophenes	0.3	1.3	0.8
	so <sub>2</sub>	-	0.2	stant to
Reference	:	(3)	(4)	(5)

<sup>†</sup>Mongantown Energy Research Center.

fier product gas is determined by the end use of the resulting clean gas, which usually specifies a maximum allowable sulfur content; sometimes this limit is determined by environmental regulations only. Table 1.3. shows the maximum allowable sulfur content for the most important applications. Note that all limits are below the requirement of environmental regulations for stationary power sources (U.S.-EPA specification : maximum 1000 ppm sulfur(1/).

# <u>Table 1.3.</u> Maximum allowable sulfur content of the gasifier product gas.

	Application	Sulfur	content	Ref.
ι.	Catalytic synthesis	1	ppm	6,7
2.	Fuel cell (molten			
	carbonate)	1	ppm	7,8
3.	Reducing gas	50	ppm	9
ł .	Combined cycle elec-			
	tricity generation	500	ppm	10

## 1.2. High temperature desulfurization.

The idea to desulfurise 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

temperature purification ( > 400  $^\circ$  c) may result in a thermal efficiency improvement of up to 4 %. This means a saving of about 20 ton coal per hour at 1000 MW capacity(711.

Unfortunately, however, almost all commercially available processes for the removal of H<sub>2</sub>S operate at low temperature. Table 1.4. lists examples of these processes. The only process which operates at relatively high temperature, i.e. the process using zinc oxide, is not suitable because it is not regenerative and, therefore, produces much sulfur containing waste.

This fact has activated research on desulfurization at temperature higher than 400  $^\circ$ C (hot gas desulfurization). The best known scheme that has been the subject of many investigations utilizes a fixed-bed system of iron oxide :

a). Desulfurization (or acceptation),

$$Fe_2^{0}_{3(s)} + 2 H_2^{S(g)} + H_2(g) \frac{600^{\circ}c}{2} 2 Fe_{S(s)} + 3 H_2^{0}(g)$$
 (1)

b). Regeneration,

$$4 \operatorname{FeS}(s) + 7 \, {}^{0}2(g) \, \frac{600 - 2}{800 \, c} \, {}^{2} \operatorname{Fe}_{2} {}^{0}3(s) + 4 \, {}^{5}30(g) \, (2)$$

Examples of iron-oxide-based processes are the MERC (Morgantown Energy Research Center) process(15/, the Battelle Columbus process(16/, and the IMMR (Institute of Mining and Mineral Research) process(17/).

An economic comparison study on coal gasification combined cycle power generation plants has, however, halted most of the work based on iron oxide. This study, again performed by Stone and Webster Engineering Corp. for EPRI, compared the use of the MERC process to that of the Benfield process (see Table 1.4.). Tables 1.5., 1.6., and 1.7. summarizes the most important results of this study(18). It is clear from these tables that, except for the plants utilizing the Lurgi gasification processes, the use of the MERC process only resulted in marginal improvements in thermal efficiency, capital requirements, and electric power cost. The significant im-

Table 1.4. Examples of commercial processes for the removal of H <sub>o</sub> S from ga	S from gases	f H_S from	of Has	removal	the	for	processes	commercial	of	Examples	1.4.	Table
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Class of process	Sorbent	Process designation	Operating temp., °C	Regeneration product
M. Friday and	Solution of monoethanolamine (MEA)	Girbotol	20 - 40	H <sub>2</sub> S
	Solution of diethnolamine (DEA)	SNPA-DEA	20 - 40	H <sub>2</sub> S
Neutralisation	Solution of diglycolamine (DGA)	Econamine	40 - 80	H <sub>2</sub> S
processes	Solution of diisopropanolamine (DIPA)	ADIP	30 - 40	H <sub>2</sub> S
	Activated solution of K2C03	Benfield	80 - 120	H <sub>2</sub> S
	Activated solution of K <sub>2</sub> CO <sub>3</sub>	Catacarb	80 - 120	H <sub>2</sub> S
	Solution of Na-salts of H <sub>2</sub> CO <sub>3</sub> , Anthra quinone 2-sulfonic acid, vanadic acid	Stretford	20 - 40	s
Oxidation pro- cesses	Solution of Na-salts of H <sub>2</sub> CO <sub>3</sub> and 1,4-naphtoquinone 2-sulfonic <sup>3</sup> acid	Takahax	20 - 40	s
	$As_2O_3$ -activated solution of $K_2CO_3$	Vetrocoke	40 - 140	S
Physical or phy-	Dimethylether of polyethyleneglycol	Selexol	0 - 30	H <sub>2</sub> S
sical-chemical	Solution of n-methyl-2-pyrolidone	Purisol	0 - 40	H <sub>2</sub> S
solvent	Methanol	Rectisol	-7020	H <sub>2</sub> S
processes	Solution of diisopropanolamine + sul- folane (tetrahydrothiophene dioxide)	Sulfinol	20 - 60	H <sub>2</sub> S
Dry purifica-	Iron oxide (Fe <sub>2</sub> O <sub>2</sub> )	11 - K & B	15 - 80	so
tion processes	tion processes Zinc oxide (ZnO)			*

<sup>f</sup>Condensed from Refs. 12, 13, and 14

"Not regenerated; used as "guard bed"

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Purification process $\rightarrow$	Benfiel	d MERC	Benfield	MERC
Gas turbine inlet o, temperature, C	- 1066	1066	1316	1316
Gasification process		Thermal	Efficiency,	$\pi^f$
Lurgi (0 <sub>2</sub> )	29.4	35.4	32.4	39.9
Lurgi (air)	31.0	37.0	34.5	41.2
BGC Slagging (0,)	36.5	37.5	39.6	40.6
Foster-Wheeler (02)	35.4	36.6	37.8	39.3
Foster-Wheeler (air)	38.0	38.4	40.8	41.6
f <sub>Thermal efficiency (%)</sub>	= (Delivere	d kW) (3	412.75) (100)	1.)

Table 1.5. Estimated thermal efficiencies of coal gasification combined cycle power plants(18).

(lb/hr coal) (HHV, Btu/lb coal)

Table 1.6.	Estimated c	apital r	equiremen	ts of	1000	MW	gasifi-
	cation comb	ined cvc	le power	plants	(181.		

Purification process	-	Benfield	MERC	Benfield	MERC
Gas turbine inlet o temperature, C	-	1066	1066	1316	1316
Gasification process		Capita	l requi	rements, \$/	kW <sup>f</sup>
Lurgi (0 <sub>2</sub> )		1117	739	1046	703
Lurgi (air)		1000	667	936	642
BGC Slagging (0,)		643	629	629	606
Foster-Wheeler (0,)		670	679	658	657
Foster-Wheeler (air)		619	616	604	597

f<sub>Mid-1975</sub> dollars.

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

Purification process $\rightarrow$	Benfield	MERC	Benfield	MERC
Gas turbine inlet ° → temperature, °C	1066	1066	1316	1316
Gasification process	Pow	ver cost	ts, Mills/k	Wh <sup>f</sup>
Lurgi (0 <sub>2</sub> )	60.2	43.7	55.5	40.4
Lurgi (air)	55.0	40.5	50.7	37.7
BGC Slagging (0 <sub>2</sub> )	39.9	39.0	38.0	36.8
Foster-Wheeler (02)	41.4	41.1	39.8	39.1
Foster-Wheeler (air)	38.4	38.1	36.7	36.1

<sup>f</sup>Based on : Delivered coal cost of \$2.00/MMbtu. Mid-1975 dollars with no escalation included and operating load factor of 70 %.

provement in the case of plants using Lurgi process is due to the fact that gas from this gasifier contains a large amount of tar, the heating value of which is ultimately converted to electricity in the combined cycle system when the gas purification steps are carried out at a high temperature. If a low temperature desulfurization is used, this tar is removed during the purification process.

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 SO2 content and its treatment resembles that of stack gas.
- 2. The conversion of the regeneration product  $(SO_{\gamma})$  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  $\rm H_{2}$  and/or CO.

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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  $H_2S$  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. Fresently, 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  $\rm H_2S$ , which results from the reaction of hydrogen with the sulfur compounds in the oil. To prevent accumulation of  $\rm H_2S$  in the recycle gas, this must be removed.
- Desulfurization of coke oven gas(23). The fluidized-bed Appleby-Frodingham process, which operates at about 400  $\degree$ C, is an example of this application. It reduces the sulfur content of coke oven gas from 1 - 2 %v down to less than 1 ppm.

#### 1.3. Aim of the present study.

During his study on the use of manganese oxide on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as an acceptor for SO<sub>2</sub> removal from flue gas, Van der Linde(24) came to the conclusion, and provided evidence,that

MnO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can remove H<sub>2</sub>S from gases at 400 - 550 °C and that the sulfided product formed can be hydrolized back to MnO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at the same temperature using a gas containing 50 % steam. In other words, the reaction

$$MnO/\gamma - Al_2O_{3(s)} + H_2S(g) \implies MnS/\gamma - Al_2O_{3(s)} + H_2O(g)$$
 (3)

is reversible. This finding is interesting, because it implies that MnO on  $\gamma - Al_2O_3$  might be used as an acceptor in a high temperature regenerative  $H_2S$  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  $H_2S$  but their products, unlike the sulfided product of MnO on  $\gamma - Al_2O_3$ , do not hydrolise with steam, at least up to 600 °C. The behaviour of MnO on  $\gamma - Al_2O_3$  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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The results of this work may also help in explaining the behaviour of MnO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.
- to study the relation between the method of preparation and the properties of MnO on  $\gamma\text{-Al}_2O_2$  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 quantitaive 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.

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#### CHAPTER 2

METAL OXIDES AS SULFUR REMOVAL ACCEPTORS

#### 2.1. Introduction

Although the use of metal oxides as sorbents (or acceptors) for  $H_2S$  removal dates back to the middle of the nineteenth century (1), most of the high temperature  $H_2S$  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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with respect to sulfidation (cf. section 1.3.) is based on the assumption that the MnO reacts with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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  $H_2S$  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 14

Table 2.1. Conditions used in the thermodynamic screening study of Westmoreland and Harrison (2).

. Temperat . Pressure	ure range	: 400 - : 2.0	1200 MPa	°c.		
. Gas comp	position	:				
N	35 - 44 mol-%		H <sub>2</sub> S	0.7	-	1.0
co	8 - 33		cos	0.02	-	0.08
н	5 - 37		CH4	0	-	16
H <sub>2</sub> O	4 - 7		NH 3	0	-	0.04
co <sub>2</sub>	1 - 20					

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.
- Elements rejected because their excess metal oxide can be reduced to a low-melting metal : Bi, Cd, Pb, Sn.
- Elements rejected because inadequate desulfurization potential ( < 95 % ) even though their equilibrium is in favour of the sulfided state : Ag, La, Ni, Sb.
- 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 aggreement with the above results of Westmoreland and Harrison.

Two of the ll thermodynamically feasible elements give



<u>Fig. 2.1.</u> The most promising range of operating temperature of  $H_2S$ -acceptors. Chemical formulae indicate stable solid phases under desulfurization conditions.

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  $^{\circ}$ C because above this temperature vanadium sulfide (i.e. the sulfidation product) is a liquid. The appreciable vapour pressure of zinc above 700  $^{\circ}$ 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-

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tors is the rate of  $H_2S$  capture. The result of a comparative study on the sulfidation rates of several metal oxides(3) 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  $H_2S$  and the solid oxide were assumed to be one.

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It can be seen from Fig. 2.2. that  $Fe_2O_3$  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<sub>2</sub>O<sub>3</sub>. Activation energies of sulfidation vary from 12 kJ/mol for Fe<sub>2</sub>O<sub>3</sub> to 37 kJ/mol for V<sub>2</sub>O<sub>3</sub>.



Fig. 2.2. Sulfidation rate constants of selected metal oxides(3). Solid curves represent experimental data; broken lines represent extrapolations of Arrhenius plots for reaction-controlled sulfidation. Deviations from linearity indicate the onset of diffusion control.

# 2.2.3. Processes

As has been pointed out in the beginning of this chapter, all high temperature  $H_2S$  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 sulfide faster than (calcined) limestone. The acceptation reaction of the Conoco process, which uses semi calcined dolomite, is :

$$H_2^{S}(g) + CaCO_3 \cdot MgO_{(s)} \implies CaS \cdot MgO_{(s)} + H_2^{O}(g) + CO_2(g)$$
 (1)

The regeneration reaction is the reverse of this reaction. Acceptation is carried out at 900  $^\circ$ C where equilibrium favours the formation of MgO.CaS, CO<sub>2</sub>, and H<sub>2</sub>O from H<sub>2</sub>S and MgO.CaCO<sub>3</sub>. Regeneration is done at lower temperature where the reverse is true.

The problems facing calcium based processes are(6) : 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 :

$$^{40}x(s) + (x-y) H_2(g) + y H_2S(g) \longrightarrow MS_y(s) + x H_2O(g)$$
 (2)

where  $M \equiv metal$  and x > y. The regeneration step is :

$$MS_{y(s)} + (y + \frac{x}{2}) O_{2(g)} \longrightarrow MO_{x(s)} + y SO_{2(g)}$$
 (3)

This oxidation reaction is highly exothermic ( $\Delta H^{\circ} \simeq \Delta G^{\circ} \simeq -420 \pm 125 \text{ kJ/mol SO}_2$  formed) and, as has been pointed out in chapter 1, is the main cause of problems associated with

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Process	Status of development	Acceptor	Accept temp.(°C)	cation press.(kPa)	Reger	temp.(°C)	Remark
Conoco	terminated	Mg0.CaC03	006	15	H20-C02	600-760	
U.S. Steel	in progress	MgO.CaO	> 816	1	propri	ietary	
Battelle- Columbus	terminated	Supported Fe203	538-816	1	Air	593	
IMMR	in progress	Gasifier ash(Fe2 <sup>0</sup> 3)	371-816	4 - 9	Air	427-649	
MERC	in progress	Supported Fe203	538-816	1 - 20	Air	538-816	
Kennecott	terminated	Cu/CuO	482-496	20 - 25	Air	816	
IFP	in progress	Supported ZnO	400-600	6.	0_con- taining gas	600-900	proprietary process
U.S. Steel	6	$MnO_{x}^{-Al}2^{O}_{3}$	700-1000	~	0 <sub>2</sub> -con- táining gas	850-1150	proprietay process

the use of transition metal oxides as regenerable acceptors for  $\rm H_2S$  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  $^{\circ}$ C is, perhaps, the major drawback of this group. The ability of the transition metals to desulfurize effectively at 400 - 700  $^{\circ}$ C is advantageous for two reasons :

- 1. Many applications, especially those in the petroleum refining and petrochemical industries, requires a desulfurization temperature not higher than 500 - 600  $\degree$ C. (cf. examples at the end of section 1.2.)
- 2. Even though a desulfurization temperature as high as 1000  $^{\circ}$ 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  $^{\circ}$ 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.  $SO_2$ ) which is less attractive than that of the alkaline earth-based processes (i.e.  $H_2S$ ). 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 20

is the use of steam to remove sulfur from the acceptor bed in the form of  $H_2S(3)$ . 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) predicts 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported MnO used in his investigation can remove H<sub>2</sub>S 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  $ZnCr_2O_4$ ,  $TiMg_2O_4$ , and  $WNa_2O_4$ . A complex oxide may be called a spinel when :

- its formula can be written as AB<sub>2</sub>O<sub>4</sub> and

- its structure is isomorphous with the natural spinel (magnesium aluminate,  ${\rm MgAl}_2 O_4$ ).

For an oxide of the formula  $AB_{2}O_{4}$ , there are eight negative charges. The three combinations of the cation charges of A and B which can balance these negative charges are: ( $A^{2+}$  + 2  $B^{3+}$ ), ( $A^{4+}$  + 2  $B^{2+}$ ), and ( $A^{6+}$  + 2  $B^{+}$ ). These result in a 2-3 spinel, a 4-2 spinel, and a 6-1 spinel. The three examples 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 ( $B^{3+} = A1^{3+}$ ). Some of them are found in nature; these are(12) MgAl<sub>2</sub>O<sub>4</sub> (the spinel itself), FeAl<sub>2</sub>O<sub>4</sub> (Hercynite), MnAl<sub>2</sub>O<sub>4</sub> (Galaxite), and ZnAl<sub>2</sub>O<sub>4</sub> (Gahnite).

### 2.3.2. Structure. 19-121

The unit cell of a spinel  $MAl_2O_4$  contains 32 oxygen ions in cubic close packing, see Fig. 2.3., and corresponds to the formula  ${\rm M_8^{A1}}_{16}{\rm O}_{32}$  (or  ${\rm A_8^B}_{16}{\rm O}_{32})\,.$  This unit cell contains 32 octahedral holes and 64 tetrahedral holes, in which 8  $\ensuremath{\text{M}}^{2+}$  ions and 16  $\ensuremath{\text{Al}}^{3+}$  ions are arranged. In one limiting mode of distribution, 8 out of the 64 tetrahedral holes are occupied by  $\ensuremath{\text{M}}^{2+}$  ions and 16 out of the 32 octahedral holes are occupied by Al<sup>3+</sup> ions. Spinels with this type of distribution are called normal. Examples of normal spinels are(11, 12) : Co-, Fe-, Mg-, Mn-, and  $2nAl_2O_4$ . 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 spinel is called inverse. Between these two limiting cases (normal and inverse spinels), various degrees of inversion are observed. NiAl<sub>2</sub>O<sub>4</sub> is an example of a partly inverted spinel (about 76 % of the Ni<sup>2+</sup> ions occupy octahedral holes(11)).

It is worthy of note that the position of the  ${\tt M}^{2+}$  ion in the aluminate spinel MAl  $_2{\tt O}_4$  is different from that in



Fig. 2.3. The structure of spinels. Large ciacle : oxygen ion Small ciacle.

black	:	octahedral	cation
white	:	tetrahedral	catio

its simple oxide MO (except for M = Zn). In the simple oxide MO, all the M<sup>2+</sup> 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, greer, black, and olive green, whereas the colour of MnAl<sub>2</sub>O<sub>4</sub>, FeAl<sub>2</sub>O<sub>4</sub>, and CoAl<sub>2</sub>O<sub>4</sub> is, respectively, dark cream, grey-green, and ultramarine blue(*12*).

# 2.3.3. Thermodynamic of sulfidation.

Using available thermodynamic data(13,14), equilibrium constants and enthalpy changes were calculated for the following reaction scheme :

$$MAl_{2}O_{4}(s) + H_{2}S(g) = MS(s) + Y-Al_{2}O_{3}(s) + H_{2}O(g)$$
(4)  
$$\kappa = \frac{a_{MS} \cdot a_{Y}-Al_{2}O_{3} \cdot PH_{2}O}{a_{MAl_{2}}O_{4} \cdot PH_{2}S}$$
(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 NnO and FeO, reaction (6) and eq. (7), are also shown in these figures.

$$MO_{(s)} + H_2S_{(g)} \implies MS_{(s)} + H_2O_{(g)}$$
 (6)

$$K \approx \frac{a_{MS} \cdot p_{H_2O}}{a_{MO} \cdot p_{H_2S}}$$
(7)

As can be seen in Fig. 2.4., the thermodynamic equilibrium constants for the sulfidation of Mn- and FeAl<sub>2</sub>O<sub>4</sub> in the temperature range of 700 to 1000  $^{\circ}$ C are close to unity (log K about zero), while those of MnO, FeO, and NiAl<sub>2</sub>O<sub>4</sub> are large

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Fig. 2.4. Thermodynamic equilibrium constants of sulfidation of several metal oxides.

(greater than 100). This means that the sulfidation of  $MnAl_2O_4$ and  $FeAl_2O_4$  is reversible, whereas that of  $NiAl_2O_4$ , 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  $\gamma$ -Al $_2O_3$ , the presence of steam will remove sulfur from the solid phase in the form of  $H_2S$ , 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  $2nAl_2O_4$  and  $CoAl_2O_4$  were not calculated. The use of  $2nAl_2O_4$  as an acceptor for the removal of  $H_2S$  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 :

- 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.
- 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\eta$ -Al<sub>2</sub>O<sub>3</sub>, 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<sub>2</sub>O<sub>3</sub> as Al<sub>8/3</sub>O<sub>4</sub>). 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\eta$ -Al<sub>2</sub>O<sub>3</sub> can be written as :

 $Al_{2/3} + x \Box_{1/3} - x \begin{bmatrix} Al_2 - x & \Box_x & 0_4 \end{bmatrix}$ 

where  $0 \le x \le 1/3$ ,  $\Box$  represents a cation vacancy, and the bracketed term represents octahedral sites. Stone(10) suggested that  $\eta$ -Al<sub>2</sub>O<sub>2</sub>, has more tetrahedral Al<sup>3+</sup> than  $\gamma$ -Al<sub>2</sub>O<sub>2</sub>.

When  $\gamma$ - or  $\eta$ -Al<sub>2</sub>O<sub>3</sub> 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<sup>2</sup>/g). Above 600 °C the surface area decreases with temperature, but still amounts to about 100 -140 m<sup>2</sup>/g at 800 °C(18,19). Further heating transform  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> into  $\delta$ -Al<sub>2</sub>O<sub>3</sub> and  $\eta$ -Al<sub>2</sub>O<sub>3</sub> into  $\theta$ -Al<sub>2</sub>O<sub>3</sub>. Gauguin et.al.(19) pointed out that the addition of a small amount of a divalent ion such as Mg or Zn to  $\gamma$ - or  $\eta$ -Al<sub>2</sub>O<sub>3</sub>, 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  $\gamma-$  or  $n-{\rm Al}_{2}O_{2},$ 

A metal oxide dispersed on a support may end up in

three different forms(17) :

 it may retain its chemical identity; the carrier acts only as a dispersing agent.

it may form a new stoichiometric compound with the support.
 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  $\gamma$ - and  $n-Al_2O_3$  as supports which exhibit strong interaction with a metal oxide dispersed on their surface. Pott and Stork(17) pointed out that  $\gamma$ - and  $n-Al_2O_3$  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  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (the most stable form of alumina).

Selwood et.al.(21) studied the formation of manganese oxide on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by impregnating this support with a solution of Mn(NO<sub>3</sub>)<sub>2</sub>, followed by drying and calcination in air at 200 °C and 600 °C. They concluded that :

- the dispersion of manganese oxide is poor. The manganese oxide appears in patches which leave much of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface bare. These patches become smaller when less manganese is present in the sample. The thermal decomposition behaviour of manganese nitrate solutions may be the cause of the poor dispersion; it is known(15) that manganese nitrate can decompose in the solution phase (before much of the water has evaporated). This will prevent the proper adhesion of manganese oxide on the alumina surface.

- the layer of manganese oxide in actual contact with the alumina is always subject to the inductive action of the a-lumina and crystallises as  $\gamma - Mn_2O_3$  which is isomorphous with the  $\gamma - Al_2O_3$ . The layers not in direct contact with the  $\gamma - Al_2O_3$  crystallise as  $\alpha - Mn_2O_3$  (600 °C) or  $\beta - MnO_2$  (200 °C), depending on the calcination temperature.

Lo Jacono et.al.(22) established the formation of surface spinel  $MnAl_2O_4$  on  $\gamma-Al_2O_3$  and  $\eta-Al_2O_3$  by using hydrogen, instead of air, as the medium of calcination. The calcination temperature was 600  $^{\circ}$ 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 %w Mn) all the manganese is in the form of surface spinel MnAl  $_{2}O_{A}$ .
- at higher Mn content, any manganese in excess of 3 to 4 %w is present as MnO.
- 3. samples based on  $\gamma\text{-Al}_2\text{O}_3$  and those based on  $n\text{-Al}_3\text{O}_3$  behave similarly.

Lo Jacono and Schiavello(23) observed that Co, Cu, and Ni behave similarly to Mn when deposited on  $\gamma$ - or  $n-Al_2O_3$ . 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<sup>2+</sup> 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.

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#### 2.2.4. Discussion.

The evidence that surface  $MnAl_2O_4$  can be formed on  $\gamma-Al_2O_3$  and that, as shown thermodynamically, the sulfidation of  $MnAl_2O_4$  is a reversible reaction, provides an indication that the active component of the  $MnO/\gamma-Al_2O_3$  acceptor used by Van der Linde(8) was the surface spinel  $MnAl_2O_4$ . 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  $CoAl_2O_4$ , for example, does not posses catalytic activity for the oxidation of CO, whereas surface  $CoAl_2O_4$  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  $\gamma\text{-Al}_2\text{O}_3$  with 0.5 molar solution of  $\text{MnSO}_4$  (up to three times, each impregnation being followed by drying and calcination in  ${\rm H}_2$  stream at 500 - 600  $^{\circ}{\rm C}). This method of prepara$ tion, 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  $FeAl_2O_4$ , 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  $\eta\text{-Al}_{2}0_3$  as support material, since the work of Lo Jacono et.al.(22) has shown that  $\gamma\text{-Al}_20_3$  and  $\eta\text{-Al}_20_3$  are similar with respect to surface spinel formation.

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#### 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.

flowsheet of the benci

#### 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 photoionization detector (14) 3.2.1. Gas dosage.

The required gas were supplied from bottles. They





entered the unit via solenoid valves (1) at a pressure of about 0.4 MPa and (except for the  $H_2S/N_2$  mixture) were passed through purification trains (2) to remove traces oxygen and water. Each gas then passed a pressure regulator (3), which reduced its pressure to 0.2 MPa, and a mass flow controller (4) (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 %v water vapour, the N<sub>2</sub> 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 FeSO<sub>4</sub>.7H<sub>2</sub>O which produces water vapour according to dehydration reaction(1) :

$$FeSO_4 \cdot 7H_2O(s) \implies FeSO_4 \cdot 4H_2O(s) + 3H_2O(g)$$
(1)  
green white

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. Reacton 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 ratios 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/21.

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 capillarry.

Solenoid valves system (1) in the reactor section allowed the feed gas to bypass the reactor for determination of the inlet concentration of  $H_{n}S$ .

3.2.3. Analysis section.

By means of three four-way valves,  $\begin{pmatrix} 12 \\ 2 \end{pmatrix}$ , the gas flow leaving the reactor section could be passed through one

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or all of the following analytical instruments : a). gas chromatograph (13). b). photoionization detector (14). c). continuous titration system (15). The gas chromatograph was equipped with a 1 ml sam-

pling loop and a 1.70 m column filled with Porapak QS 80-100 pretreated thermally at 250  $^{\circ}$ C for 3 hours. The column temperature was 100  $^{\circ}$ C and the hydrogen carrier gas flow 30 ml/min. At these conditions N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S, COS, and H<sub>2</sub>O could be separated within 7 minutes. Detection was accomplished by a katharometer maintained at 150  $^{\circ}$ 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  $H_2S$  (less than 200 ppmv) in the reactor effluent during acceptation stage. In this instrument, the gas passed through an ionization chamber irradiated by a 10.2 eV ultraviolet lamp specially selected for  $H_2S$ . The radiation was of such strength that only  $H_2S$  would be ionized. The extent of ionization was determined by a normal ionization detector (comparable to a flame ionization on detector). Thus, a continuous analysis of low concentrations of  $H_2S$  could be obtained.

The titration system is based on the well established fact that a cadmium salt solution can remove  $H_2S$  completely from a gas phase intimately contacted with it(3,4). The  $H_2S$  reacts with the cadmium ion producing cadmium sulfide precipitate and hydrogen ion :

 $H_{2}S + Cd^{++} \longrightarrow CdS_{l} + 2H^{+}$ (2)

The H<sub>2</sub>S content of the gas can be determined by titrating the H<sup>+</sup> 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 (15); the gas was dispersed by stirring in solution of CdSO<sub>4</sub> (0.1 - 0.3 M) at a pH of 4. The



Fig. 3.2. Titration vessel.

pH electrode
 magnetic stirrer

3. overflow tube

4. baffle

to waste-chemical barrel

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<sup>-1</sup> 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  $\degree$ 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-

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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 °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 result.

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  $\rm H_2S$  content of the reactor effluent was monitored.
- 3. Regeneration : the sulfur-loaded acceptor was treated with a steam-containing gas and the amount of  ${\rm H}_2{\rm S}$  released was monitored.

 "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<sub>2</sub>S-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



Fig. 3.3. A sketch of continuous titration data obtained from a complete acceptation-regeneration cycle.

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 hed 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  $t_c$  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  ${\rm H}_2\,{\rm S}$  in the reactor effluent.

Although the cadmium salt solution in the titration vessel completely removes even minute amounts of  $H_2^S$  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  $H_2^S$ . Thus, during acceptation, the titration data indicate practically zero cumulative amount of  $H_2^S$  until point B is reached. At this point, the outlet concentration of  $H_3S$  is about 100 ppmv.

Because it is easy to observe in the continuous titration data, the outlet concentration of 100 ppmv  $H_2S$  was chosen as the *bneakthnough concentration* (or *bneakthnough 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 H<sub>3</sub>S, tan  $\alpha$ , using the formula :

$$\bar{q}_{b} = \frac{t_{b} \cdot \tan \alpha}{w}$$
 (3)

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  $\bar{q}_r$  is :

$$\bar{q}_{c} = \frac{t_{c} \cdot \tan \alpha - 0}{w}$$
 (4)

U being the cumulative amount of H\_S found in the reactor off

gas during the cycle. During regeneration, the sulfur released by the acceptor produced the *negeneration* (or *elution*) *curve* DE. The percentage of completion of regeneration is :

$$\text{\$-reg} = \frac{R}{t_c \cdot \tan \alpha - U}$$
(5)

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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>4</sub> 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.

Support	Surface area, m <sup>2</sup> /g	Pore volume, ml/g	Analyțićal data
Standard Y-Al <sub>2</sub> 0 <sub>3</sub> (Alumina OOl - 1.5E)	263	0.67	SiC <sub>2</sub> 0.76 %w Na <sub>2</sub> 0 0.05 %w SO <sub>4</sub> 1.6 %w Fe 0.02 %w
High purity Y-Al <sub>2</sub> O <sub>3</sub> (Alumina 000 - 1/10"E)	. 167	0.52	Cl 0.02 %w S 67 ppmw Na 45 ppmw Fe 203 ppmw
High porosity Y-Al <sub>2</sub> 0 <sub>3</sub> (Alumina OOl - 5P)	262	1.09	SiO <sub>2</sub> 1.31 %w Na <sub>2</sub> O 0.24 %w SO <sub>4</sub> 1.4 %w Fe 0.03 %w
High silica Y-Al <sub>2</sub> O <sub>3</sub> (Alumina 007 - 1.5E)	321	0.66	SiC <sub>2</sub> 5.4 %w Na <sub>2</sub> O 0.05 %w SO <sub>4</sub> 1.12 %w Fe 0.03 %w
Silicagel AT23	385	0.90	Al 0.20 %w Ca 0.09 %w Na 0.03 %w
Silica-alumina (Low alumina grade, LA - 100 - 3P)	400	0.56	Al <sub>2</sub> O <sub>3</sub> 13 %w Na <sub>2</sub> O 0.1 %w SO <sub>4</sub> 1.0 %w Fe 0.03 %w
Synthetic MgAl <sub>2</sub> 0 <sub>4</sub>	136	0.4	



Fig. 3.4. The wet impregnation method of acceptor preparation

terial 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

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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).

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Two acceptors,  $MgAl_2O_4$ -supported manganese and iron aluminates, were prepared by the dry impregnation route. The  $MgAl_2O_4$  support was titrated to incipient wetness with a saturated solution of nitrates of aluminum and manganese/iron (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  $MnAl_2O_4$  spinel was prepared as follows. A mixture of  $Mn(NO_3)_2.4H_2O$  and  $Al(NO_3)_3.9H_2O$  (molar ratio l: 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  $H_2$ 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  $^{\circ}$ 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 CuK $\alpha$  radiation. One acceptor sample was heated to 600°C under a stream of 5 %v 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 CuK $\alpha$ .

Diffuse reflectance spectroscopy was used to determine the site occupied by  ${\rm Mn}^{2+}$  ion in manganese-based acceptors. The instrument used to obtain the spectra was a Beckman DK-2 spectroreflectometer. The standard white material used was BaSO<sub>4</sub>. 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 spectroreflectometer, allows the acceptor sample to be reduced and then isolated from air for the





measurement of its reflectance spectrum. The sample was reduced at 500  $\degree$ C for 1.5 hours. During this treatment, a 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 N<sub>2</sub> as adsorbate was applied to measure the surface area of the acceptors. Prior to measurement, the sample was evacuated down to  $10^{-5}$  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.

- K.J. Parkinson and W. Day, J. Exp. Botany 32(127) 411-418 (1981)
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- 3. V.J. Altieri, "Gas Analysis and Testing of Gaseous Matenials". American Gas Association, New York, 1944.
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#### 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 (11) :

 $T_{d} = 1.134 T_{b} - 11.6$  (A1)

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

 $T_{\rm b}$  = bath temperature, C (10 - 50 C). The standard error of each coefficient in eq. (Al) is 0.6 % (1). Thus, the volume fraction of water vapour in the outgoing gas is :

$$Y = \frac{{}^{P}H_{2}O}{{}^{P}tot}$$
(A2)

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

$$\phi_{VW} = \frac{y}{1 - y} \phi_{V}$$
(A3)

The design of the iron sulfate bed used in this work follows that of Parkinson and Day (1) 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 accuracy 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<sub>4</sub>.4H<sub>2</sub>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<sub>4</sub>.7H<sub>2</sub>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.

 K.J. Parkinson and W. Day, J. Exp. Botany 32(127) 411-418 (1981).

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# 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> acceptors, especially the desulfurization and steam-regeneration performance.
- to investigate whether other metal oxides can behave like manganese oxide when supported on  $\gamma$ -Al<sub>2</sub>O<sub>2</sub>.
- 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 discusses 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 relation 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<sub>2</sub>O<sub>4</sub>), they were prepared via the wet impregnation technique 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 compara-

	tive	desulfur:	ization-re	generation	tests
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Accep- ton	Support <sup>\$</sup>	Me <sup>¶</sup>	%w	Colour <sup>£</sup>	Рл	ep nd.	arati ition	.on s†	Technical ледепела- bility
1	st. Al,0,	Mn	7.9	green	1	x	2.0	N	No
2	ditto	Mn	8.0	cream	4	x	0.5	N	Yes
3	ditto	Mn	10.1	pale green	4	x	0.7	N	No
4	ditto	Mn	7.2	cream	3	x	0.5	S	Yes
5	ditto	Mn	7.6	cream	1	x	2.0	А	Yes
6	ditto	Mn	13.0	cream	1	x	4.0	N <sup>†</sup>	Yes
7	MnAl <sub>2</sub> 0 <sub>4</sub>	Mn	27.6	cream			*		Yes
8	Si02	Mn	8.0	white	1	x	1.5	А	No
9	Si 02	Mn	6.9	green	1	x	1.5	N	No
10	Si02.Al203	Mn	4.9	white	1	x	0.8	A	No
11	st. A1203	Mn	6.1	cream	1	x	1.5	А	Yes
12	ditto	Mn	4.4	cream	1	x	1.0	А	Yes
13	ditto	Mn	2.7	cream	1	x	0.5	А	Yes
14	ditto	Mn	12.2	pale green	2	x	1.5	А	No
15	po. Al203	Mn	8.7	cream	1	x	1.5	А	Yes
16	ditto	Mn	10.4	cream	1	x	2.0	Α	No
17	pu. Al <sub>2</sub> 03	Mn	5.1	cream	1	x	1.2	А	Yes
18	ditto	Mn	12.3	green	1	х	2.0	A	No
19	si. Al <sub>2</sub> 03	Mn	7.2	cream	1	x	2.0	A	Yes
20	st. Al <sub>2</sub> 03	Zn	8.7	white	1	x	1.2	A	Yes
21	ditto	Ni	4.2	turquoise	1	х	0.5	A	No
22	ditto	Co	3.2	deep blue	1	x	0.5	А	Yes
23	ditto	Fe	4.7	grey-green	1	x	1.0	0	Yes
24	ditto	Fe	6.3	grey-green	2	x	1.0	0	Yes

\$ st = standard, po = high porosity, pu = high purity, si = high silica. For support characteristics see Table 3.1.

<sup>¶</sup>Active metal. <sup>£</sup>The colour of Mn-acceptors is only observable in reduced condition.

<sup>†</sup>Code : number of impregnations x molarity of solution, followed by the type of salt used (A=acetate, N=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.

<sup>†</sup>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 manganesecontaining sorbents, acceptors # 11 to 13 to investigate the relation between manganese content and performance of regenerable sorbents, acceptors # 14 to 19 to examine whether the nature of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support has any influence on the general behaviour 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 H<sub>2</sub>S acceptation-regeneration performance of the acceptors 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 acceptation, a gas mixture of 1.2 % H<sub>2</sub>S, 11 % H<sub>2</sub>, and 87.8 % N<sub>2</sub> was passed through the acceptor bed at a flow rate of 100 Nml/min<sup>§</sup>. Seven minutes after the concentration of H<sub>2</sub>S in the bed effluent had reached about 100 ppmv the acceptation was stopped. The breakthrough capacity of the acceptor,  $\bar{q}_{b}$  (cf. section 3.2.5.), and the breakthrough conversion of the transition metal,  $\bar{\xi}_{\rm Me, b}$ , were the principal data gathered.

The sulfur loaded acceptor was then regenerated with a gas stream consisting of steam and nitrogen + hydrogen (N<sub>2</sub> : H<sub>2</sub> = 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 %)

<sup>Nml/min =</sup> normal milliliter per minute, i.e. the flow rate at 25  $^{\circ}$ C and 100 kPa.

- "drying" under the N2 + H2 stream until H2S 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, %-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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> reacts sufficiently rapidly to form bulk MnAl<sub>2</sub>O<sub>4</sub> spinel(7).

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.

Accep- tor	Support	Im	pro m	egnat ethod	ion f	%w-Mn	q <sub>b</sub> %w−S	ξ <sub>Mn,b</sub> %	%-reg.
1	Y-A1.02	1	x	2.0	N	7.9	3.8	82	69
2	ditto	4	x	0.5	N	8.0	1.5	32	100
3	ditto	4	x	0.7	N	10.1	3.0	51	95
4	ditto	3	x	0.5	S	7.2	1.0	24	100
5	ditto	1	x	2.0	A	7.6	1.6	34	100
6	ditto	1	x	4.0	N <sup>\$</sup>	13.0	0.5	7	100
7	MnAl 0			-		27.6	0	0	100 <sup>£</sup>
8	Si0,	1	x	1.5	А	8.0	0	0	64 <sup>£</sup>
9	sio <sub>2</sub>	1	x	1.5	N	6.9	2.9	73	24
10	sio2. Al 203	1	x	0.8	A	4.9	0	0	70 <sup>£</sup>

<sup>†</sup>see the footnote of Table 4.1.

\$ reductively calcined at 1000 °C for 1 hr.

<sup>E</sup>results from the alternative test procedure.

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<sub>2</sub>O<sub>3</sub> with a concentrated solution of manganese nitrate to exhibit a poor degree of dispersion. In such acceptors all the manganese in excess of 4 tw exists as clusters of MnO. Because MnO reacts irreversibly with H<sub>2</sub>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 investigator(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<sub>2</sub>O<sub>3</sub>. An explanation of the fact that these acceptors are relatively easy to regenerate has been proposed in section 2.4.3.; this fact was ascribed to the formation of surface MnAl<sub>2</sub>O<sub>4</sub> spinel as a result of the reaction of the finely dispersed MnO and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Two observations presented in Tables 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  $MnAl_2O_4$  (indicating a similar environment around the divalent manganese ion) , and

- MnAl\_O, itself reacts reversibly with H\_S.

As can be seen from the data in Table 4.2., however, bulk  $MnAl_2O_4$  has a lower reactivity towards  $H_2S$  than surface spinel (i.e. both are regenerable but surface spinel has a break-through 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<sub>2</sub>O<sub>4</sub> is more ordered than that of surface MnAl<sub>2</sub>O<sub>4</sub>. This is because the latter is, firstly, a surface compound and, secondly, formed on Y-Al<sub>2</sub>O<sub>3</sub>, 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  $\gamma - \lambda l_2 O_3$  with a manganese acetate solution is easily regenerable, it follows that impregnation of  $\gamma - \lambda l_2 O_3$  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 support(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\_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 negenerable acceptors.

Table 4.3. presents the test results on acceptors # 5 and 11 to 13, all of which were prepared by impregnation of standard  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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 H<sub>2</sub>S. 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as supports. In general, no significant differences in behaviour were found between acceptors prepared with different types of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The results listed, however, strengthens the supposition of paragraph 4.2.2.1. that there exists a certain maximum content of manganese above which the acceptor cannot be regenerated

Table 4.3. The	relation between manganese	content
and reactivity	of the regenerable MnO on	Y-A1203
acceptors.		

Acceptor	%w−Mn	q <sub>b</sub> %w-S	ξ <sub>Mn,b</sub> %	%-reg.
5	7.6	1.6	34	100
11	6.1	1.3	36	100
12	4.4	1.0	39	100
13	2.7	0.7	45	100

<u>Table 4.4.</u> Desulfurization and steam-regeneration behaviour of MnO on several types of  $\gamma$ -Al<sub>2</sub>O<sub>2</sub>.

Acceptor	Type of $\gamma - Al_2 O_3$	%w−Mn	q <sub>b</sub>	ξ <sub>Mn,b</sub>	%-reg.
361319/6			/oW-5	70	
5	standard	7.6	1.6	34	100
14	ditto	12.2	4.1	58	72
15	high porosity	8.7	1.6	30	100
16	ditto	10.4	2.9	49	83
17	high purity	5.1	1.2	41	100
18	ditto	12.3	5.6	78	52
19	high silica	7.2	1.0	24	100

completely. From the performance data of acceptors # 15 and 16, which use high porosity  $\gamma - \lambda l_2 O_3$  ( $S_{\rm BET} = 260 \ {\rm m}^2/{\rm g}$ ) as support, this upper limit of manganese content is estimated to be between 3.3 and 4.0 %w-Mn per 100  $\ {\rm m}^2$  support surface. In this connection, the results obtained by Friedman et.al.(9) from an extensive study on the interaction of cupric ions with  $\gamma - \lambda l_2 O_3$  supports are of interest. These authors concluded that a number of transition  $\gamma$ -aluminas appear to have a similar treshold loading for the appearance of crystalline cupric oxide of about 4 %w-Cu/100  $\ {\rm m}^2$  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  $\ {\rm m}^2$ , a value in agreement with the treshold 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 :


one can make a rough estimate of the treshold 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 x  $10^{-20}$  m<sup>2</sup>. Thus, there are 12.5 x  $10^{20}$ OH groups per 100 m<sup>2</sup> 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 treshold loading of manganese is 0.5 x (2/3) x 12.5 x  $10^{20}$ Mn ions per 100 m<sup>2</sup> or 3.5 %w-Mn per 100 m<sup>2</sup> 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  $2nAl_2O_4$  spinel has a low reactivity towards sulfidation. Anderson et.al.(14) reported that the breakthrough conversion of zinc in their acceptor (75.9 %  $2nAl_2O_4$ , 24.1 %  $Al_2O_3$ ) 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

<u>Table 4.5.</u> Desulfurization capacity and steam-regenerability of several metal oxides on  $\gamma$ -Al<sub>2</sub>O<sub>2</sub>.

Acceptor	Active metal, Me	%w−Me	q <sub>b</sub> %w−S	ξ <sub>Me,b</sub>	%-reg.
5	Mn	7.6	1.6	34	100
20	Zn	8.7	0.5	12	100
21	Ni	4.2	1.1	50	61
22	Co	3.2	0.5	28	100
23	Fe	4.7	1.1	43	100
24	Fe	6.3	1.4	38	100

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  $H_2S$  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 MnO have been postulated to explain the differences in behaviour of MnO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> acceptors containing less than 9 %w-Mn. Irregenerable acceptors are described as containing poorly dispersed clusters of MnO whereas the regenerarable ones are considered to contain finely dispersed Mn in the form of the reaction product with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, i.e. a surface MnAl<sub>2</sub>O<sub>4</sub> spinel. In order to conform this proposition, se-

veral MnO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> acceptors were characterized by X-ray diffraction anlysis 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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 of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. Comparison with Fig. 4.1.A clearly in-



Fig. 4.1.X-ray diffraction photograph of :A.  $MnAl_2O_4$  (acceptor # 7)B. Standard Y-Al\_2O\_3C. Acceptor # 4D. Acceptor # 5E. Acceptor # 1(For acceptor characteristics see Table 4.1.)

dicates that these sharp lines do not come from bulk  $MnAl_2O_4$ . 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  $^{\circ}$ C under a stream of 5 %v H<sub>2</sub> 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 spectroreflectometer. 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  $Mn^{2+}$ ),  $MnAl_2O_4$  (tetrahedral  $Mn^{2+}$ ), and  $\gamma-Al_2O_3$ . The spectrum of  $\gamma-Al_2O_3$  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 Mn<sup>2+</sup>). 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





Fig. 4.2. Diffuse reflectance spectra of manganese-containing acceptors and some standard materials. Fig. 4.3. DR spectra of acceptors # 2 and 4, fresh and after 5 acceptation-regeneration cycles.

(For details of acceptor characteristics see Table 4.1. )

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



Fig. 4.4. Diffuse reflectance spectra of  $MnAl_2O_4$  (a) compared with acceptor # 5 after (b) and before (c) treatment with air at 600 °C.

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 accetates 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  $\degree$ 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  $\text{MnAl}_2O_4$  and, therefore, provide a strong indication that the active component of regenerable acceptors, at least those derived from acetate, is surface  $\text{MnAl}_2O_4$  spinel (or tetrahedral  $\text{Mn}^{2+}$ ). 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. Acceptationregeneration 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 %w-Fe. It was prepared via impregnation of standard  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with an 0.5 M solution of ferrous sulfate. In the study, uncalcined sample of dry, impregnated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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

<sup>3</sup>The results presented were obtained in cooperation with Dr. A.M. van den Kraan, Interuniversity Reactor Institute, Delft, who also contributed to the interpretation of the data. This substantial contribution is gratefully aknowledged. 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-C0 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 nitropruside (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<sub>2</sub> drastically changes this doublet. It follows from the values of isomer shift (I.S.) as well as quadrupole splitting







<u>Table 4.6.</u> The isomer shift (I.S.), quadrupole splitting (Q.S.) and spectral contribution corresponding to the spectra in Fig. 4.5..

Sample form	I.S. mm/s	Fe <sup>3+</sup> Q.S mm/s	%	I.S. mm/s	Fe <sup>2+</sup> Q.S. mm/s	%
uncalcined	0.64	0.75	100	-	-	0
reduced	i kal <del>7</del> ko.	-	0	$1.39 \\ 1.29$	2.25	60 40
air exposed	. 0.62	0.94	70	1.24	1.97	30

(Q.S.) presented in Table 4.6. that all Fe<sup>3+</sup>ions are reduced to Fe<sup>2+</sup>. This is in contrast to the normal behaviour of iron oxide which at 600 °C is reduced to metal. Table 4.6. also shows that exposure to air only oxidizes two-thirds of the Fe<sup>2+</sup> ions to the trivalent state. Note that finely dispersed iron would be oxidized easily and completely to the trivalent state. The air-exposed sample can be reduced in 2 hours at 600 °C, again yielding Fe<sup>2+</sup> ions.

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 spect tral contributions of Fe<sup>2+</sup> and Fe<sup>3+</sup> is almost constant with temperature. The appearance of the diffuse broadened background instead of a well resolved sextupplet (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 guadrupole splitting, was found to be identical with the spectrum of coal slags after gasification(16). It is likely that the asymmetry of the doublet is due to the occurence of different environments of Fe<sup>2+</sup>, 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..



Fig. 4.6. Mössbauer spectra of an air-exposed 3.6 %w-Fe on  $\gamma$ -Al\_00, acceptor at various temperatures.

Table 4.7	. Mos	spauer p	ara	ne cer.	varues	derryca	110
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Temperature K	I.S. mm/s	Fe <sup>3+</sup> Q.S. mm/s	%	I.S. mm/s	Fe <sup>2+</sup> Q.S. mm/s	%
295	0.58	0.98	56	1.22	1.81	44
77	0.64	1.03	56	1.31	2.13	44
4.2	0.65	1.23	61	1.48	2.50	39

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<sub>2</sub>O<sub>4</sub> 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<sub>2</sub> or O<sub>2</sub>. It is likely that the thermodynamic properties of surface spinel do not differ appreciably from those of bulk FeAl<sub>2</sub>O<sub>4</sub> spinel. Using thermodynamic data for the bulk spinel tabulated in the literature(17,18) it is found that the reaction :

$$FeA1_{2}^{0}_{4(s)} + H_{2(g)} = Fe_{(s)} + Y-A1_{2}^{0}_{3(s)} + H_{2}^{0}_{(g)}$$
 (2)

has  $\Delta G^\circ$  values of +68 to +48 kJ/mol at 25 to 800 °C. Thus, reduction of FeAl<sub>2</sub>O<sub>4</sub> 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 reac-

$$FeA1_2^0_4(s) + \frac{1}{6} O_2(g) = \frac{1}{3} Fe_3^0_4(s) + \gamma - A1_2^0_3(s)$$
 (3)

has  $\Delta G^{\circ}$  values of -40 to -16 kJ/mol at 25 to 900 °C, which indicates that even bulk FeAl<sub>2</sub>O<sub>4</sub> 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 Fe<sub>3</sub>O<sub>4</sub> (Fe<sup>2+</sup>Fe<sub>2</sub><sup>3+</sup>O<sub>4</sub><sup>-2</sup>). 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<sub>2</sub>O<sub>3</sub>.

a. 4.7 %w-Fe on standard  $\gamma - Al_2O_3$  (acceptor # 23) b. 4.5 %w-Fe on high purity  $\gamma - Al_2O_3$ c. 6.2 %w-Fe on high porosity  $\gamma - Al_2O_3$ d. 6.7 %w-Fe on high silica  $\gamma - Al_2O_3$ e. 5.9 %w-Fe on high silica  $\gamma - Al_2O_3$  69

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

Acceptor	I.S. mm/s	Fe <sup>3+</sup> Q.S. mm/s	%	I.S. mm/s	Fe <sup>2+</sup> Q.S. mm/s	%
4.7 % Fe on stan- dard y-Al <sub>2</sub> 03	0.59	0.98	58	1.22	1.89	42
4.5 % Fe on high purity γ-Al <sub>2</sub> 0 <sub>3</sub>	0.58	0.94	40	1.23	1.80	60
6.2 % Fe on high porosity Y-Al <sub>2</sub> 03	0.62	1.03	46	1.22	1.85	54
6.7 % Fe on high silica γ-Al <sub>2</sub> O <sub>3</sub>	0.62	1.03	60	1.24	2.00	40
5.9 % Fe on high silica γ-Al <sub>2</sub> 0 <sub>3</sub>	0.62	0.98	62	1.22	2.02	38

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<sub>2</sub>O<sub>3</sub> 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 betweem 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 :

- 1. There are two types of manganese oxide on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, forming surface MnAl<sub>2</sub>O<sub>4</sub> 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  $H_2S$ . An efficient way to prepare this acceptor is by wet impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a concentrated solution of manganese acetate.
- 3. The surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> appears to have a maximum capacity of about 3.5 %w-Mn/100 m<sup>2</sup> to accomodate the manganese in the form of surface MnAl<sub>2</sub>O<sub>4</sub> spinel.
- 4. Zinc, iron, and cobalt behave similarly to manganese in the sense that they also form steam-regenerable acceptors when dispersed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as surface FeAl<sub>2</sub>O<sub>4</sub>, 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Supports with high surface area are preferred (cf. conclusion 3).

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#### 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 ( $25^{\circ}$ C), consisting of 1 %v H<sub>2</sub>S, 10 %v H<sub>2</sub>, and 89 %v N<sub>2</sub>. When the feed had to contain other gaseous components (e.g. H<sub>2</sub>O, CO), the flow of N<sub>2</sub> was reduced to keep the total flow rate constant.
- The regenerating gas consisted of 35%  $\rm H_2O,$  58 %  $\rm N_2,$  and 7 %  $\rm H_2,$  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.

<u>General</u>. 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



<u>Fig. 5.1.</u> Deactivation of manganese- and iron-containing acceptors at 600  $^{\circ}$ C.

iron-containing acceptors were subjected to some 260 and 150 cycles, respectively.

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

- 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 H<sub>2</sub>-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.

<u>Mechanism of deactivation</u>. There are two conceptually probable mechanisms of the above deactivation :

- a. Diffusion of the active component (Mn or Fe) into the bulk of the  $\gamma-\text{Al}_2\text{O}_3$  support, making it less readily available for sulfur capture.
- b. (Re)crystallization of the surface spinel and/or the '  $\gamma-\text{Al}_2\text{O}_3$  support forming clusters which are less reactive towards H\_S.

It has been pointed out in sction 2.4.3. that cation diffusion in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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 MgAl<sub>2</sub>O<sub>4</sub>-supported MnAl<sub>2</sub>O<sub>4</sub> and FeAl<sub>2</sub>O<sub>4</sub> acceptors was examined. The results are shown in Fig. 5.2. together with data on a MnO on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> acceptor containing a comparable amount of Mn.

It is clear from Fig. 5.2. that the deactivation trends of  $MgAl_2O_4$ - and  $\gamma$ - $Al_2O_3$ -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  $MgAl_2O_4$  as support should be far slower than that of acceptors based on  $\gamma$ - $Al_2O_2$ .



<u>Fig. 5.2.</u> Deactivation of manganese- and iron-containing acceptors at 600 °C. O MnAl<sub>2</sub>O<sub>4</sub> on MgAl<sub>2</sub>O<sub>4</sub> (2.2 %w-Mn)  $\Delta$  2.7 %w-Mn on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>  $\Box$  FeAl<sub>2</sub>O<sub>4</sub> on MgAl<sub>2</sub>O<sub>4</sub> (1.1 %w Fe) To verify the supposition that recrystallization of the surface spinel and/or the  $\gamma - Al_2 O_3$  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.

	Surface_area, m <sup>2</sup> /g.			
Acceptor	Fresh	Deactivated		
8.1 %w-Mn on Y-Al_03	224	141		
4.5 %w-Fe on Y-Al <sub>2</sub> 0 <sub>3</sub>	237	153		

The surface area of the deactivated acceptors is about 60 % of that of the fresh ones. This suggest 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  $MnAl_2O_4$ . The peaks in the diffractogram of the deactivated acceptor are sharper than those of the fresh one; the growth of the peak around  $20 \approx 60^{\circ}$  is very obvious. Furthermore, the center of the peaks of the deactivated acceptor have slightly shifted to a smaller diffractogram of the former resembles that of MnAl\_2O\_4. These facts all point to the recrystallization of surface spinel to form a bulk-aluminate-like structure.



 $\begin{array}{l} \underline{Fig. 5.3.} & X-ray \mbox{ diffraction patterns of fresh} \\ \mbox{and deactivated acceptors.} \\ \mbox{a. 8.1 $w-Mn on $\gamma-Al_2O_3$ (fresh)} \end{array}$ 

b. 8.1 %w-Mn on  $\gamma$ -Al $_2O_3$  (deactivated) c. 4.5 %w-Fe on  $\gamma$ -Al $_2O_3$  (fresh)

d. 4.5 %w-Fe on Y-Al203 (deactivated)

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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  $\degree$ C increases the capacity by a factor of two in the case of manganese-containing acceptors and threefold 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 H<sub>2</sub>S. 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 :

<u>Kinetic consideration</u>: The rate coefficients of the intrinsic chemical reaction(s) and mass transport processes involved in the transfer of H<sub>2</sub>S 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 H<sub>2</sub>S capture.

Equilibrium consideration : The thermodynamics of bulk spinels (cf. section 2.3.3.) show that sulfidation becomes more



Fig. 5.5. Acceptor capacity at various temperatures.

O 8.1 %w-Mn on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>  $\Box$  3.6 %w-Fe on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>  $\Delta$  4.5 %w-Fe on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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  $\rm H_2S$  of the surface spinel (i.e. acceptor) can be expected to increase with temperature.

5.5. Dependence of acceptor capacity on  ${\rm H_2S}$  concentration.

Performance data of manganese- and iron-containing acceptors in treating feed gases of different  $H_2S$  concentration are shown in Fig. 5.6.. Except in the case of iron-based acceptor at 400 °C, acceptor capacity becomes somewhat lower as the  $H_2S$  concentration of the treated gas increases. In other words, the capacity has a weakly negative dependence on  $H_2S$  concentration in the feed.

It is important to realize that the investigation



<u>Fig. 5.6.</u> The influence of  $H_2S$  concentration on acceptor capacity.

O 8.1 %w-Mn on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>  $\Box$  4.5 %w-Fe on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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 H\_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 H\_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 expresed 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 %.



-AL

on

aM-Mn



Relative breakthrough 3.6% w-Fe on y-Al203 1.0 o 600°C ₄ 500°C 0.8 capacity 0.6 0.4 0.2 0 15 0 10 Water content of feed, % v

Fig. 5.9. Influence of water content of feed on the capacity of iron-containing acceptor.

Gas chromatographic analysis of the reactor effluent indicated a net production of water during H2S acceptation; roughly one mole of  $H_2^{0}$  being released by the acceptor for each mole of  $H_2S$  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  ${\rm H_{2}S}$  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<sub>2</sub>S-H<sub>2</sub>O exchange reaction between the acceptor and the gas phase. The simplest conceivable representation of this exchange reaction is :

 $^{H}2^{S}(g) + Me0/\gamma - A12^{0}3(s)$  $MeS/\gamma-Al_{2}O_{3}(s) + H_{2}O(g)$ -(Me = Mn, Fe)

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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 break-through 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  $^{\circ}$ C in the case of acceptors based on iron, and at or below 500  $^{\circ}$ C in the case of manganese-containing acceptors, no improvement in performance due to the presence of carbon monoxide was found.



Fig. 5.10. Influence of carbon oxide content of feed on the capacity of manganese and iron-containing acceptors.

	Ac	ceptor			H_2-content	of feed
0	8.0	%w-Mn	on	Y-A120	10	% V
□}	3.6	%w-Fe	on	Y-A1203	10	
4 }	3.6	%w-Fe	on	Y-A1.0.	∫ <sup>10</sup>	
▲,				2 3	140	

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 :

$$^{CO}(g) + ^{H}2^{O}(g) = ^{CO}2(g) + ^{H}2(g)$$

The disappearance of water increases the driving force of the  $H_2S$  acceptation; accordingly, the acceptor captures more sulfur. This is reflected in the observed increase of acceptor capacity.

The formation of  $CO_2$  by the shift reaction was verified by gas chromatographic analysis. Measurements of the composition of gases leaving the manganese-based acceptor bed at 600  $^{\circ}$ 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  $^{\circ}$ C)(1).

Based on the fact that CO increases acceptor capacity by consuming water via the shift reaction, it is easy to predict that  $CO_2$  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  $CO_2$  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 H<sub>2</sub>O and 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 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 :



<u>Fig. 5.11.</u> Net influence of  $H_20$  and CO content of feed gas on the capacity of 8.0 %w-Mn on  $\gamma$ -Al<sub>2</sub>0<sub>3</sub> at 600  $^{\circ}$ C.

 $Fe_3^0_4$  + CO  $\longrightarrow$  3 Fe0 + CO<sub>2</sub> 3 Fe0 + H<sub>2</sub>O  $\longrightarrow$  Fe<sub>3</sub>O<sub>4</sub> + H<sub>2</sub>

The applicability of this mechanism to the iron-containing acceptor studied here is questionable as it requires the presence of  $\text{Fe}_3O_4$ , 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 :

$$CO + H_2O \implies HCOOH_{(ads)} \implies CO_2 + H_2$$

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  $\gamma$ -Al<sub>2</sub>O<sub>2</sub>

catalyses the CO-shift reaction at 400-600  $^{\circ}$ C and, using insitu 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  $^{\circ}$ C and that at the temperature range studied, the rate determining step of the reaction is the decomposition of the formate complex. As  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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 vapour 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  $^{\circ}$ 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  $^{\circ}$ 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  $^{\circ}$ 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  $^{\circ}$ 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 H<sub>2</sub>S concentration, being 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, 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.

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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 H2S are derived from the features of the breakthrough and elution curves of  $H_2S$  and  $H_2O$ , 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 qas 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 experimental procedure. This chapter presents the procedure of some further experiments specifically done to support the modelling study.

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, the reactor effluent contained very low, almost constant concentrations of H\_S, amounting to about 20 ppmv at 400  $\,^\circ\text{C}$  and 10 ppmv at 600  $\,^\circ\text{C}$  . When the feed gas concentration was raised to about 3 %v H2O, these became 60 and 40 ppm, respectively. As the lowest feed concentration used in this work was 0.5 %v H<sub>2</sub>S (5000 ppmv), this means that at least 99 % of the  ${\rm H_2S}$  in the feed gas was removed by the acceptor. At breakthrough the concentration of  $\rm H_{2}S$  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  $t_{\rm b}$  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  $(C/C_{H_2}S_{,0}) = 1$  and the  $H_2S$  breakthrough curve, i.e. a measure of the total amount of  $H_2S$  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

$${}^{\rm H}{}_{2}{}^{\rm S}(g) + {}^{\rm Mn0/\gamma - Al}{}_{2}{}^{\rm O}{}_{3}(s) = {}^{\rm MnS/\gamma - Al}{}_{2}{}^{\rm O}{}_{3}(s) + {}^{\rm H}{}_{2}{}^{\rm O}(g)$$
(1)





<u>Fig. 6.1.</u> Typical breakthrough (elution) curves of  $H_2S$  ( $H_2O$ ). The symbols of  $C_{H_2S,o}$  and  $C_{H_2O,o}$  denote the concentration of hydrogen sulfide and water in the feed, respectively.

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

 $C_{H_2S,o}$  +  $C_{H_2O,o}$  =  $C_{H_2S,out}$  +  $C_{H_2O,out}$ or in the case of dry feed gas  $(C_{H_2O,o} = 0)$ , 94

$$\frac{{}^{C}_{H_{2}S,out}}{{}^{C}_{H_{2}S,o}} + \frac{{}^{C}_{H_{2}O,out}}{{}^{C}_{H_{2}S,o}} =$$

1

which is equivalent to

$$\begin{bmatrix} \frac{C_{H_2O,out}}{C_{H_2S,o}} & - & 0.5 \end{bmatrix} = \begin{bmatrix} 0.5 & - & \frac{C_{H_2S,out}}{C_{H_2S,o}} \end{bmatrix}$$

This relationship implies that the elution curve of water should take the form of a mirror image of the  $H_2S$  breakthrough curve with respect to the horizontal line  $(C/C_{H_2S,0}) = 0.5$ . Therefore, the experimental fact (cf. Fig. 6.1.) that the form of water elution curve prior to breakthrough deviates strongly from this expectation, is an indication of the occurrence of at least one other process. This process can be visualized as follows. The acceptor surface contains not only sites capable of exchanging oxygen with sulfur according to reaction (1) above but also sites, \*, which can adsorb both  $H_2S$  and  $H_2O$ :

$$H_2S(g) + *(s) = *H_2S(s)$$
 (2)

 $H_2^{0}(g) + *(s) = *H_2^{0}(s)$ 

Thus, when the acceptation is started  $H_2S$  first reacts with the oxygen-containing sites to produce water, which is then adsorbed by the sites \*. The net effect is that initially neither  $H_2S$  nor  $H_2O$  appears in the reactor effluent (cf. Fig. 6.1.). Some time later, when the exchange reaction is almost complete, two other processes occur :

- (a). hardly any water is now produced by the reaction. This disturbs equilibrium (3), which then shift to the left, causing water to desorb ("free desorption").
- (b). sites \*, which initially cannot compete for  ${\rm H_2S}$  with the reaction sites, now start to adsorb  ${\rm H_2S}$ . This provides another disturbance to equilibrium (3) because it reduces the number of free sites available. Therefore, more water is desorbed ("forced desorption" or desorption by indirect displacement).

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  $H_2S$  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  $H_2S$  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  $H_2S$ .

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 ( $t_b$ ), the concentrations of  $H_2S$  and  $H_2O$  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 :

- 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.
- 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.

(3)

Two mechanisms of  $H_2S$  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  $H_2S$  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.  $N_2 + H_2$ ) to elute the adsorbed  $H_2S$ , and subsequently treating the bed with a steam-containing gaseous stream to regenerate the chemically bound sulfur. Fig. 6.2.



<u>Fig. 6.2.</u> Typical elution curve of H<sub>2</sub>S during (a) inert flush and (b) steam-regeneration of sulfur-saturated acceptor bed.

presents typical elution curves obtained from regenerations carried out in this manner.

The fact that a part of the sulfur in the acceptor can be eluted by inert flush (Fig. 6.2a.) confirms the postulate that the acceptor surface possesses sites capable of adsorbing  $H_2S$ . Fig. 6.2a. further shows that the  $H_2S$  concentration in the reactor effluent decreases strongly in the initial part of the elution (i.e. when the acceptor still contains a relatively large amount of adsorbed  $H_2S$ ). This indicates that the desorption of the rest of the  ${\rm H_2S}$  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 acceptation (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  $^{\circ}$ 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 acceptation 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.

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 acceptation-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/6,71; 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 :

$$N_{i} = v.C_{i} + D_{a} \left(-\frac{\partial C_{i}}{\partial z}\right)$$
(4)

where v is the interstitial gas velocity (m/s), D<sub>a</sub> the axial dispersion coefficient (m<sup>2</sup>/s), C<sub>i</sub> the concentration of the i-th sorbable component (mol/m<sup>3</sup>), 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  $\Delta V = \Omega \cdot \Delta z$ , where  $\Omega$  is the cross sectional area of the bed (m<sup>2</sup>), gives :

$$\left. \epsilon_{\Omega N_{i}} \right|_{Z} = \left. \epsilon_{\Omega N_{i}} \right|_{Z^{+} \Delta Z} + \left. \epsilon_{\Omega} \frac{\partial c_{i}}{\partial t} \Delta z + \left. \alpha \frac{\partial q_{i}}{\partial t} \Delta z \right|_{Z^{+} \Delta Z}$$
flux at flux at accumulation accumulation   
z z + \Delta z in the gas in the accep phase tor phase

in which  $\varepsilon$  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<sup>3</sup> of bed);  $q_i = \rho_b \cdot q_{i,m}$  where  $\rho_b$  is the bulk density of the acceptor (kg/m<sup>3</sup>) and  $q_{i,m}$  the amount of i-th component adsorbed per unit mass of acceptor (mol/kg). By taking the limit as  $\Delta z \longrightarrow 0$  and assuming that v and  $D_a$  are constants, the above equation yields :

$$\frac{\partial C_{i}}{\partial t} + \frac{1}{\varepsilon} \frac{\partial q_{i}}{\partial t} + v \frac{\partial C_{i}}{\partial z} = D_{a} \frac{\partial^{2} C_{i}}{\partial z^{2}}$$
(5)

When  $D_a = 0$  (no axial dispersion, that is, plug flow), eq.(5) reduces to :

$$\frac{\partial C_{j}}{\partial t} + \frac{1}{\varepsilon} \frac{\partial q_{j}}{\partial t} + v \frac{\partial C_{j}}{\partial z} = 0$$
 (6)

A separate mass balance for the solid phase gives :

$$\frac{\partial q_{i}}{\partial t} = R_{i}$$
 (7)

accumulation in the solid phase global rate of sorption of the i-th component

where  $R_i$  has a unit of mol.m<sup>-3</sup>.s<sup>-1</sup>.

Conceptually, given an expression of  $\Re_i$  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

$$A(g) + MeB(s) \implies MeA(s) + B(g)$$
 (8)

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

$$-r_{A} = k_{1}C_{A}(Q - q_{A}) - \frac{k_{1}}{K}C_{B}q_{A}$$
(9)

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

$$= \frac{C_{B,eq}q_{A,eq}}{C_{A,eq}(Q - q_{A,eq})}$$
(10)

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 :

100

$$C_{\rm B} \simeq C_{\rm A,o} + C_{\rm B,o} \sim C_{\rm A}$$
 (11)

in which  $C_{A,O}$  and  $C_{B,O}$  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,

$$\mathcal{R}_{A} = \kappa_{1} C_{A} (Q - q_{A}) - \frac{\kappa_{1}}{\kappa} C_{B} q_{A}$$
(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 :

$$\mathcal{R}_{A} = \left(\frac{\partial Q_{A}, eq}{\partial C_{A}, eq}\right)_{C_{A}, eq} \cdot \frac{\partial C_{A}}{\partial t}$$
(13)

Physically,  $(\partial q_{A,eq}/\partial C_{A,eq})$  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 sor-

ber 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. Jsotheam. Substitution of eq.(11) into eq.(10) gives :

$$c = \frac{(c_{A,o} + c_{B,o} - c_{A})q_{A}}{c_{A}(Q - q_{A})}$$
(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;  $C_{B,O}^{=} = 0$ . By introducing dimensionless quantities,

$$= \frac{c_A}{c_{A,o}} \quad \text{and} \quad y = \frac{q_A}{Q} \quad (15a,b)$$

eq.(14) can be written as :

x

$$= \frac{y(1 - x)}{x(1 - y)}$$

which, when solved for y, gives the isotherm equation :

$$y = \frac{K_X}{1 + (K - 1)_X}$$
(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 :

$$\frac{dy}{dx} = y' = \frac{\kappa}{\{1 + (\kappa - 1)x\}^2}$$
(17)





Fig. 6.3. Isotherm of exchange reaction (8).

*Initial conditions.* The acceptation experiments of the present work were started by switching at t = 0 to a feed stream containing a constant  $H_2$ S concentration,  $C_{A,o}$ , to pass through a completely regenerated acceptor bed  $(q_A = 0)$ . This means that the initial condition is :

at 
$$z = 0$$
,  $C_A = \begin{cases} 0 & t < \\ C_{A,0} & t > \end{cases}$ 

or, in dimensionless form :

at 
$$\zeta = 0$$
,  $x = \begin{cases} 0 & \theta < 0 \\ 1 & \theta > 0 \end{cases}$  (18)

where :

$$\zeta = \frac{z}{L} ; \theta = \frac{vt}{L\alpha} ; \alpha = \frac{Q}{\varepsilon C_{A,O}}$$
(19a,b,c)

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 ( 6 = 0 ). Breakthrough curves. From eqs. (6), (7), and (13) it follows that :

or



 $\frac{\partial C_A}{\partial t} + \frac{1}{\varepsilon} \left( \frac{d q_A}{d C_A} \right) \frac{\partial C_A}{\partial t} + v \frac{\partial C_A}{\partial z} = 0$ 

which, in terms of the dimensionless quantities x, y, 0,  $\zeta$ , and  $\alpha$  defined in (15a,b) and (19a,b,c) can be rewritten as :

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

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

Now, from differential calculus(9) :

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

When  $dx \approx 0$  (that is, x = constant),

$$\begin{pmatrix} \frac{d}{d} \frac{\theta}{\zeta} \\ \chi \end{pmatrix}_{X} = -\frac{\frac{\partial x}{\partial \zeta}}{\frac{\partial x}{\partial \theta}}$$
(22)

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

$$\left(\frac{\mathrm{d}\,\mathfrak{g}}{\mathrm{d}\,\mathfrak{t}}\right)_{\mathbf{X}} = \frac{1}{\alpha} + \mathbf{y}'(\mathbf{x}) \qquad (23)$$

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) :

$$\int_{\alpha}^{\theta} \frac{d\theta}{d\theta} = \left[\frac{1}{\alpha} + y'(x)\right]_{0} \int_{0}^{\zeta} d\zeta \qquad (24)$$

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

$$\theta = \left[\frac{1}{\alpha} + y'(x)\right]\zeta$$
 (25)

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

$$x = \frac{\sqrt{\frac{K\zeta}{(\theta - \frac{\zeta}{2})}} - \frac{K\zeta}{(\theta - \frac{\zeta}{2})}}{K - 1}$$

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

$$= \sqrt{\frac{K}{\left(\theta - \frac{1}{\alpha}\right)}} - 1$$

$$K - 1$$
(26)

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 ( $\alpha > 1000$ ). This means that in the region of practical interest, i.e. ( $\theta - \frac{1}{\alpha}$ ) around unity, ( $\theta - \frac{1}{\alpha}$ )  $\approx 0$ .

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.





Fig. 6.4. Breakthrough curves of the exchange reaction  $A_{(g)} + MeB_{(s)} \xrightarrow{K} MeA_{(s)} + B_{(g)}$ as predicted by the equilibrium theory. A : purely mathematical (innealistic) solution.

B : physically acceptable solution.

For convex isotherm (K > 1) eq.(26) results in an unrealistic form of breakthrough curve (See Fig. 6.4b. : Curve A implies that for 0.5 < ( $\theta - \frac{1}{\alpha}$ ) < 2.0, there are three different concentrations associated with any single value of time). The physically acceptable solution is represented by the step front B which, as has been stated above, is the best form of breakthrough one can hope for. The vertical line was

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 acceptation/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  $(\theta - \frac{1}{2})^{\frac{1}{2}}$ ; 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  $K \geq$  1, and the experimental  ${\rm H_2S}\mbox{-breakthrough curves in Fig.}$ 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. :

$$H_2S(g) + 2 MnO(s) = "Mn_2OS"(s) + H_2O(g)$$
 (27)

or, more generally written :

$$A_{(g)} + 2S_{(s)} = P_{(s)} + B_{(g)}$$
 (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 :

 $= C_{A, 0} + C_{B, 0} - C_{A}$ 

$$= \frac{q_{A}(C_{A,0} + C_{B,0} - C_{A})}{C_{A} \cdot 4(Q - q_{A})^{2}}$$
(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/3,101.

Exchange reaction (27) implies that two moles of manganese are required in order to capture one mole of sulfur



Fig. 6.5. Breakthrough curve corresponding to a complex isotherm. (a). isotherm, (b). breakthrough curve.

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 $({\rm H}_2{\rm S})$ . 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 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  ${\rm H}_2{\rm S}$  in the reactor effluent became equal to that of 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.(11) recently investigated the adsorption isotherm of  $H_2S$ on Pt on Al<sub>2</sub>O<sub>3</sub> 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

$$K = \frac{y(1 + y - x)}{4 Q (1 - y)^2 x}$$
(30)

where  $\gamma = C_{B,O}^{/C} C_{A,O}^{-}$ . Solving eq.(30) for y results in the isotherm equation :

$$y = \frac{1}{b} \left\{ (b + 2p) - \sqrt{4p(b + p)} \right\}$$
(31)

in which b = 16.K.Q and p =  $(\frac{1+\gamma}{x} - 1)$ . 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  $\gamma$ . More precisely, for b  $\leq 2$  the isotherm is wholly concave, independent of the value of  $\gamma$ . If b > 2, the isotherm is complex when  $\gamma$  is relatively small ( $\gamma < 1/[b - 2]$ ); at higher va-



<u>Fig. 6.6.</u> Isotherms of exchange reaction :  $A_{(g)} + 2 S_{(s)} = P_{(s)} + B_{(g)}$ 

lues of y it becomes convex throughout.

 $\label{eq:theta} The equation of the isotherm's slope can be derived from (31). It is :$ 

$$y'(x) = \frac{dy}{dx} = \frac{(p+1)^2}{b(1+\gamma)} \left\{ \sqrt{\frac{b+p}{p}} + \sqrt{\frac{p}{b+p}} - 2 \right\}$$
(32)

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  $y(x^*) = x^* \cdot y'(x^*)$ . The result is :

$$x^* = (1 + \gamma) \frac{b - 2}{b - 1}$$
 (33)

The condition b>2 and  $\gamma<1/\left(b-2\right),$  which was mentioned above as determining the range of condition in which the isotherm is complex, was actually derived from this analytical

. (40)

expression of x<sup>2</sup>. The other important characteristics of the isotherm are :

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

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

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

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

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 :

$$(\theta - \frac{1}{\alpha}) = \gamma'(x) = \frac{b-1}{b(1+\gamma)}$$
 (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 :

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

Thus, a complete description of the breakthrough curve is :

$$\begin{cases} 0 \qquad (\theta - \frac{1}{\alpha}) \leq \frac{b-1}{b(1+\gamma)} \\ x \text{ given by} \\ eq.(38) \qquad (\theta - \frac{1}{\alpha}) > \frac{b-1}{b(1+\gamma)} \end{cases}$$
(39)

When the isotherm is wholly convex (b > 2 and  $\gamma$  > 1/[b - 2]), the dispersive front disappears and (39) simplifies to :

$$(\theta - \frac{1}{\alpha}) \leq y \Big|_{x=1}$$

$$(\theta - \frac{1}{\alpha}) > y \Big|_{x=1}$$

where  $y|_{x=1}$  is given by (34). On the other hand, if the isotherm is wholly concave (b  $\leq 2$ ) the step front does not exist and (39) is replaced by :

$$x = \begin{cases} 0 & (\theta - \frac{1}{\alpha}) \leq \frac{b}{4(1 + \gamma)} \\ x \text{ given by} \\ eq.(38) & (\theta - \frac{1}{\alpha}) > \frac{b}{4(1 + \gamma)} \end{cases}$$
(41)

As eq.(38) cannot be inverted to yield an explicit expression of x as a function of  $(\theta - \frac{1}{\alpha})$ , 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  $\alpha$ (= Q/[ $cC_{A,O}$ ]) 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 ZXSSQ 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 6.3.). 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

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6

Y

x =

	Fig. 6.7.	Fig. 6.8.	Fig. 6.9.	Fig. 6.10.	Fig. 6.11.
Mn content of acceptor, %w.	8.1	8.1	8.1	8.1	8.1
Acceptor state <sup>\$</sup>	stable	stable	stable	fresh	fresh
Temperature, °C	450	550	600	400	400
Residence time, L/v, s.	0.410	0.383	.0.324	0.439	0.432
C <sub>H2</sub> S,o' mol/m <sup>3</sup>	0.1574	0.1259	0.1262	0.1553	0.1532
$\gamma (= \frac{C_{H_2O,O}}{C_{H_2S,O}})$	0	0	0	0	0.89
Acceptor bulk density, p <sub>b</sub> , kg/m <sup>3</sup>	700	700	700	700	700
Bed void frac- tion, ε <sup>É</sup>	0.4	0.4	0.4	0.4	0.4

Table 6.1. Experimental conditions associated with the data in Figs. 6.7. to 6.11..



Fig. 6.7. Comparison of theoretical breakthrough curve with experimental data obtained with a stable acceptor (8.1 %-Mn) at 450  $^\circ$ C.

0	experimental data	a
-	curve of best fit	t :
	$Q = 175.6 \text{ mol/m}^3$	$(\alpha = 2790)$
	$K = 7.114 \times 10^{-4}$	m <sup>3</sup> /mol
		(b = 1.999)



fassumed value

<u>Fig. 6.8.</u> Comparison of theoretical break-through curve with experimental data obtained with a stable acceptor (8.1 %-Mn) at 550  $^{\circ}$ C.

experimental data
curve of best fit :
$Q = 246.6 \text{ mol/m}^3 (\alpha = 4897)$
$K = 5.023 \times 10^{-4} m^3/mol$ (b = 1.982)



Fig. 6.9. Comparison of theoretical break-through curve with experimental data obtained with a stable acceptor (8.1 %-Mn) at 600  $^{\circ}$ C.

- O experimental data
  - curve of best fit :  $Q = 268.5 \text{ mol/m}^3 (\alpha = 5361)$  $K = 4.621 \times 10^{-4} \text{ m}^3/\text{mol} (b = 1.985)$

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550 °C). 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.

T (°C)	$K_{(10^{-4} m^{3}/mol)}$	$(mol/m^3)$
( 0)		( 110 1 / 11 )
400	4.2	180
450	7.1	176
500	5.5	202
550	5.0	247
600	4.6	269

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  $\degree$ C and water-free feeds. This is illustrated in Fig. 6.10.. The values of K and Q



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

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

Table 6.3	. Par	ameters	s of	exchar	nge	read	tion	(27)
	for	frach	000	ontona	<b>c</b> +	100	° ~	
	101.	TLEPH	acce	eptors	al	400	0.	

Mn-content of acceptor, %w.	Qtheor. (mol/m <sup>3</sup> )	Q <sub>exp.3</sub> (mol/m <sup>3</sup> )	K (10 <sup>-4</sup> m <sup>3</sup> /mol)
8.1	515	490	2.7
6.1	388	360	3.5
4.4	261	242	4.3
2.7	172	163	6.4

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 :

- a fast oxygen-sulfur exchange reaction (the principal process)

- a slow oxygen-sulfur exchange reaction

- adsorption/desorption of  $H_2^S$  as well as  $H_2^O$ 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 :

 $(A = H_2 S \text{ or } S, B = H_2 O \text{ or } O)$ 

1. A fast exchange reaction,

 $-r_{\mathbf{A}} = k_{\mathbf{r}} \begin{bmatrix} c_{\mathbf{A}}(Q_{1} - q_{1}) & - \frac{\mathbf{B} - \mathbf{1}}{\mathbf{K}} \end{bmatrix}$ 

2. A slow exchange reaction in the solid phase,

$$S_1^{A}(s) + S_2^{B}(s) \stackrel{K_s}{=} S_2^{A}(s) + S_1^{B}(s)$$
 (44)

$$\begin{array}{cccc} \mathbf{q}_1 & (\mathbf{Q}_2 - \mathbf{q}_2) & \mathbf{q}_2 & (\mathbf{Q}_1 - \mathbf{q}_1) \\ \mathbf{\Gamma} & & \mathbf{I} \end{array}$$

$$-r_{S_2B} = k_s \begin{bmatrix} q_1(Q_2 - q_2) & - & q_2(Q_1 - q_1) \end{bmatrix}$$
(45)

The equilibrium constant of this reaction is simply assumed to be unity. Note that the terms "fast" and "slow" mean that  $k_{\rm r}$  is supposed to be much larger than  $k_{\rm g}$ .

3. Competitive, Langmuirian adsorption of A and B,

$$A_{(g)} + S_{3(s)} \stackrel{K_{A}}{=} S_{3}A_{(s)}$$
(46)  

$$C_{A} \quad (Q_{3}-q_{3A}-q_{3B}) \quad q_{3A}$$
  

$$B_{(g)} + S_{3(s)} \stackrel{K_{B}}{=} S_{3}B_{(s)}$$
(47)  

$$C_{B} \quad (Q_{3}-q_{3A}-q_{3B}) \quad q_{3B}$$

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

$$K_{A} = \frac{q_{3A}}{(Q_{3} - q_{3A} - q_{3B})C_{A}}$$
(48)

$$K_{\rm B} = \frac{q_{\rm 3B}}{(Q_{\rm 3} - q_{\rm 3A} - q_{\rm 3B})C_{\rm B}}$$
(49)

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

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

$$H_{3B} = \frac{K_B}{1 + K_A C_A + K_B C_B} Q_3$$
(51)

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 :

$$C_{A,O} + C_{B,O} = C_{A} + C_{B}$$

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 :

$$\frac{\partial C_A}{\partial t} + \frac{1}{\varepsilon} \frac{\partial q_A}{\partial t} + v \frac{\partial C_A}{\partial z} = 0$$
 (52a)

$$\frac{\partial C_{B}}{\partial t} + \frac{1}{\varepsilon} \frac{\partial q_{B}}{t} + v \frac{\partial C_{B}}{\partial z} = 0$$
 (52b)

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

$$\frac{\partial \mathbf{q}_{\mathbf{A}}}{\partial t} = \underbrace{\mathbf{k}_{\mathbf{r}} \left[ \mathbf{C}_{\mathbf{A}} (\mathbf{Q}_{1} - \mathbf{q}_{1}) - \frac{\mathbf{C}_{\mathbf{B}} \mathbf{q}_{1}}{\mathbf{K}} \right]}_{\frac{\partial (\mathbf{q}_{1} + \mathbf{q}_{2})}{\partial t}} + \left( \frac{\partial \mathbf{q}_{3\mathbf{A}}}{\partial \mathbf{C}_{\mathbf{A}}} \right) \frac{\partial \mathbf{C}_{\mathbf{A}}}{\partial t} + \left( \frac{\partial \mathbf{q}_{3\mathbf{A}}}{\partial \mathbf{C}_{\mathbf{B}}} \right) \frac{\partial \mathbf{C}_{\mathbf{B}}}{\partial t}}{\partial t}$$
(53a)  
$$\frac{\partial \mathbf{q}_{\mathbf{B}}}{\partial t} = \underbrace{-\mathbf{k}_{\mathbf{r}} \left[ \mathbf{C}_{\mathbf{A}} (\mathbf{Q}_{1} - \mathbf{q}_{1}) - \frac{\mathbf{C}_{\mathbf{B}} \mathbf{q}_{1}}{\mathbf{K}} \right]}_{\frac{\partial (\mathbf{q}_{1} - \mathbf{q}_{1}) + (\mathbf{Q}_{2} - \mathbf{q}_{2}) \right]}{\frac{\partial (\mathbf{q}_{1} - \mathbf{q}_{1}) + (\mathbf{Q}_{2} - \mathbf{q}_{2}) \right]}} \qquad \underbrace{\frac{\partial \mathbf{q}_{3\mathbf{B}}}{\partial \mathbf{c}_{\mathbf{A}}} + \left( \frac{\partial \mathbf{q}_{3\mathbf{B}}}{\partial \mathbf{c}_{\mathbf{B}}} \right) \frac{\partial \mathbf{C}_{\mathbf{B}}}{\partial t}}{\frac{\partial \mathbf{q}_{\mathbf{B}}}{\partial t}}$$
(53b)

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

and safer (preventing diagram also to simplify the interpretation of results of calculation, the following dimensionless quantities are introduced :

$$\begin{aligned} \zeta &= \frac{z}{L} \quad ; \quad x_{A} = \frac{c_{A}}{c_{o}} \quad ; \quad x_{B} = \frac{c_{B}}{c_{o}} \quad ; \quad y_{1} = \frac{q_{1}}{Q_{1}} \quad ; \quad y_{2} = \frac{q_{2}}{Q_{2}} \\ y_{3A} &= \frac{q_{3A}}{Q_{3}} \quad ; \quad y_{3B} = \frac{q_{3B}}{Q_{3}} \quad ; \quad \lambda_{1} = \frac{Q_{1}}{Q_{o}} \quad ; \quad \lambda_{2} = \frac{Q_{2}}{Q_{o}} \quad ; \quad \lambda_{3} = \frac{Q_{3}}{Q_{o}} \\ \alpha_{o} &= \frac{Q_{o}}{\epsilon c_{o}} \quad ; \quad \theta_{o} = \frac{t_{v}v}{L\alpha_{o}} \quad ; \quad \kappa_{1} = \kappa_{r}c_{o}\alpha_{o}L/v \quad ; \quad \kappa_{2} = \kappa_{s}Q_{o}\alpha_{o}\lambda_{1}L/v \\ \quad (54a-54n) \end{aligned}$$

Some of this quantities (e.g.  $\zeta$ ) have already been defined previously (see also List of Symbols at the end of the thesis).  $C_{_{\rm O}}$  and  $Q_{_{\rm O}}$  represent a reference concentration and a reference

capacity, respectively. The value of C<sub>o</sub> was chosen to correspond to a gas concentration of 1 %v and  $\Omega_o$  was assigned a value of 0.2 mol/kg acceptor (or 140 mol/m<sup>3</sup> 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 :

 $\frac{\partial Y_2}{\partial \theta} = F_2$ 

$$\frac{\partial \dot{\mathbf{x}}}{\partial \theta_{O}} = M^{-1} \cdot \dot{\mathbf{u}}$$
 (55)

$$\frac{\partial y_1}{\partial \theta_0} = F_1 - \frac{\lambda_2}{\lambda_1} F_2$$
(56)

(57)

where :  

$$\vec{x} = \begin{pmatrix} x_{A} \\ x_{B} \end{pmatrix} ; \quad \vec{u} = \begin{pmatrix} -\frac{\partial x_{A}}{\partial \zeta} - \lambda_{1}F_{1} \\ -\frac{\partial x_{B}}{\partial \zeta} + \lambda_{1}F_{1} \end{pmatrix}$$

$$4 = \begin{bmatrix} (\frac{1}{\alpha_{o}} + \lambda_{3}\frac{\partial y_{3A}}{\partial x_{A}}) & \lambda_{3}\frac{\partial y_{3A}}{\partial x_{B}} \\ \lambda_{3}\frac{\partial y_{3B}}{\partial x_{A}} & (\frac{1}{\alpha_{o}} + \lambda_{3}\frac{\partial y_{3B}}{\partial x_{B}}) \end{bmatrix}$$

$$F_{1} = \kappa_{1} \begin{bmatrix} x_{A}(1 - y_{1}) - \frac{x_{B}y_{1}}{\kappa} \end{bmatrix} ; \quad F_{2} = \kappa_{2} \begin{bmatrix} y_{1}(1 - y_{2}) - (1 - y_{1})y_{2} \end{bmatrix}$$

When the acceptation is started by passing a dry feed containing 1 %v  $\rm H_2S$  through a fully regenerated bed, the initial conditions of the above equations are :

$$x_{A} = \begin{cases} 0 & \text{at } \theta_{0} < 0 , 0 \le \zeta \le 1 \\ 1 & \text{at } \theta_{0} > 0 , \zeta = 0 \end{cases}$$

$$x_{B} = 0 & \begin{cases} \text{at } \zeta = 0 & \text{for all } \theta_{0} \\ \text{at } 0 \le \zeta \le 1 \text{ for } \theta_{0} < 0 \end{cases}$$
(58b)

$$y_1 = 0$$
 at  $\theta_0 = 0$ ,  $0 \le \zeta \le 1$  (58c)  
 $y_2 = 0$  at  $\theta_0 = 0$ ,  $0 \le \zeta \le 1$  (58d)

# 6.5.2. Method of numerical solution.

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)

- From a mathematical point of view, square consist of a pair of nonlinear hyperbolic partial differential equations (PDE's) containing a source term F<sub>1</sub> which, in turn, is affected by the two relatively simple PDE's (56) and (57).
- 2. 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<sup>É</sup> nor the IMSL<sup>\$</sup>, 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.  $\partial x_i/\partial \zeta$ ). The simplest stable scheme applicable to eq.(55) is the first order backward difference :

$$\frac{\partial x}{\partial \zeta} = \frac{x_j - x_{j-1}}{\zeta_j - \zeta_{j-1}} \qquad j = 1, \dots, N$$
(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

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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 limitationn.

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  $\zeta$  ranges from zero to unity, the length of each interval ( $\zeta_j - \zeta_{j-1}$ ) is just 1/N. This approach converts eqs. (55) to (57) into the following set of 4N ordinary differential equations (j = 1,.....,N) :

$$\frac{\mathrm{d}\mathbf{x}_{\mathrm{A},j}}{\mathrm{d}\boldsymbol{\theta}_{\mathrm{O}}} = -\frac{a_{\mathrm{A}}}{\hbar} \left[ \mathbb{N} \left( \mathbf{x}_{\mathrm{A},j} - \mathbf{x}_{\mathrm{A},j-1} \right) + \lambda_{1} \mathbb{F}_{1,j} \right]$$

$$+ \frac{a_{2}}{\hbar} \left[ \mathbb{N} \left( \mathbf{x}_{\mathrm{B},j} - \mathbf{x}_{\mathrm{B},j-1} \right) - \lambda_{1} \mathbb{F}_{1,j} \right]$$
(60a)

$$\frac{dx_{B,j}}{d\theta_{O}} = + \frac{a_{3}}{\Lambda} \left[ N(x_{A,j} - x_{A,j-1}) + \lambda_{1}F_{1,j} \right] \\ - \frac{a_{1}}{\Lambda} \left[ N(x_{B,j} - x_{B,j-1}) - \lambda_{1}F_{1,j} \right]$$
(60b)

 $\frac{dy_{1,j}}{d\theta_{0}} = F_{1,j} - \frac{\lambda_{2}}{\lambda_{1}} F_{2,j}$ (60c)

$$\frac{dy_{2,j}}{d\theta_0} = F_{2,j}$$
(60d)

where :  $a_1 = \frac{1}{\alpha_0} + \lambda_3 \left( \frac{\partial y_{3A}}{\partial x_A} \right)_j$ ;  $a_2 = \lambda_3 \left( \frac{\partial y_{3A}}{\partial x_B} \right)_j$ 

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$$a_{3} = \lambda_{3} \left( \frac{\vartheta y_{3B}}{\vartheta x_{A}} \right)_{j} ; a_{4} = \frac{1}{\alpha_{o}} + \lambda_{3} \left( \frac{\vartheta y_{3B}}{\vartheta x_{B}} \right)_{j}$$

$$\Lambda = a_{1}a_{4} - a_{2}a_{3}$$

$$F_{1,j} = \kappa_{1} \left[ x_{A,j} (1 - y_{1,j}) - \frac{x_{B,j}y_{1,j}}{K} \right]$$

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

The four partial derivatives  $(\vartheta y_{3}/\vartheta x)_{j}$  were obtained from the dimensionless forms of (50) and (51) :

$$\begin{pmatrix} \frac{\partial y_{3A}}{\partial x_A} \end{pmatrix}_j = \frac{K_a (1 + K_b x_{B,j})}{G_j} \quad ; \quad \begin{pmatrix} \frac{\partial y_{3A}}{\partial x_B} \end{pmatrix}_j = -\frac{K_a K_b x_{A,j}}{G_j} \\ \begin{pmatrix} \frac{\partial y_{3B}}{\partial x_A} \end{pmatrix}_j = -\frac{K_a K_b x_{B,j}}{G_j} \quad ; \quad \begin{pmatrix} \frac{\partial y_{3B}}{\partial x_B} \end{pmatrix}_j = \frac{K_b (1 + K_a x_{A,j})}{G_j} \\ \text{here } : G_j = (1 + K_a x_{A,j} + K_b x_{B,j})^2 \quad ; \quad K_a = K_A C_o \quad ; \quad K_b = K_B C_o$$

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  $H_2S$  and  $H_2O$ , 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<sup>\$</sup> to

 $\hat{s}_A$  system of ODE's is called stiff in some region/range of the independent variable if, in that region, its solution possesses components which vary much more rapidly than the others.

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 \_O and H \_S 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  $\rm H_2O$  adsorption and  $\rm H_2S$  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  $^{\circ}$ 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  $^{\circ}$ C, C<sub>H2</sub>0,o = 1.7 %v.,  $\alpha_{o}$  = 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 ( $\theta_0 = 0.72$ ) 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 ( $x_{B,0} = 0.75$ ) was interpreted as having been caused by readsorption of water on the tubing. The solid line drawn in the figure is the breakthrough curve of water as expected from equilibrium theory



Fig. 6.13. Breakthrough curve of water on an 8.0 %w-Mn on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> acceptor. T = 600 °C CH<sub>2</sub>O,o = 0.75 %v.

(A Langmuir isotherm is a convex isotherm for which equilibrium theory discussed in section 6.3. predicts that the breakthrough curve will consist of a step front). From eqs. (56) with  $C_A = 0$ , it follows that the breakthrough capacity  $q_{3B,b}$  according to equilibrium theory is :

$$A_{3B,b} = \frac{K_{B}C_{0}x_{B,0}}{(1 + K_{B}C_{0}x_{B,0})} Q_{3}$$
(61)

Table 6.4. lists the experimental breakthrough capacity at 400 and 600  $\degree$ C as a function of the inlet concentration of water. From these data, the parameters K<sub>B</sub> and Q<sub>3</sub> of water adsorption were estimated to be :

400 °C :  $Q_3 = 140 \text{ mol/m}^3$   $K_B = 14.74 \text{ m}^3/\text{mol}$ 600 °C :  $Q_3 = 168 \text{ mol/m}^3$   $K_B = 12.36 \text{ m}^3/\text{mol}$ 

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  $Q_3$  at 400 °C and 600 °C is probably due to the difference in "degree of dryness" of the

when a completely sulfur-saturated acceptor was flushed by an inert stream (88 %  $h_2$  + 12 %  $H_2$ ). To that end, the acceptor was treated with a gaseous stream containing a constant concentration of  $H_2$ 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  $H_2$ 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  $H_2S$ ). 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	sulf	fur	capa	aci	ty o:	f an	8.0	%w-1	In	on
Y-A1203	aco	ceptor	and	amo	ount	of	H2S	des	orbed	by	in	ert
aldt Si				flu	ush.		-					

Inlet con- centration Temp. of H <sub>2</sub> S		Total sulfur accepted, mol/m <sup>3</sup>	Mol ratio S/Mn	Amount of $H_2S$ desorbed by inert flush, mol/m <sup>3</sup> of acceptor.			
°c	% <b>v</b>	of acceptor	30 2 A 4	measured	calculated		
		11 19 25 1 1 19			der and the second		
400	0.93	489	0.48	36	27		
400	1.60	458	0.45	36	40		
400	2.24	468	0.46	50	50		
600	1.03	462	0.45	31	27		
600	1.52	570	0.45	34	38		
600	1.96	529	0.52	52	50		

<u>Table 6.4.</u> Water-breakthrough capacities of an 8 %w-Mn on  $\text{\gamma-Al}_{2}\text{O}_{2}$  acceptor.

Temperature	Inlet conc. of of H <sub>2</sub> 0,	Breakthrough capacity, $mol/m^3$			
°c	%v	exp.	calc.		
400	1.21	84	105		
400	2.26	126	120		
400	3.17	133	125		
600	0.75	105	95		
600	1.36	112	118		
600	2.29	133	134		
600	3.31	147	143		
	and the second				

acceptor at these two temperatures (i.e. at 600  $^{\circ}$ C the dry acceptor contains less hydroxyl groups and, therefore, can capture more water than at 400  $^{\circ}$ C).

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

$$\ln \left(\frac{\kappa_2}{\kappa_1}\right) = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \frac{\Delta H^{\circ}}{R}$$
(62)

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

6.5.3.3. H S adsorption.

The adsorption of  $H_2S$  by the tubing was found to be negligible, in contrast to that of  $H_2O$ . Thus, the concentration of  $H_2S$  in the reactor effluent, as detected by the titrator and/or gas chromatograph in the analysis section, is the real concentration of  $H_2S$  released by the acceptor.

The equilibrium constant ( ${\rm K}_{\rm A})$  of  ${\rm H}_2{\rm S}$  adsorption could be estimated by measuring the amount of  ${\rm H}_2{\rm S}$  desorbed
presumably reflects the fact that the manganese is bound by the alumina support.

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

$$_{3A,b} = \frac{K_{A}C_{o}x_{A,o}}{1 + K_{A}C_{o}x_{A,o}} Q_{3}$$
(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 :

$$400 \text{ °C}$$
 :  $K_{A} = 1.38 \text{ m}^3/\text{mol}$   
 $600 \text{ °C}$  :  $K_{A} = 1.36 \text{ m}^3/\text{mol}$ 

# 6.5.4. Verification of model.

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Apart from the known adsorption parameters  ${\rm K}_{\rm a}$  ,  ${\rm K}_{\rm p}$  , and  $Q_3$ , the model equations contain five other parameters K,  $k_r$ ,  $k_s$ ,  $Q_1$  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(24,251). 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).

La benet bet	400 °C	600 °C
K, dimensionless	4.7	3.6
k, m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	0.4	0.4
$Q_1$ , mol.m <sup>-3</sup>	160	209
k, m <sup>3</sup> mol <sup>-3</sup> s <sup>-1</sup>	10-3	10-3
Q <sub>2</sub> , mol.m <sup>-3</sup>	140	210
K <sub>n</sub> , m <sup>3</sup> mol <sup>-1</sup>	1.38	1.36
K <sub>B</sub> , m <sup>3</sup> mol <sup>-1</sup>	14.74	12.36
$Q_3$ , mol.m <sup>-3</sup>	140	168
-		



<u>Fig. 6.14.</u> 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<sub>2</sub>O<sub>3</sub>.







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  $H_2O$  and  $H_2S$  resulting from the regeneration of a completely saturated bed with a gas containing 3.5 %v  $H_2O$ . These simulation results agree qualitatively with experimental observation (cf. Fig. 6.2.).



<u>Fig. 6.15.</u> Simulated breakthrough (elution) curve of  $H_2O$  ( $H_2S$ ) during regeneration of a completely sulfur-saturated acceptor bed. The gas used to saturate the bed contains 1 %v  $H_2S$  and 0 %v  $H_2O$ . The  $H_3S$ -free regenerant contains 3.5 %v  $H_2O$ .

# 6.5.5. Conclusions.

The material presented in this section shows that it is possible to describe the dynamics of  $H_2S$  acceptation on the acceptor by a model based on :

 two oxygen-sulfur exchange reactions proceeding at very significantly different rates, and

- competitive adsorption of H2S and H2O.

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. 6.6. Reactor effluent composition in the presence of oxides of carbon.

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<sub>2</sub> 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 :

$$CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)}$$
 (64)

Carbonyl sulfide was probably formed by reaction of CO with  ${\rm H_{\gamma}S}$  :

$$CO_{(g)} + H_2S_{(g)} = COS_{(g)} + H_2(g)$$
 (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<sub>2</sub>S and COS. Case et.al.(26) reported that reaction (65) rapidly attains equilibrium. According to Kohl and Riesenfeld(27), the equilibrium constant

$$= \frac{[H_2][\cos]}{[H_2S][\cos]}$$

is about 0.054 at 600  $^{\circ}$ 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



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	:	со	59.5 %v.
		Н2	32.3
		H <sub>2</sub> S	1.1
		H <sub>2</sub> 0	2.05
		c0 <sub>2</sub>	0
		COS	0
		N <sub>2</sub>	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  $\mathrm{CO}_{\gamma}$  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.); the formation of the complex is probably preceded by adsorption of both CO and H<sub>2</sub>O on the acceptor surface. In addition, the relatively bulky formate complex may hinder further adsorption of  $H_{2}O$  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 :

$$r_{CO_2} = k_I (x_{CO} x_{H_2O} - x_{CO_2} x_{H_2} / K_I)$$
(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  $(0.04 \text{ m}^3 \text{mol}^{-1} \text{s}^{-1})$ . 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 COS concentration. The predicted elution curves of CO<sub>2</sub> and  $H_2O$  were, however, far from reality : the model predicted that both  $H_2O$  and CO<sub>2</sub> 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  $MnO/\gamma-Al_2O_2$  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 H\_O and  $H_2S$  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  $H_2S$ ,  $H_2O$ , 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 acceptation 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 timedependent 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 technique, 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 implementtation 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  $\gamma$ -Al\_0, but also iron-containing acceptor.

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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 Rl-R2 which is operated in a swing mode. In Fig. 7.1. only two absorption<sup>\$</sup> vessels are shown, one in the desulfurization/acceptation phase (Rl) the other in the regeneration phase (R2). In practice, more than two vessels will be rquired (see next paragraph).

<sup>\$</sup>The term absorption/absorber is chosen here although the process itself involves adsorption on the surface of the acceptor.



Fig. 7.1. Fixed-bed hot gas desulfurization process based on a steam-regenerable metal oxide on  $\gamma\text{-Al}_2\text{O}_3$  acceptor.

▶ valve (open) ▶ valve (closed)

Depending on the type of coal and gasifier used, the feed gas entering the desulfurization unit may contain  $0.4 - 1.4 \text{ %v H}_2$ S 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 Rl where its H\_2S 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 H\_S.

When the concentration of H\_S 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 presssure 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 %v H\_S. To concentrate the  $\rm H_2S,$  the pressure and the temperature of the regenerator off-gas are reduced to about 0.2 MPa and 50  $^\circ$ C, respectively, by passing it through heat recovery system HR (waste-heat boiler/condenser/cooler). The  ${\rm H}_{_{\rm S}}{\rm S}$  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 v,respectively (1,2).

The water leaving the bottom of separator SP will dissolve some  $H_2S$  and probably also contains some sulfur particles produced by gas-phase decomposition of hydrogen sulfide. The dissolved  $H_2S$  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. Companison with other processes.

As has been discussed in paragraphs 2.2.3. and 2.2.4., most hot gas desulfurization processes produce  $SO_2$  as a regeneration product, the conversion of which to sulfur in a Claus plant requires reducing agents (e.g.  $H_2$ , 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  $H_2S$ , 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 SO<sub>2</sub> 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<sup>\$</sup> iron oxide process, for example, where the iron oxidized by air during regeneration is reduced by  $H_2/CO$  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 (3).

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 %v water vapour(3), the present process is applicable only to relatively dry feeds. Gaseous stream with a  ${\rm H_2O}$  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 fulfil this requirement, see e.g. Table 1.1.. In addition, recent surveys(3,4) 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 Lankhuijzen(5) is quite promising : he found no coke formation

<sup>\$</sup>Morgantown Energy Research Center, Morgantown, West Virginia, U.S.A. occurs when a stream of gaseous hydrocarbons is passed through a bed of manganese oxide on alumina at temperature of up to 600  $\degree$  C.

Another weakness of the process is the relatively low sulfur-removal capacity of the acceptor. An acceptor containing 8 %w-Mn on  $\gamma\text{-Al}_2\text{O}_3$  has a capacity of about 1 %w-S at 600 °C. In contrast, the MERC acceptor (25 % Fe<sub>2</sub>O<sub>3</sub>, 75 % SiO<sub>2</sub>) has a capacity of 8-10 %w-S/3/. 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. 6 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(3,6/ 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 ( $\approx$  700 kg/m<sup>3</sup>) is approximately half of that of the MERC sorbent (~ 1500 kg/m<sup>3</sup>). 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 :

l. As discussed in section 5.3., the capacity of an 8 %w-Mn on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> acceptor is initially about 2 %w-S, but it deactivates due to sintering and reaches a stable capacity of

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<sup>3+</sup> or Ce<sup>4+</sup> 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 on of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). 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



Fig. 7.2. Fluidized-bed hot gas desulfurization system.

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 particles 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.

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LIST OF	SYMBOLS		tR	total regeneration time	s
			т	temperature	Corl
a,	activity of the i-th component	-	U	cumulative amount of H_S found in the re-	
b	dimensionless parameter			actor effluent during the acceptation	
	(eq.(31) of chapter 6)	-		stage	mol
с,	concentration of the i-th component	- 3	v	interstitial velocity of gas through	mor
	in the gas phase	mol.m 2 -1		acceptor bed	m/c
D	axial dispersion coefficient	m .s	w	weight of acceptor in the reactor	m/s
а Н	enthalpy	J.mol -1	x	stoichiometric factor (eqs. (2) and (3)	y or ky
I.S.	isomer shift	mm.s 3 -1 -1		of chapter 2	
k	forward reaction rate constant	m mol s	x	dimensionless gas phase concentration	
к	equilibrium constant (may or may not			(= C/C)	
	have a dimension, depending on its		у	stoichiometric factor (egs (2) and (2)	-
	specific definition)			of chapter 2	
L	length of acceptor bed	m -2 -1	у	volume fraction of water vapour	-
Ν.	flux of the i-th component	mol.m s		(Appendix A of chapter 3)	
1 P.	partial pressure of the i-th component		y	dimensionless solid phase concentration	-
- 1	(eq.(5) of chapter 2)	Ра		(=q/0)	
p	dimensionless variable		Z	axial distance from reactor inlat	-
	(eq.(31) of chapter 6)			The second second second second	m
Р	pressure	Pa	%-reg	degree of completion of regeneration	8
a.	concentration of the i-th component	- 3	1		
"i	in the solid phase	mol.m	α	angle of H <sub>2</sub> S titration curve	
0	stoichiometric capacity of the solid	- 3		(paragraph 3.2.5.)	0
	phase	mol.m	α	dimensionless stoichiometric capacity	
ā	breakthrough capacity of acceptor	%w-S or mol/kg		of acceptor ( = $Q/[\varepsilon C_])$	_
чр		or mol/m	Y	modification of alumina	-
ā	sulfur load of the acceptor at the end		Y	ratio of inlet concentration	
°C	of the acceptation stage	mol/kg		$(=C_{H} O O/C_{H} S O)$	_
0.5.	guadrupole splitting	mm/s	1	modification of alumina	
-r	intrinsic reaction rate of the i-th	-3 -1	6	void fraction of accenter by	-
ī	component	mol.m s		dimensionloss smill direction bed	-
p	total amount of sulfur recovered from			modification of alumin	
K	the acceptor in the regeneration stage	mol		modification of alumina	
R	global rate of sorption of the i-th	-2 -1			-
^i	component	mol.m s			
+	time	S			
L +	breakthrough time	S .			
b	DICUNCTION ON THE				

tc

total acceptation time

155

S

0	dimensionless time (eqs. (19) and		
	(54) of chapter 6)	STREET,	
ĸ	dimensionless rate constant		
	(eq.(54) of chapter 6)	-	
λ	capacity ratio (eq.(54) of chapter 6)	3	
ρ.	bulk density of acceptor	2	
0	cross sectional area of acceptor bed	m	

### STELLINGEN

 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)
N.K. Hiester and T.J. Vermeulen, Chem. Eng. Prog. 48(10)
505 (1952)

N.R. Amundson, J. Phys. Chem. 52 1153 (1948)

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- 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.

R.C. Aiken and L. Lapidus, A.J.Ch.E.J. 20(2) 368 (1974)
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M.L. Michelsen, A.J.Ch.E.J. 22(3) 594 (1976)

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.

Y. Kogue and Y. Yoshikawa, Bull. Chem. Soc. Japan 38(6) 948 (1965)

J.R. Conder and C.L. Young, "Physicochemical Measurements by Gas Chromatography", John Wiley & Sons, Chichester, 1979.

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

H.H. Lee and B.O. Yau, Chem. Eng. Sci. 36 483 (1981)

5. Ruth et.al. concluded that the reduction of manganese oxides by hydrogen is controlled by diffusion at lower temperature 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)

D. 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
P.J. van den Berg, Chem. Eng. Sci. 35 1591 (1980)

6. The Runge-Kutta-Gill method is unsuitable for solving stiff systems of ordinary differential equations (ODE's). Therefore, 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.

C. Hwang and Y.P. Shih, Chem. Eng. J. 27 81 (1983)

- 7. The steam-regenerability of a  $Mn0/\gamma Al_2O_3$  acceptor for  $H_2S$  removal is caused by the interaction of the MnO and the  $\gamma Al_2O_3$  support to form surface  $MnAl_2O_4$  spinel. This thesis, chapter 4
- 8. The warning :

Roken bedreigt de gezondheid. De Minister van Volksgezondheid and Milieuhygiene. 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 experienced persons to these countries is a far better mean than a mere increase in the number of "experts".

Delft, 13 juni 1985

T.H. Soerawidjaja