STELLINGEN

behorende bij het proefschrift

"CLEAN COAL COMBUSTION with IN SITU IMPREGNATED SOL-GEL SORBENT"

van

Anton Duisterwinkel.

1. Het vervangen van fosfaten in wasmiddelen uit milieuoverwegingen is niet alleen zinloos, maar brengt ook onbekende risico's met zich mee.

2. De in de stukken van de Tweede Kamer voorgestelde maatregelen voor het beperken van zwaveldioxide-emissies bij steenkoolverbranding leiden tot het gebruik van hoogzwavelige kolen, en dus tot grotere emissies.
   Tweede Kamer, "De problematiek van de verzuring", vergaderjaar 1987-88, 18225, nr. 22, 1988

3. Als bij alle steenkoolverbranding regeneratieve ontswaveling wordt toegepast, en de daarbij vrijkomende zwavel wordt gebruikt voor de produktie van zwavelzuur, kan hiermee 2/3 van de wereldbehoefte aan zwavelzuur worden gedekt.
   Chemical and Engineering News, december 1990
   "Energie in kort bestek", Shell Brochures Serie, Shell Nederland B.V., augustus 1989

4. De rol van katalysatorbereiding voor het vastleggen van katalysatoreigen schappen wordt schromelijk onderschat.
   V. Ponec, NATO ASI Ser., Ser. B 191, 310-13, 1988
5. In een Eirich mixer worden agglomeraten gevormd door het afbreken van macroporiën totdat alle nog aanwezige macroporiën met vloeistuff gevuld zijn. Dit levert de mogelijkheid op het porievolume in het eindproduct te sturen.

6. De correctheid van het in dit proefschrift voorgestelde relogiemodel moet beter worden onderbouwd, vooral met betrekking tot de rol van de intrinsieke viscositeit bij hoge volumefracties van ellipsoidale deeltjes.

   Dit proefschrift

7. Het moet mogelijk zijn de zogenaamde 'structural interaction' tussen colloidale deeltjes te correleren aan de adsorptie-enthalpie van het medium aan die colloidale deeltjes.

8. Voor de politieke stabiliteit van de wereld is de energievoorziening van groot belang. In tegenstelling tot wijdverbreide opvattingen is het in dat licht bezien niet zozeer zorgwekkend dat 1/3 van de olieproductie in handen van landen in het Midden-Oosten is. Veeleer is het zorgwekkend dat 2/3 van de winbare oliereserve in het Midden-Oosten ligt.

   "Energie in kort bestek", Shell Brochures Serie, Shell Nederland B.V., augustus 1989


10. Veel universitaire practica kunnen sterk worden verbeterd: de inhoud dient meer te zijn gericht op het opzetten van onderzoek (waarbij 'mislukkende' experimenten noodzakelijk zijn), terwijl de verslaggeving ook op haar taalkundige merits dient te worden beoordeeld.
11. Het grote aantal 'stellingen', dat niet meer is dan ontkenningen van beweringen van anderen, doet weinig goeds vermoeden met betrekking tot de creativiteit van hedendaagse promovendi. Talloze recente proefschriften

12. Als chaos daadwerkelijk de toekomst van de wetenschap is, dan zijn vele wetenschappers al aardig op de goede weg.

13. Toevoeging aan de wetten van Murphy:
   Als experimentele resultaten en theoretische berekeningen in overeenstemming zijn, zijn er één of meer rekenfouten gemaakt.

14. Ons gevoel voor logica stopt vaak bij chronologica.

15. Een ieder, die beweert geen tijd te hebben, heeft per definitie gelijk. Tijd kan men niet bezitten, maar hoogstens indelen, vrijmaken of ... doden. Tijd is geen kwestie van bezit, maar van prioriteit.

16. (Koor)zang is niet alleen goed voor de culturele ontwikkeling en persoonlijke ontwikkeling, voor de ademhaling en spijsvertering, ter ontspanning en ter bevordering van sociale contacten, maar vooral ook voor drop- en koffieproducecenten.

17. De bijbelteksten die uitdrukking geven aan de relativiteit van de menselijke wijsheid, zouden alle wetenschappers, maar in het bijzonder de theologen, moeten nopen tot een grote mate van bescheidenheid bij het presenteren van hun resultaten en theorieën aan de maatschappij.
CLEAN COAL COMBUSTION
with
IN SITU IMPREGNATED SOL-GEL SORBENT
CLEAN COAL COMBUSTION
with
IN SITU IMPREGNATED
SOL-GEL SORBENT

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan
de Technische Universiteit Delft, op gezag van
de Rector Magnificus, prof. drs. P.A. Schenck,
in het openbaar te verdedigen ten overstaan van een
commissie aangewezen door het College van Dekanen
op donderdag 28 maart 1991 te 16.00 uur

door

ANTONIE ELLERT DUISTERWINKEL

scheikundig ingenieur
geboren te Meppel

Universiteitsdrukkerij Delft
DANKWOORD

Help!
Luister naar iedereen, maar doe wat je zelf het beste vindt...

The Beatles

Maksim Gorki

Velen, zeer velen, hebben geholpen bij de totstandkoming van dit proef­schrift. Sommigen heel letterlijk, bij de productie van dit boekje. Anderen in de vorm van meertalige van standaard analysetechnieken. Weer anderen waren direct betrokken bij het onderzoek en bij het bespreken van de verkregen resultaten. Ik heb in de gelukkige situatie verkeerd, naar veel mensen te mogen luisteren.


Het samenwerken met de leden van de EG-projectgroep (onder de energieke leiding van prof. Cock van den Bleek) verliep uitstekend. Het samenleven met het Laboratorium voor Fysische Chemie was aangenaam. Even leek het shrinking core (krimpende kern) model toepasbaar op het lab, maar dat bleek, gelukkig, een kapitale misvatting.

Gedurende mijn promotieonderzoek was prof. Van den Berg een plezierige en waardevolle begeleider. Giel Doesburg (nu werkzaam bij ECN, Enschede), heeft vooral bij de aanvang van het onderzoek de bakens gezet, hoewel hij ook later niet uit het zicht verdween. En prof. Frens was in de latere jaren een ware promotor. Misschien niet altijd even extreem gecontroleerd, maar wel altijd zeer enthousiast, inspirerend en opbouwend kritisch.

De financiële ondersteuning voor dit onderzoek was afkomstig van de Europese Gemeenschap (contract no. EN3F-0014-NL(GDF)), de NOVEM (contract no. 20.35-016.30) en van de STW (contract no. DST77.1386).

Minder wetenschappelijk, maar daarom niet minder schappelijk, waren de contacten met de klaverjass(t)ers, coffiedrink(st)ers, ping-pong(st)ers, bijtank(st)ers, Van Gogh-gang(st)ers en wie al dies meer zij.

Goed functioneren kan een mens alleen, als het goed met hem gAÁt. En dat wordt voor een groot gedeelte bepaald door anderen: vrienden en familie.

En dan is er die Ene, die zowel de gave als de ruimte geschonken heeft.

Dank.
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Dit proefschrift is goedgekeurd door de promotoren

Prof. drs. P.J. van den Berg

en

Prof. dr. G. Frens

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Printed in the Netherlands
"Our science mocks magic and the human heart, 
our knowledge is the brutal mastery of the unknown. 
(...)

The planet does not turn for us alone. 
Science is a form of wonder, knowledge a form of love. 
Are we too late to love ourselves? 
Shall we change, or shall we die?"

Ian McEwan
DANKWOORD

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The Beatles

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Dank.
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LYST OF SYMBOLS

SUMMARY

SAMENVATTING

CURRICULUM VITAE
PART I

A NEW SORBENT
for
CLEAN COAL COMBUSTION
I.O  CLEAN COAL COMBUSTION

... rather bear those ills we have
Than fly to others that we know not of?
William Shakespeare

These words of Shakespeare do not only apply to Hamlet [1] or Tess of the d'Urbervilles [2], but also for us when we deal with environmental problems. A good example is the conversion of coal to electricity. Because coal contains sulphur, considerable amounts of gaseous sulphur compounds are emitted during this conversion, whatever the process used. This is clearly unacceptable, but so is the generally accepted solution to this problem: capturing the gaseous compound with some sorbent, yielding a liquid or solid waste. Sometimes, acceptable uses can be found for this waste on a small scale, like building purposes [3,4], but when produced on a larger scale, the waste must be dumped. It contains sulphuric compounds, which, being dumped, may convert into H₂S, smelling badly in more than one sense of the word. Also, heavy metals, chlorine and other pollutants, originating from the coal ash, may leach out of the waste [5]. To what extent this occurs is unknown. Therefore, dumps are an 'other ill that we know not of'.

Of course, the best solution would be not to use coal at all, but this is hardly feasible. As shown quite clearly during the writing of this thesis, modern Western society is vulnerable through its need for energy. Therefore, the energy sources used, should be large and well dispersed over the world. Coal has exactly these advantages [6,7]. At the contemporary rate of coal consumption, the reserves are large enough for about 250 year, compared to 50-60 year for oil and natural gas. Furthermore, oil and natural gas are more suited as raw materials for the chemical industry than coal is, due to the high hydrogen to carbon ratio in these materials. Using coal as an energy source, however, must imply that the environmental problems encountered are at least reduced to the level that can be achieved for other mineral energy sources. Rather than to 'bear those ills we have', we should try to cure them. In other words: we need clean coal conversion.

To accomplish clean coal conversion, a suitable conversion process must be chosen. On a technological scale, we are at this moment limited to combustion processes. A suitable clean coal combustion process is fluidized bed combustion (FBC) [8]. The relatively low combustion temperature, ca. 850°C, prevents the oxidation of nitrogen in the combustion air into nitrogen.
oxides. This reduces the total emission of $\text{NO}_x$ with ca. 50%, while other measures can be taken to improve this.

FBC has more advantages, but the most important for this thesis is that a sorbent for sulphur oxides can be added in situ to the combustor. Up to now, sorbents are only applied commercially in a "once-through" type of process: natural sorbents like limestone ($\text{CaCO}_3$) or dolomite ($\text{CaCO}_3\cdot\text{MgCO}_3$) are fed to the combustor where the calcium oxide in these materials reacts with the sulphur oxides to form gypsum-like products. When the rate of the sorption reaction decreases to an uneconomical level, typically at less than 40% conversion of the calcium oxide [9-11], the sorbent is dumped with the coal ash. This procedure has three disadvantages. For every mole of sulphur oxide captured, at least one mole of carbon dioxide is emitted, increasing the greenhouse effect. Also, the scenery is spoiled, both by sorbent quarries and waste dumps. And thirdly, the possible dangers of dumping waste sorbent necessitates expensive dumping procedures.

![Diagram of regenerative desulphurization during coal combustion in a fluidized bed combustor (C). The route followed by the sorbent is shown by the fat lines. The sulphated sorbent is separated from the coal ash, and transported to the regenerator (R). There, reducing conditions are applied to remove the sulphur from the sorbent. While the sorbent is again fed to the combustor, the regenerator off-gas, containing, say, 10% of $\text{SO}_2$, is used for the production of economically attractive products, like $\text{S}$ or $\text{H}_2\text{SO}_4$](image)

Figure 0.1 Diagram of regenerative desulphurization during coal combustion in a fluidized bed combustor (C). The route followed by the sorbent is shown by the fat lines. The sulphated sorbent is separated from the coal ash, and transported to the regenerator (R). There, reducing conditions are applied to remove the sulphur from the sorbent. While the sorbent is again fed to the combustor, the regenerator off-gas, containing, say, 10% of $\text{SO}_2$, is used for the production of economically attractive products, like $\text{S}$ or $\text{H}_2\text{SO}_4$. 
Therefore, regenerative desulphurization is considered (fig. 0.1) [12-22]. Converted sorbent is regenerated in a separate reactor under reducing conditions. Then, on the one hand, the regenerator off-gas can be used to produce economically attractive products like sulphur or sulphuric acid, as long as the SO₂ concentration in the off-gas is larger than ~4vol% [13,14]. On the other hand, the regenerated sorbent is recycled to the combustor, strongly reducing the need for make-up sorbent and the dumps of waste sorbent.

Two problems arise when limestone or dolomite is used regeneratively.

(a) Regeneration of sulphated natural sorbents only yields CaO, when it is performed at relatively high temperatures (>1050°C) [12-14]. At lower temperatures, the formation of CaS is favoured thermodynamically [15]. The reaction to CaS uses a large amount of expensive reducing agent and the CaS can not be used again to capture sulphur oxides. High regeneration temperatures, however, are economically not attractive. Also, they can cause attrition (particle size reduction) of the sorbent due to repeated thermal shock, and agglomeration of sorbent and coal ash [21].

(b) Natural sorbents, certainly when calcined (decarbonated), generally are weak materials [21-23]. Therefore, strong attrition will occur during fluidization and conveyance of sorbent from combustor to regenerator and vice versa. The resulting fines cannot be separated from the coal ash and can elutriate from the fluidized bed. The latter causes dust problems in the further process and large losses of sorbent.

Consequently, a synthetic sorbent must be developed for regenerative desulphurization [15-21]. This synthetic sorbent should show selective regeneration at 850°C and good attrition resistance. To develop such a sorbent is the objective of the first part of this thesis.

Since the non-selective regeneration of natural sorbents at 850°C is determined thermodynamically, we will use thermodynamics to select suitable (mixed) oxides for regenerative desulphurization (chapter I.1). The demands on thermal and mechanical stability limit the possibilities even further, and also determine which preparation techniques can be used (I.2). The most promising technique appears to be in situ impregnation during sol-gel preparation. This new process is described in chapter I.3, as are the characteristics of sorbents produced according to this method. In chapter I.4, the sulphation and regeneration behaviour of these sorbents is described and modelled. These results are incorporated in ReSuLT (I.5), a model for the sorbent performance in Regenerative deSulphurization at Low
Temperature as a function of sorbent properties. It is used, amongst other things, for an economic comparison between regenerative desulphurization and "once-through" desulphurization with limestone (I.6).

The physico-chemical background of the in situ impregnation technique is examined in part II of this thesis. But first, let me prove the advantages of this preparation technique, especially for regenerative desulphurization.

References

[2] Thomas Hardy, "Tess of the d'Urbervilles"
[16] H.J. Yoo, M. Steinberg, final report, BNL 33748, Brookhaven National Laboratory, Upton, N.Y., October 1983
I.1 CHOICE OF A COMPOUND

When the going gets tough, the tough get going

English saying

The objective of this chapter is to find the compounds that could meet the requirements, set forward in the previous chapter.

I.1.1 Reactivity and regenerability

It is thermodynamically determined which (mixed) oxides can be used for regenerative desulphurization. Compounds can be used, when they are capable of (a) reducing SO$_2$ emission levels sufficiently in the coal combustion (< 100 ppm SO$_2$ at 850°C and oxidizing conditions) and (b) releasing >-4v% SO$_x$ at the same temperature under reducing conditions. It can be shown that these thermodynamic demands are contradictory. This limits the range of compounds that can be used to a few mixed oxides, independent whether H$_2$ or CO is used as reducing agent.

These mixed oxides (Av$_a$O$_y$Sp$_b$O) can be envisaged as existing of an active oxide (Av$_a$O) and a supporting oxide (Sp$_b$O), where a and b are determined by the valency of the Av and Sp cations. During sulphation, the Av$_a$O is converted into Av$_a$SO$_4$, while the Sp$_b$O remains unchanged. During regeneration the formation of the mixed oxide is thermodynamically favoured over the formation of Av$_a$S, which facilitates selective regeneration. The Sp$_b$O can give strength to the sorbent when more than the equivalent for the formation of Av$_a$O$_y$Sp$_b$O is added.

As far as thermodynamic data are available, it is found that only Av = Li, Na, Ca, Sr or Ba can be used in combination with Sp = Al*, Si, Ti at 850°C and a total pressure of 1 atm, using the demands given above [1-4]. Fe can be used as a support when Av = Li or Na. However, Li or Na cannot be used as their compounds with the given Sp$_b$O's slowly decompose at the combustion temperature, causing serious corrosion problems of the combustor [5]. Thus, the aluminates, silicates and titanates of calcium, strontium or barium are possible synthetic regenerable sorbents.

* Not all existing calcium aluminates are suitable for desulphurization at 850°C. CaO, yAl$_2$O$_3$ exist for y = 1/3, 1/2, 7/12, 3/5, 1, 5/3, 2 and 6 [6-8]. Only calcium aluminates for y ≤ 1 react with 0.5v% SO$_2$/air at 850°C [9,10].
I.1.2 Availability

The traveller (....), who, after plodding (....) over calcereous downs and corn-lands, suddenly reaches the verge of one of these encarpments, is surprised and delighted to behold, (....), a country differing absolutely from that which he has passed through.

Thomas Hardy

Further study of the compounds that thermodynamically spoken can be used for regenerative desulphurization, is only useful when they can be produced in sufficient amounts. This is questionable as the amount of coal available for power plants is very large [11].

The production of the support oxides is small compared to the possible consumption, but the total mineable reserves are large enough and production technology is available. This also holds for calcium, but not for barium and strontium (table 1.1). Therefore, on an economically attractive scale, only calcium aluminates, silicates and titanates are suitable for regenerative desulphurization.

Table 1.1 Resources and yearly production of possible sorbents and coal

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<tr>
<td>Ca</td>
<td>$4.66 \times 10^4$ ppm</td>
<td>19 Mton lime/yr, 1979, worldwide</td>
</tr>
<tr>
<td>Sr</td>
<td>384 ppm</td>
<td>no data available*</td>
</tr>
<tr>
<td>Ba</td>
<td>390 ppm</td>
<td>96 kton barite/yr, 1972, USA</td>
</tr>
<tr>
<td>coal</td>
<td>$1.4 \times 10^5$ ppm [12]</td>
<td>3.3 Gton coal/yr, 1988, worldwide</td>
</tr>
<tr>
<td>S in coal</td>
<td>$1.4 \times 10^3$ ppm [12]</td>
<td>33 Mton S in coal/yr, 1988, worldwide</td>
</tr>
</tbody>
</table>

* for the most important mineral celestite it is stated that "The scale of celestite mining has never been big enough to justify highly efficient mining methods or extensive exploration. Hand digging of the mineral is not uncommon and the ore is usually sorted by hand." [12]
I.1.3 Stability

Cracking

It's a one time thing
It just happens
A lot
Walk with me
And we will see
What we have got
Ah

Suzanne Vega

A synthetic sorbent can only compete with natural sorbents when both thermal and mechanic stability are much better.

Thermal stability is achieved when the sintering temperature of a compound is well above the combustion temperature, 850°C. In dry air, the sintering temperature of a compound is very roughly estimated by the Tamman rule of thumb: the temperature of sintering roughly equals 2/3 of the melting temperature. 12CaO.7Al₂O₃ and to a lesser extent 3CaO.Al₂O₃ could be sensitive to sintering at 850°C [6,7,14]. However, when water vapour is present, certain groups of compounds show fast sintering at relatively low temperature. Especially silica and silicates are well known for this [15]. As during coal combustion and regeneration water vapour concentrations up to 15v% exist, it seems wise not to use calcium silicates for regenerative desulphurization.

<table>
<thead>
<tr>
<th>shape and technique</th>
<th>surface roughness</th>
<th>crystalline form</th>
<th>( V_p ) (ml/g)</th>
<th>( 10^4 \alpha ) (1/h)</th>
<th>( 10^{10} k^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>cylindrical pellets</td>
<td>medium</td>
<td>( \gamma )-Al₂O₃</td>
<td>0.45</td>
<td>4.5 ± 0.4</td>
<td>8.3</td>
</tr>
<tr>
<td>cylindrical pellets</td>
<td>medium</td>
<td>( \alpha )-Al₂O₃</td>
<td>0.36</td>
<td>2.2 ± 0.1</td>
<td>1.3</td>
</tr>
<tr>
<td>spherical granules</td>
<td>rough</td>
<td>( \gamma )-Al₂O₃</td>
<td>0.57</td>
<td>5.8</td>
<td>4.5</td>
</tr>
<tr>
<td>sol-gel spheres</td>
<td>smooth</td>
<td>( \gamma )-Al₂O₃</td>
<td>0.55</td>
<td>0.7</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* crystalline form determined with X-ray diffraction; pore volume \( V_p \) with water intrusion (appendix II), attrition rate \( \alpha \) from fluidized bed attrition experiments at a superficial gas velocity of ~1.5 m/s; \( k \) is the rate constant of attrition, calculated from \( \alpha \), see appendix III.
Mechanical stability is resistance to attrition. Attrition - particle size reduction by fragmentation or abrasion - leads to small particles. These cannot be separated from the coal ash or will even be blown out of the fluidized bed (elutriate). For more details, see appendix III.

To compare attrition resistances of compounds is difficult, as not only the compound, but also the shape, smoothness and the coherence of the individual particles influence the attrition behaviour. These factors are influenced by the preparation method and conditions. This can be seen from table 1.2 and table III.2 (appendix III). In both tables a number of CaO on Al₂O₃ samples is compared. The spherical shape appears to be ideal; the more edges and asperities, the faster the attrition is. Lack of particle coherence causes equal effects.

When we compare the most optimal sorbents of the several materials, made during this research (fig. 1.1), the aluminates are found to be the most attrition resisting materials. A calcium titanate sample, fluidized without the addition of sand at 2 m/s, elutriated totally in 50 hours.

For good attrition resistance, α-Al₂O₃ is better than γ-Al₂O₃ (table 1.2). α-Al₂O₃ is formed from γ-Al₂O₃ when the latter is heated to at least 1150°C. During this phase transition, usually strong sintering takes place. The resulting material is therefore stronger, has a smaller pore volume and much smaller surface area, but a larger pore radius. In chapter I.2.3 we will return to this point.

Figure 1.1 Relative weight of sorbent beads (>1.4 mm) during attrition in a slugging fluidized bed (ID 5 cm) at a superficial gas velocity of 2 m/s and 20°C; sorbent : sand (<1.4 mm) = 1 : 1 [16]
(a) o calcium aluminate sorbent made by the sol-gel method
(b) x SiO₂ spheres made by a sol-gel method
(c) + as (b), but impregnated with Ca(NO₃)₂
(d) △ calcined "Carmeuse Engis", a strong limestone [17]
The mechanical stability of the calcium titanate and calcium silicates is not as good as the stability of calcium aluminates. Together with the expected sensitivity to sintering in a water containing environment for the silicates, this is reason enough to focus our attention on calcium aluminates (with \( y \leq 1 \) in \( \text{CaO}_y\text{Al}_2\text{O}_3 \)). These calcium aluminates are generally referred to as \( \text{CaO} \) on alumina (\( \text{Al}_2\text{O}_3 \)). Sintering of these materials may occur slightly at 850°C. This can generally be prevented by ensuring a good dispersion of the calcium oxide over the alumina. This is determined by the preparation process and conditions, the subject of the next chapter.

References

[6] ASTM powder diffraction standards, several cards
I.2 SHAPING STRONG SORBENTS

"You are to pronounce your verdict on the evidence and on the evidence alone. You are to forget all that you have ever heard or read on the subject, for it is probably erroneous and is, at all events, unsupported by proof."

Graham Greene

The heavy demands on the sorbent do not only dictate the choice of the compound, but also the choice of shaping technique and conditions, needed to make strong, porous particles (I.2.1). A general background on shaping techniques is given in I.2.2, after which the promising shaping techniques are briefly outlined. On the basis of this information a choice is made (I.2.3). Sample preparations are described in appendix I, test methods and conditions in appendix II.

I.2.1 Kinetic constraints

Because the sorbent must be separated from the flyash, it is convenient to use pellets with a diameter of a few mm. Such pellets must be porous to

![Figure 2.1 Local calcium concentration, determined by EPMA, for a length of ca. 100 μm](image)

(a) in situ impregnated γ-alumina sol-gel sphere, $\xi_2 = 0.9$
(b) impregnated γ-Al₂O₃ pellet, $\xi_2 = 0.85$
(c) impregnated α-Al₂O₃ pellet, $\xi_2 = 0.6$

vertical axis is equal for (a) - (c)
effect an appreciable reaction rate during sulphation and regeneration. Both for natural and synthetic sorbents, several investigators find that the overall rate of sulphation is determined by diffusion processes \[1-7\]. Both diffusion into the pores and diffusion through the productlayer formed on the pore wall can be important. In the first case, large pores are necessary; in the second case a large surface area is important.

Another effect encountered in natural sorbents, is pore plugging, due to the large molar volume of CaSO\(_4\) as compared to that of CaCO\(_3\). Although this effect is less important for synthetic sorbents, this is an additional reason for ensuring the sorbent particles to be sufficiently porous.

For regeneration according to

\[
\text{CaSO}_4 \, + \, y\text{Al}_2\text{O}_3 \, + \, \text{H}_2/\text{CO} \, = \, \text{CaO} \cdot y\text{Al}_2\text{O}_3 \, + \, \text{SO}_2 \, + \, \text{H}_2\text{O}/\text{CO}_2
\]

(2.1)
an intimate contact between the solids (CaSO\(_4\) and Al\(_2\)O\(_3\)) is needed. If this is not the case, solid-solid diffusion will have to take place. The more solid-solid diffusion is needed for reaction (2.1), the larger is the chance that CaS formation is kinetically favoured, and consequently, the lower the regeneration selectivity is. This is demonstrated by two effects: regeneration selectivity increases (a) with improved CaO dispersion as determined by EPMA (fig. 2.1) and (b) with decreasing CaO content (fig. 2.2). Therefore, the most ideal dispersion of the CaO over the alumina surface would be the dispersion in a mono(molecular) layer. In such a dispersion, all the CaO (and consequently the CaSO\(_4\)) is in molecular contact with alumina.

![Figure 2.2](image.png)

**Figure 2.2** Regeneration efficiency (conversion of CaSO\(_4\) into CaO) versus CaO weight content for sol-gel samples. ○ in situ impregnated, batchwise. + in situ impregnated, continuously. Δ impregnated after calcination of continuous prepared sol-gel beads. Dotted line is drawn to guide the eye.
In this thesis, dispersion is defined as the way in which the calcium oxide is spread on the surface. Bad dispersion implies large crystallites and good dispersion implies thin layers. The distribution of calcium is defined as the calcium gradient over the macroscopic particle. In the discussions on the dispersion, the active material is always referred to as 'calcium oxide'. It would probably be more correct to refer to it as calcium aluminate, but since the microscopic situation of the calcium is not known, it is convenient to use the term calcium oxide.

A good dispersion can only be achieved when a good distribution exists. It is not only important for good regeneration, but also to prevent sintering, and, as we will see later, for a fast sulphation.

1.2.2 Techniques for particle size enlargement [8-10]

"En deskundige," verklaarde heer Ollie. "Iemand die kundig in des is."

Marten Toonder

When oxidic materials like alumina are prepared, one obtains crystallites (1 nm - 0.1 μm). These are so small that the Van der Waals forces cause them to be agglomerated in rather fluffy but small agglomerates (1 μm - 1 mm). A shaping or particle size enlarging technique must be applied to (partially) break down the existing agglomerates, either by brute force or by chemistry, followed by building up a new, strong particle (1 mm - 5 mm). The strength of the product particle depends on the extent of the breakdown of the original agglomerates during the shaping process. For extrusion and granulation, the extent of breakdown is quite small, so that these techniques yield particles which are too weak for our purposes. In spray drying and comparable techniques, one generally starts with a suspension in which the crystallites are well dispersed, so that strong particles can be formed. These are, however, too small for our purposes (10-100 μm).

This leaves us with two possible shaping techniques: pelletizing and sol-gel processes. These techniques generally yield porous support particles only, so that impregnation is needed to add an active material. Impregnation of porous materials is performed by filling the pores with a solution of a metal salt which can give the active material. The metal ions may adsorb on the pore walls and/or precipitate during drying, yielding a precursor which is converted to the active material during the subsequent calcination (decomposition of the precursor salt to the metal oxide). The combination of
adsorption and drying determines the dispersion and distribution of the active material in the porous particle [11-15].

A good dispersion can be obtained by a combination of a strong adsorption and slow drying [11]. At slow drying, adsorption can equilibrate and no "lumps" of fluid are transferred to the outside of the drying particles. The latter occurs when the overall drying rate is faster than the diffusion rate of evaporated fluid through the pore system [15]. The effect may cause considerable precipitation near the outside of the pellet.

Strong adsorption is achieved by choosing a support material which has a large specific surface area (≈ 200 m²/g) and a good affinity for adsorption like γ-alumina or pseudoboehmite (AlOOH·xH₂O), aluminium oxy hydroxide with additional crystal water. The pH of the system determines which type of ions will adsorb. At a pH above the iso-electrical-point, where the surface has a negative charge, alkaline metal ions will adsorb strongly on alumina [16].

1.2.2.a Pelletizing

Pelleting or pelleting is shaping by pressing from one or more sides on a powder mass of an easy compressible powder. Very hard powders like BaTiO₃ and, to a lesser extent, CaTiO₃ cannot be pelleted, even when lubricants are added [10,17]. Cylindrical particles with reasonable porosity are formed (0.2-0.8 ml/g), which are quite strong. The average crushing strength, i.e. the force needed to crush a particle, measured and averaged for 50 particles, is 60-200 N. By comparison, granules and extrudates seldom are stronger than 60 N. However, the particles are more dense at the outside since the pressure is applied from the outside. This means that a broken particle is weaker than the original one. Impregnation of pellets yields a far from ideal dispersion (fig. 2.1), and consequently a non-selective regeneration, especially in the case of α-Al₂O₃. In a preliminary research [18], it is found that starting material and impregnation conditions have little influence on the sorbent properties: the possibilities of optimization are rather small.

1.2.2.b Sol-gel methods

In sol-gel or oil-drop methods, a concentrated sol is dropped into an organic (oil) phase [19-21]. The particles in the sol are stabilized (peptized) by a surface charge, causing a repulsion which overcomes the Van
der Waals attraction. When this surface charge is removed, the Van der Waals forces will cause particles to stick on contact. In these concentrated systems, this causes rapid 'gelation'.

Sol-gel processes for the production of alumina start with aqueous sols of pseudoboehmite \([22-24]\) \((\text{AlOOH} \cdot x\text{H}_2\text{O})\). In a favourable process \([25]\), the sol is peptized with some nitric acid and urea, so that the particles bear a positive surface charge. This sol is dropped through an oil layer into an aqueous ammonia solution. The oil layer causes the particles to spherulize and to stay intact when falling into the aqueous phase, where they gelate as the ammonia neutralizes the acid and therewith the positive surface charge. Careful drying and calcination yields strong spherical beads (crushing strength 60-150 N), with reasonable porosity \((0.2-0.5 \text{ ml/g})\) and a uniform but small pore radius \((5-10 \text{ nm})\). To attain a good dispersion with impregnation will in principle be as problematic as it is for the pellets.

I.2.2.c In situ impregnation during sol-gel preparation

This type of sol-gel process, however, gives the possibility for in situ impregnation during the gelation in the aqueous phase \([26]\). In situ impregnation is performed by dissolving an appropriate salt in the ammonia solution. During gelation, this salt diffuses into the gelating particles and thus impregnates it under alkaline conditions. The \(\text{Ca}^{2+}\) ions adsorb on the pseudoboehmite surface, which in the alkaline environment bears a negative surface charge \([16]\). Because the drying of the gel particles is necessarily slow, to prevent cracking and breaking, the conditions for strong adsorption are ideally met. Therefore, a very good dispersion, possibly even a monolayer dispersion, of the active material on the alumina can be expected. Apart from this product technological advantage, a process technological advantage of in situ impregnation is that two energy consuming steps - drying and calcining after separate impregnation - can be discarded. A complication is that the solubility of many metals at \(\text{pH} > 7\) is rather small. This can be improved by using a proper complexing agent. In the case of calcium, ammonia appears to act in this way \((11.10.2)\).

After careful drying and calcination of the gelated particles, the sol-gel method with in situ impregnation yields spherical beads with a crushing strength of 60-200 N, a uniform pore size distribution (pore radius 5-10 nm) and a pore volume of 0.2-0.5 ml/g. The dispersion of the CaO is remarkably good \((\text{fig. 2.1})\).
Calcination of in situ impregnated sol-gel material at 850°C results in γ-Al₂O₃ as a support material. Calcination to higher temperatures in order to get the stronger α-Al₂O₃ results in a great loss of activity (fig. 2.3.b) which can be attributed either to a sharp decrease in surface area (fig. 2.3.a) or to phase transitions and reactions. With X-ray diffraction (XRD), only γ-Al₂O₃ is found after calcination at 850°C. After calcination at 1050°C, δ-Al₂O₃ and 3Ca0.5Al₂O₃ are found. After calcination at 1200°C, α- and θ-Al₂O₃ and Ca0.6Al₂O₃ are found. The calcium aluminates found are nonreactive towards sulphur oxides (I.1.1). Apparently, other compounds are also present in the sample, since it does show some reactivity. This is expected, because compounds that make up less than 5% of a sample, and compounds that are badly crystallized do not give an XRD-pattern. Yet, it is clear that when in situ impregnation is applied, only γ-Al₂O₃ can be used as a support because calcination to α-Al₂O₃ causes sintering, and the formation of nonreactive calcium aluminates.

![Graph 2.3.a](image1)

**Figure 2.3.a**

![Graph 2.3.b](image2)

**Figure 2.3.b**

**Figure 2.3** Influence of calcination temperature on the properties of sol-gel samples:

- lines are drawn to guide the eye
- 2.3.a BET surface area
- 2.3.b relative weight increase after 1.5 h sulfation in SRO test
  - ○ sample, made by impregnating calcined sol-gel beads
  - + sample, made by in situ impregnation during sol-gel preparation
I.2.3 The choice of a shaping method

Als Mozes eerst de uitkomst had willen weten, dan zou Israel nu nog in Egypte zijn.
Maarten Luther, geciteerd door Okke Jager

From the above it is clear that only two combinations of shaping and impregnation could meet the demands on low attrition rate and selective regeneration:

(a) pelletizing, followed by firing to α-Al₂O₃, impregnation, slow drying and calcination at 850°C. Thus, strong cylindrical pellers are made with relatively large pores and a small surface area; the calcium must be dispersed in a thick layer or even in large crystallites (fig. 2.1).

(b) sol-gel preparation, resulting in spherical and smooth beads with a good attrition resistance (table 1.2). The surface area is large, and the distribution and dispersion of the calcium are good (fig. 2.1) when in situ impregnation is applied. Possibly, the sulphation rate is smaller due to the small pore radius.

Yet, the good dispersion is important to provide good regeneration, to prevent sintering as far as possible, and possibly to prevent productlayer diffusion problems during sulphation. Combined with the good attrition resistance and the challenge of the new, we can only choose for developing the sol-gel method with in situ impregnation for sorbent preparation.

References

[22] Personal communication with J.W. Geus, 1990
I.3 IN SITU IMPREGNATION
DURING SOL-GEL PREPARATION

She is the latest in technology
Almost mythology
But she has a heart of stone
She has an IQ of one-thousand-one
She has a jumpsuit on
And she is also a telephone

Electric Light Orchestra

Having chosen in situ impregnation during sol-gel preparation, it is appropriate to give a more extensive description of the process (I.3.1). The objective is to show the possibilities of the process by investigating the limiting process conditions. It will be shown that the calcium oxide content of the sorbent can be controlled with the calcium concentration in the ammonia solution and the residence time of the gelating particles therein. These parameters are typical for the in situ impregnation process. The calcium oxide content appears to influence the texture and particle strength (I.3.2) and also CaO dispersion (I.4.2), and consequently the sulphation and regeneration behaviour (I.4.2).

Testing and modelling of the sulphation reaction is dealt with in the next chapter. All experimental details on preparation and characterization are given in appendix I and II respectively. Part II of this thesis is devoted to the physico-chemical background of the process.

I.3.1 Continuous sol-gel production with in situ impregnation

The general principle of the sol-gel process used, is that of the process developed by Condea Chemie, FRG [1]. The main difference between that process and the in situ impregnation we invented [2] is that we impregnate during the gelating step, and that consequently a much larger residence time of the gelating particles in the calcium containing ammonia solution has to be created. This is achieved by applying a reactor that is developed by KEMA, Arnhem, the Netherlands [3] (fig. 3.1, reactor 3). The gelating particles fall into the conical part of the reactor, where an upward flow of NH₃ solution is maintained, which restrains them from falling through the smaller part. The residence time is controlled by adjusting the upward flow. When impregnated long enough, the gel particles fall through the smaller
part of the reactor, and are carried to the sieve by the downward stream.

The overall process consists of three steps: sol preparation and dropping, gelation and impregnation, and drying and calcination.

1.3.1.8 Sol preparation and dropping

Pseudoboehmite powder (AlOOH.\(xH_2O\)) is dispersed in an aqueous solution of urea and a monovalent inorganic acid. The type of powder or powder mixture may exert considerable influence on the sol and product properties [4]. On advice of experts [5] we decided to use only one type of pseudoboehmite: PURAL SB-70, kindly provided by CONDEA Chemie. The type of acid is not very important [4], so we used nitric acid as does CONDEA Chemie.

The concentrations of powder, urea and nitric acid control the viscosity of the sol (II.9). The amount of pseudoboehmite powder is set at 33\(^\circ\) to prevent possible problems during drying (too large shrinkage due to small solids concentration, \(~30\%) or during dropping (too high viscosity due to large solids concentration, \(~35\%)).
Urea is added to prevent too fast an increase of the viscosity of the sol [1], in concentrations between 0.25 and 1 M to the aqueous solution. The influence of urea concentration on pore volume is shown in fig. 3.5.

Approximately 0.175 M nitric acid is added to the solution to yield the appropriate viscosity (~200 mPa.s at a shear rate of ~5 s⁻¹). Much lower (~0.02 M) and higher (~0.4 M) HNO₃ concentrations will cause the viscosity of the sol to be too high (~300 mPa.s).

High shear mixing is applied (13,500 rpm, shear rate ~16,000 s⁻¹) to disperse the solids in 5 to 10 minutes. Neither the type of mechanical dispersion or the intensity shows significant influence on the product properties.

After the sol has aged for about half an hour in a buffer vessel, it is dropped by pumping it through an orifice. The droplets, about 5 mm in diameter, fall into an oil layer, which must be lighter than, and immiscible with, water. Petrol ether (boiling point 40-60°C) serves this purpose quite well. A layer of about 20 cm is sufficient. Some ionic surfactant (TEEPOL) is added to the oil to ensure that the sol droplets easily pass the oil/water interface.

1.3.1.6 Gelation and impregnation

After passing the oil layer, the droplets fall into an ammonia solution which contains a calcium salt which decomposes to CaO and a gaseous component on calcination. To ensure a high enough Ca²⁺ concentration (~1 M), we used calcium nitrate.

Too high a salt concentration (≥2.0 M) causes the density of the solution to (almost) equal to the density of the sol-droplets, stopping them from falling further. But even at lower concentrations, the so-called osmotic imbalance (II.10.2.a) can cause cracking of the particles. The total ion concentration in the ammonia solution should be smaller than ca. 5 M. We use only 0.85 M ammonia and up to 1.2 M calcium nitrate to ensure a large enough calcium content in the final product.

To reach complete gelation and impregnation, a residence time of at least 5 minutes must be maintained. This can be achieved as explained above. Together with this residence time \( t \), the Ca²⁺ concentration [Ca²⁺] determines the calcium oxide weight content of the sorbent \( X_{CaO} \). Applying the penetration theory, which linearizes the calcium concentration profile into the
gelating particle, Rijpkema obtained the following semi-empirical relation for one specific set-up of the continuous sol-gel apparatus [6] (fig. 3.2)

\[ X_{CaO} = 7.31 \times 10^{-4} \frac{[Ca^{2+}]}{d^3 \rho_B} r^{0.35} \]  

(3.1)

Since \( d \), the diameter of the calcined sorbent beads, and \( \rho_B \), the bulk density of same, are constants, the calcium oxide content is easily controlled.

The gel particles are separated from the \( \text{NH}_3 \) solution carefully. They are rigid but not strong, which means that they easily deform at the cost of cracking. To avoid this, no small passages like valves or sharp angles are allowed in the downward stream, and the flow rate of the fluid at the sieve must be small.

After sieving, the gel particles can be immersed in ethanol for a few seconds to remove entangling ammonia solution. This prevents them from sticking together in the subsequent drying and calcination process. Also, it prevents the build-up of an outer layer of calcium oxide which might cause nonselective regeneration and pore blocking during sulphation.

I.3.1.1 Drying and calcination

The drying process of the gel particles can be divided into two steps. In the first step, the water loss (~40%) is accommodated for by a considerable shrinkage (~60%), but the particles stay wet all through. This first step can be performed relatively fast, for instance in approximately 3/4 h, in a microwave oven. The calcium distribution profile is influenced by this fast drying (fig. 3.3). This will have a negative influence on the dispersion, as is shown by the lower sulphation rate of the microwave dried sorbent (I.4.2).

The second drying step begins when the rate of contraction becomes slower
Figure 3.3 Calcium distribution profile (intensity of WDS signal for calcium) for in situ impregnated sol-gel samples o dried at 27°C in a ventilator oven + dried 15 min in a microwave oven, and then at 82°C in the ventilator oven lines are drawn to guide the eye

than the rate of water evaporation. This causes the outside of the particles to fall dry. To avoid the build-up of large stresses in the particles, slow drying (< 0.6 g/(g.h)) must be applied, for instance by blowing cold air over the particles. The total weight loss during drying is about 55w%, while the total volume loss is about 75%.

About 32w% of the dried particle weight is removed during the subsequent calcination at 850°C, the temperature at which the sorbent is used. Assuming that all the gas formed is retained in the pores of the beads, a pressure of more than 1000 atm can easily be reached during this process. Of course the gas will diffuse out of the beads, but the rate of diffusion is limited by the small pore radius (~7 nm). This limits the heating rate to 1°C/min.

Figure 3.4 Weight loss of an in situ impregnated sol-gel sample versus calcination temperature (calcination at 1°C/min in a thermobalance) left hand: relative weight loss right hand: rate of weight loss
A thermogravimetric experiment at 10°C/min (fig. 3.4) shows that the calcination can also be divided into two steps. The total weight loss can be accounted for fairly well by assuming it to be caused by the decomposition of Ca(NO₃)₂ and AlOOH·xH₂O. Here, x = 0.35 is taken, the value determined thermogravimetrically for the pseudoboehmite. The total calculated weight loss is ~30 wt%. The first step is probably due to the removal of excess water of the boehmite (~9 wt%) and the formation of some nitrous oxides; the second step is due to the decomposition of Ca(NO₃)₂ and AlOOH [7,8].

Above 500°C, the main part of the decomposition has taken place, and a higher calcination rate can be applied. We have employed slow heating (0.5 or 1.0°C/min) up to 500°C and a larger rate (~3°C/min) up to 850°C, at which the sorbent is calcined for 10 hours. Relative fast cooling to room temperature (~3 h) is applied to prevent large uptakes of water or CO₂.

The drying and calcination procedures can probably be optimized in a technological sense: faster heating can be applied at certain stages. However, it is not expected that this would affect the product properties in a positive way. Consequently, this process step has not been a main point of attention in the development of the sorbent.

---

**Figure 3.5** Pore volume versus $X_{CaO}$ for in situ impregnated sol-gel spheres
(a) + made with 0.25 M urea in sol
(b) linear regression on all data
(c) o made with 0.75 or 1 M urea
(d) pore filling model

**Figure 3.6** Pore radius ($r_p = 2 V_p/S_{BET}$) versus calcium oxide weight content of in situ impregnated sol-gel samples; dotted lines are two linear regressions for low and high calcium oxide content
1.3.2 The influence of CaO content on sorbent texture and strength

The presence of calcium ions during gelation appears to induce structural changes in the sorbent. Here, we will only demonstrate the effects, which are discussed in further detail in chapter II.10.

(a) The pore volume \( V_p \) decreases rapidly with increasing CaO content \( X_{CaO} \) (fig. 3.5), more than expected for simple pore filling according to

\[
V_p = V_{p,0} - \frac{X_{CaO} \rho_{CaO}}{\rho_{CaO}}
\]

where \( V_{p,0} \) is the pore volume at \( X_{CaO} = 0 \) (g/g) and \( \rho_{CaO} \) the solid density of CaO (g/ml).

(b) At higher urea concentration the loss of pore volume is smaller (fig. 3.5). This is not expected for simple pore filling. Apparently, this model does not apply. An alternative explanation is given in II.10.2.a.

(c) The pore radius decreases when \( X_{CaO} \) is increased from zero to 7 wt%, but increases again at higher \( X_{CaO} \) (fig. 3.6). Both the extent of the decrease and the occurrence of an increase of pore radius at higher \( X_{CaO} \) are not expected for simple filling of the pores.

Figure 3.7 Average crushing strength of in situ impregnated sol-gel samples versus calcium oxide weight content; dotted line is a linear regression
The average crushing strength increases on increasing calcium oxide content (fig. 3.7), as expected for a decrease in pore volume.

In the next chapter the influence of the CaO content on reactivity and on the calcium oxide dispersion will be discussed.

References

I.4 SULPHATION AND REGENERATION OF SOL-GELO SORBENTS

"Ja, ja", zei heer Bommel. "Zo is het ook met mij ... ik doe dikwijls dingen die mijn denkraam te boven gaan!"
Marten Toonder

To test sorbents on their capacity, rate of sulphation and selectivity of regeneration, we have developed the SRO test [1] (appendix II). In this thermogravimetric test, the weight changes during sulphation, regeneration and oxidation are followed. The oxidation step is introduced to determine the amount of CaS, formed during regeneration, by oxidizing it to CaSO₄.

We have developed a model for the sulphation reaction, on the assumption that productlayer diffusion cannot play an important role in that reaction: the shrinking core model [2] (I.4.1). It yields the effective pore diffusion coefficient, which is compared to the theoretical one (I.4.2). Based on this comparison, conclusions are drawn on the dispersion of the CaO.

These conclusions are confirmed by the results of regeneration experiments and cyclic tests (I.4.3). These tests also show that the in situ impregnated sol-gel sorbent can be applied successfully in a cyclic process.

In appendix I and II experimental data on materials and techniques can be found. A more extended research on the reactivity of the sorbents has been carried out by E.H.P. Wolff cocurrently [3].

I.4.1 Shrinking core model for the sulphation of sol-gel sorbent

The SRO test yields, amongst other things, the sample weight versus time during sulphation of 6 or 7 particles (~200 mg, fig. 4.1). Therefore, the differences of individual beads in calcium content and porosity are impor-

![Figure 4.1 Typical weight versus time curve during sulphation in SRO test](image)

- $W_0$ initial weight; $W_\infty$ final weight
- $W_\infty$ final weight
tant. Larger samples, however, would induce severe rate limitation by gas diffusion, which would considerably decrease the value of the experiment. This means that for modelling not the overall conversion, based on the calcium oxide content, but the relative conversion $\xi_1$, based on the total weight increase, must be used

$$\xi_1 = \frac{(W-W_0)}{(W_\infty-W_0)}$$  \hspace{1cm} (4.1)

where $W$, $W_0$, and $W_\infty$ denote the weight of the sample at time $t$, the initial weight and the final weight, respectively.

There are several reasons to assume that severe pore diffusion limitation determines the sulphation rate, certainly when sol-gel sorbents are used. Experimental indications are: (a) the strong dependency of reaction rate on particle size [3], and (b) the increase of sulphation rate with decreasing surface area but increasing pore radius (fig. 4.2). Theoretic considerations are: (a) the involved chemical reaction rates are known to be relatively fast at 850°C [4-6]; this is confirmed experimentally by adding platinum to

---

**Figure 4.2.a**

Figure 4.2 Properties of calcined sol-gel samples, made by batchwise in situ impregnation during sol-gel preparation at varying residence time in the gelation step

4.2.a BET surface area $S_{BET}$ and average pore radius ($r_p = \frac{2V}{S_{BET}}$)

4.2.b relative weight increase after 1.5 h sulphation in SRO test (duplicated)
a sorbent sample. Platinum is a known catalyst for oxidation of SO$_2$ to SO$_3$ [7], but hardly any rate increase is noted [3,8], so that at least the gas phase reactions are of no importance for the overall rate; (b) the small pore size (~6 nm) combined with the rather narrow pore size distribution (fig. 4.3); and (c) the good dispersion of the calcium oxide. Diffusion through the product layer of CaSO$_4$ is often mentioned as a possible rate influencing step [9-11]. However, it is to be expected that in situ impregnation yields a good dispersion (I.2.2.c). This is corroborated by the 'direct observation' and the results on regeneration (I.2.1). If we assume that it is a mono-(molecular) layer, productlayer diffusion cannot be important. We will return to this important assumption in I.4.2.

Assuming furthermore, that the reaction rate is much faster than the diffusion rate, these processes can be described as being serial processes: the SO$_2$ must diffuse through an outer core of reacted material to a reaction front and can only then react with calcium aluminate. Thus, a shrinking core of unreacted calcium aluminate arises (fig. 4.4).

Based on these assumptions, the shrinking core model is derived elsewhere [2], taking external gas transport into account. This derivation results in

$$\left( \frac{df_1}{dt} \right)^{-1} = \frac{\kappa f(f_1)}{D_{\text{eff}}} + \frac{\kappa}{R_k g}$$

(4.2)

![Figure 4.3 Duplicated pore size distribution of SG-105 (a continuous in situ impregnated sol-gel sample), calculated from the desorption branch of N$_2$ physisorption, assuming cylindrical pores](image)

Figure 4.3 Duplicated pore size distribution of SG-105 (a continuous in situ impregnated sol-gel sample), calculated from the desorption branch of N$_2$ physisorption, assuming cylindrical pores.
Figure 4.4 Diagram of the shrinking core model

\[ (d\xi_1/dt)^{-1} \text{ and } f(\xi_1) \text{ can be calculated from the experimental results. A plot of } (d\xi_1/dt)^{-1} \text{ versus } f(\xi_1) \text{ should give a straight line, the slope giving } D_{\text{eff}} \text{ (the effective diffusion constant), the intercept of the y-axis giving } k_0 \text{ (the external mass transfer coefficient). Here} \\
\]

\[ f(\xi_1) = (1-\xi_1)^{-1/3} - 1 \tag{4.3} \]

and

\[ \kappa = \frac{W_\infty - W_0}{4\pi n MR C_0} \tag{4.4} \]

where \( n \) is the number of beads which is tested, \( M \) the molar weight of \( \text{SO}_3 \) (the weight difference between \( \text{CaO} \) and \( \text{CaSO}_4 \)), \( R \) the particle radius and \( C_0 \) the inlet \( \text{SO}_2 \) concentration.

In this model, the accumulation term has been neglected, although the \( \text{SO}_2 \) concentration in the thermobalance is zero at the start of the experiment. However, it takes only a few minutes to reach the equilibrium \( \text{SO}_2 \) concentration. The total experiment time is at least a few hours. The first few minutes of the experiments are not used in the modelling.

1.4.1.a Preliminary results and verification

A plot of \( (d\xi_1/dt)^{-1} \) versus \( f(\xi_1) \) (fig. 4.5) shows that the experimental data are fitted quite well up to \( f(\xi_1) = 1.5 \) or \( \xi_1 = 0.93 \). At even higher conversions the reaction rate is too small to be determined precisely enough. No deviations of the model are found for small \( f(\xi_1) \) where the neglect of the accumulation term could have caused them. Also, the intercept of the y-axis is very small, indicating that the effect of external diffusion limitation is negligible. The internal diffusion is apparently important enough to make any external effect subordinate.
Figure 4.5 Test of the shrinking core model: \((d\xi_1/dt)^{-1}\) versus \(f(\xi_1)\); line is linear regression for all points with \(f(\xi_1) < 1.5\) or \(\xi_1 < 0.93\)

The error in fitting the slope in fig. 4.5 is only about 1%. Other experiments are equally well fitted, indicating that the mathematical model describes the experiments quite well. In some cases, however, a kink appears in the \((d\xi_1/dt)^{-1}\) versus \(f(\xi_1)\) plot, especially for samples with lower CaO content. Possibly it is caused by a non uniform distribution profile of the CaO over the sorbent particle.

The reproducibility of the experiment is good (table 4.1), but uncertainties in test and particle parameters cause the total relative error in the diffusion coefficient to be \(-10\%\). The intercept of the \(y\)-axis is very small, and of the same order of magnitude as the error in the intercept. Therefore this method cannot be used to determine \(k_g\) accurately, though the calculated values are of the correct order of magnitude for mass transport coefficients.

Table 4.1 Duplicate results of the shrinking core model on sample SG-105*

<table>
<thead>
<tr>
<th>cycle number</th>
<th>(D_{\text{eff}} \times 10^{-7} \text{ m}^2/\text{s})</th>
<th>(k_g \times 10^{-2} \text{ m/s})</th>
<th>(\Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment</td>
<td>(a)</td>
<td>(b)</td>
<td>(a)</td>
</tr>
<tr>
<td>1</td>
<td>5.8</td>
<td>5.9</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>8.9</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>8.4</td>
<td>-</td>
<td>0.9</td>
</tr>
<tr>
<td>8</td>
<td>9.7</td>
<td>-</td>
<td>1.6</td>
</tr>
</tbody>
</table>

*sample SG-105; see appendix I; symbols defined in Lyst of Symbols
in thermobalances [12]. However, our objective is to find the kinetics of the sorbent rather than to describe the thermobalance.

For sample SG-105 (appendix I), it is found that \( D_{\text{eff}} = 5.9 \pm 0.6 \times 10^{-7} \) m\(^2\)/s. Wolff finds on the same sample, tested in a fixed bed reactor and modelled in a comparable way: \( D_{\text{eff}} = 7.5 \pm 0.6 \times 10^{-7} \) m\(^2\)/s [3]. These values are nearly equal, and have the correct order of magnitude. The latter can be shown by estimating \( D_{\text{eff}} \) from the Knudsen diffusion coefficient \( D_K \) [13]

\[
D_{\text{eff}} = \frac{\epsilon}{\theta} D_K = \frac{\epsilon}{\theta} 97 r_p \left( \frac{T}{M'} \right)^{0.5}
\]

\( \epsilon \) is the porosity of the sample (-), \( \theta \) the tortuosity factor of the pore system (-), \( r_p \) the average pore radius (m), calculated from the pore volume \( V_p \) and the BET-surface area according to \( r_p = 2 V_p / S_{\text{BET}} \). \( T \) is the absolute temperature (K), and \( M' \) the molar weight of the diffusing species (g/mol)*.

The tortuosity factor \( \theta \), the only unknown in equation (4.5), is defined as the actual distance a molecule diffuses through a pore system, divided by the minimal distance. For a typical pore system, \( \theta \) should equal \( 1/2 \), though in practice values between 0.1 and 12 are found [13,15]. Here, we calculate it to be 2.4, which is quite close to the theoretic value. The deviation will be discussed in I.4.2.

1.4.1.b Physical imaging by EPMA

Electron Probe Micro Analysis (EPMA) is used to determine the distribution of calcium and sulphur over sorbent beads (appendix II). Thus, the physical image of the shrinking core model can be shown. Sorbent beads of the sample which was used in I.4.1.a, are sulphated in a thermobalance for a given time, embedded in resin and ground until a (nearly) diametrical cross-section of the bead is obtained. The results (fig. 4.6), which show the approximate image of a shrinking core, are compared to predictions of the

---

* The diffusing species is taken to be the \( \text{SO}_2 \) molecule, based on the following argument. Two sources for \( \text{SO}_3 \) exist on the boundary of the shrinking core: \( \text{SO}_3 \) from the gas bulk, and \( \text{SO}_3 \) that is formed in the pores from \( \text{SO}_2 \) and \( \text{O}_2 \) that have diffused into the particle. At equilibrium at 850°C the \( \text{SO}_2 \) concentration is about 12.5 times the \( \text{SO}_3 \) concentration [14]. Also, the reaction between \( \text{SO}_2 \) and \( \text{O}_2 \) is fast. Consequently, it is safe to assume that the second source for \( \text{SO}_3 \) is the most important one. This leaves us with two possible rate determining species: \( \text{SO}_2 \) and \( \text{O}_2 \). The diffusion coefficient of \( \text{O}_2 \) is larger and its concentration is about 40 times larger than the \( \text{SO}_2 \) concentration: the species which determines the rate of diffusion will be the \( \text{SO}_2 \) molecule.
shrinking core model (table 4.2). The radius of the shrinking core $r_c$ is calculated from the conversion (which is calculated from the model), with

$$1 - \xi_1 = \left(\frac{r_c}{R}\right)^3 \tag{4.6}$$

The predictions are calculated with the given values for the sorbent properties (table 4.2), where the CaO content of each sample is simultaneously determined with EPMA. It is impossible to find the exact middle of the bead while grinding. Missing the exact middle causes an overestimate of $(R - r_c)$, especially for small $r_c$ and large dev (the deviation from the middle

---

**Figure 4.6** Physical imaging of the shrinking core model with EPMA

---

**Figure 4.6.a** calcium (fat line) and sulphur (thin line) profiles for an in situ impregnated sol-gel bead, that was sulphated for 10 minutes (see table 4.2)

---

**Figure 4.6.b** sulphur profiles on the same sample, for different sulphation times
(a) 10 min (thin line)
(b) 30 min (dotted line)
(c) 150 min (striped line)
(d) 300 min (fat line)
(e) 2160 min (stripe dot stripe)
Table 4.2 Comparison of theoretic and experimental shrinking core radii

<table>
<thead>
<tr>
<th>Sulphation time (min)</th>
<th>R (mm)</th>
<th>$X_{CaO}$ (w%)</th>
<th>$(R-r_c)_{model}$ (μm)</th>
<th>$(R-r_c)_{EPMA}$</th>
<th>approximate overestimate dev: 100</th>
<th>300</th>
<th>500</th>
<th>μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.55</td>
<td>8.82</td>
<td>55</td>
<td>50-80</td>
<td>0.3</td>
<td>2.5</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1.70</td>
<td>8.82</td>
<td>116</td>
<td>80-150</td>
<td>0.4</td>
<td>3.4</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>1.70</td>
<td>8.26</td>
<td>326</td>
<td>350-420</td>
<td>1.3</td>
<td>12</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1.60</td>
<td>8.12</td>
<td>506</td>
<td>780-805</td>
<td>4.2</td>
<td>41</td>
<td>138</td>
<td></td>
</tr>
<tr>
<td>2160</td>
<td>1.60</td>
<td>7.28</td>
<td>∞</td>
<td>∞</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

* Sulphation of sample SG-105 (appendix I) in a thermobalance at 850 °C, 100 ml/min (NTP) of 0.25 v% SO₂, 2.5 v% O₂, balance N₂. Approximate overestimate $(A₀)$ calculated from $A₀ = r_c - R + √(R² - dev²) - √(r_c² - dev²)$ using the maximum value of $R - r_c$, determined by EPMA. Shrinkage core radii calculated with: $D_{eff} = 5.8 \text{ m}²/\text{g}$, $k = 0.015 \text{ m/s}$ (table 4.1).

of the beads. Bearing this in mind, the agreement between experiment and theory is satisfactory (table 4.2).

Together with the arguments in 1.4.1.a, these results sufficiently prove the correctness of the shrinking core model.

1.4.2 Evidence for the monolayer concept

... eenvoudige boeren horen niet graag ingewikkelde waarheden.  

Louis Paul Boon

The assumption that the calcium in the in situ impregnated sol-gel sorbent is distributed in a monolayer, is tested using samples with varying calcium oxide content, $X_{CaO}$ (appendix IV). For low $X_{CaO}$ the assumption appears to be adequate: the model predicts correct diffusion coefficients (fig. 4.7). It is calculated (appendix IV), that the critical calcium content $X_{CaO,c}$ for which the monolayer capacity is exceeded is approximately 9.5w%. Therefore, for $X_{CaO} > X_{CaO,c}$, product layer diffusion can be expected to be important.

This can be seen as follows. The diffusion coefficient divided by the diffusion length can be used to compare the influence of several diffusion processes in series. Thus, product layer diffusion will be important when

$$
D_{K}/R = D_s/δ_s
$$

(4.7)
Figure 4.7 Inverse dispersion coefficient $\Delta^{-1}$ versus calcium oxide weight content of in situ impregnated sol-gel samples. Theoretically, it should hold that $\Delta^{-1} \rightarrow \Delta = 1$ for $X_{CaO} < X_{CaO,c}$, where the latter is the critical calcium oxide weight content for a monolayer dispersion.

- Slowly dried samples; linear regression for points at $X_{CaO} > 8\%$.
- Fast dried samples; linear regression for all points.

$D_s$ and $\delta_s$ are the diffusion coefficient and the thickness of the product layer. Even for a monolayer of product ($\delta_s \approx 0.5$ nm) this can be true, since solid diffusion coefficients are usually $10^5 - 10^7$ times smaller than gas diffusion coefficient [13]. A range, given for the diffusion coefficient of SO$_2$ in CaSO$_4$ is $6 \times 10^{-13}$ to $2.5 \times 10^{-10}$ m$^2$/s [16], while $D_K = 2 \times 10^{-6}$ m$^2$/s.

When product layer diffusion does influence the overall reaction rate, the experimental $D_{eff}$ will be smaller than the theoretical one. Indeed, for $X_{CaO} > X_{CaO,c}$, this effect is found (fig. 4.7). Also, a higher drying rate can be expected to cause a less good dispersion (I.2.2). Then, the influence of product layer diffusion will be larger, which shows in larger deviations from the theory. Again, this idea is confirmed by experiment (fig. 4.7).

To use the shrinking core model in a predictive fashion at higher $X_{CaO}$, the 'dispersion coefficient' $\Delta = D_{eff}/D_{th}$ is introduced in equation (4.5)

$$D_{eff} = \frac{\epsilon}{\delta} \Delta D_K$$

(4.8)

$\Delta = 1$ for $X_{CaO} < X_{CaO,c} = 9.5\%$ and $\Delta < 1$ for larger $X_{CaO}$ (fig. 4.7).
I.4.3 Regeneration and cyclic use of sol-gel sorbents

Aan alles komt een eind, zeggen ze wel eens.
Liselore Gerritsen

As stated before (I.2.1), our hypothesis regarding regeneration is that CaSO₄, which is in direct contact with aluminium oxide reacts completely to calcium aluminate. CaSO₄ that is dispersed in any other way will only partially react to calcium aluminates and partly to CaS. For $X_{\text{CaO}} < X_{\text{CaO,rec}}$, the regeneration selectivity to CaO decreases with increasing $X_{\text{CaO}}$ (Fig. 2.2). This again confirms the correctness of the monolayer concept.

It also implies the following. When sorbent is used in a cyclic fashion, the CaS will be converted into CaSO₄ when it enters an oxidative environment. After a few cycles, all the CaO not dispersed in a monolayer will have followed this route to CaS, leaving only the monolayer to be sulphated. Then, $A$ should equal 1. This is true after a few cycles (table 4.1).

Still, even when $A = 1$, some CaS is formed during regeneration. Possibly, a small part of the calcium oxide is present as CaO, which readily sulphates but regenerates into CaS at 850°C. Indeed, when the sorbent is treated with solution of phenolphthaleinen, it turns purple, which proves that an alkaline compound is present. CaO reacts alkaline, calcium aluminates do not [3].

Figure 4.8.a  
Figure 4.8.b

Figure 4.8 The influence of hydrogen concentration on the regeneration behaviour of an in situ impregnated sol-gel sample
4.8.a regeneration selectivity (conversion of CaSO₄ to CaO); line drawn to guide the eye
4.8.b regeneration rate (regression with a reaction order of 0.5)
Figure 4.9.a and Figure 4.9.b

Figure 4.9 The influence of regeneration temperature on the regeneration behaviour of an in situ impregnated sol-gel sample

4.9.a regeneration selectivity (conversion of CaSO₄ to CaO); line drawn to guide the eye
4.9.b regeneration rate, shown as Arrhenius plot

(a) activation energy of 90 kJ/mol (best fit)
(b) activation energy of 22 kJ/mol (best fit)

The hydrogen concentration during regeneration does not significantly influence the regeneration selectivity (fig. 4.8.a), although it has a strong influence on the regeneration rate (fig. 4.8.b). More or less the same applies for the regeneration temperature above 800°C (fig. 4.9.a and .b). A slightly better selectivity is found at a higher temperature. In practice, a higher temperature than 850°C is not advisable: it is economically unattractive and will cause sintering. Generally, regeneration is fast enough and not sensitive to changes in the conditions.

During regeneration, CaS, H₂S and Sₓ can be formed. It is assumed that all CaSO₄ that does not regenerate to CaO yields CaS. The amounts of H₂S and Sₓ formed are not monitored. More details on this subject can be found in the work of Wolff [3].

Apart from the sulphation rate, regeneration selectivity, etcetera in the first cycle, the stability of the sorbent through the cycles is important. Several tests, in thermobalances and in fixed bed reactors [3], have shown that the rate of sulphation and the selectivity of the regeneration both decrease somewhat in the first 5 to 10 cycles. From that point onwards, they
stabilize (fig. 4.10) on values which are acceptable for a cyclic process (regeneration selectivity of ~0.75). In a fixed bed reactor, a steady regeneration selectivity of ~0.7 was attained [3]. Voet performed a fluidized bed experiment of 102 cycles at 850°C (150 minutes sulphation, total cycle time including calibration, etc. 258 min). He found a steady regeneration selectivity of ~0.5 [17]. Regarding the small size of the sample in the thermobalance experiment (only three beads), and the differences in experimental set-up and sulphur analysis, the agreement between these experiments is satisfactory.

The BET surface area of the sample that had undergone 50 cycles in the TG is determined to be 29 m²/g, as compared to 99 m²/g for the original sorbent. The sample was too small to determine a pore size distribution from N₂ physisorption, but the change in surface area points at sintering of the sorbent.

Most important, however, is that the regeneration selectivity is stable at higher number of cycles, that the sorbent still reacts easily with SO₂, and that is not severely weakened by the large number of cycles as is confirmed in the 102-cycle experiment.

Thus, we have seen in this chapter that in situ impregnation during sol-gel preparation yields sorbents, which can successfully be applied in regenerative desulphurization for a large number of cycles. Also, we have seen that the excellent sulphation and regeneration is due to the very good,
possibly monolayer, dispersion of the 'CaO' on the alumina surface, achieved by this preparation process.

Still, these separate experiments do not show the performance in an actual process, where any improvement through a change in one sorbent property may be destroyed by the change in another sorbent property. For instance, a more porous sorbent will sulphate faster, but will also attrite faster. The best way to examine this complex problem would be to determine, in a pilot plant, the amount of make-up sorbent needed. Since this is beyond the scope of this research, a model is developed, which tries to combine the several effects into one result. This model is the subject of the next chapter.

References

[12] Personal communication with A. Potma, 1989
I.5 ReSuLT: A MODEL FOR REGENERATIVE DESULPHURIZATION AT LOW TEMPERATURE

The performance of a sorbent is a complex parameter, depending on its attrition rate, sulphation behaviour and regeneration selectivity, which again depend on the texture and degree of dispersion, et cetera. The sorbent performance becomes an accesable parameter when we express it as the amount of make-up sorbent per kg of coal fed to the combustor. To calculate this, we have developed ReSuLT, a simple reactor model for the Regenerative desulphurization at Low Temperature. In ReSuLT, the sorbent loss is described with an attrition model (appendix III) and the sulphation is described with the shrinking core model (I.4). The basic idea of the model is that slower sulphation leads to a larger sorbent hold-up in the combustor, which leads to larger attrition losses. Thus, ReSuLT predicts the sorbent performance as a function of its properties. It can be used to explore the routes for sorbent improvement (I.5.2) and to examine the technology window of the preparation method adopted (I.6.1). In this chapter it will be derived (I.5.1) and verified (I.5.2).

To be able to describe the system of combustor and regenerator (fig. 5.1), some rigorous simplifications and assumptions are made.

Figure 5.1 Simplified flowchart of regenerative desulphurization (see also fig. 0.1); C: combustor, R: regenerator

\[ \phi_i \] molar flow of calcium

\[ Q_1 \] total (gas + solid!) molar flow of S

\[ k_i \] mass flow of coal
a) Sulphation and regeneration are carried out isothermally in fluidized beds, which are in steady state and mixed ideally for solids and gases.
b) The sulphation is described by the shrinking core model (appendix V).
c) Attrition loss occurs in the fluidized beds only. The attrition loss in the regenerator is neglected ($\phi_e = 0$), as the sorbent hold-up therein is much smaller than it is in the combustor. The attrition rate is directly proportional to the sorbent mass in the combustor (appendix III).
d) The efficiency of the separation of sorbent and coal ash is 100% for particles, larger than 1.4 mm, and 0% for smaller ones (appendix III).
e) The regenerator is regarded as a black box; all particles are regenerated from CaSO$_4$ into CaO with an average conversion of $\tilde{\xi}_2$. The CaO which is at that moment available in the regenerated particles equals $\Xi X_{\text{CaO}}$, where
$$\Xi = 1 - \tilde{\xi}_1 + \tilde{\xi}_1 \tilde{\xi}_2$$ (5.1)

$\tilde{\xi}_1$ is the average conversion of CaO to CaSO$_4$ in the combustor and $X_{\text{CaO}}$ is the CaO weight content of the sorbent. This amount of CaO is thought to be dispersed evenly over the sorbent particle.
f) The sorbent residence time in the combustor $\tau_1$, defined on a molar basis, is not influenced by the flow of coal ash (the densities of sorbent and coal ash are assumed to be equal). Accordingly,
$$\tau_1 = n_1 / (\phi_4 + \phi_5)$$ (5.2)
n$_1$ is the number of moles of calcium in the combustor, and $(\phi_4 + \phi_5)$ is the molar flow of calcium out of same. In general, $\phi_4$ indicates a molar calcium flow, and $Q_4$ a total molar sulphur flow; the indices are defined in fig. 5.1. Many other parameters are defined in table 5.1.
g) To meet governmental regulations [2], 90% of the sulphur fed to the combustor is captured ($R_s = 0.9$) and the SO$_2$ off-gas concentration is 215 ppm.

I.5.1 Derivation of ReSuLT

NU WORDEN mijn gedachten vreemd, als oude tulpen met kleuren, die er eigenlijk niet bestaan ...
M. Vasalis

In general, molar balances for reactors or systems, are written as
$$\text{accumulation} = \text{in} - \text{out} - \text{conversion}$$ (5.3)

In steady state, for calcium
while for *calcium oxide*, regarding the combustor

\[
0 = (\phi_1 + \phi_4) - (\phi_3 + \phi_5)(1 - \xi_1) - n_1 \dot{r}_{\text{CaO}} \tag{5.6}
\]

The molar balance of *sulphur in the gas phase* of the combustor is

\[
0 = Q_1 - (Q_5 - \xi_1 \phi_5) - n_1 \dot{r}_{\text{CaO}} \tag{5.7}
\]

\(\dot{r}_{\text{CaO}}\) is the average rate of conversion of \(\text{CaO}\) per mol of calcium. It is calculated from the residence time distribution in the fluidized bed \(E(t)\), and from \(r_{\text{CaO}}\), the rate per particle as given by the shrinking core model (I.4).

\[
\dot{r}_{\text{CaO}} = \int_0^\infty E(t) r_{\text{CaO}} \, dt = \int_0^\infty \frac{\exp(-t/\tau_1)}{\tau_1} r_{\text{CaO}} \, dt \tag{5.8}
\]

From assumption g), where \(k_1\) is the *mass* flow of coal into the combustor

\[
Q_5 = (1 - R_S) Q_1 + \xi_1 \phi_5 = (1 - R_S) X_S/M_S k_1 + \xi_1 \phi_5 \tag{5.9}
\]

\(\xi_1\) relates to a common operational parameter for desulphurization, \(\text{Ca/S}\)

\[
\xi_1 = R_S / (\text{Ca/S}) \tag{5.10}
\]

When \(\alpha\) denotes the attrition rate in \(1/s\) and \(m_1\) the mass content of \(\text{CaO}\) of the combustor, it follows from assumption c) and equations (5.2), (5.4) that

\[
\phi_5 = \alpha m_1 / M_0 = \alpha \tau_1 M_0 (\phi_3 + \phi_5)/M_0 = \alpha \tau_1 (\phi_1 + \phi_4) \tag{5.11}
\]

This *molar* loss of calcium is not affected by extra weight due to the sorbent not being pure \(\text{CaO}\) or by conversion of \(\text{CaO}\) into \(\text{CaSO}_4\) or \(\text{CaS}\).

1.5.1.a Solution of Result

The system of equations is solved in appendix V, yielding

\[
\phi_1 = \frac{\alpha \tau_1 \text{Ca/S} X_S/M_S}{\xi_2 + \alpha \tau_1 (1 - \xi_2)} k_1 \tag{5.12}
\]

and

\[
R_S X_S/M_S k_1 = \frac{\phi_1}{\alpha \tau_1} \int_0^1 \exp\left(- \frac{3/2(1-(1-\xi_1)^{-2/3}) + \xi_1}{K C_0 \tau_1}\right) d\xi_1 \tag{5.13}
\]
where $\xi_1$ is the conversion of a particle as a function of time. $\phi_1$ and $r_1$ are found iteratively by numerical integration of (5.13). $\phi_1$ and $r_1$ depend on the sorbent properties in the following three ways.

The regeneration selectivity $\xi_2$. The CaS formed during regeneration, $(1-\xi_2)$, is oxidized into CaSO$_4$ during the subsequent combustion step. Together with the CaSO$_4$, formed by sulphation in that combustion step, this CaSO$_4$ is regenerated with the same selectivity $\xi_2$. The constant value for $\xi_2$, which is reached after a number of cycles (I.4.3), is used. Thus, no sorbent deterioration is included in ReSuLT.

The reaction rate parameter $K C_0$ from the shrinking core model (appendix V)

$$K = \frac{3 D_{\text{eff}} M_0}{\rho_B R^2 X_{\text{Ca0}}}$$  \hspace{1cm} (5.14)

The effective diffusion coefficient $D_{\text{eff}}$ is calculated from the Knudsen diffusion coefficient, corrected with the dispersion coefficient $\Delta$ (I.4.2). $\Delta = 1$ for a monolayer dispersion and it is smaller for a less good dispersion. The porosity $\epsilon$ equals by definition $\rho_B V_p$

$$D_{\text{eff}} = \frac{\epsilon}{\theta} \Delta D_K = 406 \Delta \rho_B V_p r_p / \theta$$  \hspace{1cm} (5.15)

The SO$_2$-concentration in the combustor, $C_0$, is calculated from

$$C_0 = (1-R_s) \frac{X_s}{M_s} \frac{k_1}{\phi_{v,\text{out}}}$$  \hspace{1cm} (5.16)

For the attrition rate $\alpha$ (appendix III)

$$\alpha = \frac{3}{2} R_k a (U - U_{mf})$$  \hspace{1cm} (5.17)

$U_{mf}$ is the minimal superficial gas velocity for fluidization. The best approximation available applies for a 1:1 mixture of sand and sorbent (appendix III). Then

$$U_{mf} = \frac{\eta_k}{2 R \rho_k} \left( 30^2 - 0.43 R^3 \rho_k \rho_B \eta_k^{1/2} \right)^{1/2} - 30$$  \hspace{1cm} (5.18)

where the bulk particle density $\rho_B$ is calculated from

$$\rho_B = \frac{1}{\rho_s + V_p}^{-1}$$  \hspace{1cm} (5.19)
In ResuLT, no limit exists for the regenerator capacity or the sorbent transport rate from combustor to regenerator and vice versa. Therefore, ResuLT compensates for a reduced regeneration selectivity by increasing the transport rate ($\phi_1$). This results in a smaller $r_1$ and therefore a smaller $\phi_1$, which is unrealistic. We correct this by fixing $r_1$ at the value calculated for $\xi_2 - 1$, because in that case assumption e) is most realistic. Using the fixed $r_1$ and the actual $\xi_2$ in equation (5.12), $\phi_1$ is calculated.

Rather than $\phi_1$, we have calculated the sorbent performance $Y$ with ResuLT. $Y$ is the sorbent make-up per kg of coal added to the combustor. It follows from $\phi_1$ according to

$$ Y = \frac{M_0 \phi_1}{X_{\text{CaO}} k_1} $$  \hfill (5.20)

Also important is the bed content or sorbent hold-up of the combustor, $m_1$.

$$ m_1 = \frac{M_0}{X_{\text{CaO}}} n_1 - \frac{M_0}{X_{\text{CaO}}} r_1 (\phi_1 + \phi_4) = \frac{M_0}{X_{\text{CaO}}} \frac{\xi_2 - 1}{\xi_2 \phi_1 + \frac{\text{Ca/S}}{X_{\text{CaO}}} \frac{k_1}{k_t}} $$ \hfill (5.21)

I.5.2 Parameter estimation and model verification

De pop is wel honderd.
Dat zie je niet, maar dat kun je uitrekenen.
Liselore Gerritsen

Typical values for the sorbent, coal and bed properties are estimated from literature data [3-7] and experimental data (table 5.1). The values and ranges given for the sorbent properties, apply for sorbents prepared with the sol-gel method. The shrinking core model is developed for this type of sorbent.

The particle radius is chosen such, that good separation from the coal ash is possible on the one hand, and fluidization is possible on the other. The optimal superficial gas velocity for fluidization at 850°C is roughly three times the minimal one [8]. Thus: $U = 3 U_{mf}$.

Both for $k_a$ and $\xi_2$, values are used which apply for sorbents that have undergone a number of cycles and are in 'steady state'. For make-up sorbent, $k_a$ will be larger (larger attrition rate), as will be $\xi_2$ (better regeneration). These effects will tend to compensate each other. Also, the amount of make-up sorbent will be small, compared to the total amount of sorbent in the combustor. Any remaining effect will probably be insignificant.

The physical reality of ResuLT is demonstrated by the calculated sorbent residence time. At standard conditions, $r_1$ is 41 hours, and it ranges from ~ 25 to ~ 75 h. Such values are physically realistic [5].

The bed height $H$ is estimated from the sorbent hold-up in the combustor $m_1$.
where $\rho_{\text{bed}}$ is the bed density, which is approximately 580 kg/m³ at $U = 1.2$ m/s and 1123 K [9]. Thus, the bed height is approximately 3.5 m for $m_1 = 690$ ton (standard conditions). Because the bed also contains some coal ash (-20%), the total bed height will be somewhat larger. Bed height up to 6 m are frequently encountered [5]. The bed heights obtained are realistic.

The amount of natural sorbent needed per kg of coal is approximately 55 g/kg coal (limestone, Ca/S = 2). $Y$ is considerably smaller, varying between 2 and 10 g/kg coal. We will discuss this point in more detail when examining the economic feasibility of the regenerative desulphurization (I.6.2).

Table 5.1 Parameter values and ranges, used in ReSuLT

<table>
<thead>
<tr>
<th>sorbent properties</th>
<th>symbol</th>
<th>range</th>
<th>standard</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle radius</td>
<td>$R$</td>
<td>0.6-1.8</td>
<td>1.0</td>
<td>mm</td>
</tr>
<tr>
<td>pore radius</td>
<td>$r_p$</td>
<td>4-8</td>
<td>6</td>
<td>mm</td>
</tr>
<tr>
<td>pore volume</td>
<td>$V_p$</td>
<td>0.1-0.5</td>
<td>0.3</td>
<td>ml/g</td>
</tr>
<tr>
<td>pore tortuosity [3]</td>
<td>$\theta$</td>
<td>-</td>
<td>$\sqrt{2}$</td>
<td>-</td>
</tr>
<tr>
<td>dispersion coefficient</td>
<td>$\Delta$</td>
<td>0.3-1</td>
<td>0.57</td>
<td>-</td>
</tr>
<tr>
<td>solid density [4]</td>
<td>$\rho_s$</td>
<td>-</td>
<td>3.5</td>
<td>g/ml</td>
</tr>
<tr>
<td>attrition rate constant</td>
<td>$k_a$</td>
<td>0.25-1.25</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>regeneration efficiency</td>
<td>$\xi_2$</td>
<td>0.2-1.0</td>
<td>0.75</td>
<td>-</td>
</tr>
<tr>
<td>calcium oxide content</td>
<td>$X_{CaO}$</td>
<td>0.05-0.2</td>
<td>0.1</td>
<td>g/ g sorbent</td>
</tr>
</tbody>
</table>

bed and coal properties

| Ca/S [5]                   | Ca/S  | -       | 2        | mol Ca/mol S       |
| retention [2]              | $R_s$ | -       | 0.9      | mol S/mol S        |
| sulphur content of coal [6]| $X_s$ | -       | 0.01     | kg S/kg coal       |
| coal feed rate (100 MWe) [7]| $k_1$ | -       | 10       | kg coal/s          |
| gas flux out combustor [7] | $\phi_{V,\text{out}}$| -  | 380     | m³/s (1123 K)       |
| combustion temperature     | $T$   | 1123    |          | K                   |

physical constants [4]

| molar mass of calcium      | $M_0$ | -       | 56       | g CaO/mol          |
| molar mass of sulphur      | $M_S$ | -       | 32       | g S/mol            |
| density of air (1123 K)    | $\rho_\ell$| - | 0.314   | kg/m³              |
| viscosity of air (1123 K)  | $\eta_\ell$| - | 45.5   | $\mu$Pa.s          |
| acceleration due to gravity| $g$   | -       | 10       | m/s²               |
1.5.2.a Observed trends with ResulT

Y and $m_1$ are calculated, varying the sorbent properties independently. This is not very realistic, but it demonstrates the trends in the changes of Y and $m_1$ with changing sorbent properties, which should be realistic. Also, it shows which properties are most relevant for the sorbent performance. The ResulTs are shown in fig. 5.2. Y and $m_1$ usually show the same trend.

Y increases sharply when the particle radius $R$ is increased: the average reaction rate decreases (larger bed mass) and $U_{mf}$ increases (larger $U_{mf}$).

It follows that the attrition rate increases.

As expected, Y and $m_1$ increase with decreasing regeneration efficiency $\dot{\xi}_2$.

The smaller $\dot{\xi}_2$ is, the more important the effect becomes.

The calcium content $X_{CaO}$ does not significantly influence Y or $m_1$. This may seem strange, but it is a natural consequence of the fact that Ca/S is a constant.

Both by increasing the pore radius and the pore volume, Y and $m_1$ decrease (faster reaction, shorter residence time). The smaller $r_p$ and $V_p$ are, the stronger the effect is. Furthermore, a larger $V_p$ results in a smaller particle bulk density, which means that $U_{mf}$ becomes smaller. Then $U = 3U_{mf}$ becomes smaller, and the rate of attrition is lower. The consequence of this calculation, however, is that the reactor design ($U$ !) is determined by the

---

**Figure 5.2** Sorbent performance Y (amount of make-up sorbent, fed per kg coal) at standard conditions (table 5.1) versus independently varied sorbent properties; points are calculated and lines are drawn to guide the eye.

- 5.2.a particle radius $R$
- 5.2.b regeneration efficiency $\dot{\xi}_2$
- 5.2.c CaO weight content $X_{CaO}$
- 5.2.d average pore radius $r_p$
- 5.2.e pore volume $V_p$
- 5.2.f dispersion coefficient $\Delta$
- (Deff(exp)/Deff(th))
- 5.2.g rate constant of attrition $k_a$

---

**Figure 5.2.a**
sorbent properties, which is not always very realistic.

The smaller the dispersion coefficient $\Delta$ is, the worse the dispersion and the larger $Y$ and $m_i$ are. The value of $\Delta$, when smaller than 1, appears to be one of the major sorbent properties determining the sorbent performance.
The rate constant of attrition $k_a$ is a very important factor. Naturally, an increase in $k_a$ causes a strong increase of $Y$, although $m_1$ does not significantly change. $k_a$ should be as small as possible.

Summarizing: the observed trends appear to be realistic. The two most important sorbent properties are $k_a$ and the calcium dispersion, the latter working through $\Delta$ and $\tilde{\xi}_2$. The sorbent capacity is not important.

1.5.2.b Discussion and conclusion on model validation

ReSuLT predicts realistic values and trends. Yet, is it correct? Two weak points can be easily shown. An important drawback is the black box assumption on the regenerator (assumption e). Incorporating the regeneration kinetics and the residence time distribution of the regenerator would improve matters. Also, it would make it possible to use distributions of $\xi_1$ and $\xi_2$, rather than average values, greatly enhancing the reality of the model, but also its complexity. At this moment, however, no reliable kinetic model for the regeneration of sol-gel sorbent is available.

Confining all sources of sorbent loss to fluidized bed attrition (assumption c) and d)) is not very realistic either. However, as long as no data are available on the separation efficiency and the rate of attrition due to transport, it is the best we can do. Furthermore, the model used to describe
the fluidized bed attrition should be verified more thoroughly. It does not include any chemical effects like repeated conversion of CaO into CaSO₄ and vice versa. The influence of bed properties on $k_a$, like bed size, type of grit, cooling tubes, amount and type of coal ash, etc. is unknown. These are serious drawbacks.

Summarizing, two major sources of uncertainties exist in ReSuLT, the magnitude of which cannot be easily estimated. There are no indications that one source is more important than the other. This means that taking away only one of them does not improve the model. The uncertainty will remain equally large. To improve any model, all sources of uncertainties should be discarded, or at least their magnitude should be estimated. This is not an easy task. Within the objective of this research, it is deemed unnecessary. As a first approximation the ReSuLTs are satisfying.

A last remark on assumption g). The influence of the sulphur dioxide concentration on the bed content, and thus on $Y$, is rather dramatic. When a coal with a small sulphur content is used, and 90% sulphur capture is to be reached, it is necessary to lower the SO₂ off-gas concentration of the combustor well below the emission standards. This can only be reached using large amounts of sorbent. Therefore it is economically attractive to use coal with a higher sulphur content. In other words: the governmental demand of 90% sulphur capture actually provokes the use of more "dirty" coal.

References

[5] Personal communication with C.M. van den Bleek and J.C. Schouten, 1990
[8] Personal communication with P.J. van den Berg, 1990
I.6 ReSuLTS AND CONCLUSIONS

De kennis is een macht waarmee w'elkander meten. Alleen de wijze weet dat wij niet waarlijk weten.
Toon Hermans

In this chapter, the results of sorbent preparation and characterization, and those of ReSuLT are combined. Thus, we search the sorbent with the highest feasible performance. With this sorbent, we compare regenerative desulphurization to "once-through" desulphurization with limestone (I.6.1). This economic comparison leads us directly to the conclusions of the first part of this thesis (I.6.2).

I.6.1 ReSuLTSs

Table 6.1 Comparison of sorbents with ReSuLT

<table>
<thead>
<tr>
<th>sorbent property</th>
<th>symbol</th>
<th>units</th>
<th>pellet</th>
<th>sol-gel</th>
<th>sol-gel</th>
<th>type of impregnation</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate const. of attrition</td>
<td>$10^{10} k_a$</td>
<td>-</td>
<td>-2.2**</td>
<td>1.1</td>
<td>0.4</td>
<td>in situ</td>
</tr>
<tr>
<td>calcium content</td>
<td>$X_{CaO}$</td>
<td>%</td>
<td>0.10</td>
<td>0.17</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>pore volume</td>
<td>$V_p$</td>
<td>ml/g</td>
<td>0.36</td>
<td>0.35</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>pore radius</td>
<td>$r_p$</td>
<td>mm</td>
<td>80</td>
<td>7.3</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>dispersion coefficient</td>
<td>$\Delta$</td>
<td></td>
<td>0.14+</td>
<td>0.31</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>solid density</td>
<td>$\rho_s$</td>
<td>g/ml</td>
<td>4.0</td>
<td>3.5</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>regeneration selectivity</td>
<td>$\xi_2$</td>
<td>-</td>
<td>0.5++</td>
<td>0.6++</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>sorbent performance</td>
<td>$Y_#$</td>
<td>g/kg coal</td>
<td>6.8</td>
<td>14.9</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>sorbent residence time</td>
<td>$\tau_1$</td>
<td>h</td>
<td>10.3</td>
<td>93.4</td>
<td>36.4</td>
<td></td>
</tr>
<tr>
<td>sorb. hold-up in comb.</td>
<td>$m_1$</td>
<td>ton</td>
<td>258</td>
<td>1117</td>
<td>609</td>
<td></td>
</tr>
</tbody>
</table>

* after calcination of support
** estimate from the data in table 1.2
+ best approximation with shrinking core model for cylindrical pellets
++ estimated by multiplying the regeneration selectivity of the first cycle by 0.75/0.88, the values for the regeneration selectivity of in situ impregnated sol-gel sorbent at 'steady state' and at the first cycle
# calculated with $R_a = 0.9$, $R = 1$ mm, $Ca/S = 2$ and $U = 3 U_{mf}$
I.6.1.a Confirming the choice of sorbent preparation technique

In table 6.1, sorbent properties and calculated sorbent performance are given for three typical sorbents: impregnated α-alumina pellets (the state-of-the-art at the start of our research); γ-alumina sol-gel beads which are calcined first and impregnated afterwards; and in situ impregnated sol-gel beads. It is clear that the latter, although not optimized, shows the best sorbent performance (Y, the amount of make-up sorbent per kg of coal). This confirms the choice of the preparation method (I.2.3).

I.6.1.b Sorbent Optimisation within the experimental range

The calcium oxide content of in situ impregnated sol-gel sorbent, \(X_{CaO}\), is easily controlled during preparation (I.3.1). It influences most properties of the sol-gel sorbent (I.3.2, I.4.2 and I.4.3). To find an optimal \(X_{CaO}\), these influences are fitted into the following empirical relations (linear regressions from fig. 3.5, 3.6, 4.7 and 2.1, respectively).

\[
V_p = 0.408 - 0.96 X_{CaO} \quad \text{(6.1)}
\]

\[
r_p = 5.34 + 1.4 X_{CaO} \quad \text{for } X_{CaO} > 0.07 \quad \text{(6.2)}
\]

\[
\Delta = 1 - 1.70 - 0.85 X_{CaO} \quad \text{for } X_{CaO} \leq 0.095 \quad \text{for } X_{CaO} > 0.095 \quad \text{(6.3)}
\]

Figure 6.1 Sorbent performance Y (amount of make-up sorbent per kg coal) for an optimization within the experimental range, performed by calculating \(r_p\), \(V_p\), \(\Delta\) and \(\xi_2\) as a function of \(X_{CaO}\). See sub-paragraph I.6.1.a.
\[ \dot{\xi}_2 = 0.75 \]
\[ = 0.75 / 0.88 \]
\[ = (1.04 - 1.2 \times X_{CaO}) \] for \( X_{CaO} \leq 0.095 \)
\[ = 0.75 / 0.88 \] for \( X_{CaO} > 0.095 \)

(6.4)

The factor 0.75/0.88 in (6.4) is added to convert the \( \dot{\xi}_2 \) which applies for the first regeneration, to the 'steady state' \( \dot{\xi}_2 \) which is reached after a number of cycles (I.4.3). Other sorbent properties are taken at their typical values, independent of \( X_{CaO} \). See figure 6.1.

The sorbent performance \( Y \) decreases with decreasing calcium oxide content (fig. 6.1). Below the critical calcium oxide content \( (X_{CaO,c} = 9.5\% \) ), the decrease is slow; the changes in \( \rho_p \) and \( \nu \) compensate each other almost totally. Above \( X_{CaO,c} \), the calcium cannot be distributed in a monolayer, so that \( \Delta \) and \( \dot{\xi}_2 \) decrease with increasing \( X_{CaO} \), and \( Y \) increases sharply. A very low calcium content seems to be advisable. However, the production cost of sorbent is mainly determined by the price of the boehmite. Thus the sorbent price increases by decreasing the calcium oxide content. It seems that a calcium content of \( \sim 8\% \), ensuring that \( \Delta = 1 \) and \( \dot{\xi}_2 = 0.75 \), is the optimal value for the calcium oxide content. Then, \( Y \approx 2.5 \text{ g sorbent/kg coal} \).

**Table 6.2 Comparison of in situ impregnated sol-gel sorbents with ReSuLT**

<table>
<thead>
<tr>
<th>sorbent property</th>
<th>symbol</th>
<th>units</th>
<th>sol-gel SG-105</th>
<th>sol-gel 'optimal'</th>
<th>sol-gel 'ideal'</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate const. of attr.</td>
<td>( 10^{10} \ k_a )</td>
<td>-</td>
<td>0.4</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>calcium content</td>
<td>( X_{CaO} )</td>
<td>%</td>
<td>0.10</td>
<td>0.08</td>
<td>0.10</td>
</tr>
<tr>
<td>pore volume</td>
<td>( V_p )</td>
<td>ml/g</td>
<td>0.32</td>
<td>0.33</td>
<td>0.40</td>
</tr>
<tr>
<td>pore radius</td>
<td>( r_p )</td>
<td>nm</td>
<td>6.4</td>
<td>5.5</td>
<td>7.0</td>
</tr>
<tr>
<td>dispersion coefficient</td>
<td>( \Delta )</td>
<td>-</td>
<td>0.56</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>solid density</td>
<td>( \rho_s )</td>
<td>g/ml</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>regener. selectivity</td>
<td>( \dot{\xi}_2 )</td>
<td>-</td>
<td>0.75</td>
<td>0.75</td>
<td>0.9</td>
</tr>
<tr>
<td>sorbent performance</td>
<td>( Y )</td>
<td>g/kg coal</td>
<td>3.1</td>
<td>2.5</td>
<td>1.1</td>
</tr>
<tr>
<td>sorbent residence time</td>
<td>( \tau_1 )</td>
<td>h</td>
<td>36.4</td>
<td>18.7</td>
<td>14.9</td>
</tr>
<tr>
<td>sorb. hold-up in comb.</td>
<td>( n_1 )</td>
<td>ton</td>
<td>609</td>
<td>392</td>
<td>250</td>
</tr>
</tbody>
</table>

\# calculated with \( R_s = 0.9, R = 1 \text{ mm}, \ Ca/S = 2 \) and \( U = 3 \text{ U}_{mf} \)
I.6.1.c Sorbent optimization beyond experimental limits

The above optimization is performed using experimental results. The sorbent performance of this 'optimum sorbent' is not much better than that of the typical sorbent made in a larger scale preparation (sample SG-105, see table 6.2 and appendix I). Of this preparation we know, however, that it was not ideal, especially regarding the drying conditions. This resulted in a less than optimal dispersion ($\Delta = 0.56$), and relatively many broken beads. A considerably better sorbent performance must be possible. This idea is quantified (table 6.2, 'ideal sorbent'), and results in $Y \approx 1.1$ g/kg coal. Naturally, this is to be regarded as a target figure, rather than a fact.

I.6.1.d Comparison with non-regenerative desulphurization

A first indication of the economic feasibility of regenerative desulphurization in FBC can be obtained by comparing the sorbent costs with those for a "once-through" or non-regenerative process. This assumes that the costs of regeneration and of the production of sulphur or sulphuric acid are compensated for by the profits of the latter, which is not impossible [1].

The price of natural sorbents is mainly determined by transportation and dumping costs [2-4]. Especially the latter can increase considerably, when the governmental regulations become more strict. When the contaminated gypsum, produced in "once-through" desulphurization, is regarded as chemical waste, expensive dumping procedures will be needed [5-7].

The price of the sol-gel sorbent is determined by the manufacturing costs, predominantly the costs of pseudoboehmite (3,500-4,500 Dfl/ton [8,9]). This means that the current price of sol-gel sorbent (16,000-17,000 Dfl/ton [9]) can be reduced considerably, when sorbent is produced on a very large scale.

Using current prices and dumping costs (A and C in table 6.3), "once-through" operation with limestone is clearly the cheapest solution. An increase of the dumping costs to the level of dumping costs for chemical waste does not change this (B and C in table 6.3). The same holds for an improvement of the sol-gel sorbent performance to the level of the 'ideal' sorbent (A and D). The combination of these two factors (B and D), however, brings the sorbent costs of both desulphurization methods to the same level. When, at that point, it is decided to apply regenerative desulphurization with in situ impregnated sol-gel sorbent on a large scale, the price of the latter will decrease. In the most ideal case, the sorbent costs would be
Table 6.3  Sorbent costs of (non-)regenerative desulphurization processes

<table>
<thead>
<tr>
<th>case</th>
<th>amount needed*</th>
<th>sorbent price (Dfl/ton)</th>
<th>sorbent costs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/kg coal</td>
<td>m+t**</td>
<td>dump</td>
</tr>
<tr>
<td></td>
<td>kton/yr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>limestone, &quot;once-through&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>55</td>
<td>30-70</td>
<td>80-100</td>
</tr>
<tr>
<td>B</td>
<td>55</td>
<td>30-70</td>
<td>250-500</td>
</tr>
<tr>
<td>in situ impregnated sol-gel sorbent, regenerative</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2.5 0.73</td>
<td>16,000-17,000</td>
<td>80-100</td>
</tr>
<tr>
<td>D</td>
<td>1.1 0.32</td>
<td>16,000-17,000</td>
<td>80-100</td>
</tr>
<tr>
<td>E</td>
<td>1.1 0.32</td>
<td>4,000-5,200</td>
<td>250-500</td>
</tr>
</tbody>
</table>

* calculated for a 100 MWe FBC (10 kg coal/s [12]) and 8000 h/yr; Ca/S = 2 and R = 0.9; for sol-gel sorbents ReSuLT is used with U = 3U_{mf}, R = 1 mm
** m+t denotes manufacturing and transport costs [2,4]
# 1 Mfl/yr = 0.13 10^-2 Dfl/kWh

case A: limestone, current price [2,4] and dumping costs [3]
case B: ibid, dumping costs when gypsum is treated as chemical waste [6,7]
case C: 'optimal' sol-gel sorbent, current price [9] and dumping cost [3]
case D: 'ideal' sol-gel sorbent, current price [9] and dumping cost [3]
case E: ibid, large scale production and expensive dumping [6,7]

even lower than the current sorbent costs for "once-through" desulphurization (E and A): 0.17-0.23 10^-2 Dfl/kWh(e). This is approximately 1% of the current Dutch price of electricity (0.16 Dfl/kWh(e)).

Of course, these conclusions only hold when ReSuLT is reliable. For this to be true, the design of the installation, needed for regenerative desulphurization, must be improved, to minimize attrition and to optimize the separation of coal ash and sorbent. It follows that application of regenerative desulphurization using in situ impregnated sol-gel sorbent depends on two factors: a political one (high dumping costs) and a process technological one (low attrition and good separation technology). The latter problem is currently being tackled at Delft University of Technology [10].
I.6.2 Conclusions

"We know by experience it selfe, that it is a marvelous paine, to finde oute but a short waie, by long wandering."  
Roger Ascham, 1570

The synthetic sol-gel sorbent, developed during this research, is considerably better than sorbents, prepared according to the state-of-the-art up to this research, as can be proven with ReSuLT. We have seen that this is due to two reasons.

(a) The good attrition resistance, caused by the spherical shape, combined with a smooth surface and good particle coherence. This advantage of sol-gel methods in general is even improved by the in situ impregnation.

(b) The extremely good - possibly monolayer - dispersion, yielding a high regeneration selectivity at a relatively low temperature, and minimizing the influence of product layer diffusion during sulphation (as can be seen from the shrinking core model). This good dispersion is, again, achieved by the in situ impregnation during the gelation step of the sol-gel process.

Although the objective of this research has been achieved in this way, it appears that political and process technological arguments determine whether regenerative desulphurization using the sol-gel sorbent will be applied. Realizing that the most promising preparation process has brought us only this far, two approaches remain, within the framework of this research.

(a) Try to further improve the sorbent. According to ReSuLT, this would mean improving attrition resistance \( k_a \rightarrow 0 \) and ascertaining optimal dispersion \( \Delta, \tilde{c}_2 + 1 \). It is not to be expected, however, that the 'ideal sorbent' described in I.6.1.c, can be improved in this way.

(b) Investigate the physical chemistry of the sol-gel process with in situ impregnation. Better insight in the preparation process may lead to better products. Also, it may show the way to other applications of the preparation method, and it may solve some of the scaling-up problems of the in situ impregnation process.

The latter, more scientific, approach is adopted here.
References

[1] B.P. Voet, internal report, Delft University of Technology, July 1990
[2] Personal communication with Nekami B.V., Gouda, the Netherlands, 1990
[3] Personal communication with Verwerking Bedrijfsafvalstoffen Maasvlakte (VBM), the Netherlands, 1990
[9] Personal communication with K. Noweck, 1989
PART II

THE SOL-GEL METHOD

with

IN SITU IMPREGNATION
PART II: THE SOL-GEL METHOD WITH IN-SITU IMPREGNATION

Have not the small Particles of Bodies certain Powers, Virtues, or Forces by which they act at a distance (...) upon one another for producing a great part of the Phenomena of Nature?

Isaac Newton

In the first part of this thesis we have shown that the sol-gel process yields strong, spherical, porous $\gamma$-Al$_2$O$_3$ particles. In situ impregnation of the gel with calcium nitrate even increases the strength of these particles, and changes the pore structure. The dispersion of the calcium oxide on the alumina surface is very good.

The objective of the second part of this thesis, is to understand these phenomena as a result of the preparation process. In doing so, we must realize the importance of the shape and size of the building units in the calcined particle, and the way in which these building units are packed. These three parameters determine the pore structure (texture) directly. Also, they determine the number of contact points and their strength, which determines the intrinsic particle strength. The latter can, however, be strongly influenced negatively by stresses and cracks in the calcined particle, formed during preparation.

The packing of the building units in the calcined particles depends on their geometry and on the preparation process. Precursors of the building units are to be found in the dried gel, and, consequently, in the sol. The primary pseudoboehmite particles in the sol will be described, and it will be shown that they form aggregates (II.7). The size and shape of these aggregates is studied in detail using rheology (II.9). The necessary theory is developed in chapter II.8. The aggregates appear to be both the flow units in the sol, and the precursors of eventual building units in the calcined particle (II.10).

An extensive background on sol-gel method in general is given in a recent book of Brinker and Scherer [1].

References

II.7 THE PRIMARY PSEUDOBOEHMITITE PARTICLE

... though only a year ago (...) they were nothing more than inorganic particles.  

Thomas Hardy

As explained above, the properties of the calcined particles are determined by the building units therein. These building units must have their precursors in the pseudo Boehmite sol, and it is useful to examine whether the primary particles in the sol are in fact these precursors. The properties of these primary particles - crystallites in which no phase boundaries occur - are related to the crystal lattice of (pseudo)boehmite.

II.7.1 The crystal lattice of pseudo boehmite

Boehmite (A1OOH) has a layered crystal lattice (fig. 7.1). Pseudo boehmite has a comparable structure, but contains excess water (A1OOH.xH2O). For a long time, it has been believed that this excess water was placed between the crystal planes in the boehmite [1-4]. But in 1974, Baker and Pearson proposed a new model [5], placing the excess water, partially bound chemically and partially adsorbed physically at the outside of the crystallites. More precise, the excess water is only bound chemically at the ends of the Al-O-Al-O-Al chains in the a- and c-direction of the crystal lattice (within the layers of A1OOH). The chains in the b-direction (perpendicular to the layers) are generally much shorter and end with hydroxyl groups (fig. 7.1).

For the wealth of convincing arguments for this model, we refer to Baker and Pearson [5]. We will look into its consequences.

(a) The primary particles are likely to be platelets due to the layered

Figure 7.1 Schematic representation of the b,c plane of the crystal lattice of boehmite (A1OOH) [5,6]. Al-O-OH units are clearly visible in the b-direction. Chemically adsorbed water is to be seen on the edges, at the end of the crystal in the c-direction; in the a-direction, the lattice is rather comparable.
structure and the growth mechanism [5,6]. While the faces of these platelets contain hydroxyl groups (OH) (fig. 7.2), the edges bear the chemically bound excess water, as they consist of water groups (OH₂). This has consequences for the colloidal behaviour, as we will see later (II.9.1.c).

(b) The crystal planes interact in the b-direction through hydrogen bonds (fig. 7.1). H bonds are weak compared to other crystalline bonds, so that the crystallites are expected to be small in the b-direction, yielding platelets. These platelets can again interact through H bonds, which are strong compared to interparticle forces. This makes it likely that a parallel packing of platelets is formed. See also II.7.3.

(c) The hydroxyl and water groups resemble water molecules. This has two consequences. First, it eliminates any contrast for neutrons between the solution and the particles in a sol. Thus, neutron scattering and diffraction cannot be used to study this sol [7], which is a great drawback. The use of D₂O does not improve matters, due to the fast exchange of deuterium between solution and particle [7]. Second, the adsorption of water to the surface can be quite strong. This has many consequences (II.7.3.a, II.9.3).

(d) With thermogravimetry, the total amount of excess water is determined to be 0.35 mol H₂O per mol AlOOH (x = 0.35). The chemically bound excess water (which desorbs in vacuo at 100°C) is 0.19 mol H₂O/mol AlOOH. This relatively small value indicates that there are relatively few edges, so that the platelet diameter must be reasonably large (> 20 nm [5]).

II.7.2 The geometry of the primary particle

Find the line, find the shape / Through the grain
Find the outline, things will / Tell you their name
Suzanne Vega

Pseudoboehmite platelets can be triangular, diamond-like, rhombic [1,2], elongated [8] or even more or less circular [9], depending on preparation
conditions. TEM results show that the powders used in this research, contain more or less rhombic platelets [10], which for reasons of simplicity will be regarded as discs with thickness $\delta$ and diameter $d_{pp}$.

Calculations for the XRD line broadening of the 020-peak give $\delta \approx 3$ nm [10], which compares well with the characteristic length of 5-7 nm calculated from the 021 and 120-peak [10]. The latter should be roughly 2$\delta$.

The diameter $d_{pp}$ is estimated from the results of others on comparable materials. Also, the BET surface areas are compared to the geometrical surface areas $S_g$. From the data in Table 7.1, it follows that assume $d_{pp} = 25$ nm. This agrees well with the prediction in the last paragraph.

To calculate $S_g$, the density of the pseudoboehmite $\rho_{pb}$ is needed. Using He-pycnometry, we have found that $\rho_{pb} = 2.64$ and 2.84 g/ml for non preheated and preheated pseudoboehmite (150°C, in vacuo), respectively. Both values are smaller than the theoretical value for boehmite (3.07 g/ml [11]), which is due to the excess water. The amount of water, which would explain this difference for the non preheated sample corresponds to x = 0.37. This is in excellent agreement with the thermogravimetrically determined value of x (0.35). This amount of excess water is explained by assuming one molecular layer of water to exist on the total surface of the primary particle, when $d_{pp} = 25$ nm is assumed. This will prove important in further discussions (II.9.3).

Table 7.1 Properties of primary pseudoboehmites particles

<table>
<thead>
<tr>
<th>reference</th>
<th>produced by</th>
<th>$\delta$ (nm)</th>
<th>$d_{pp}$ (nm)</th>
<th>$\rho_{pb}$ (g/ml)</th>
<th>$S_g$ (m$^2$/g)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drouin et al. [12]</td>
<td>Condea</td>
<td>4</td>
<td>$\sim$25</td>
<td>3.07*</td>
<td>215</td>
<td>290</td>
</tr>
<tr>
<td>Leenaars [9]</td>
<td>Leenaars</td>
<td>2.5</td>
<td>$\sim$25</td>
<td>3.07*</td>
<td>315</td>
<td>360</td>
</tr>
<tr>
<td>this work</td>
<td>Condea</td>
<td>3</td>
<td>$\sim$25</td>
<td>2.84**</td>
<td>315</td>
<td>270</td>
</tr>
<tr>
<td>Fukasawa et al. [15]</td>
<td>Fukasawa</td>
<td>2.5</td>
<td>4.0*6.0</td>
<td>3.07*</td>
<td>530</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

$\delta$: thickness of the platelets, $d_{pp}$: diameter of the platelets, $\rho_{pb}$: density of pseudo-boehmite, $S_g$: geometric surface area, $S_{BET}$: BET surface area. **literature value for well crystallized boehmite determined by He-pycnometry.

n.d. not determined
II.7.3 The packing of the primary pseudoboehmite particles

Hoe berekent men de inhoud van een rond lichaam? Was dat hoogte mal straal? Maal diameter mal wandoppervlak? Hoogte maal vloeroppervlak maal soortelijk gewicht water maal lengte Archimedes in liters? Geen idee ... 
Kees van Kooten

The packing of the primary particles in the sol cannot be random. This is easily seen from an argument, used by Drouin et al. [12]. The excluded volume of a thin disc in a random array is $\pi^2d^3/8 \approx 1.9 \times 10^4 \text{ nm}^3$, whereas the volume of the disc itself is $\delta \pi d^3/4 \approx 1.5 \times 10^3 \text{ nm}^3$, the ratio of which is 14.5 for the pseudoboehmite platelets. The maximum possible ratio, however, is the inverse of the volume fraction of solids in the sol ($\phi_{pp} = 0.16$), and equals ca. 6. The structure in the aggregates must be more or less regular.

The latter makes it unlikely that the packing of the primary particles is fractal, in contradiction to many other systems. This is confirmed by results of Ramsay et al. [13] with detailed light scattering experiments on diluted boehmite sols. They found that the number of primary particles (calculated from the "molecular weight" of the aggregates) varied approximately with the third power of the radius of gyration of the aggregates. In other words: for diluted sols the fractal dimension is about 3.

Having established that the packing of platelets is neither random nor fractal, the most likely packing remaining is face to face packing [14], in which the platelets are placed parallelly (see also II.7.1, point (b)). There are several additional arguments for this hypothesis.

(a) The intensity of the (020) peak in the X-ray diffraction pattern is relatively much stronger than that of other peaks [9,15].

(b) The nitrogen physisorption isotherm [9,13] of the starting powder (fig. 7.3) and of dried gels (fig. 10.2) resembles that of a system of narrow slit-shaped pores [1] (for more details: see appendix II). Calculations according to this model on our data and those of Leenaars [9], yield pore sizes, with a width $D$, equal to the thickness of the platelets (fig. 7.3).

(c) Some (pseudo)boehmite sols show birefringence under shear [15], indicating parallel ribbons of platelets. Such packings also exist in other systems (e.g. $V_2O_5$ [16]).

(d) The swelling of dried gel spheres in water. This swelling is caused by the formation of a "surface layer" of water on the platelets (see II.7.1). The effect is comparable to the swelling in parallelly packed arrays of clay particles. Drouin et al. conclude from NMR results that for many materials the thickness of this layer is about 1 nm (three molecular $H_2O$ layers) [12].
Figure 7.3.a

Figure 7.3 N₂ physisorption results on pseudoboehmite powder

7.3.a Hysteresis loop: adsorbed volume (STP) versus partial pressure
7.3.b Pore size distribution, calculated from the desorption
   (a) ○ according to a cylindrical pore model (r_p)
   (b) + according to a slit-shaped pore model (D)

Due to the relatively small thickness of the primary particles, considerable swelling can occur when the powder is immersed in pure water.

This is confirmed by the following experiment. A non-impregnated, dried gel was prepared. The pore volume of the dried gel particles was determined both by N₂ physisorption and by water intrusion (appendix II). The water intrusion caused the dried spheres to swell and burst. The thus measured pore volume was much larger (0.73 ml/g) than that of the N₂ physisorption (0.30 ml/g). From the thickness of the primary particles and of the water layer, we estimate that the excess volume V_e should be approximately equal to the volume of the primary particles. Expressed per gram of dry sphere, the latter equals 1/ρ_pb = 0.38 ml/g. V_e is the difference in wet and dry pore volume, determined by water intrusion and N₂ physisorption respectively: V_e = 0.43 ml/g (for a duplicate experiment). Within experimental error this indeed equals 1/ρ_pb.

It follows that pseudoboehmite particles, dispersed in pure water, have a surface water layer of ca. 3 water molecules. This results in a doubling of the volume fraction in solution as compared to the dry volume fraction.
The swelling and the other arguments indicate that face to face packing is to be expected. The slit-shaped pores \((D \approx 3 \text{ nm})\), however, are not at all comparable to the pores in the calcined material. The latter are cylindric, with radii of 5 to 9 nm (fig. 4.3). The slit-shaped pores are expected to collapse at the calcination temperature of 850°C [1].

In view of the volume fraction of primary particles in the sol, it is impossible that the face to face packing extends throughout the sol or the gel particle. Rather, definite entities of this packing are expected to exist. These entities will be referred to as aggregates. It turns out that the aggregates are the building units of the calcined particle. In order to prove this, their morphology - geometry and size - must be known. For these opaque sols, SANS failing, rheology is the most appropriate method for investigations, neutron scattering failing, rheology is the most appropriate method. For the purpose of such investigations, a model is developed (II.8) and used to describe the pseudoboehmite sols (II.9).

References

[10] Personal communication with K. Noweck, 1989
II.8 THE RHEOLOGY OF CONCENTRATED (COAGULATING) COLLOIDS

Who am I to blow against the wind?
Paul Simon

Rheology is one of the few methods which can be used to obtain data on the structure in concentrated, opaque, sols. To obtain these data, it is imperative to link the microscopic properties of the sol to its macroscopic, rheological behaviour. Considering the huge amount of (semi)empirical relations to describe the rheologic behaviour [1-3] and the considerable effort in purely theoretical approaches [2,4], this link is surprisingly seldom laid, and only successfully for dispersions of non-interacting spheres. Here, we will try to give a more general approach, adopting and adapting existing models of Krieger and Dougherty [1], and of Stein and his group [6].

Good introductions to rheology of (coagulating) dispersions are given by Krieger [1], Van de Ven [6] and Mewis [7].

II.8.1 The rheology of non-coagulating dispersions

We define the viscosity \( \eta \) as the differential increase of the shear stress \( \tau \) with a differential increase of the shear rate \( \dot{\gamma} \)

\[
\eta = \frac{d\tau}{d\dot{\gamma}}
\]  

(8.1)

The relative viscosity of a dispersion, \( \eta_r \), is the measured viscosity \( \eta \), relative to the viscosity of the medium, \( \eta_0 \). For dilute systems (volume fraction of solids \( \phi \) smaller than 0.1), the Einstein equation holds [8]

\[
\eta_r = \frac{\eta}{\eta_0} = 1 + [\eta] \phi
\]  

(8.2)

The intrinsic viscosity \([\eta]\) is 2.5 for spheres and larger for ellipsoids. The increase of viscosity, as described by the Einstein equation, is due to the rotation of particles in the shear field. In the case of ellipsoids, this means that the orientation distribution changes under shear [6]. During this change, damped oscillations of the viscosity with time are sometimes found [6], before a steady state is reached. In steady state, \([\eta]\) is a known function of the axial ratio of oblate or prolate particles \((a/b)\). For small axial ratios, \(1 < (a/b) < 10\), one obtains [9]

\[
[\eta] = 1.5 + (a/b)
\]  

(8.3)
At $\phi < 0.1$, spherical particles do not significantly hinder each other in their rotation and the dispersion behavior is Newtonian, i.e. the viscosity does not depend on the shear rate $\dot{\gamma}$. At a higher volume fraction, $0.1 < \phi < 0.35$, the particle movements are hindered by other particles, and deviations from the Einstein equation (8.2) are found. At an even higher volume fraction ($> 0.35$), shear thickening is observed: the viscosity decreases with increasing shear to a limiting value at high shear, $\eta_{r,\infty}$ (fig. 8.1). At an even higher shear, dilatancy or shear thinning can occur [10], especially for large particles. This effect is beyond the scope of this model.

The extrapolation of the asymptote to which the $r-\dot{\gamma}$ curve approaches to $\dot{\gamma} = 0$, yields $r^*$ (fig. 8.1). When the shear thinning is only caused by a high volume fraction, $r^*$ is denoted as $r_0$ and called the extrapolated yield stress. When the shear thinning is caused by particle interactions, $r^*$ is usually referred to as the (extrapolated) Bingham yield value of the shear stress, $r_B$. For concentrated coagulating colloids, both effects occur simultaneously and $r^*$ tentatively equals $r_B + r_0$.

Many (semi-)theoretical models have been proposed for $\eta_r$ at higher $\phi$ [1-3, 10]. Of the models that yield the Einstein equation (8.2) at the limit of low $\phi$, the Krieger-Dougherty relation [1] is the most promising one. For the limiting viscosities at high shear ($\eta_{r,\infty}$) and at low shear ($\eta_{r,0}$)

$$\eta_{r,a} = (1-\phi/\phi_{max,a})^{-[\eta]} \phi_{max,a} \quad a = \dot{\gamma} \rightarrow 0 \text{ or } \dot{\gamma} \rightarrow \infty$$

(8.4)

where $\phi_{max}$ is the maximum volume fraction, which depends on the shear rate. Many different interpretations of the physical meaning of this parameter exist [1,10-13]. We think that for the low shear limit, $\phi_{max}$ equals the random loose packing ($\phi_{max,0} = 0.60$ [14]). For the high shear limit, $\phi_{max}$

---

**Figure 8.1** Typical shear thinning curve: shear stress ($r$) versus shear rate ($\dot{\gamma}$). $\eta_0$ and $\eta_\infty$ are the viscosity at limiting low and high shear, respectively. $r^*$ is the extrapolated yield stress, which can be due to volumetric effects ($r_0$), to interaction effects ($r_B$), or to a combination of these effects.
equals the random close packing ($\phi_{\text{max, } \infty} = 0.64$ [14]). The shear thinning is therefore, in our opinion, due to the change of the structure from a random loose into a random close packing. This is only a small difference in 'structure' or in the radial pair distribution function, of the order of magnitude of the experimentally observed effects [13]. The above holds for small particles, where the Brownian forces are important.

For larger particles, the change in packing can be considered an disorder-order transition, which can be envisaged as the formation of shear planes through the sheared suspension [5,6,10]. The effective rheological behaviour is equal, although the exact value of $\phi_{\text{max, } \infty}$ may be different in this case.

In these calculations, care should be taken that $\phi'$, the effective volume fraction of the particles in the dispersion is used. Layers of solvent or steric stabilizer, swelling, and liquid in void volumes (between surface asperities and in aggregates) must be taken into account. Doing so, the Krieger-Dougherty relation, without any adjustable parameter, predicts the high shear viscosity of several model systems (monodisperse, non interacting spheres) rather well (fig. 8.2).

To our knowledge, no data are available on model systems of particles with axial ratios $> 1$ for higher volume fractions. For ellipsoids, $[\eta]$ is expected to increase with increasing a/b, possibly according to equation (8.3), while $\phi_{\text{max, } \infty}$ is expected to decrease [16]. It must be possible to predict $\phi_{\text{max, } \infty}$ with numerical simulations, as is done for spheres, but as

Figure 8.2 Verification of the Krieger-Dougherty equation (8.4) at the high shear limit for several dispersions of spherical particles

8.2.a (a) x latex [1]; volume fraction corrected for polymer layer with $\phi' = \phi (1+\Delta/\sigma)^3$; $[\eta] = 2.5$ and $\phi_{\text{max, } \infty} = 0.64$

(b) glass ballotini [17] for several particle radii; volume fraction corrected for double layer with $\phi' = \phi (1+j/(\kappa r))^3$; $j = 4.5$, $[\eta] = 2.8$ and $\phi_{\text{max, } \infty} = 0.60$. $r=9 \mu m$, $o=15 \mu m$, $\Delta \sigma=35 \mu m$

8.2.b two latex samples [14], $[\eta] = 2.5$ and $\phi_{\text{max, } \infty} = 0.65$

8.2.c polydisperse bitumen [3], $[\eta] = 2.5$ and $\phi_{\text{max, } \infty} = 0.77$
far as we know this has not been performed.

Polydispersity will also affect $\phi_{\text{max}, \infty}$. The more polydisperse, the larger $\phi_{\text{max}, \infty}$ [3] (fig. 8.2).

Any deformability of the particles cannot be incorporated into the model.

II.8.2 The influence of particle interactions

"Een conceptie wordt geboren uit de tegen-
strijdigheden van de elementen der ervaring."

prof. J. Burgers

The above is valid for hard-sphere interacting particles that exert no forces on each other, other than a strong repulsion on direct contact (see (a) in fig. 8.3). In general, at least two other forces are encountered: the repulsive electrostatic forces, due to a surface charge, and the attractive dispersion or Van der Waals forces. The balance of these forces is described by the well-know DLVO-theory [10] (see fig. 8.3).

II.8.2.a Repulsive interactions

When the particles have sufficient surface charge, and the ion concentration in the liquid medium is sufficiently low so that the double layer extends into the medium over a reasonable range, the particles are fully
Figure 8.3 Typical curves for the total interaction energy $V_{\text{tot}}$ versus the interparticle distance ($H$) between colloidal particles [10]
(a) hard-sphere interaction
(b) electrostatically stabilized system
(c) non stabilized system with Van der Waals attraction
(d) slightly stabilized system with a primary (*) and a secondary (**) minimum.

Not drawn is the very steep increase of $V_{\text{tot}}$ at very small $H$.

stabilized ((b) in fig 8.3). Then, three separate effects can occur [1,6].

- The first electroviscous effect is a slight increase in $[\eta]$ due to the deformation of the diffuse double layer under shear. A rigorous theoretic analysis is available for spheres [6], but yields little additional information while complicating matters dramatically.

- The second electroviscous effect is due to interactions between the double layers of particles. As a first approximation, this can be described as an effective increase of the particle size and therefore in the volume fraction. The particle radius $R$ is thought to increase with $j$ times the Debye length ($1/\kappa$). Thus, for spheres

$$\phi'' = \left(\frac{R + 1/\kappa}{R}\right)^3 \phi = \left(1 + j/(\kappa R)\right)^3 \phi$$

(8.5)

$\phi''$ is the volume fraction, corrected for the second electroviscous effect. Boersma [10] rather arbitrarily chooses $j = 1$. He finds that this suffices to bring his results on electrostatically stabilized lattices into agreement with the 'model system' of De Kruiff et al. [13]. Another estimate of $j$ follows from the work of Schreuder and Stein [16] on glass ballotini in glycerol/water. They find an influence of the particle radius on the $\eta_{\text{L,\phi}}$ versus $\phi$ results. This influence, which should not exist, disappears when they assume that a layer of $\approx 0.15 \mu m$ exists around the particles. They contribute this to 'occlusion of fluid in surface irregularities', but with equal right this layer can be contributed to the second electroviscous effect. Taking $\kappa = 3 \times 10^7 1/m$ [10], one finds $j = 4.5$ for this system.
Fitting the viscosity and corrected volume fraction data with the Krieger-Dougherty relation one obtains, independent of particle radius, $[\eta] = 2.8$ and $\phi_{\text{MAX},\infty} = 0.6$ (fig. 8.2.a), which shows the influence of the first electroviscous effect. This shows that our explanation of these results is more appropriate than the assumption of asperities, which should yield $[\eta] = 2.5$. Regarding $j$, $1 < j < 5$ appears to be an appropriate range.

- The third electroviscous effect is the distortion of the particle itself as a result of the electrostatic forces. This will only occur when the particles can deform. It cannot be incorporated easily in this model.

II.8.2.b Attractive interactions

When the repulsion is not much larger than the Van der Waals forces, energy minima arise (lines (c) and (d) in fig. 8.3). The primary particles flocculate, when these energy minima are deeper than a few kT. Whether the resulting flocs or aggregates can be broken by shear depends on the balance between shear forces and attraction forces.

For relatively large attraction forces (as is generally the case for very small particles, $r < 10$ nm), the aggregates cannot be broken by physically realistic shear. At lower volume fraction of solids, separate aggregates will exist, their total volume fraction being larger than $\phi$. The shape and polydispersity of the aggregates can be different from those of the primary particles. Furthermore, the aggregates may be deformable, giving rise to extra energy dissipation [17]. At higher volume fraction, no loose aggregates exist, and the system can be regarded as a giant floc. A more or less rigid gel arises, and it is difficult to obtain useful results from non oscillatory experiments.

When the attraction forces are relatively weaker, for instance between large particles or aggregates, again, a 'giant-floc' will arise at high enough volume fraction. The bonds are weaker and can be broken by shear. The shear will be concentrated in shear planes [5]. The domains between these shear planes move at different rotation rates, and consequently slide along each other. Therefore, particles that protrude through the shear plane encounter other particles. At such moments, they are pushed back into their respective domains. A particle that is pushed tends to drag its neighbours over a fraction $\ell$ of the distance it is moved itself (fig. 8.4). $\ell$ depends on the strength of the interaction. In much the same way, the dragged particles drag roughly half their neighbours and so on.
Figure 8.4 Schematic representation of the dragging of the particles in a concentrated dispersion, according to the giant floc model [6]. The length of the arrows indicates the relative distance over which the particles are dragged. \( A \) is the thickness of the domains (the distance between two shear planes). The relative rates of the domains are indicated as \( \dot{\gamma}A \) and \( 2\dot{\gamma}A \).

This idea was conceived by Van Diemen and Stein [5]. A detailed derivation is given in appendix VI. The dragging by the interacting particles can be incorporated in the Krieger-Dougherty relation as follows

\[
\eta_{t,\infty} = \frac{(1 - \phi/\phi_{\text{max},\infty})^{-[\eta]_{\phi_{\text{max},\infty}}}}{1 - 0.5q \dot{\gamma}^2} = \frac{(1 - \phi/\phi_{\text{max},\infty})^{-[\eta]_{\phi_{\text{max},\infty}}}}{1 - 0.5q_{0} \phi/\phi_{\text{max},\infty}} \dot{\gamma}^2
\]  

(8.6)

\( q \) is the number of neighbours in a random packing. It is estimated from \( q = q_{0}(\phi/\phi_{\text{max},\infty}) \), which compares reasonably well with the calculations of Schreuder and Stein [5]. \( q_{0} \) is the average number of neighbours in a random close packing, which equals 6 for spheres [14].

Figure 8.5 Logarithmic plot of the relative limiting viscosity at high shear for monodisperse poly-styrene lattices, depletion flocculated with hexaethylene-glycol mono-n-dodecyl ether [13], as a function of volume fraction, fitted with equation (8.6).

(a) \( d = 3.5 \mu m; \dot{\gamma}^2 = 0.40 \)
(b) \( d = 0.97 \mu m; \dot{\gamma}^2 = 0.20 \)
(c) \( d = 0.6 \mu m; \dot{\gamma}^2 = 0.16 \)
(d) \( \dot{\gamma}^2 = 0 \) (no interaction; Krieger-Dougherty equation)
The viscosity, predicted by the Krieger-Dougherty relation, diverges when \( \phi \) approaches \( \phi_{\text{max}} \). The viscosity, calculated from the 'adapted' Krieger-Dougherty (equation (8.6)), diverges when \( \phi \) approaches \( \phi_{\text{max},0}/(0.5q_0k^2) \) or \( \phi_{\text{max},0} \) whichever is the smallest of the two. Thus, for \( q_0 = 6 \), the viscosity diverges at \( \phi_{\text{max},0} \) for weakly coagulated colloids \((k^2 < 1/3)\), and at a smaller value of \( \phi \) for strongly coagulated colloids \((k^2 > 1/3)\). Such an effect is found in practice for latices by Buscall et al. (fig. 8.5) [12]. This strongly supports the proposed model.

Other literature data on the high shear limiting viscosity can also be fitted with equation 8.6 when an appropriate value of \( k^2 \) is taken. \( k^2 \) must vary between zero (no interaction) and \( \phi_{\text{max},0}/3\phi \) (maximum interaction). It clearly depends on the energy of separation of a doublet, but that is all we can say at the moment.

References

II.9 THE RHEOLOGY OF PSEUDOBOEHMITE SOLS

... wie al te diep op de dingen ingaat moet verloren lopen, dat kan niet anders.

Louis Paul Boon

For concentrated, coagulating colloids, the limiting high shear viscosity \( \eta_{x,\infty} \), see figure 8.1) can be written as

\[
\eta_{x,\infty} = \frac{(1-\phi''/\phi_{\text{max},\infty})^{-[\eta]\phi_{\text{max},\infty}}}{1 - 0.5 q \ell^2} = \frac{(1-\phi''/\phi_{\text{max},\infty})^{-[\eta]\phi_{\text{max},\infty}}}{1 - 0.5 q_0 \phi''/\phi_{\text{max},\infty} \ell^2} \quad (9.1)
\]

The numerator of (9.1) is the Krieger-Dougherty relation, which describes the influence of volumetric effects on the viscosity. The denominator describes the influence of attraction forces; for non interacting sols, \( \ell = 0 \).

This model is used here to gain information on the flow units in pseudo-boehmite sols. First, we will describe some experimental details on the determination of the shear stress \( (r) \) versus shear rate \( (\dot{\gamma}) \) curves, from which the viscosity \( (dr/d\dot{\gamma}) \) is obtained.

II.9.0.a Experimental

Figure 9.1 Hysteresis in \( r-\dot{\gamma} \) plots for several 'hysteresis times' (the time in which the shear rate is changed from 0 to 1000 s\(^{-1}\) or vice versa) for a fresh standard sol. The arrow indicates the direction of the change.
$\tau - \gamma$ curves have been obtained for pseudoboehmite sols (see appendix II) at varying acid, urea and solids concentrations, as a function of time. Shear thinning was observed in nearly all cases. $\eta_{r,0}$ and $\eta_{r,\infty}$ could be determined graphically or with Wouterson's empirical relation [1]:

$$\tau = c_0 + c_1 \gamma + c_2(1 - \exp(-c_3\gamma))$$

(9.2)

where $c_0$ to $c_3$ are adjustable parameters which can be related to $\eta_{r,0}$ and $\eta_{r,\infty}$.

Artificial causes for shear thinning (e.g. wall slip and viscous heating) are found to be negligible (appendix II). An important argument for this, is that no significant hysteresis is observed when the shear rate is not changed too fast (fig. 9.1). In a typical experiment, the shear rate is increased linearly from 0 to 1000 1/s in two minutes, kept constant at 1000 1/s for 20 seconds and decreased to 0 1/s again in two minutes. When the stress values of both branches are within experimental error, we say that no hysteresis occurs. It shows that the systems are in a steady state throughout the experiment, that no viscous heating or centrifugal separation interferes with the experiment, et cetera. In table 9.1, typical hysteresis times (minimum time in which the shear rate can be varied from 0 to 1000 1/s without creating significant hysteresis) are given for a standard sol at various ageing times. The short hysteresis times show that the build up of the broken bonds during the decrease of the shear rate is quite fast, although it appears to slow down upon ageing of the sol (II.9.2.b).

Whenever hysteresis did occur, the stress was, at every shear rate, higher during decreasing shear rate than during increasing shear rate. This phenomenon is at this moment not understood.

The reproducibility of the experiments is investigated in table 9.2. While the values for the limiting high shear viscosity are reproduced, there is considerable variation in the values for the extrapolated yield stress $\tau$. This is most probably due to slight changes in preparation procedure, e.g. in the conditions of the high shear dispersion step (see also table 9.3). The reproducibility is remarkably better when the experiments are performed by one operator. For a series of 7 reproducings experiments, immediately after preparation, $\eta_{r,\infty} = 113+3$ mPa.s and $\tau = 57+5$ Pa [2]. Therefore, at least $\eta_{r,\infty}$ is a reliable experimental parameter, and can be used for calculations with the above model.

<table>
<thead>
<tr>
<th>Table 9.1</th>
<th>Variation of hysteresis time during ageing</th>
</tr>
</thead>
<tbody>
<tr>
<td>ageing time (min)</td>
<td>hysteresis time (s)</td>
</tr>
<tr>
<td>0</td>
<td>45 ± 10</td>
</tr>
<tr>
<td>35</td>
<td>85 ± 15</td>
</tr>
<tr>
<td>165</td>
<td>135 ± 20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 9.2</th>
<th>Reproduced rheological experiments on sols with 0.175 M HNO₃ and 1 M urea</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment</td>
<td>$\eta_{r,\infty}$ (mPa.s)</td>
</tr>
<tr>
<td>[HNO₃] variation</td>
<td>86.8</td>
</tr>
<tr>
<td>[urea] variation</td>
<td>80.1</td>
</tr>
<tr>
<td>duplicate</td>
<td>76.5</td>
</tr>
<tr>
<td>$\phi'$ variation</td>
<td>86.6</td>
</tr>
</tbody>
</table>
Table 9.3 Influence of shear rate in high shear dispersion

<table>
<thead>
<tr>
<th>Shear rate during preparation (1/s)</th>
<th>Duration (min)</th>
<th>( \eta_{r,\infty} ) (( \text{cP} ))</th>
<th>( \tau_B ) (( \text{Pa} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>9,400</td>
<td>5</td>
<td>97.3</td>
<td>29.3</td>
</tr>
<tr>
<td>16,000</td>
<td>10</td>
<td>116.2</td>
<td>59.1</td>
</tr>
<tr>
<td>28,000</td>
<td>10</td>
<td>108.9</td>
<td>50.2</td>
</tr>
</tbody>
</table>

II.9.1 The influence of acid concentration on the rheology

Ik was een eenzaam dier, dat dagen en nachten broeien moest aan een gedachte, die slechts pijnlijk ter wereld kwam.

Louis Paul Boon

Rather complex behavior of the viscosity is found as a function of acid concentration in the sol (fig. 9.2). Analogous observations are reported by Drouin et al. in viscoelastic measurements on pseudoboehmite sols of comparable or slightly higher volume fractions [3]. Decreasing viscosity with increasing acid concentration is observed in regions I and III of fig. 9.2. Increasing viscosity is observed in regions II and IV. The changes in viscosity are, according to equation (9.1), due to changes in \( \phi'' \) (changing \( \phi' \) or changing Debye length); changes in \( \phi_{\text{max}} \) and in \([\eta]\) (axial ratio of the flow units); or changes in \( \ell^2 \) (strength of interaction).

Figure 9.2 Limiting viscosities for pseudoboehmite sols with varying acid concentration; \( \phi = 0.16 \) and 1 M urea. If \( \eta_{r,0} = \eta_{r,\infty} \), then \( \tau^* = 0 \). The meaning of the four regions (I to IV) is given in the text.

- \( \eta_{r,0} \) (dotted line)
- \( \eta_{r,\infty} \) (normal line)
Over the full range, the total ion concentration increases and consequently the Debye length decreases. Therefore, $\phi''$ decreases, explaining region I of fig. 9.2. At very high concentrations, the diffuse double layer is compressed so much, that it is too small to prevent flocculation. The resulting increase of $J$ explains region IV. What happens in regions II and III will be discussed later. Here, we will quantify the qualitative description of concentration effects.

At acid concentrations where no or hardly any shear thinning occurs $\phi'' < 0.35$ and $J^2 \approx 0$. The smaller the acid concentration is, the higher is the effective volume fraction. Since for all acid concentrations at which no

<table>
<thead>
<tr>
<th>Table 9.4 Influence of acid concentration on rheological properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image_url" alt="Table Image" /></td>
</tr>
</tbody>
</table>

* calculated assuming $J = 0$

** calculated with equation (8.4) for $\dot{\gamma} \rightarrow 0$, assuming $\phi_{\text{max},0}/\phi_{\text{max},\infty} = 0.60/0.64$, as it is for spheres (11.21.1)

# assumed value from which the other values of $\phi''$ are calculated

## gel-like appearance; flow curve measured, but no useful data obtainable
shear thinning is observed, $\phi''$ must be smaller than 0.35, it is logical to assume that $\phi'' = 0.35$ for the lowest acid concentration at which no shear thinning is observed: $[\text{HNO}_3] = 0.058$. With $\phi_{\text{max,}\infty} = 0.65 \pm 0.10$, it is calculated for this acid concentration that $[\eta] = 4.9 \pm 0.5$. This facilitates the calculation of $\phi''$ at $[\text{HNO}_3] = 0.029$, assuming $[\eta]$ is constant. One finds: $\phi''([\text{HNO}_3] = 0.029) = 0.44 \pm 0.01$. As an internal check, the low shear limiting viscosity is now calculated for this acid concentration with equation (8.4), and compared to the measured value. Good agreement is found for $\phi_{\text{max,}\infty} = 0.55$ (table 9.4). This value agrees well with the large value of the intrinsic viscosity. It is not to be expected that $\phi_{\text{max,}\infty}$ is constant at a varying acid concentration, but for the calculation of $[\eta]$, the exact value is not very important.

II.9.1.a The second electroviscous effect

The difference in volume fraction at $[\text{HNO}_3] = 0.058 \text{ M}$ and $[\text{HNO}_3] = 0.029 \text{ M}$ is due to the second electroviscous effect. For spherical flow units, this is given by equation (8.5). The value of $[\eta]$, however, shows that the flow units are ellipsoidal. We shall take them to be prolate, $a > b = c$, where $(4\pi/3 \text{ abc})$ is the volume of an ellipsoid. Let $a_1 = a + j/\kappa_1$, $b_1 = b + j/\kappa_1$ and $i = 1$ for $[\text{HNO}_3] = 0.058 \text{ M}$ ($\phi'' = 0.55$) and $i = 2$ for $[\text{HNO}_3] = 0.029 \text{ M}$ ($\phi'' = 0.44$). Then, analogous to equation (8.5)

<table>
<thead>
<tr>
<th>$[\text{HNO}_3]$ (mol/L)</th>
<th>$\eta_{\text{T,0}}$ (-)</th>
<th>$\eta_{\text{T,}\infty}$ (-)</th>
<th>$1/\kappa$ (nm)</th>
<th>$\phi''$ (-)</th>
<th>$[\eta]^*$ (-)</th>
<th>$\kappa^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.144</td>
<td>108.3</td>
<td>68.6</td>
<td>0.79</td>
<td>0.29</td>
<td>8.2</td>
<td>0.364</td>
</tr>
<tr>
<td>0.173</td>
<td>188.6</td>
<td>86.8</td>
<td>0.72</td>
<td>0.28</td>
<td>8.5</td>
<td>0.456</td>
</tr>
<tr>
<td>0.195</td>
<td>155.6</td>
<td>76.8</td>
<td>0.68</td>
<td>0.27</td>
<td>8.7</td>
<td>0.453</td>
</tr>
<tr>
<td>0.202</td>
<td>108.3</td>
<td>69.0</td>
<td>0.67</td>
<td>0.27</td>
<td>8.8</td>
<td>0.420</td>
</tr>
<tr>
<td>0.231</td>
<td>45.4</td>
<td>37.0</td>
<td>0.62</td>
<td>0.26</td>
<td>9.1</td>
<td>0.233</td>
</tr>
</tbody>
</table>

$^*$ $[\eta]$ values are obtained by linear interpolation between the values at 0.116 mol HNO$_3$/L and 0.260 mol/L for $\phi_{\text{max,}\infty} = 0.55$, see table 9.4
\[
\frac{\phi''}{\phi_1} = \frac{a_2 b_2^2}{a_1 b_1^2} = \frac{(a_j + j/k_2 - j/k_1)}{(a_j + j/k_2 - j/k_1)^2} \frac{(b_j + j/k_2 - j/k_1)^2}{a_1 b_1^2} = \left(\frac{1}{b_1} \frac{1}{k_2} - \frac{1}{k_1}\right)^2
\]

Since \( \phi''/\phi_1 = 0.44/0.35 = 1.26 \), it follows that \( j/b_1 \approx 2.4 \times 10^8/\text{m} \). Because \( b \) must at least equal the radius of the primary particle (~12 nm), it follows that \( j \geq 4.1 \). Since also \( 1 < j < 5 \) (II.8.2), \( j = 4 \) and \( b = 12 \text{ nm} \).

With equation (9.3) and the value of \( j/b_1 \) calculated, \( \phi'' \) is calculated for all acid concentrations (table 9.4). For infinitely high acid concentration, \( 1/\kappa \to 0 \) and \( \phi''(1/\kappa \to 0) = \phi' = 0.21 \).

From the calculated \( \phi'' \) and the measured \( \eta_{\gamma, \infty} \), we have calculated \( [\eta] \) and \( \eta_{\gamma, 0} \) for the other acid concentrations (table 9.4). \( [\eta] \) increases with increasing acid concentrations. For the measurements, at which no shear thinning was observed experimentally, the calculated values for \( \eta_{\gamma, 0} \) are within 10% of \( \eta_{\gamma, \infty} \); within experimental error, this indeed means Newtonian behaviour. The non-Newtonian behaviour at the acid concentrations between 0.144 and 0.231 mol/L (regions II and III in fig. 9.2) could be due to a very large value of \( [\eta] \) while \( \ell^2 = 0 \). It turns out that such an explanation does not yield correct values for \( \eta_{\gamma, 0} \) (table 9.4). Therefore, in those sols, \( \ell^2 \) must be larger than zero.

To calculate \( \ell^2 \) in that range, a value for \( [\eta] \) must be assumed. A possibility is a linear interpolation between \( [\eta] = 7.9 \) for \( [\text{HNO}_3] = 0.116 \text{ M} \), and \( [\eta] = 9.4 \) for \( 0.260 \text{ M HNO}_3 \). With \( \phi_{\text{max}, \infty} = 0.55 \), \( \ell^2 \) is given by table 9.5.

II.9.1.b Physical interpretation of the calculated results

As stated above, \( [\eta] > 2.5 \) indicates that the flow units are ellipsoidal, where the axial ratio \( (a/b) \) ranges from 3 \( ([\eta] = 4.4) \) to ~10 \( ([\eta] = 12) \). Assuming the ellipsoids are prolate, we find for the shorter axis: \( b = 12 \text{ nm} \). This implies the following.

(a) The flow units must be aggregates.

(b) These aggregates consist of one particle in the b-direction, and 3 to 10 in the a-direction (fig. 9.3).

(c) The primary particles, which are flocculated face to face (II.7.3), do so parallel to the a-b plane (fig. 9.3).

(d) The number of layers of primary particles in the aggregates can be estimated from \( c = b = 12 \text{ nm} \) when the thickness of the water layer between the platelets is known. The latter can be calculated from the volume fraction of the aggregates at infinitely small Debye length: \( \phi''(1/\kappa \to 0) \)
Figure 9.3 Sketch of the cross-section through the a-c plane of an aggregate. Every black line is the cross-section of a primary particle. In the b-direction, perpendicular to the paper, the thickness of the aggregate equals the diameter of one primary particle: 25 nm

$= \phi' = 0.21$. The volume fraction of the aggregates $\phi_a$ is related to the volume fraction of primary particles $\phi_{pp}$ as

$$\frac{\phi_a}{\phi_{pp}} = 1.11 \left(1 + 0.28 \times 10^{-9} \frac{t}{\delta}\right)$$

(9.4)

where $t$ is the number of molecular water layers between the parallel platelets. The approximate thickness of one such a layer is 0.28 nm; 1.11 is the shape factor for the rhombic primary particles. With $\delta = 3$ nm, $\phi_p = 0.16$ and $\phi_a = 0.21$, one finds $t = 1.95 \approx 2$. Thus, the number of layers of platelets is 6-7.

The aggregate model will be checked independently in II.9.3, after extending it to explain the typical rheological behavior at varying [HNO$_3$].

II.9.1.c The anisotropical surface charge

The explanation of the high viscosities at intermediate acid concentrations starts from three observations.
- The acid concentration at which we find the second minimum in viscosity is found by many investigators to be approximately the optimum in peptization [3-8] when corrected for differences in surface area. This indicates that the maximum surface charge behind the Stern plane is reached at or around this HNO$_3$ concentration.
- The maximum in $\eta$ is found at 70% of the acid, needed for 'optimal' peptization, while 70% of the total surface area is face area.
- The crystal structure of the faces of the primary particles is different from the crystal structure of the edges (fig. 7.1). Many different sites exist for protons to adsorb on these surfaces, but the most likely sites appear to be the O-atoms, exposed at the surface. On the faces, these sites are surrounded by many electronegative hydroxyl ions, whereas on the edges the situation appears to be less advantageous for proton adsorption. Therefore, we expect that for pH < 7, a surface charge builds up much easier on the faces than on the edges of the primary particles. At
intermediate acid concentrations, the faces will be protonated, whereas
the edges will not: the surface charge is distributed anisotropically.
Now, it is important to realize that the regular stacking of primary plate-
lets in the aggregates amplifies this effect. Suppose that a surface charge
only begins to build up on the edges of the primary platelets, and therefore
on the edges and points of the aggregates, when the faces are (nearly) satu-
rated with protons. Then at lower acid concentrations, the edges and points
bear no surface charge. They are protected from flocculation by the double
layer emanating from the faces. At intermediate acid concentrations (region
II in fig. 9.2), the double layer is compressed, and its protecting action
is decreased so that especially point to point flocculation can occur. At
the maximum in viscosity (0.17 M HNO₃), however, a surface charge begins to
build up on the edges of the primary particles, so that the edges and points
of the aggregates protect themselves from flocculation (region III). When
the total surface is saturated with protons, the further compression of the
double layer only weakens the repulsion (region IV).

The anisotropic distribution of the surface charge on the aggregates
explains the observed rheological behaviour as it gives a reason for $\ell > 0$
at intermediate acid concentrations. Since $\ell > 0$, a net attraction must
exist between the aggregates. Yet, no fast flocculation occurs. Most likely,
at these high counterion concentrations, part of the aggregates is floccu-
lated in a shallow primary minimum, protected by a small but significant
repulsion barrier [9]. In such systems, a dynamic equilibrium of floccula-
tion and 'repeptization', spontaneous deflocculation, exist [9,10]. The
short hysteresis time (see II.9.0.a) indicates that in the pseudoboehmite
sol, these processes are very fast. This means that flocculation can be
expected to be very rapid, when the repulsion barrier is removed.

II.9.2 Other rheological results on pseudoboehmite sols

Het verschil is niet groot genoeg om er een
onderscheid mee te maken. Louis Paul Boon

II.9.2.a Influence of solid volume fraction

Dispersions were prepared at 0.173 M HNO₃ and 1 M urea, for $\phi_{pp} = 0.15$,
0.16 and 0.17 ($\phi'' = 0.26, 0.28$ and 0.30). At all three volume fractions, the
measured values of $\eta_{r,\infty}$ are predicted well by equation 9.1 (table 9.6). For
Table 9.6 Influence of solid volume fraction on the rheology

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$\phi^n$</th>
<th>$\eta_{r,\infty}$</th>
<th>$\eta_{r,\infty}^*$</th>
<th>$\eta_{r,\infty}^#$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0.26</td>
<td>60.4 ± 0.3</td>
<td>57.9</td>
<td>60.0</td>
</tr>
<tr>
<td>0.16</td>
<td>0.28</td>
<td>86.6 ± 0.5</td>
<td>86.8</td>
<td>-</td>
</tr>
<tr>
<td>0.17</td>
<td>0.30</td>
<td>118.4 ± 1.0</td>
<td>137.0</td>
<td>119.4</td>
</tr>
</tbody>
</table>

* calculated for $[\eta] = 8.5$, $\phi_{\text{max,}\infty} = 0.55$, $q_0 = 6$ and $z^2 = 0.456$

# corrected for relative change in [HNO$_3$]

This prediction, the data for $\phi = 0.16$ are used (table 9.5). The agreement even improves when it is taken into account that the acid concentration, relative to the solids content, is changed ca. 6%. For instance, for $\phi = 0.15$, [HNO$_3$] is too large, and $[\eta]$ is underestimated. With $[\eta] = 8.6$ it follows that $\eta_{r,\infty} = 60.0$, within experimental error of the measured value.

11.9.2. b Ageing and the influence of urea concentration

$\eta_{r,\infty}$ increases on ageing although stirring is applied (250 rpm) to prevent sedimentation. A possible explanation for this ageing is slow, irreversible flocculation of aggregates, which would cause an increase in the effective volume fraction, and possibly changes in the axial ratio (and consequently in $[\eta]$ and $\phi_{\text{max,}\infty}$). Some authors [11] regard such a flocculation as the transition from a colloidal to a crystallitic contact as originally proposed by Rehbinder.

A second explanation assumes that no extra flocculation takes place, so that $\phi'$, $[\eta]$ and $\phi_{\text{max,}\infty}$ are constant in time, but that only $z^2$ changes. A reason for this might be the slow formation of Al$_{13}$O$_4$(OH)$_{28}$ species [3,4,12]. This will exert all kinds of influences on the chemistry of the sol, the simplest being that protons are consumed.

Yet, this second explanation for the ageing effect is most probably not valid. As already shown in table 9.1, the hysteresis time increases during ageing. This indicates that the reformation of the broken bonds becomes slower. This might occur when the average aggregate size increases (first explanation), but it is unrealistic when the bond strength increases (second
Figure 9.4 Relative limiting viscosity at high shear versus ageing time for sols with different urea content; lines are linear regressions
(a) × 0.0 M urea
(b) o 0.5 M urea
(c) + 1.0 M urea
(d) * 1.5 M urea
(e) Δ 2.0 M urea

It follows that slow flocculation probably takes place during ageing, although this cannot be quantitatively verified.

The urea slows down the ageing (fig. 9.4), nearly totally stopping it at 2.0 M urea. The stirring, applied during preparation, is much more vigourous (13,500 rpm) than it is during ageing (250 rpm). At such high shear, shear induced flocculation can occur, and the 'ageing' can be relatively rapid during that first step. This can explain the effect of the urea concentration for the fresh sols (t = 0). The increase in viscosity at 0 M urea is not as dramatic as expected from relevant literature [13]. Possibly, some urea is added already to the starting material, which is a commercial product rather than an analytically pure chemical. This remark has no dramatic meaning for this study, except that it is impossible to determine the absolute influence of the urea content.

Be this as it may, an influence is found of the urea concentration on the ageing process. Apparently, urea prevents flocculation. It is known, that urea increases the positive surface charge on AgI sols [12]. This effect, caused by the adsorption of urea on the positively charged sol, is due to a shift of the point of zero charge to lower concentrations of potential determining ions, i.e. to a higher pH in our system.

Such a shift in point of zero charge is indeed observed, using a mass titration technique [15] (table 9.7). That no change in electroforetic mobility (and therefore in \( \zeta \)-potential) was observed on changing the urea
Table 9.7 Electroforetic properties at varying urea concentration

<table>
<thead>
<tr>
<th>urea concentration (mol/L)</th>
<th>electroforetic mobility (10^{-8}) m²/Vs</th>
<th>point of zero charge* (pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.0 ± 0.2</td>
<td>7.74</td>
</tr>
<tr>
<td>0.5</td>
<td>2.3 ± 0.2</td>
<td>n.d.</td>
</tr>
<tr>
<td>1.0</td>
<td>2.2 ± 0.2</td>
<td>7.82</td>
</tr>
<tr>
<td>2.0</td>
<td>2.4 ± 0.2</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

* 0.01 M KNO₃ is used as background electrolyte

concentration is not surprising, as even a change in acid concentration does not yield a change in \(\zeta\)-potential at this pH [4]. For an explanation of this effect we refer to Hiemenz [16].

In short, the adsorption of urea, causing an increase of surface charge, possibly explains the stabilizing effect. This confirms, that the ageing effect can indeed be caused by insufficient stability. Also, it demonstrates how critical the balance between stabilizing and destabilizing forces is.

II.9.3 Concluding discussion

... wij zoeken steeds wat anders, 
dan dat wij zullen vinden ... 

Louis Paul Boon

We explain the rheological behaviour of the pseudoboehmite sols by assuming aggregates of primary particles to be the flow units. These aggregates are prolate, with an axial ratio \(a/b\), ranging from 3 to 10, with a width of one primary particle, and a thickness of 6 to 7 layers of parallelly packed primary particles (fig. 9.3). Rather comparable aggregates have been observed by Buining et al. [17] and by Hille et al. [7] using TEM. Fukasawa finds aggregates, consisting of strings of primary particles [18].

The water layer between these parallel layers of primary particles has probably a thickness of 2 molecular layers (~0.6 nm) or one molecular layer per surface. This agrees very well with the calculations on the starting material (II.7.2), but not with the results of the swelling experiment (II.7.3.a), which yielded a thickness of ~1 nm per particle, resulting in a
total layer thickness of ~2 nm. From DLVO theory, however, we would expect no water layer to exist at all for the small particles, small \( \tau \)-potentials and high ion concentrations encountered (when the particles have no asperities). A water layer can only exist because the total adsorption energy of the layer is larger than the total attraction energy between the particles. This so-called structural interaction [19,20] therefore depends strongly on the adsorption energy and consequently on the structure in the water layer. Protons are known to strongly disrupt such surface layers of water [19]. This appears to be a valid explanation for the small water layer thickness in acidic environment.

A remarkable feature of the aggregates is the anisotropic distribution of the surface charge at intermediate and low acid concentrations. This anisotropy, which resembles strongly that of clay particles, is inherited from the primary particles and even amplified by the layered structure within the aggregates. This anisotropy is largest, when 70\% of the acid needed for full peptization, is added. Apparently, the faces are then saturated with protons, while the edges and points bear no or only little surface charge. At this point, the aggregates are very sensitive to flocculation.

One may wonder, how the aggregates can be stable against strong flocculation, while the primary particles are definitely not. Three effects may be important. First, the aggregates are larger than the primary particles, making them relatively more stable. The Hamaker constant, which determines the Van der Waals attractive forces, will be smaller for the aggregates than for the primary particles. The former consist for \( (\phi_a - \phi_{pp})/\phi_a \approx 0.3 \) of water, the dispersion medium, which will have a significant effect on the Hamaker constant. These two effects may lower the total attractive force just enough, to let the structural interaction work at full strength, yielding 'stable' aggregates: aggregates that interact weakly enough to be separated by viscous forces, which act stronger on larger particles.

These are the conditions at which true gelation can occur [21]: a small repulsion barrier and anisotropical particles. In true gelation, linear flocs are formed. Linear flocs are flocs in which the number of bonds per aggregate is 2 or slightly higher. They soon fill the system, forming a gel. Many examples of this type of flocculation exist in literature [9,21-23].

Indeed, true gelation is observed in sedimentation experiments. For a standard sol (500 g pseudoboehmite in 1 L of 0.173 M HNO\(_3\) and 0.9 M urea), only slight sedimentation is noted, but the 'supernatant' does not become
clear, and gelates in a few hours time. Stronger sedimentation is observed when the concentrations, mentioned above, are decreased by a factor ten, but even then the supernatant gelates. Gelation also occurs in the supernatant of a centrifuged standard sol (3000 g), although the volume fraction in this supernatant is clearly much lower than for sedimentation by gravity.

These observations agree with the above model, in that gelation is indeed to be expected for semi-stable ellipsoidal particles. The sedimentation, on the other hand, proves that also larger particles exist in a sol when it is not sheared. Apparently, these agglomerates are broken down under shear.

References

[23] Personal communication with P.J. van den Berg, 1990
II.10 SHAPING SOL INTO SORBENT

"Tut, tut," hernam de professor. "Welk een beuzelpraat! Ik begin te geloven dat ge toch een student zijt."
Marten Toonder

Up to this point, we have discussed the properties of the pseudoboehmite sol. To make sorbent particles from such a sol, a number of shaping steps has to be performed: dropping, gelation, drying and calcination. All these steps are of importance to the performance of the final product (see also chapter I.3). Understanding the physical processes underlying these process steps will improve process control and product quality. An initial impetus to such a comprehension is developed in this chapter, starting with the simple system (10.1) and concluding with in situ impregnation (10.2).

II.10.1 From sol to sorbent without salt

In the sol-gel (or oil-drop) process as described in chapter 1.3, sol-droplets fall through an oil layer into an aqueous solution of ammonia. Remarkably enough, the sol droplets stay intact in the latter medium. Although the residence time in the oil phase is short, ca. 1 sec, it is essential: dropping without oil layer causes the droplets to break and mix with the ammonia solution before it gelates. Sanchez et al.* [1] explain the effect by assuming that some ammonia is dissolved in the oil phase, causing gelation of an outer skin of the droplets. However, due to the low ammonia concentration in the oil and the much higher diffusion rate of protons in the water, it seems unlikely that a significant change in pH can be reached in the sol in only 1 second. Therefore, gelation appears an unlikely, though not impossible, explanation.

* The explanation of Sanchez et al. appears to be inspired by the older patents in this area [2-5], which all use the so-called ‘oil-drop method’ of Hoekstra [2]. A general feature of this method is ‘internal gelation’. A weak organic base, like hexamethylenetetramine, was added to the sol. This sol was dropped into hot oil (> 90°C) to decompose the organic base into NH₃, thus provoking gelation. The droplets had to gelate and age for a few hours (!) in the hot oil before they could be contacted with water. The rate of gelation in the new processes is much higher (10 minutes being enough for total gelation), by changes in sol preparation method and composition [6]. But even compared to 10 minutes, 1 sec is very short.
A possible explanation follows from the observation that the sol droplets drag some oil into the ammonia solution. This oil is released after a short time, ca. 10 seconds, rising to the oil layer as a small droplet. The effect can be most clearly seen in the batch version of the process (appendix I) after addition of some surfactant. Possibly, an oil film exists around the sol droplets, protecting them long enough for a significant pH change to take place. The ammonia concentration of the surrounding medium is much higher. Consequently, 10 seconds of exchange of protons and ammonia through the membrane may well be long enough to bring about the formation of gelated skin on the sol droplets which protects it from breaking. This remarkable explanation agrees well with our experimental observation (also those to be mentioned below). It has to be examined in more detail.

At any rate, an addition of appropriate surfactants ensures that the droplets retain their spherical shape. Without surfactant, the sol droplets tend to come at rest at the interface between the oil layer and the NH₃ solution, taking a flattened shape. In this position, the droplet will coalesce with other sol droplets, when these fall on top of the former within a few seconds. The reshaping and coalescence indicate that gelation of the sol droplets cannot have proceeded far.

Coalesced droplets usually fall through the interface, indicating that the balance between interfacial tension and gravitational forces is rather sensitive. An addition of surfactant will lower the interfacial tension between oil and water (and also between oil and sol) significantly [7]. The decrease in surface tension between the sol and the oil implies that the droplets are more easily deformed, which would cause them to flatten more easily. On the other hand, the decrease in interfacial tension between oil and ammonia solution makes that the falling droplet can easily push a dent in that interface. Then, its equilibrium shape is still a sphere. Apparently, the impetus of the falling droplet is always enough to break through the interface, which is more easily deformed when surfactant is added.

Thus, spherical gel particles are formed. This spherical shape is one of the advantageous properties of the final product. If the final product is used in moving or fluidized beds, attrition is minimized by this shape. In fixed beds, spherical beads are better packed, preventing channelling of reactants. Also, less dust is formed when the fixed bed reactor is loaded with such beads.
II.10.1.a Gelation without the addition of salt

Gelation is provoked by a change in pH. The NH$_3$ and OH$^-$, diffusing into the gelating particles, neutralize the positive surface charge. This changes the fragile balance of the interaction forces between the aggregates (II.9). In this research, typically sols with ~0.14 M HNO$_3$ are used. This acidity yields the maximum viscosity (fig. 9.2). Therefore, small concentrations of ammonia will cause fast flocculation. This results eventually in a floc as large as the macroscopic size of the droplet. We will refer to this flocculated particle as a 'gel particle', in accordance with the sol-gel nomenclature, even though it is more like a flocculated colloid of high particle concentration. The final pH of the gel particles is so high (~11), that the pseudoboehmite surface is negatively charged. Under these conditions, the flocculated aggregates do not reptize because of the high overall concentration of counter ions, in particular Al$^{3+}$ ions, which considerably lower the surface potential.

Since the flocculation is fast, an open structure arises with many contact points per aggregate. This follows from the high axial ratio ($a/b = 7 \pm 3$), combined with the high aggregate volume fraction ($\phi_a \approx 0.21$). Most probably, regions with higher and with lower density will exist in the gel. We will refer to the latter as 'macropores'.

During flocculation, syneresis of the gel takes place (table 10.1). The

Table 10.1 Syneresis during gelation without impregnation

<table>
<thead>
<tr>
<th>during gelation residence time (min)</th>
<th>properties of sorbent beads after calcination</th>
<th>bulk density (g/ml)</th>
<th>pore volume* (ml/g)</th>
<th>crushing strength# (N/mm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td></td>
<td>1.32</td>
<td>0.47</td>
<td>$1.0 \pm 0.6$</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>1.36</td>
<td>0.45</td>
<td>$1.7 \pm 0.5$</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>1.40</td>
<td>0.43</td>
<td>$1.6 \pm 0.7$</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>1.43</td>
<td>0.41</td>
<td>$1.9 \pm 0.4$</td>
</tr>
<tr>
<td>120</td>
<td></td>
<td>1.43</td>
<td>0.41</td>
<td>$2.1 \pm 0.9$</td>
</tr>
</tbody>
</table>

* calculated from the bulk density and an estimated solid density (3.5 g/ml)  
# average crushing force per mm$^2$ of particle area ($\pi r^2$)
longer the residence time of the gel particles in the ammonia solution is, the denser, and consequently the stronger, the calcined particles become. Syneresis is the spontaneous shrinking of a gel by expulsion of dispersion fluid. Its driving force in this case is probably the osmotic imbalance: the difference in osmotic pressure across the gelated skin of the droplets [8]. The total concentration of dissolved species is higher outside the particles (-1.6 M NH₄OH) than inside (-0.2 M HNO₃ + 0.75 M urea). The gelated skin of the particles acts as a semi-permeable membrane: due to the negative surface charge on the aggregates in this gelated skin, no negatively charged ions can pass through the small pores. Consequently, the total diffusion of dissolved species into the gel particles is slowed down, and the transport of water out of the particles (osmosis) becomes the most important flow to equilibrate the solutions inside and outside the spheres. We call this process "osmotic syneresis".

Figure 10.1.a

Figure 10.1.b

Figure 10.1 N₂ physisorption results on calcium free ‘sol-gel’ samples
10.1.a hysteresis loop: adsorbed volume (STP) versus partial pressure
10.1.b pore size distribution, calculated from the desorption
(a) x pseudoboehmite according to a cylindrical pore model (r_p)
(b) + pseudoboehmite according to a slit-shaped pore model (D)
(c) o calcium free, dried gel (microwave); slit-shaped pore model (D)
(d) △ calcium free, calcined (850°C); cylindrical pore model (r_p)
II.10.1.b Drying of a nonimpregnated gel

As described in I.3.1.c, during drying a considerable shrinkage occurs. Apparently, during drying the macropores collapse: none are found in the pore size distribution of dried gels (fig. 10.1).

When the vapour phase begins to enter into the pore system, the outside of the gel particles dries up first. It becomes rigid and can only shrink slowly. The inside of the particles is still wet. It can shrink faster than the outer skin. Stresses build up, which relax only slowly. Much literature exists on this subject [9,10]. For our purpose, it is important to notice that the narrower the pores are, the stronger they are pulled together. The smallest pores in the gel are the slit-shaped pores inside the aggregates. These cannot be pulled together more than they are. Therefore, the smaller pores in between the aggregates will be pulled together until they are at the same distance as the pores within the aggregates. This yields pores of the same size as the slit-shaped pores. The resulting pore structure should be more regular than the pore structure in the starting material.

The \( N_2 \) physisorption hysteresis loop (fig. 10.1.a) and the calculated pore size distribution (fig. 10.1.b), show this to be valid, within the limited value of this technique (appendix II). From the hysteresis loop it cannot be decided which pore model holds: both narrow slit-shaped pores and ink bottle pores can give such results (appendix II). Pore size distributions, calculated according to these models are essentially equal, so that either can be used for comparing samples.

From the packing of the primary platelets, it is likely that the pores are slit-shaped. The pore volume of the dry material (0.27 ml/g) is much larger than the pore volume of the aggregates (~0.16 ml/g)*. Clearly, also some ink bottle pores must remain. These ink bottle pores are larger pores that do not form a network throughout the system, but are only connected by the slit-shaped pores. Estimates of the radius of these larger pores depend rather on the pore models taken for both the small and the large pores. These estimates yield values between 5 and 20 nm, which is the order of magnitude expected for the interaggregate pores.

---

* The pore volume of the dry gels is calculated from \( N_2 \) physisorption and from the difference between bulk and solid density (1.62 & 2.80 g/ml). Both methods yield 0.27 ml/g. The pore volume of the aggregates is calculated from their porosity and from the solid density of the pseudoboehmite (2.84 g/ml). The porosity equals 0.11, as follows from equation (9.4) with \( i = 0 \).
II.10.1.c Calcination of nonimpregnated and dried gel

Calcination of nonimpregnated, dried gels is accompanied by a shrinkage of 14±6\%\%. This is smaller than the theoretic shrinkage upon transition of pseudoboehmite to $\gamma$-alumina (-24%\%, calculated from the respective specific densities, -2.8 and -3.7 g/ml). Consequently, the pore volume increases during calcination to 0.35±0.02 ml/g (water intrusion and $N_2$ physisorption).

During calcination, the pore structure changes. The pores become cylindric (fig. 10.1.a), with only a slight tendency to ink bottle pores. The pore size distribution is bimodal with a main peak around 5.5 nm (cumulative pore volume 0.33 ml/g) and a minor peak around 3.0 nm (0.03 ml/g, fig. 10.1.b). The total surface area, calculated from these two peaks, is 140 m$^2$/g, whereas direct measurement of the BET-surface area yields 143 m$^2$/g. This proves the correctness of the cylindrical pore model for calcined materials.

It appears that the disconnected interaggregate pores become reconnected during calcination, most probably because the slit-shaped pores collapse. It is known that this occurs at 850°C, the calcination temperature [11]. The collapse of part of these pores leads to a size increase of the remaining ones. This is a sintering process, which makes it likely that the resulting pores are more or less cylindric. The small peak around 3 nm (radius) is most probably due to some remaining slit-shaped pores.

II.10.2 From sol to sorbent with salt

Men moet altijd weten waarom men iets doet, anders kan men het niet goed doen.

Martens Toonder

Dissolving a salt in the ammonia solution has a number of consequences for the gelation, drying and calcination process. We will discuss these effects, with emphasis on the effect of calcium nitrate. The solubility of many (bivalent) metal ions under alkaline conditions is low. Significant amounts of such ions can only be dissolved in the ammonia solution because the $NH_3$ acts as a complexing agent. The solubility of $Ca(OH)_2$ is only $-1.3 \times 10^{-6}$ mol$^3$/L$^3$ [12], but the formation of $Ca(NH_3)_6^{2+}$ [13-15] prevents precipitation up to the technologically needed concentrations of $Ca(NO_3)_2$ (< 1.5 mol/L). When both the solubility and the equilibrium constant of the formation of the complex ion are known, as is the case for $Zn^{2+}$, maximum concentrations
can be calculated in reasonable agreement with experimental values. Such calculations lead to the following conclusions: (a) nearly all NH₃ in the solution is coordinated with polyvalent metal ions; (b) the pH is ca. 11 (as is experimentally verified); and (c) the solution is strongly buffered, so that the free NH₃ concentration can not be controlled by pH measurements.

11.10.2. a Gelation with a salt containing ammonia solution

A nonspecific effect of the addition of soluble salts to the NH₃ solution during gelation is the increase of the osmotic pressure of that solution. Consequently, the rate of osmotic syneresis increases. High calcium contents in the final product can only be reached with long residence times or high calcium concentrations in the ammonia solution. In both cases, considerable osmotic syneresis will have taken place, resulting in a small pore volume of the final product (fig. 3.5). On the other hand, the higher the urea concentration is, the smaller the osmotic imbalance, the smaller the osmotic syneresis and the larger the resulting pore volume, as experimentally demonstrated (fig. 3.5). Thus, we have a method to control the final pore volume, viz. by adding indifferent solutes to the sol. Apart from urea, also alcohols and other small organic molecules can probably be used.

At a very large osmotic imbalance, the rate of syneresis becomes too high for the gel skin. Stresses build up, and the gel skin breaks open, yielding pac-man like particles, which crack even further upon drying. When gel particles are dried, which are in situ impregnated with nickel nitrate, a skin separates from the core of the particles, proving the existence of the semi-permeable skin.

Cracking occurs in 5 w% NH₄OH solutions at more than ca. 1.5 M for calcium nitrate (II ≈ 80 atm), and at ca. 1 M (II ≈ 40 atm) or even less for nickel nitrate. Clearly, there is an ion specific effect. This may be as simple as a difference in activity coefficient. Another ion specific effect which may be important in this regard, is the adsorption of the metal ion on the negatively charged pseudoboehmite surface [16]. Since the considered ions are all polyvalent, they will preferentially adsorb on spots between negatively charged surfaces. This yields strong bonds between primary particles [17]. The aggregates become stiffer and the gel as a whole is rigidified. Stresses are relaxed slower in such gels. To avoid cracking, the osmotic imbalance must be reduced, e.g. by adding indifferent solutes to the sol.
II.10.2.b Drying of in situ impregnated gel particles

To avoid cracking, the drying rate of in situ impregnated gels must also be lowered. This is found experimentally [18]. Another effect of the specific adsorption is the formation of not more than a monolayer of adsorbate. On or near a place where a bivalent ion has adsorbed, a second ion will not easily adsorb. Given enough ions and time, the available surface will be 'titrated' with metal ions. A very good dispersion, resembling a monolayer dispersion, is formed during calcination. This has been amply demonstrated in the first part of this thesis, and needs no more comment at this place.

II.10.2.c Calcination of in situ impregnated and dried gels

Adding metal (oxides) to the system can aid sintering during calcination: many mixed oxides have a lower melting temperature than pure alumina has.
Indeed, the increase of pore radius with increasing calcium oxide content (fig. 3.6), combined with the decrease in BET surface area and pore volume, points at sintering. Apparently, it only occurs when enough calcium is present. The pore size distribution does not alter very much as compared to a nonimpregnated sample, it merely shifts to somewhat larger pore sizes (fig. 10.2). Prolonged calcination (500 h) at 850°C [19], does not cause more severe sintering. Apparently, the main effect at 850°C is the collapse of slit-shaped pores (see also II.10.1.c). Indeed, at such low temperatures compared to the melting temperature of pure alumina, only very small alumina particles are expected to sinter. Only when the gas atmosphere is changed (I.4.3), or when the calcination temperature is increased (fig. 2.4), more dramatic sintering occurs.

That slit-shaped pores do not collapse at lower temperatures is confirmed by the measurements on gels which are in situ impregnated with nickel [20]. These gels are dried, calcined at 650°C and reduced at 700°C in 30 vol% 

![Diagram](image1)

**Figure 10.3.a**

**Figure 10.3.b**

**10.3.a** Hysteresis loop: adsorbed volume (STP) versus partial pressure

**10.3.b** Pore size distribution, calculated from the desorption; cylindrical pore model

(a) △ metal free, calcined (850°C)

(b) + with 0.5 M Ni(NO₃)₂ in situ impregnated, calcined (650°C)

(c) Ο with 1.5 M Ni(NO₃)₂ in situ impregnated, calcined (650°C)

(d) x with 1.5 M Ni(NO₃)₂ in situ impregnated, sintered (800°C, H₂O/H₂)
$H_2/N_2$, yielding a reasonable well dispersed Ni/γ-alumina. This is a catalyst for the low temperature oxidation of methane. Its initial activity is lower than for comparable catalysts, but its sinter stability is much better [20].

The $N_2$-hysteresis curves for the reduced samples (which are not heated above 700°C), show that the pores are of the slit-shaped/ink bottle type (fig. 10.3.a). Pore size distributions (calculated with a cylindrical pore model [20]), show a strong resemblance to the pore size distribution of dried, nonimpregnated samples (fig. 10.3.b). Adding more nickel results in smaller pores, a result of pore filling, rather than of sintering. This is confirmed by the large surface area of these samples, ~180 m$^2$/g.

On the other hand, a sample which is sintered purposely for 550 h at 800°C in an atmosphere of 30% steam and 70% $H_2$, resembles the calcium containing samples, calcined at 850°C (fig. 10.3). Although the sintering is small for this kind of circumstances, very little remains of the slit-shaped pores of ca. 3 nm. The BET surface area is decreased to 71 m$^2$/g. A sample which is calcined at 800°C before reduction did not show any sintering [20]. This again points at the importance of the gas atmosphere for sintering.

The collapse of the slit-shaped pores during calcination at 800-850°C yields pores, which have essentially the same sizes as the original inter-aggregate pores. The latter are present in the dried gels as ink bottle pores, connected only by the slit-shaped intra-aggregate pores. The collapse of the latter is possibly enhanced by the presence of metal (oxides). The gas atmosphere is, however, much more important to the rate and extent of pore collapse and sintering.

The resulting pore size distribution is rather uniform. This is important to the strength of the calcined beads. The intrinsic strength of porous materials is determined by the number and strength of the contacts in the system. The size and packing of the aggregates ensures a large number of contacts, evenly distributed over the particle. The addition of calcium, as in the gel, yields strong contacts by bridge formation and helps sintering of the stacked pseudoboehmite platelets into a solid γ-$Al_2O_3$ structure. Consequently, the intrinsic strength of sol-gel beads is very high.

The actual strength of a porous particle is reduced strongly by the macro-pores or cracks. These are formed during the shaping process (gelation, drying and calcination) and ruin the intrinsic strength of a bead. When crack formation is avoided, very strong sol-gel beads can indeed be made.
II.10.3 Conclusion

But there is much to be read in that book, and I
cannot claim to have seen more than a page or two.

J.R.R. Tolkien

We have seen that the particular sol-gel process we have examined, starts
with a sol which very rapidly flocculates. This makes it possible to drop
the sol particles through a relatively small layer of oil into an ammonia
solution. Possibly, the formation of an oil film around the sol droplets is
the cause that the sol droplets remain intact when they reach this ammonia
solution. At any rate, the oil layer is responsible for the advantageous
spherical shape of the final beads.

The use of an ammonia solution opens the possibility of in situ impregna-
tion because the ammonia acts as a complexing agent. Advantages of this type
of impregnation are that two energy consuming process steps can be avoided;
that the dispersion of the active component over the surface of the alumina
is very good because the impregnation is carried out under alkaline
conditions; that larger pores are created at higher calcium contents while
the strength of these beads increases in the same direction. The latter is
due to the formation of strong bridges and to the uniformity of the pore
size distribution.

The latter is formed during drying and calcination. During drying, the
smaller inter-aggregate pores are compressed even further, so that a system
remains of inter-aggregate pores which are only connected by smaller slit-
shaped pores. The latter, however, collapse during calcination at 850°C,
leaving the uniform pore size distribution.

Possible disadvantages of the in situ impregnation are that the osmotic
imbalance, and consequently the osmotic syneresis, is increased, and that
the gel is rigidified due to the adsorption of polyvalent ions between
primary platelets. Both effects increase the tendency to build up stresses
during gelation and drying, which may result in cracks, ruining the strength
of the bead. On the other hand, both effects can also be used in a
constructive way. The osmotic imbalance, which can be controlled by adding
'indifferent' solutes to the sol, can be used to control the pore volume of
the calcined product. And the adsorption can be used to yield very good
dispersions of active material and strong bridges yielding strong beads.
We now have the physico-chemical tools to tailor the valuable properties of in situ impregnated sol-gel sorbents: the spherical shape, the very good dispersion of the active material and the good particle strength, combined with sufficient porosity. We are not limited to calcium, but we can also use other metals, like Ni, Cu, Co, Mn and Zn, for in situ impregnation. This leads to the conclusion that in situ impregnation during sol-gel preparation is a valuable additional technique for the well controlled preparation of catalysts and sorbents.

References

[18] Personal communication with A. Meyer, 1989
[20] Personal communication with R. Berger, 1990
APPENDICES
APPENDIX I MATERIALS

A brief description is given of every preparation method used, including standard preparation conditions. Then, samples prepared according to that method which are mentioned in the text or in figures/tables are documented.

Sol-gel method (with in situ impregnation), continuous version

The apparatus used is described briefly in chapter I.3, figure 3.1. The following preparation procedure was followed.

Sol-preparation was performed in a Janke & Kunkel 500 ml mixer (RW 20-DZM-P4 at 137 rpm) and an Ultra-Turrax T25 high shear mixer fitted with a dispersing head S25N-10G (at 13,500 rpm). Urea (13.5 g p.a., Baker) was dissolved in 250 ml of a 0.175 M HNO₃-solution (p.a., Baker). Then 125 g of pseudo-boehmite (PURAL SB 70, Condea Chemie GmbH) was added and high shear mixing was applied for 5 minutes. The prepared sol was aged for half an hour in a buffering vessel, meanwhile stirring at 250 rpm.

Sol-dropping was performed by pumping the sol with a Masterflex pump (model 2015-21, tubing 6415.11) through four orifices of small tubes (ID 3.6 mm) into a layer (20 cm) of petroleum-ether (40-60°C) to which some surfactant (TEEPO3) was added.

Gelation was performed in a solution of ± 1 M Ca(NO₃)₂·4H₂O (chemically pure, Merck) and 0.85 M NH₄OH (chemically pure, Lamers & Pleuger); this solution was circulated with a pump (AEG ADEB56N2). The calcium and ammonia concentrations were determined by titration (see appendix II) to control the inflow of fresh solutions (2.85 M NH₄OH / 1 M Ca(NO₃)₂ and 1.4 M Ca(NO₃)₂ / 0.85 M NH₄OH), which were made from the purge stream. The volume of the solution in the set-up was kept constant by an overflow through which the purge stream left the set-up (see "purge stream"). The gelating particles were let through the smaller part of the gelation reactor after a residence time of ca. 10 minutes, and separated from the solution with a sieve.

Drying was performed in 3 steps: (1) immersion in ethanol (technically pure) for 15 sec, leaking (15 sec) and a second immersion for 15 sec to remove the water from the outside of the gel particles; (2) distribution over paper towel (M-TORK standard) and drying for 10 minutes in a microwave oven (Bauknecht MWT 732) at 115 W; (3) further drying at 80°C in a ventilator oven (Heraeus, 5 h or longer).

Calcination was performed in a Naber N100G with program controller C15. First, the dried particles were heated to 500°C at 1°C/min; then further heated to 850°C (at ca. 3°C/min), which temperature was applied for 10 h. Then the samples were cooled quickly in ca. 3 h.

Purge stream. To minimize the need for chemicals the purge stream was reused by filtration with a filter candle and addition of Ca(NO₃)₂·4H₂O (chemically pure, Merck) and/or NH₄OH (chemically pure, Lamers & Pleuger) to produce the addition solutions mentioned under "gelation".

Sample SG-105 (fig. 1.1, 4.3, 4.6, 4.7, 4.10, table 4.1, 4.2, 6.1, 6.2, appendix III) was prepared according to the above recipe in a long standing experiment (one week!), in which a total of ~40 kg of sorbent was produced.

Sample SG-102 (fig. 4.7, 4.8, 4.9 and appendix III) was prepared nearly identically. 15 g of urea was used in stead of 13.5 g, and high shear mixing was performed for 10 minutes in stead of 5. Drying in the microwave oven was performed for 5 in stead of 10 minutes. Drying at 80°C was performed in a
normal stove and took very long (> 24 h). Calcination was performed by heating at 1°C/min from 20°C to 850°C, and then further as described above.

Many of the data on other continuously prepared sol-gel sorbents in figures 2.2, 3.2, 3.5, 3.6, 3.7, 4.7 relate to samples made by Rijpkema according to the above recipe (with some slight alterations) [1].

The SG-Cx series (fig. 2.2, table 1.2, 6.1, 6.2, appendix III) was prepared by Condea Chemie, GmbH, Germany. They did not apply in situ impregnation, but impregnated calcined alumina spheres, usually with Ca(NO₃)₂ solutions; sample SG-C3 was impregnated with calcium acetate.

Sol-gel method (with in situ impregnation), batch version

Sol preparation and dropping, and gel drying and calcination were performed as in the above recipe. Gelation was performed in a measuring cylinder (500 ml or 1 L) with solutions of varying calcium content (0 to 3.33 M Ca(NO₃)₂) and 5w% NH₄OH for various residence times (0.5-18 h). Microwave drying was usually replaced by drying at room temperature for a 3-24 hours (typically 16 h or overnight).

The sol-gel sample in fig. 2.2 was made batchwise as the samples in fig. 4.2 (see below).

The samples in fig. 2.3 were produced batchwise and calcined additionally for 2 h at the given temperature. The in situ impregnated sample was made with a sol containing 1 ml 66w% HNO₃, 4.5 g urea and 50 g AlOOH.xH₂O per 100 ml water, which was gelated in a 4w% NH₄OH in water solution, containing 0.7 mol/L Ca(NO₃)₂. Drying was performed at room temperature (2-3 h) and then at 80°C (> 15 h), after which the sample was calcined at 550°C and 850°C, respectively, for 2 hours. The afterwards impregnated sample was prepared with a sol, containing 1.5 ml 66w% HNO₃, 6 g urea and 50 g of AlOOH.xH₂O per 100 ml water, which was gelated in a 8w% NH₄OH in water solution. The gel was dried for 3.5 h at 850°C and calcined at 550°C for 2 h. Then it was impregnated with a 4.8 M Ca(NO₃)₂ solution, dried at 80°C and calcined for 70 h at 850°C.

The samples in fig. 3.3 were produced batchwise from a standard sol (see continuous preparation) and dried as stated in the figure.

The data in fig. 4.2 relate to samples made batchwise at various residence time in the gelation medium. Sol was prepared as for the afterwards impregnated sample mentioned just above, and gelation was carried out in a 4w% NH₄OH in water solution containing 1.65 M Ca(NO₃)₂. The gel particles were dried overnight at room temperature and 3h at 80°C, and calcined at 850°C for 2 hours, heating at 1°C/min to 200°C, and faster onward.

The fast dried samples (fig. 4.7) were also prepared batchwise. These samples were dried for 30 minutes in the microwave oven.

The non-impregnated samples (chapter II.10) are produced in this way, see Slager [2]. Also, the nickel impregnated samples (1 h in 0.5, 1.0 and 1.5 M Ni(NO₃)₂) were produced in this way, in cooperation with Berger [3].

Impregnation of alumina pellets

000-3p and 001-3p γ-alumina pellets of AKZO (Amsterdam) were used for these preparations. Part of the pellets were calcined at 1235°C to convert them to α-alumina. Then, they were impregnated with solutions of Ca(NO₃)₂, dried at 80°C for 3 to 6 hours and calcined at 750°C or higher temperature.
The type of impregnation (with excess fluid or to incipient wetness) had no influence on sorbent properties.

Sample 1-6 (fig. 2.1, table 3.1 and 6.1) was 001-3p, calcined to α-Al₂O₃, twice impregnated with excess fluid, and calcined at 850°C. The γ-alumina sample (fig. 2.1, table 3.1) was 000-3p, impregnated with a 3.12 M Ca(NO₃)₂ solution and calcined at 750°C (5h, heating rate 2°C/min).

Silica

The silica samples mentioned in fig. 1.1 were Shell Silica Spheres (Shell, Amsterdam), produced by a sol-gel method, with a pore volume of 0.8 ml/g. These were impregnated with a 3.84 M Ca(NO₃)₂ solution in ca. 3 hours, dried at 80°C (18 h) and calcined as described for the sol-gel samples.

Calcium titanate

The calcium titanate sample, mentioned in the text of chapter I.1, was prepared by the so-called impregnation method. To a suspension of TiO₂ in a Ca(NO₃)₂ solution, a solution of ammonium carbonate was added. This resulted in a pink precipitate of CaCO₃ on TiO₂. The precipitate was filtered, washed with demineralised water of 80°C, dried overnight at 80°C and calcined at 850°C (24 h). The resulting powder was pelletized on a Hoko KJ machine, using the powder fraction of 0.3-0.8 mm to ensure free flowing behaviour of the powder. Graphite was added (-2%) as a burnable lubricant. The pellets were calcined at 1150°C for 4 h.

References

APPENDIX II METHODS

Analytical methods

ICP-AES

Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) has been used to determine the Ca and Al content of synthetic sorbents. 4-6 (= 200 mg) sorbent beads were crushed and ground. About 10 mg of the well homogenized powder and 10 ml 66w% HNO₃ (p.a. Baker) were added to 10-20 ml twice distilled H₂O. This was heated to 60-80°C to increase the dissolution rate. After 2-20 hours, depending on Ca content (the more Ca the faster the dissolution), the powder had totally dissolved. The liquid was cooled, H₂O was added to a total volume of 100 ml; the solution was thoroughly homogenized.

The Ca and Al contents of these solutions were determined on a Plasma 2, Perkin Elmer instrument by J.P. Koot and J. Padmos. The apparatus was calibrated, using matrix compensation for the HNO₃. Each ICP-AES measurement was reproduced 5 times and the results were averaged. Per solution good reproducibility of the Ca content (< 3%) was achieved, but when several solutions were made, the reproducibility was less good (< 10%). This was most probably due to variations in Ca content between sorbent beads.

The obtained Ca and Al concentrations were used to calculate the CaO content of the sorbent assuming all Ca to be present as CaO and all Al as Al₂O₃. Taking the small water content of the samples into account, this agreed well to the starting weight of the sample.

Titrations

Ca²⁺ The Ca²⁺ concentration in the NH₃ solutions was determined titrimetrically. 1 ml of sample solution was added to a mixture of 1 ml 0.2 M Mg(NO₃)₂, 2 ml buffering solution (NH₄OH and NH₄NO₃ at pH 10) and some Eriochrome Black-T in twice distilled H₂O. This solution was titrated from red to purple with V ml of 0.1 M EDTA. The transition was reasonably fast (~2 sec). The Ca²⁺ concentration [Ca] was calculated from

\[ [Ca] = 0.1 (\text{V-2}). \]

NH₃ The NH₃ content of NH₃ solutions was also determined titrimetrically. 1 ml of sample was added to a solution of 10 ml 0.2 M HNO₃ and 3 drops of a Methyl-red solution in twice distilled H₂O. This solution was titrated from red to yellow with V ml of 0.1 M NaOH, a very fast transition. The NH₃ concentration [NH₃] was calculated from

\[ [\text{NH}_₃] = 0.1 (\text{20-V}). \]

Experiments were performed by the author, students and technical personnel.

EPMA (WDS)

Electron-Probe X-ray MicroAnalysis was used to determine Ca and S distributions over sorbent particles. In this extension to a normal electron microscope, use is made of the X-rays that are emitted by the sample due to the electron bombardment. The wavelength of the X-ray radiation is specific for each element, and its intensity is related to the local concentration of that element. These parameters can be determined when WDS's (wavelength dispersive spectrometers) are used.

Specimen were prepared by embedding (sulphated) sorbent beads in a transparent mounting compound (Struers Denmark, Mounting resin-3). The mould was ground using 5IC emery paper until a (nearly) diametrical cross-section of the beads was obtained. Then, the specimens were polished (final stage: 1
\( \mu m \) diamond) and cleaned ultrasonically in ethanol. To improve electrical conductivity, a layer of \(-30 \mu m\) of carbon was deposited on the surface.

Ca, S, Al and O profiles were determined with a Jeol JXA 733 EPMA, equipped with four WDS's and a fully automated analysis system (Tracer Northern TN 5500 and TH 5600). The intensities of the respective Ka radiation, excited by a focussed electron beam (1 keV and 1 nA), was determined of spots lying 5 \( \mu m \) apart from each other on a diametrical line over the particle, from the outer particle to about its centre (1500 \( \mu m \)). The penetration depth was <50 \( \mu m \), so that wall effects of the bead can be neglected.

The resulting X-ray intensities were compared to a CaSO\(_4\) reference (Ca and S) and a \( \gamma_3Al_5O_{12} \) reference (Al and O). The Ca, S, Al and O contents were determined applying the so-called modified \( \phi(\rho z) \) approach [1]. Experiments and calculations were performed by Sloof, Helmig and Van Dam.

**Thermogravimetry**

Thermogravimetry (TG) has been used to determine the water contents of AlOOH.xH\(_2\)O and of sorbents, to gain information on the calcination of impregnated and dried spheres and to determine the content of reactive CaO in sorbents. The latter was performed with the SRO test, briefly described lateron. The apparatus was described by Duisterwinkel et al. [2]. When not stated otherwise, 100 ml/min of air was used as a purge gas during the experiment, while heating at 1 K/min. Experiments were performed by the author.

**XRD**

X-ray diffraction (XRD) was used to determine the crystallographic structure of compounds, present in (sulphated) sorbents. Sorbent particles were crushed, ground and mixed with gliseal to obtain a paste which was put into a metal frame. XRD patterns were obtained with a Guinier-de Wolff camera instrument by J.F. van Lent and compared to ASTM standard diffraction patterns [3] to determine the compounds present.

**Characterization**

**Water intrusion**

Exactly weighed samples (-2 g) of sorbent were added to twice distilled water. During a period of half an hour up to an hour, this was gently shaken now and then to assure that all air was released from the sorbent particles. Then the particles were decanted, entangling water was removed with drying paper, and the sample was weighed again. The weight difference (g) divided by the initial weight (g) yields the pore volume (ml/g), since the density of water at room temperature is 1 g/ml. The experiment was duplicated and repeated again when the two determinations differed more than 0.02 ml/g. These simple, fast and cheap experiments were carried out by the author, students and technical personnel.

**Nitrogen physisorption**

\( \text{N}_2 \) physisorption at 77 K has been used to determine the BET surface area, pore size distribution and total pore volume. Sample preparation includes, when not stated otherwise, drying at 150\(^{\circ}\)C in vacuo until no significant pressure increase was found.

BET measurements were performed on a self build apparatus, using M.K.S. absolute pressure transducers. Physisorption hysteresis curves were obtained
using a Micromeretics Digisorb 2600 instrument. From the shape of the hysteresis loop, the appropriate pore model was deduced. Four 'standard' hysteresis loops are given in fig. II.1 [4-7]. Type H1 applies for a small distribution of cylindrical pores. Type H3 is found for aggregates of plate particles. Type H4 is observed for narrow slit-shaped pores. Type H2 is contributed to ink bottle pores [4], and to narrow slit-shaped pores [5]. More recently, Sing contributed this type of hysteresis loops to 'poles of ill-defined size and shape'. He advised only to calculate pore size distributions from type H2 loops. This appeared nonsatisfactory in our case.

Having deduced the appropriate pore model from the shape of hysteresis loop, pore size distributions were calculated according for both adsorption and desorption. In this thesis, only the results of the calculations on desorption are given, because those of the adsorption branch often showed erroneous (negative) peaks. This demonstrates the difficulties of this technique. The only check of these calculations is a SANS measurement on sample SG-105 (appendix I). The neutron scattering observed, could be fitted quite well using a log-normal pore size distribution [8]. The volume averaged pore radius, calculated from this distribution, was 5.1 nm. This agrees rather well to the modal pore size of 5.6 nm (the modal pore size is the radius at which dV/dr is maximal, fig. 4.3 in chapter I.4). Also, the average pore radius for cylindrical pores (= 2 V_p/πR_BET = 5.8 nm using the pore volume from N₂ desorption) is reasonable close, regarding the breadth of the distribution. We conclude that at least for calcined samples, N₂ desorption yields reliable pore size distributions.

Experiments and calculations were performed by J. Teunisse and N. van Westen.

Helium Pycnometry

Helium pycnometry has been used to determine the solid or skeletal density of a number of materials. Samples were degassed as for N₂ physisorption, and slowly filled with He. Apparatus: Auto-He-pycnometer, model 1320 (Micromeretics). Experiments were performed by J. Teunisse and N. van Westen.

Small Angle Neutron Scattering (SANS)

In SANS, use is made of the scattering of neutrons by small sample inhomogeneities (1-100 nm) such as pores and small particles. Neutrons are only scattered when the contrast for neutrons between inhomogeneity and
matrix is large enough. This appeared not to be the case for AlOOH\textsubscript{x}H\textsubscript{2}O/H\textsubscript{2}O or AlOOH\textsubscript{x}D\textsubscript{2}O/D\textsubscript{2}O and alike, in contradiction to the pores in the calcined sorbent. From the scattering of the latter, the pore size distribution has been calculated, assuming a log-normal distribution. Neutron refraction and multiple scattering were checked for (the latter by varying sample thickness) and found negligible. Theoretical and experimental details are given by W.A.H.M. Viak [8,9], who kindly performed these experiments and their interpretation.

**Electrophoresis**

The electrophoretic mobility of aggregates in the boehmite sol has been determined with a Laser Z meter, model 501. Sample preparation consisted of standard sol preparation, centrifuging at 3000 g and ultracentrifuging the supernatant of the centrifuging at 200,000 g for half an hour. From a starting amount of 300 ml sol, approximately 20 ml of reasonably clear supernatant was obtained, to which a small spatula of the first sediment was added. This sol was subjected to electrophoresis, and the average mobility was determined by several operators.

**The SRO test**

Based on literature data [10,11], we have developed the SRO test [2]. This thermogravimetric test consists of consecutive sulphation, regeneration and oxidation steps. In cyclic experiments, these steps are repeated.

The test was performed in a thermobalance using a Pt-gauze sampleholder through which the gas was led at a relatively high flow rate of 100 ml STP/min throughout the test to ensure good gas transfer [2]. The sample weight was recorded as a function of time, varying the gas composition as required to obtain subsequent sulphation, regeneration and oxidation, typically at 850°C. The test conditions are given in table II.1. N\textsubscript{2} purges were applied between the several test stages for safety reasons. All test stages were performed until constant weight was achieved. Sulphation was sometimes performed for a shorter, fixed period. Weight changes were due to:

1. Loss of water and decarbonisation during heating.

2. Sulphation of active component AvO according to
   \[ \text{AvO} + \text{SO}_2 + 0.5 \text{O}_2 \rightarrow \text{AvSO}_4 \]  

3. Regeneration of the sulphated sorbent according to
   \[ \text{AvSO}_4 + \text{H}_2 \rightarrow \text{AvO} + \text{SO}_2 + \text{H}_2\text{O} \]  
   and
   \[ \text{AvSO}_4 + 4 \text{H}_2 \rightarrow \text{AvS} + 4 \text{H}_2\text{O} \]  

4. Oxidation of the byproduct AvS according to
   \[ \text{AvS} + 2 \text{O}_2 \rightarrow \text{AvSO}_4 \]  
   and
   \[ \text{AvS} + 3/2 \text{O}_2 \rightarrow \text{AvO} + \text{SO}_2 \]

The amount of SO\textsubscript{2} formed during oxidation has been monitored with a mass-spectrometer and found to be less than 10% of the total AvS conversion. Therefore, reaction (II.5) was neglected. Then, the weight change during oxidation gave the amount of AcS formed during regeneration. From that the total product distribution of the regeneration was calculated.

Using reactive CaTiO\textsubscript{3} powder, it was checked that gas bulk diffusion did not control the reaction rate [2]. The regeneration results of the SRO test were consistent and reproducible with a relative error of 2.5%. The reproducibility of the sulphation step was less good, because of the small size of the samples (initial sample weight of 200 mg, 6 or 7 beads). Larger samples, however, would have induced rate limitation by gas bulk diffusion.
Table II.1 Standard conditions for SRO test

<table>
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<th>sulphation</th>
<th>regeneration</th>
<th>oxidation</th>
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</thead>
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<td>heating rate</td>
<td>830°C in half an hour</td>
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</tr>
<tr>
<td>temperature</td>
<td>850±2°C, if not stated otherwise</td>
<td></td>
<td></td>
</tr>
<tr>
<td>total gas-flow</td>
<td>100 ml/min at 25°C and 1 atm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas composition</td>
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<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>0.5v%</td>
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<td></td>
</tr>
<tr>
<td>H₂</td>
<td></td>
<td>10v%</td>
<td></td>
</tr>
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</tr>
<tr>
<td>N₂</td>
<td></td>
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</tbody>
</table>

Experiments were performed by the author, by students and collegues, all under the experienced guidance of G. Hakvoort.

Rheology

Rheological experiments were performed with a CONTRAVES apparatus (Rheomat 115 controlled by a Rheoscan 100), typically using the DIN 125 bob and cup. At maximum revolution rate (780 rpm), the shear rate (\(\dot{\gamma}\)) was 1014 1/s. \(\dot{\gamma}\) was controlled by the revolution rate of the bob, on which also the shear stress was measured (Searle principle). The following procedure was used.

a) 17.5 ml of an (aged) sol was poured in the cup, the bob was inserted, and the combination was fitted in the Rheomat 115.

b) Maximum shear rate was applied for 30 seconds to prevent the pouring to affect the measurements.

c) No shear rate was applied for 30 seconds to let the structure recuperate.

d) Shear rate was linearly increased from 0 to maximum in measuring time \(t_m\).

e) Maximum shear rate was applied for 20 seconds.

f) Shear rate was linearly decreased from maximum to 0 in measuring time \(t_m\).

During step b) to f) the shear stress (\(\tau\)) was measured and plotted continuously. Care had to be taken that during measurement the system was in equilibrium. Had the rate of change been too fast, the sol would not have been able to change its properties at the same rate of change and false results would have been obtained. This would have been the case when hysteresis had occurred. Hysteresis occurs when the \(\tau-\dot{\gamma}\) curves during increasing and decreasing shear rate do not overlay. The following procedure was followed to determine the minimum measuring time where no hysteresis occurred: the hysteresis time \(t_h\). First steps a) to c) were applied. Then steps d) to f) were repeated for decreasing \(t_m\) until hysteresis was found, giving \(t_h\). For not too viscous sols, \(t_m\) ranged from 45 to 120 seconds. Taking the measuring time to be 2 minutes ensured that no hysteresis occurred, while no serious aging could take place during the measurement.

The nonexistence of hysteresis proved that the following artefacts were not important:

- Non equilibrium.
- Viscous heating (also checked theoretically and found negligible [12]).
- Aging or sedimentation (measuring time much shorter than typical times for these processes).
- Centrifugal effects (was noted on prolonged (> 1 h) shearing at maximum shear, \(\approx 2.2 g/m/s^2\)), but was not important on normal time scale).
- Shear induced diffusion.
Concentration changes due to evaporation etc. (not likely at short times and room temperature for aqueous sols). Other artefacts that were checked for and found negligible:

- Wall slip was checked for by using different sets of bobs and cups [13]; both \( \eta \) (< 4%) and \( \gamma \) (< 9%) were reproduced rather well.
- Sample inhomogeneity and shear history (as shown by the good reproducibility of the \( r-\gamma \) plots, see II.9.0.a).
- Taylor vortices. These do not occur when the Taylor number \( Ta < 1708 \) [14].

\[
Ta = \frac{4 \frac{R^2_b}{R^2_c} (R_b - R_c)^4}{\frac{R^2_b}{R^2_c} - \frac{R^2_c}{R^2_b}} \left( \frac{\Omega}{\eta/\rho} \right) \quad \text{(II.6)}
\]

where \( R_b \) and \( R_c \) are the bob and cup radius, \( \Omega \) is the angular velocity of the bob, \( \eta \) is the measured viscosity and \( \rho \) the density of the sol. Using \( Ta < 1708 \), it can be found that no Taylor vortices occur in the DIN-125 system for \( \eta > 10 \) mPa.s. This was always true for our experiments.

Experiments were performed by the author, students, J. Slager, B. Sonneville and N. van Westen. Bad reproducibility between experiments of several operators appeared mainly to be due by differences in sample preparation.

References

[3] ASTM powder diffraction standards, several cards
[12] Personal communication with J. Laven, 1989
APPENDIX III SORBENT ATTRITION IN FLUIDIZED BEDS

Attrition, unwanted particle size reduction, can occur by three important mechanisms: fragmentation, abrasion and weakening. During fragmentation (breakage), the parent particles - unattrited particles - split into more or less equal children particles and few fines. Abrasion (surface attrition), on the other hand, hardly alters the parent particles, but yields more fines [1]. Weakening is due to repeated stress, causing cracks to arise or grow in the particles, so that they weaken [2]. All causes leading to fragmentation and abrasion will also lead to weakening. Fragmentation is most harmful, since it yields irregular particles which have less resistance to further attrition than smooth, regular particles.

A good design of the system of combustor, coal ash separator and regenerator, is important to avoid fragmentation as much as possible. Here, it is assumed that this can be achieved. Consequently, it is appropriate to describe the attrition process as an abrasion process, and to determine attrition rates under conditions where predominantly abrasion takes place.

Here, we define the attrition rate $\alpha$ as

$$\alpha = \frac{-\Delta m}{m_0 \Delta t} = \frac{\Delta m}{m_0 \Delta t}$$  \hspace{1cm} (III.1)

$m_0$ and $m$ are the initial and actual sorbent mass, respectively. The right hand side of equation (III.1) strictly only applies when the attrition rate is constant in time from the start of the experiment. The latter is not always true (fig. III.1), but after a certain period of relatively fast initial attrition, a constant rate of attrition is (nearly) always found.

We believe that this constant rate of attrition exists, because the effective energy transfer in the bed hardly changes. The particle diameter changes nonsignificantly, and therefore the specific surface area does not change. Semi-empirical models for abrasion in fluidized beds generally take the shape of [1,3-9]

$$\frac{dX}{dt} = -\eta_1 \eta_2 (U - U_{mf})$$  \hspace{1cm} (III.2)

where $X$, depending on the author, either equals $m$ [7-9] or the particle diameter $d$ [3-5]. $(U - U_{mf})$ - the excess gas velocity - stands for the extra

![Figure III.1 Typical weight versus time plot for a fluidized bed attrition test. The constant slope, $\alpha$, is defined as the rate of attrition (1/h).](attachment:figure.png)
energy added to the fluidized bed which may cause attrition. \( \eta_1 \) and \( \eta_2 \), both variable between 0 and 1, are the sensitivity of the material to attrition and the effectiveness of the energy transfer in the fluidized bed, respectively. As these cannot be separated we redefine \( \eta_1 \eta_2 = k_a \), the rate constant of attrition, which depends both on the material and the bed.

Assuming \( X = d \) and assuming the number of particles and their diameters to change unsignificantly in time one finds from equations (III.1 and .2) [3-5]

\[
\alpha = \frac{-\Delta m/m_0}{dt} = \frac{3k}{d} (U-U_{mf}) (III.3)
\]

The inverse relationship of \( \alpha \) with \( d \) reflects the importance of the specific surface area of the particles, and confirms the choice of \( X = d \). This is a simple model, which does not take into account: (a) particle property distributions; (b) non spherical particles; (c) weakening by thermal, chemical or other influences.

To use the model in a predictive fashion, \( U_{mf} \) must be predicted as a function of sorbent properties. Especially for mixed systems (like sorbent/coal ash), this is not simple. For single systems of uniform spheres [10,11]

\[
U_{mf} = \frac{\eta_f}{\rho_f d} [(A^2 + B Ar)^{1/2} - A] (III.4)
\]

where \( \eta_f \) and \( \rho_f \) are the viscosity and density of the gas, \( A \) and \( B \) are empirical constants and \( Ar \) is the number of Archimedes)

\[
Ar = \frac{d^3 \rho_f (\rho_B - \rho_f)}{\eta_f^2} (III.5)
\]

\( g \) the acceleration due to gravity; \( \rho_B \) is the bulk density of the particle.

Figure III.2: The influence of adjustable parameters \( A \) and \( B \) on the predicted minimal fluidization velocity for a typical sorbent

Figure III.3: Comparison of theoretical and experimental \( U_{mf} \) for:
- sorbent: sand : 1 : 1 mixture, with \( A = 30 \) and \( B = 0.0193 \) (equation (6))
- sorbent only, with \( A = 30 \) and \( B = 0.0532 \) (equation (6))
\[ \frac{1}{\rho_B} = \frac{1}{\rho_S} + V_p \]  

(III.6)

\( \rho \) is the solid density of the particle and \( V_p \) its pore volume. When \( A \) and \( B \) are known, \( U_{mf} \) can easily be calculated. Ren & Yu give: \( A = 33.7 \) and \( B = 0.0408 \); Babu et al. give \( A = 25.25 \) and \( B = 0.0651 \). Generally, \( U_{mf} \) does not depend on \( A \) very strongly (fig. III.2).

Experimental

Materials are described in appendix I. The sand is a sieve fraction < 1.4 mm. Its average diameter is 0.79 ± 0.12 mm. The bulk density, assuming zero porosity, is 2.38 g/ml.

The particle radius is determined as an average value over 25 particles using a marking gauge. The sorbent sieve fraction > 1.4 mm is used for these experiments. The bulk density of the sorbent is calculated from equation (III.6), estimating \( \rho_B \) to be 3.5 g/ml, intermediate between the values for \( \gamma \)-alumina \((= 3.7 \text{ g/ml})\) and calcium aluminates \((= 3.0 \text{ g/ml})\). The pore volume is determined by water intrusion (appendix II). The crushing force is determined as an average over 100 particles in a Schleuniger 2E apparatus. In this apparatus, every particle is loaded with an increasing force, until it crushes. The maximum force applied is the crushing force of that particle.

The minimal superficial gas velocity for fluidization, \( U_{mf} \), is estimated by slowly decreasing \( U \) of a well mixed bed, up to the point that the bed stops fluidizing. Usually, only a part of the bed stops fluidizing, which is probably due to the distributions in particle size and density. The range of \( U \)-values in which part of the bed fluidized is determined, and \( U_{mf} \) is taken as the middle of that range. The width of the range is ca. 0.10 m/s.

The attrition rate \( a \) is determined at regular intervals by weighing the size fraction of sorbent > 1.4 mm. This size is chosen because sorbent, smaller than 1.4 mm, is difficult to separate from the coal ash. The initial composition is sorbent (> 1.4 mm): sand (≤ 1.4 mm) = 1:1, and \( M_0 = 100 \text{ g} \). Three beds are used with an internal diameter of 5 cm and sintered glass frits as gas distributor plates. Before fluidization, the samples are conditioned to the fluidizing gas (dried air) by a small flow of this gas for 24 hours. Then, fluidization is started at a predetermined \( U \), usually 1.5 m/s. At regular intervals, the bed content is taken out, sieved by hand on a 1.4 mm sieve for 2 minutes, and the fraction > 1.4 mm is weighed. The short sieving time ensures that attrition by sieving is not important.

The comparison of cold and hot attrition is carried out by others [12]. They used SG-105 (2.8-3.4 mm): sand (≤ 1.4 mm) = 1:1, at \( U = 2 \text{ m/s} \), and sieved mechanically for half an hour. The attrition loss by sieving is determined separately and corrected for, although it is not sure that the same sieving loss takes place on sorbent that has been fluidized.

The determination of the attrition rates for comparing several sorbent materials (fig. 2.1) is carried out as we performed it, at \( U = 2 \text{ m/s} \) [13].

Results and discussion

The minimal superficial gas velocity for fluidization is compared to the theoretic predictions in table III.1. It appears that for sorbent only, the experimental values lay in between the two theoretic predictions, calculated using literature data for the empirical constants \( A \) and \( B \) [9,10]. Defining (for this reason!) \( A = 30 \), we have calculated \( B = 0.0532 \) to obtain a better
### Table III.1 Experimental and theoretical values for the minimal fluidization velocity

<table>
<thead>
<tr>
<th>sample code</th>
<th>$d$ (mm)</th>
<th>$V_p$ (ml/g)</th>
<th>$\rho_B$ (g/ml)</th>
<th>experimental $U_{mf}$</th>
<th>theoretical $U_{mf}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no sand</td>
<td>with sand</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SG-C0</td>
<td>2.71±0.23</td>
<td>0.40</td>
<td>1.5</td>
<td>1.25</td>
<td>1.00</td>
</tr>
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<td></td>
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<td></td>
<td>0.51</td>
<td>1.36</td>
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<td>1.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.64</td>
</tr>
<tr>
<td>SG-C2</td>
<td>2.55±0.11</td>
<td>0.64</td>
<td>1.1</td>
<td>0.81</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.63</td>
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<td>0.94</td>
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<td></td>
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<td></td>
<td></td>
<td>0.51</td>
</tr>
<tr>
<td>SG-C3</td>
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<td>0.35</td>
<td>1.5</td>
<td>1.05</td>
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<tr>
<td></td>
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<td></td>
<td>0.73</td>
<td>1.34</td>
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<td></td>
<td>0.66</td>
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<tr>
<td>SG-C4</td>
<td>2.67±0.09</td>
<td>0.51</td>
<td>1.2</td>
<td>1.19</td>
<td>0.87</td>
</tr>
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<td>0.57</td>
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<td>SG-102</td>
<td>3.50±0.26</td>
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<td>1.7</td>
<td>1.65</td>
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<td></td>
<td>0.86</td>
</tr>
<tr>
<td>SG-105</td>
<td>3.37±0.36</td>
<td>0.32</td>
<td>1.7</td>
<td>1.34</td>
<td>1.26</td>
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<td></td>
<td>0.81</td>
</tr>
<tr>
<td>error</td>
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<td>0.1</td>
<td>0.05</td>
<td>25 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
<td>25 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25 %</td>
</tr>
</tbody>
</table>

### Figure III.4 Reproducibility test for the fluidized bed attrition experiments on SG-105. $U = 1.5$ m/s in a 5 cm internal diameter bed, fitted with a sintered glass frit at room temperature. Linear regression ($t > 50$ h).

- x, A bed R, + bed M, o bed L.

### Figure III.5 Test of the dependency of the attrition rate $a$ on the excess gas velocity $(U-U_{mf})$.

- a o sample SG-rp, prepared by agglomeration on a rotary plate.
- b + sample SG-C0', nonimpregnated sol-gel spheres.
prediction. For sorbent: sand = 1, no literature data are available. With again A = 30, B = 0.0193 gives a reasonable estimate of $U_{mf}$ (Fig. III.3). We conclude that equation III.4-6 can be used for predicting $U_{mf}$ for mixtures, when the value of B is known for any particular mixture. This is not true for sorbent/coal ash mixtures and may be problematic because of the variations in properties of coal ashes. As far as we know, no reliable theory exists on the $U_{mf}$ of mixtures of materials.

The reproducibility of the test is shown in figure III.4 (SG-105, 1.5 m/s, three different beds). The intercept of the y-axis is very reproducible. Apparently, about 5% of the sample is so small and or weak that it is lost rather fast. $\alpha$ is $1.25 \pm 0.1 \times 10^{-4}$/h for two different beds, and $0.99 \pm 0.07 \times 10^{-4}$/h for a duplicate experiment in a third bed. This shows that the experiment is rather reproducible, when carried out in one bed. Different distributor plates result in different $k_a$ values (Table III.2), but these differences are not dramatic. The only exceptions are the measurements by Anton Fransen [13], which also show a totally differing intercept of the y-

<table>
<thead>
<tr>
<th>sample code</th>
<th>bed</th>
<th>T (K)</th>
<th>U (m/s)</th>
<th>$y_0$ (%)</th>
<th>$10^4 \alpha$ (1/h)</th>
<th>$10^{10} k_a$ from $U_{mf}(exp)$</th>
<th>average $U_{mf}(th)$</th>
<th>$10^{10} k_a$ (N)</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG-C0</td>
<td>L</td>
<td>300</td>
<td>1.5</td>
<td>0.4</td>
<td>3.90±0.05</td>
<td>0.99</td>
<td>1.14</td>
<td>1.07</td>
<td>64 ± 19</td>
</tr>
<tr>
<td>SG-C2</td>
<td>M</td>
<td>300</td>
<td>1.5</td>
<td>0.6</td>
<td>4.50±0.16</td>
<td>1.22</td>
<td>1.07</td>
<td>1.15</td>
<td>45 ± 12</td>
</tr>
<tr>
<td>SG-C3</td>
<td>M</td>
<td>300</td>
<td>1.5</td>
<td>0.8</td>
<td>4.29±0.10</td>
<td>1.38</td>
<td>1.26</td>
<td>1.32</td>
<td>96 ± 22</td>
</tr>
<tr>
<td>SG-C4</td>
<td>R</td>
<td>300</td>
<td>1.5</td>
<td>-0.1</td>
<td>3.85±0.11</td>
<td>1.07</td>
<td>1.02</td>
<td>1.05</td>
<td>67 ± 21</td>
</tr>
<tr>
<td>SG-C10</td>
<td>L</td>
<td>300</td>
<td>1.5</td>
<td>0.8</td>
<td>0.97±0.06</td>
<td>0.49</td>
<td>0.49</td>
<td>0.49</td>
<td>147 ± 49</td>
</tr>
<tr>
<td>SG-105</td>
<td>R</td>
<td>300</td>
<td>1.5</td>
<td>4.8</td>
<td>0.98±0.07</td>
<td>0.37</td>
<td>0.44</td>
<td>0.41</td>
<td>79 ± 47</td>
</tr>
<tr>
<td>SG-105</td>
<td>R</td>
<td>300</td>
<td>1.5</td>
<td>4.7</td>
<td>1.01±0.06</td>
<td>0.37</td>
<td>0.46</td>
<td>0.42</td>
<td>79 ± 47</td>
</tr>
<tr>
<td>SG-105</td>
<td>M</td>
<td>300</td>
<td>1.5</td>
<td>5.0</td>
<td>1.22±0.06</td>
<td>0.45</td>
<td>0.55</td>
<td>0.50</td>
<td>79 ± 47</td>
</tr>
<tr>
<td>SG-105</td>
<td>L</td>
<td>300</td>
<td>1.5</td>
<td>4.7</td>
<td>1.27±0.13</td>
<td>0.47</td>
<td>0.57</td>
<td>0.52</td>
<td>79 ± 47</td>
</tr>
<tr>
<td>SG-105[AF]</td>
<td>AF</td>
<td>300</td>
<td>2.0</td>
<td>0.0</td>
<td>0.54±0.09</td>
<td>-</td>
<td>-</td>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td>SG-105[AF]</td>
<td>AF</td>
<td>300</td>
<td>2.0</td>
<td>0.0</td>
<td>1.10±0.74</td>
<td>-</td>
<td>-</td>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td>SG-105[LH]</td>
<td>AF</td>
<td>300</td>
<td>2.0</td>
<td>7.3</td>
<td>1.82±0.17</td>
<td>-</td>
<td>-</td>
<td>0.43</td>
<td>-</td>
</tr>
<tr>
<td>corrected for attrition in sieves</td>
<td>6.7</td>
<td>1.28±0.10</td>
<td>-</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SG-105[LH]</td>
<td>AF</td>
<td>1120</td>
<td>2.0</td>
<td>5.3</td>
<td>2.15±0.20</td>
<td>-</td>
<td>-</td>
<td>0.54</td>
<td>-</td>
</tr>
<tr>
<td>corrected for attrition in sieves</td>
<td>4.4</td>
<td>1.74±0.24</td>
<td>-</td>
<td>0.44</td>
<td>-</td>
<td>-</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>error</td>
<td>-</td>
<td>5</td>
<td>0.05</td>
<td>0.2</td>
<td>$\sim 5%$</td>
<td>$\sim 12%$</td>
<td>$\sim 12%$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* d. $U_{mf}(th)$ and $U_{mf}(exp)$ can be read from Table III.1; $y_0$ is the intercept of the y-axis

# d = 2.8-3.3 mm, $U_{mf}(th) = 0.78$ m/s, $M_0 = 75$ g, other bed, 2 minutes mechanic sieving

## d = 1.4-2.4 mm, $U_{mf}(th) = 0.51$ m/s, $M_0 = 75$ g, other bed, 2 minutes mechanic sieving

+ d = 2.8-3.3 mm, $U_{mf}(th) = 0.78$ m/s, $M_0 = 150$ g, other bed, 30 min mechanic sieving
axis. Later, it appeared that the sieving procedure he used was not very reliable. As far as these measurements can be trusted, it seems that the influence of the particle diameter on $a$ is as expected from equation (III.3). This, however, must be verified more thoroughly.

The theoretic prediction of the influence of the superficial gas velocity on $a$ can be checked in figure III.5 (no sand, equal beds). For SC-CO', the theoretic prediction appears to work very well. For SC-rp, the results seem less reproducible, but not altogether incorrect. Possible, the large variation in particle diameter (and thus $U_{mf}$) causes this effect.

The influence of bed temperature is small. This is an important conclusion for the applicability of the theory for regenerative desulphurization.

The overall conclusion is, that a simple but workable model is proposed for the attrition rate, which gives reasonable results. More verification is needed: the influence of the gas distributor plate must be examined more profoundly and a better prediction of $U_{mf}$ might improve the model. As a first approximation, this model, however, proves itself useful.

The data in table III.2 also show, that there is a distinct difference between sol-gel sorbents that are impregnated in situ during gelation or impregnated after calcination. The particles, made by the latter method, contain more loose powder and have rougher surfaces. Possibly, the calcium is partly dispersed in loose crystallites on the outside of the particles.

Crushing strength and attrition rate

In the crushing test, the static force, needed to crush (fragmentate) the particle, is recorded. Determining this force for a large number of particles and averaging gives the crushing strength. No identifiable relation exists between the crushing strength and the attrition rate constant (table III.2). Therefore, we have not used the crushing test to assess the sorbent attrition resistance in fluidized bed. Of course, it gives useful information on particles, to be used in fixed bed reactors.

References

[2] P.P.M. Vervoorn, internal report no. FRR 13.01, Delft University of Technology, December 1986
APPENDIX IV THE MONOLAYER CAPACITY

Let us calculate the surface area, \( S \), needed to disperse a certain calcium oxide content \( X_{\text{CaO}} \) (in w%) in a monolayer over the alumina surface.

\[
S = \frac{\text{volume}}{\text{thickness}}_{\text{monolayer}} = \frac{M_i \times X_{\text{CaO}}}{N_{\text{CaO}} \rho_i \delta_i} = A \times X_{\text{CaO}} \tag{IV.1}
\]

\( \rho_i \) is the specific density of compound \( i \) (g/m\(^3\)), \( \delta_i \) the thickness of its monolayer (m) and \( M_i \) its molar weight (g/mol). \( A \) is to be derived (m\(^2\)/g.w%).

For \( i = \text{CaO} \) the monolayer thickness can be calculated either as the mean ion diameter of Ca\(^{2+}\) and O\(^{-}\) [1], or as half the lattice parameter "a" of the cubic CaO crystal structure [2]. In both cases we arrive at \( \delta = 2.4 \pm 0.04 \) Å. Thus

\[
A = 12.8 \pm 0.5 \text{ m}^2/(\text{g.w%).}
\]

For \( i = \text{CaO.Al}_4\text{O}_5 \) the monolayer thickness is estimated as half the lattice parameter "c" of the orthorhombic aluminate structure [2]: \( \delta = 7.58 \pm 0.02 \) Å. With \( \rho_{i} = 2981 \text{ kg/m}^3 \) we find

\[
A = 12.5 \pm 0.1 \text{ m}^2/(\text{g.w%).}
\]

For \( i = 3\text{CaO.Al}_2\text{O}_3 \) the monolayer thickness is estimated as 3/11 \( a = 4.19 \) Å [2]. The factor 3/11 follows from the fact that a molecule of 3CaO.Al\(_2\)O\(_3\) contains 3 calcium atoms on a total of 11 atoms. With \( M = 1/3 \times 270.2 \text{ g/mol} \) and \( \rho_{i} = 3038 \text{ kg/m}^3 \) it follows that

\[
A = 12.7 \text{ m}^2/(\text{g.w%).}
\]

A can also be calculated from the surface area per "CaO-molecule": \( S_m \).

\[
S = S_m \times N_{A} \times X_{\text{CaO}} / M_{\text{CaO}} \tag{IV.2}
\]

\[
S_m = 1.09 \left( \frac{M_{\text{CaO}}/(N_{A} \rho_{\text{CaO}})}{1} \right)^{2/3} \tag{IV.3}
\]

As \( N_A \) is the number of Avogadro, one finds

\[
A = 10.8 \pm 0.2 \text{ m}^2/(\text{g.w%).}
\]

Both methods give similar results. To compare \( S \) to \( S_{\text{BET}} \) (the surface area according to the BET method) the two extremes of \( A \) are used, giving straight lines in fig. IV.1). Left of these a monolayer certainly is possible, while right of the lines too much CaO is added for a monolayer to exist. In between, no explicit conclusions can be drawn on the possibility of a mono-

![Figure IV.1 BET-surface area versus CaO content for in situ impregnated sol-gel sorbents](image-url)

- Batchwise preparation
- Continuous preparation

(a) less CaO than monolayer capacity
(b) high theoretical limit
(c) low theoretical limit
(d) more CaO than monolayer capacity
layer dispersion. Comparison with the experimental data yields the monolayer capacity or critical calcium content $X_{\text{CaO,c}}$:

$$X_{\text{CaO,c}} = 9.5 \pm 0.5 \text{ w\%}.$$ 

The monolayer concept is tested with the shrinking core model (I.4.2). The data on the samples, used for this test, are collected in Table IV.1.

<table>
<thead>
<tr>
<th>code</th>
<th>$X_{\text{CaO}}$ (w%)</th>
<th>$\varepsilon$</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$r_p$ (nm)</th>
<th>$R$ (mm)</th>
<th>$\xi_1$ (mol%)</th>
<th>$\xi_2$ (mol%)</th>
<th>$10^7D_{\text{eff}}$ (m$^2$/s)</th>
<th>$\Delta$</th>
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<tr>
<td>SG-106</td>
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<td>141</td>
<td>5.0</td>
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<td></td>
<td></td>
<td></td>
<td>0.55$^\theta$</td>
</tr>
<tr>
<td>SG-99</td>
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<td>0.526</td>
<td>128</td>
<td>4.8</td>
<td>1.76</td>
<td>80</td>
<td>91</td>
<td>8.1</td>
<td>0.87</td>
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<td>11.1</td>
<td>0.516</td>
<td>108</td>
<td>5.6</td>
<td>1.65</td>
<td>82</td>
<td>88</td>
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<td>14.3</td>
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<td>93</td>
<td>6.0</td>
<td>1.56</td>
<td>85</td>
<td>82</td>
<td>5.6</td>
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<td>SG-91</td>
<td>15.4</td>
<td>0.423</td>
<td>61</td>
<td>6.9</td>
<td>1.56</td>
<td>81</td>
<td>78</td>
<td>5.2</td>
<td>0.61</td>
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<td>fast drying</td>
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<tr>
<td>SG-105</td>
<td>9.5</td>
<td>0.470</td>
<td>99</td>
<td>5.6</td>
<td>1.66</td>
<td>91</td>
<td>88</td>
<td>5.3</td>
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<tr>
<td>SG-125</td>
<td>9.7</td>
<td>0.472</td>
<td>103</td>
<td>4.5</td>
<td>1.13</td>
<td>102</td>
<td>96</td>
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<td>0.57</td>
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<tr>
<td>SG-124</td>
<td>10.6</td>
<td>0.462</td>
<td>99</td>
<td>4.5</td>
<td>1.15</td>
<td>101</td>
<td>94</td>
<td>3.0</td>
<td>0.51</td>
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<tr>
<td>SG-121</td>
<td>12.1</td>
<td>0.441</td>
<td>85</td>
<td>4.8</td>
<td>1.41</td>
<td>102</td>
<td>93</td>
<td>1.6</td>
<td>0.27</td>
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<tr>
<td>SG-123</td>
<td>12.7</td>
<td>0.450</td>
<td>86</td>
<td>5.0</td>
<td>1.34</td>
<td>90</td>
<td>92</td>
<td>1.9</td>
<td>0.29</td>
</tr>
<tr>
<td>error</td>
<td>5%</td>
<td>7%</td>
<td>1</td>
<td>0.2</td>
<td>2%</td>
<td>5%</td>
<td>3%</td>
<td>10%</td>
<td>10%</td>
</tr>
</tbody>
</table>

* symbols defined in List of Symbols; parameters determined with SRO test [3]
+ first part of $(d\xi_1/dt)^{-1}$ versus $f(\xi_1)$ plot
$^\theta$ second part of $(d\xi_1/dt)^{-1}$ versus $f(\xi_1)$ plot

References

[2] ASTM powder diffraction standards, several cards
APPENDIX V DERIVATION OF ReSuLT

Derivation of the rate equation: the shrinking core model [1]

The molar flow of sulphur per spherical particle, \( \phi_p \), equals

\[
\phi_p = D_{\text{eff}} \frac{dC}{dr} A_r \tag{V.1}
\]

\( A_r \) is the surface area of a sphere with radius \( r \), and \( D_{\text{eff}} \) is the effective pore diffusion coefficient. Assuming no reaction or accumulation of SO₂ in the shell between the particle radius \( R \) and the radius of the shrinking core \( r_c \) it follows that \( \phi_p (r_c) = \phi_p (R) \). Thus it follows from (V.1)

\[
\phi_p = 4\pi D_{\text{eff}} \frac{C_s - C_c}{(1/r_c - 1/R)} \tag{V.2}
\]

where \( C_s \) is the SO₂ concentration at the outer surface of the particle, which equals the bulk gas concentration as external transport limitation is assumed negligible: \( C_c = C_0 \). \( C_c \) is the SO₂ concentration on the boundary of the shrinking core.

Assuming the reaction rate is extremely fast compared to the diffusion rate, we may put \( C_c = 0 \).

\( r_c \) is related to the relative conversion \( \xi_1 \) according to

\[
1 - \xi_1 = (r_c/R)^3 \tag{V.3}
\]

\( \xi_1 \) is obtained from the weight changes (I.4, equation (4.1)). Experimentally, \( \phi_p \) is found from the rate of weight change \( (dW/dt) \)

\[
\phi_p = \frac{1}{M} \frac{dW}{dt} = \frac{1}{M} (W_\infty - W_0) \frac{d\xi_1}{dt} \tag{V.4}
\]

\( M \) is the molar weight of SO₃: the weight difference between CaO and CaSO₄. \( W_\infty \) and \( W_0 \) are the final and initial sample weight, respectively. Then

\[
\frac{d\xi_1}{dt} = \frac{K C_0}{(1 - \xi_1)^{-1/3} - 1} \tag{V.5}
\]

where

\[
K = 4\pi M R D_{\text{eff}} / (W_\infty - W_0) \tag{V.6}
\]

When \( (W_\infty - W_0) \) is expressed as the maximum possible weight change related to the calcium oxide content \( X_{\text{CaO}} \), we find, using the bulk density \( \rho_b \),

\[
K = \frac{3D_{\text{eff}} M_{\text{CaO}}}{\rho_b R^2 X_{\text{CaO}}} \tag{V.7}
\]

Starting equations of ReSuLT

Repeating the equations in chapter I.5, for reasons of clarity

\[
0 = - \phi_1 - \phi_5 - 0 \tag{5.4}
\]

\[
0 = - (\phi_1 + \phi_4) - (\phi_3 + \phi_5) - 0 \tag{5.5}
\]

\[
0 = (\phi_1 + \xi_1 \phi_4) - (\phi_3 + \phi_5)(1 - \xi_1) - n_1 \tilde{r}_{\text{CaO}} \tag{5.6}
\]

\[
0 = Q_1 - (Q_5 - \xi_1 \phi_5) - n_1 \tilde{r}_{\text{CaO}} \tag{5.7}
\]
\[
\dot{r}_{\text{CaO}} - \int_{0}^{\infty} E(t) \frac{r_{\text{CaO}}}{t_1} \exp\left(-t/t_1\right) dt = \int_{0}^{\infty} \exp\left(-t/t_1\right) \frac{r_{\text{CaO}}}{t_1} dt \tag{5.8}
\]

\[
Q_s = (1-R_s) Q_1 + \dot{\xi}_1 \phi_5 = (1-R_s) \frac{X_s}{M_s} k_1 + \dot{\xi}_1 \phi_5 \tag{5.9}
\]

\[
\Xi = 1 - \dot{\xi}_1 + \dot{\xi}_1 \dot{\xi}_2 \tag{5.11}
\]

\[
\dot{\xi}_1 = \frac{R_s}{(\text{Ca}/S)} \tag{5.10}
\]

\[
\phi_5 = \alpha \frac{\tau_1}{(\phi_3+\phi_4)} \tag{5.11}
\]

**Solution of ReSuLT**

Combining equations (5.7) to (5.9) gives

\[
R_s Q_1 = n_1 \dot{r}_{\text{CaO}} - n_1 \int_{0}^{\infty} \frac{\exp\left(-t/t_1\right)}{t_1} r_{\text{CaO}} dt \tag{V.8}
\]

For \(n_1\) we find, combining (5.2), (5.5) and (5.11),

\[
n_1 = \frac{\phi_4}{\alpha r_1} \tag{V.9}
\]

Realizing that we may use equation (V.5) for \(r_{\text{CaO}}\), and that consequently

\[
K C_o \frac{\text{d}t}{\text{d}t} = \left(1-\xi_1\right)^{-1/3} - 1 \left(1-\xi_1\right)^{-2/3} \text{d} \xi_1 \tag{V.10}
\]

For \(t = \infty\), \(\xi_1 = 1\), so that we find from (V.8), (V.9) en (V.10)

\[
R_s \frac{X_s}{M_s} k_1 = \frac{\phi_1}{\alpha r_1} \left[\int_{0}^{1-3/2(1-(1-\xi_1)^{-2/3}) + \xi_1} \exp\left(-\frac{3/2(1-(1-\xi_1)^{-2/3}) + \xi_1}{K C_o r_1}\right) \text{d} \xi_1 \right] \tag{5.13}
\]

the right hand side of which can be numerically integrated.

On the other hand, combination of (5.4) (\(\phi_1 - \phi_5\)) with (5.5) yields \(\phi_3 - \phi_4\).

Using these two equations and the left hand side of (V.8) in (5.6) yields

\[
\phi_1 + \dot{\xi}_2 \phi_4 = \frac{R_s Q_1}{\dot{\xi}_1} = \frac{\text{Ca}/S}{Q_1} \tag{V.11}
\]

where (5.10) is used in the right hand side of (V.11). From (5.4) and (5.11)

\[
\phi_4 = (1-\alpha r_1) \phi_1 / \alpha r_1 \tag{V.12}
\]

Combining (V.11), (V.12) and (5.9) yields

\[
\dot{\xi}_2 = \alpha r_1 \frac{\text{Ca}/S}{X_s/M_s} k_1 \tag{5.12}
\]

The combination of (5.12) and (5.13), through an iterative procedure, yields \(\dot{\xi}_1\) and \(\tau_1\), from which \(Y\) and \(m_1\) can be calculated. Jaap Schouten has written the necessary computer program, which is greatly appreciated.

**References**

APPENDIX VI DERIVATION OF THE RHEOLOGICAL MODEL

The giant floc model, developed by Schreuder and Stein [1], appeared to be quite suitable to describe our results. Apart from one or two minor changes in the derivation of this model, we have made one additional step by incorporating the Krieger-Dougherty relation in the final equation. This is based on a physical interpretation of the model which goes beyond that of Schreuder and Stein. To appreciate this, we first briefly introduce the giant floc model.

According to the giant floc model, the shear in a concentrated dispersion (volume fraction \( \phi > 0.3 \)) is not distributed homogeneously, but is limited to certain shear planes. In between the shear planes, domains exist. Out of these domains, particles extend and protrude through the imaginary shear plane. Particles, extending from adjacent domains will now and then encounter each other. The energy dissipation during steady flow is thought to be caused by rearrangements due to these encounters. The energy dissipated by one particle in one encounter, \( \varepsilon_p \), equals

\[
\varepsilon_p = \text{force (Stokes) \times distance} = 6\pi R\eta_f(\delta/t) \times \delta \quad (VI.1)
\]

where \( R \) is the radius of the sheared particle, \( \eta_f \) is viscosity of the surrounding fluid and \( \delta \) and \( t \) are the distance and time of the encounter. A particle will drag approximately half of its neighbours each over a distance \( \delta \xi \), where \( 0 < \xi < 1 \) (fig. 8.4 in II.8). A dragged particle will drag half of its own neighbours in the same way over a distance \( (\delta \xi)^2 \) and so forth. When \( q \) is the average number of neighbours within a domain we find for the total energy dissipated per encounter, \( \varepsilon_e \)

\[
\varepsilon_e = 2 \times 6\pi R\eta_f \sum (0.5q^2) \left( \frac{1}{1-0.5q^2} \right) \quad (VI.2)
\]

Here, it should be remarked that Schreuder and Stein use \((q-1)\) rather than \(q/2\). We prefer the latter to avoid double counting of particles. Also, we will put \( q = q_0 \phi/\phi_{\text{max,omega}} \), where \( q_0 \) is the average number of neighbours at random close packing, which is reached at \( \phi_{\text{max,omega}} \), the maximum volume fraction at limiting high shear. Schreuder and Stein use estimates which are based on crystal lattices. Both these differences are, however, minor ones.

Expressed per unit volume and time, the energy dissipation \((\dot{\varepsilon})\) becomes

\[
\dot{\varepsilon} = 12 \pi \frac{R \delta_0 \Delta^3}{\Delta^3} \eta_f (1-0.5q^2) \gamma^2 = \tau \dot{\gamma} \quad (VI.3)
\]

where \( \Delta^2 \) is the area of shear plane per particle protruding in that plane and \( \dot{\gamma} \) is the shear rate. The thickness of the domains, \( \Delta \), varies with the shear rate and is unknown. In the case of limiting high shear, \( \Delta \) will be as small as possible: \( \Delta = 2R \). The right hand side of equation (VI.3) is the general expression for the energy dissipation. In the same limit

\[
\lim_{\dot{\gamma} \to \infty} (\tau) = \lim_{\dot{\gamma} \to \infty} (\tau_0 + \eta_\infty \dot{\gamma}) = \eta_\infty \dot{\gamma} \quad (VI.4)
\]

Introducing \( A = 2R \) and equation (VI.4) in (VI.3), we obtain

\[
\lim_{\dot{\gamma} \to \infty} (\dot{\varepsilon}) = 24 \pi \frac{R}{\Delta^3} \delta_0 \eta_f / (1-0.5q^2) \gamma^2 = \eta_\infty \gamma^2 \quad (VI.5)
\]
With this equation, we can predict \( \eta_f \), which appears to be independent of the shear rate, as required. To simplify (VI.5), we follow Schreuder and Stein [1] in putting \( (R/\Delta) = 0.5 \) and \( (\delta_0/R) = 0.1 \), so that

\[
24 \pi \frac{R^3}{\Delta} \frac{\delta_0}{R} \approx 1
\]

(VI.6)

Furthermore, \( \eta_f \) can be regarded as the viscosity of the fluid that has to flow due to the rearrangements during the encounter. Schreuder and Stein set this equal to \( \eta_0f \) where \( \eta_0 \) is the viscosity of the suspension medium and \( f \) a friction factor. We postulate, that for the flow of the fluid in first approximation it is not important whether the particles are flocculated or not. Then the Krieger-Dougherty relation predicts \( f \) (see II.8.1). Thus

\[
\eta_f - \eta_0 f = \eta_0 (1 - \phi:\phi_{max, \infty})^{[\eta]_{\phi_{max, \infty}}}
\]

(VI.7)

Combining the equation (VI.5) - (VI.7) gives for the relative viscosity at limiting high shear (\( \eta_{R, \infty} \))

\[
\eta_{R, \infty} = \frac{f}{1 - 0.5q\ell^2} - \frac{(1 - \phi:\phi_{max, \infty})^{[\eta]_{\phi_{max, \infty}}}}{1 - 0.5q_0(\phi:\phi_{max, \infty})\ell^2}
\]

(8.6)

The physical interpretation of this semi-empirical relation is rather straightforward: the viscosity at limiting high shear of a flocculated dispersion can be regarded as the viscosity at limiting high shear of a non-flocculated system multiplied by a drag factor \( (1/(1 - 0.5q\ell^2)) \). For a non-flocculated system \( f = 0 \). The drag factor will generally depend on particle size and shape and on the strength of attraction between the sheared particles.

Schreuder and Stein comment that \( f \) is much more important for \( \eta_{R, \infty} \) than \( \ell \) is. In their case, this statement is valid, because they used dispersions of large spheres (~30 to ~80 \( \mu \)m), with a relatively weak interaction. For large spheres, viscous forces are relatively strong (cf. equation (VI.1)), so that it is to be expected that \( f \) is more important than \( \ell \) in such systems.

For smaller particles, on the other hand, attraction forces are strong relative to the viscous forces, and \( \ell \) is expected to be more important. In chapter II.9, this is shown to be valid in a number of cases.

References

LIST OF SYMBOLS

The limited size of the Latin and Greek alphabets; the incapability of the wordprocessor used to incorporate other alphabets; and the existing conventions on nomenclature; all these were factors in the decision to use a small number of symbols for more than one purpose. In such cases, it is indicated in the list below, which definition applies in which part of the thesis.

**Latin symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>appendix III: fit parameter in equation (III.4)</td>
</tr>
<tr>
<td></td>
<td>appendix IV: surface area, needed per w% CaO</td>
</tr>
<tr>
<td></td>
<td>appendix VI: thickness of a domain between shear planes</td>
</tr>
<tr>
<td>A_r</td>
<td>external surface area of sphere with radius r</td>
</tr>
<tr>
<td>A_r</td>
<td>dimensionless number of Archimedes (equation (III.5))</td>
</tr>
<tr>
<td>A_v</td>
<td>the active metal in $A_v , \text{ySp}_b$</td>
</tr>
<tr>
<td>a</td>
<td>part I: constant, determined by the valency of $A_v$</td>
</tr>
<tr>
<td></td>
<td>part II: longer half axis of ellipsoid</td>
</tr>
<tr>
<td>a/b</td>
<td>axial ratio of ellipsoids</td>
</tr>
<tr>
<td>b</td>
<td>part I: constant, determined by the valency of $Sp$</td>
</tr>
<tr>
<td></td>
<td>part II: shorter half axis of ellipsoid</td>
</tr>
<tr>
<td>c</td>
<td>SO$_2$ concentration on the boundary of the shrinking core</td>
</tr>
<tr>
<td>C_c</td>
<td>SO$_2$ concentration on the outer surface of the particle</td>
</tr>
<tr>
<td>C_S</td>
<td>bulk gas SO$_2$ concentration</td>
</tr>
<tr>
<td>c_a/S</td>
<td>ratio of moles of Ca and S fed to the combustor</td>
</tr>
<tr>
<td>c</td>
<td>shorter half axis of ellipsoid</td>
</tr>
<tr>
<td>c$_0$-c$_3$</td>
<td>adjustable parameters in Wouterson's equation (9.2)</td>
</tr>
<tr>
<td>D</td>
<td>width of slit-shaped pores</td>
</tr>
<tr>
<td>D$_{eff}$</td>
<td>effective pore diffusion coefficient</td>
</tr>
<tr>
<td>D_K</td>
<td>Knudsen pore diffusion coefficient</td>
</tr>
<tr>
<td>D_s</td>
<td>diffusion coefficient in product layer</td>
</tr>
<tr>
<td>d</td>
<td>part I: sorbent particle diameter</td>
</tr>
<tr>
<td></td>
<td>part II: diameter of thin disc</td>
</tr>
<tr>
<td>d$_{pp}$</td>
<td>diameter of primary pseudoboehmite platelet</td>
</tr>
<tr>
<td>d$_{dev}$</td>
<td>deviation of the middle of the particle</td>
</tr>
<tr>
<td>E(t)</td>
<td>sorbent residence time distribution in a fluidized bed</td>
</tr>
</tbody>
</table>
F  average crushing strength  N
f  friction factor  -
f(\xi_1)  function of \xi_1, defined in equation (4.3)  -
g  acceleration due to gravity  m/s^2
H  sorbent bed height in combustor  m
i  no. of H_2O layers between primary platelets in aggregate  #
j  multiplication factor in second electroviscous effect  -
K  constant, defined by equations (5.14 and V.6)  m^3/(mol.s)
k_a  rate constant of attrition, defined by equation (III.1)  -
k_g  external mass transfer coefficient  m/s
k_i  mass flow of coal into combustor  kg coal/s
l  drag fraction: distance a dragged particle is moved, relative to the distance the dragging particle moves  -
M  molar weight of SO_3  g/mol
M'  molar weight of rate determining diffusing species  g/mol
M_i  molar weight of compound i  g/mol
M_S  molar weight of S  g S/mol S
M_0  molar weight of Ca  g Ca/mol Ca
m  mass of sorbent in fluidized bed (attrition test)  g
m_0  initial mass of sorbent in fluidized bed  g
m_i  sorbent hold-up (mass of sorbent) in combustor  ton sorbent/mol
N_A  number of Avogadro  -
n  number of particles which is tested in SRO test  #
n_1  number of moles of CaO in the reactor  #
pH  - log [H^+]  -
Q_1  molar flow of sulphur; indexes defined in fig. 5.1  mol S/s
q  number of neighbouring particles in concentrated sol  #
q_0  average q for a random close packing  #
R  (sorbent) particle radius  m
R_b  radius of bob in rheological measurements  m
R_c  radius of cup in rheological measurements  m
R_s  sulphur retention: mole S captured per mole S fed  -
r_c  radius of the shrinking core during sulphation  m
r_{CaO}  sulphation rate per mole of reactive CaO in a particle  l/s
\dot{r}_{CaO}  average r_{CaO} per mole CaO in combustor  l/s
r_p  sorbent pore radius (calculated with r_p = 2 V_p/S_{BET})  nm or m
S  surface area  m^2/g
S_{BET}  surface area, calculated by the BET method  m^2/g
$S_m$  surface area per 'molecule' of CaO  m$^2$
$Sp$  the support metal in $Av_{a}O_ySp_bO$ -
$T$  temperature  K
$Ta$  Taylor number, defined by equation II.6 -
$t$  time  s, min or h
$U$  superficial gas velocity  m/s
$U_{mf}$  minimal superficial gas velocity for fluidization  m/s
$V_e$  excess pore volume in swelling experiment  ml/g
$V_P$  sorbent pore volume  ml/g
$W$  sample weight in thermogravimetric experiment  mg
$W_0$  ibid, starting weight  mg
$W_{\infty}$  ibid, final weight  mg
$X$  either $m$ or $d$ (see comment to equation (4))  g or m
$X_{CaO}$  calcium oxide weight content of sorbent  w\%  
$X_{CaO,c}$  critical CaO weight content for monolayer dispersion  w\%
$X_s$  sulphur weight content of coal  w\%
$x$  molar ratio of excess H$_2$O to AlOOH in pseudoboehmite  mol/mol
$Y$  sorbent performance: g make-up sorbent/kg coal  g/kg coal
$y$  molar ratio of SpO to AvO in mixed oxides in general;  
and molar ratio of Al$_2$O$_3$ to CaO in calcium aluminates  mol/mol
$y_0$  intercept of y-axis in m/$m_0$ versus time plot  -
$[i]$  concentration of species $i$ in aqua  mol/L

Greek symbols

$\alpha$  attrition rate  kg/(kg.s)
$\dot{\gamma}$  shear rate  s$^{-1}$
$\Delta$  part I: dispersion factor = $D_{\text{eff}}(\text{exp})/D_{\text{eff}}(\text{theory})$ -
  app. VI: square root of area of shear plane per particle  m$^2$
$\delta$  part II: thickness of primary pseudoboehmite platelet  m
  app. VI: distance a particle is moved in an encounter  m
$\delta_i$  thickness of a monolayer for compound $i$  m
$\delta_s$  thickness of the product layer in sulphated sorbent  m
$\epsilon$  sorbent porosity  -
$\epsilon_e$  total energy, dissipated per encounter in shearing  J
$\epsilon_p$  energy, dissipated per particle per encounter in shearing  J
$\theta$  pore tortuosity  -
\[ \eta \]  

Differential viscosity of a sol 

\[ \eta_f \]  

Viscosity of surrounding fluid in concentrated sol 

\[ \eta_g \]  

Viscosity of fluidization gas

\[ \eta_r, \alpha \]  

Relative \( \eta \) at limiting low (\( a = 0 \)) and high shear (\( a = \infty \))

\[ \eta_0 \]  

Viscosity of the dispersion medium

\[ \eta_1 \]  

Sensitivity of a material to attrition

\[ \eta_2 \]  

Effectivity of energy transfer in a fluidized bed

\[ \eta_\infty \]  

Limiting viscosity at high shear

\[ \eta \]  

Intrinsic viscosity

\[ \kappa \]  

Part I: constant, defined by equation (4.4) 

Part II: inverse Debye length

\[ \rho_B \]  

Sorbet bulk or apparent density 

\[ \rho_{bed} \]  

Density of a fluidized bed

\[ \rho_i \]  

Solid density of compound \( i \)

\[ \rho_g \]  

Density of fluidization gas

\[ \rho_{pb} \]  

Density of pseudoboehmite

\[ \rho_s \]  

Sorbet solid or skeletal density

\[ r \]  

Part I: residence time of gel particles in NH\(_3\) solution 

Part II: shear stress

\[ r_B \]  

Extrapolated Bingham yield stress 

\[ r_1 \]  

Average sorbent residence time in the combustor 

\[ r_0, r_0 \]  

Extrapolated yield stress

\[ \phi \]  

Volume fraction of particles in a sol

\[ \phi' \]  

Effective volume fraction, corrected for solvent layers

\[ \phi'' \]  

Ibid, corrected for second electroviscous effect

\[ \phi_a \]  

Volume fraction of aggregates in sol

\[ \phi_i \]  

Molar flow of calcium; indexes defined in fig. 5.1

\[ \phi_{max, \alpha} \]  

Maximum \( \phi \) at limiting low (\( a = 0 \)) or high shear (\( a = \infty \))

\[ \phi_p \]  

Molar flux of sulphur per spherical particle

\[ \phi_{pp} \]  

Volume fraction of primary particles in sol

\[ \phi_{v, out} \]  

Volumetric gas flow out of combustor 

\[ \Xi \]  

Moles of CaO in regenerated particle per mole Ca

\[ \xi_1 \]  

Conversion of CaO in a particle

\[ \xi_1 \]  

Average conversion of CaO to CaSO\(_4\) in sulphation

\[ \xi_2 \]  

Average conversion of CaSO\(_4\) to CaO in regeneration

\[ \Omega \]  

Angular velocity of the bob in rheological experiment
In the introduction of this thesis (I.0), the contemporary energy supply problem is sketched, and clean coal combustion is given as an alternative. A favourable process for clean coal combustion is fluidized bed combustion (FBC), amongst others, because it gives the opportunity for regenerative desulphurization. In regenerative desulphurization, a sorbent is used to capture sulphur oxides in situ in the combustor at 850°C. Converted sorbent is transported to a second reactor, where reducing conditions are applied to regenerate it. The regenerated sorbent is again fed to the combustor, while the sulphur-rich regenerator off-gas is used to produce sulphuric acid. This minimizes both SOX emissions, and soil contamination by spent sorbent.

Existing sorbents cannot meet the severe demands of this process. The two main problems are the nonselective regeneration at 850°C, and the strong particle attrition during fluidization and transport, which causes sorbent loss and dust problems. The objective of this research is to develop a sorbent which can successfully be used in regenerative desulphurization.

It appears that only certain mixed oxides are, at 850 °C, capable of both capturing SOX under oxidizing conditions, and releasing it under reducing conditions (I.1). Taking into account the demands on availability and on mechanical and thermal stability, calcium alumimates (CaO-yAl2O3) are the most promising of oxides. They easily react into CaSO4 in the combustor. During regeneration at 850°C, this CaSO4 reacts to calcium aluminate rather than to CaS. This is the reason for the good regeneration selectivity.

When sorbents contain more alumina (Al2O3) than the equivalent for calcium aluminate formation, the alumina can act as a strong, porous support for the calcium aluminate. Often, such sorbents are referred to as CaO on alumina. Alumina exists in several crystal forms, of which α-Al2O3 and γ-Al2O3 are the most important. Rather than α-Al2O3, the state-of-the-art at the start of this research, we have employed γ-Al2O3 as a support. The latter has a much larger surface area. Consequently, the CaO, and the CaSO4 formed during combustion, can be much better dispersed over the surface as compared to α-Al2O3. This means that no or little solid-solid diffusion is necessary for the regeneration reaction between CaSO4 and γ-Al2O3, so that calcium
aluminates can be formed easily. When solid-solid diffusion is needed, as is the case for $\alpha$-Al$_2$O$_3$ supported sorbents, relatively more CaS is formed.

$\gamma$-Al$_2$O$_3$ is, however, intrinsically less strong than $\alpha$-Al$_2$O$_3$. It is necessary to use a sorbent preparation technique which yields (preferentially spherical) strong, porous, particles. A modification of a sol-gel method appeared to be the most promising technique for this goal (1.2).

In this sol-gel method (1.3), a pseudoboehmite (AlOOH.xH$_2$O) sol is dropped through an oil layer, where the droplets spherulize, into an aqueous NH$_3$ solution. There the spherulized droplets 'gelate'. We have invented a variation of this process, in which a calcium salt is dissolved in the NH$_3$ solution. Then, the gel particles are impregnated during the gelation: in situ impregnation. The gel particles are dried, and calcined at 850$^\circ$C, to yield strong, porous $\gamma$-Al$_2$O$_3$ beads containing CaO.

The CaO in sorbents, prepared by in situ impregnation, is dispersed on the internal surface as a mono(molecular) layer (1.4). This is concluded from the succes of the shrinking core model in describing the sulphation reaction for sorbents containing (less than) the equivalent of a monolayer. The model should only hold for such cases, because product layer diffusion is not taken into account. Under circumstances where product layer diffusion must occur, the shrinking core model yields incorrect results. Together with a number of other arguments, this is sufficient evidence for the monolayer concept. The monolayer dispersion also enables a very good regeneration, so that the sorbent can be used successfully for many cycles in regenerative desulphurization. This is proven in fixed and in fluidized bed reactors.

Together with the low attrition rates of in situ impregnated sol-gel sorbents, this demonstrates the technological feasibility of regenerative desulphurization. Large scale cyclic experiments are beyond the scope of this research, but the sorbent performance can be estimated with ReSuLT (1.5). This is a model for Regenerative deSulphurization at Low Temperature. It is based on the shrinking core model, mentioned above, and a simple attrition model which is only valid when low attrition technology is used. ReSuLT yields the sorbent performance - the amount of make-up sorbent per kg of coal fed to the combustor - as a function of the sorbent properties.

With ReSuLT, it is shown that the optimum sol-gel sorbent performs at least 6 times better than other types of sorbent (1.6). Yet, even this most optimal sorbent cannot compete economically with non-regenerative desulphurization using limestone. Per kWh of electricity, the costs are 0.64-0.68 10$^{-2}$ Dfl and 0.23-0.34 10$^{-2}$ Dfl, respectively. The sorbent costs for the two
processes only reach the same level, when the spent sorbent is regarded as chemical waste, and the dumping costs are increased accordingly. When this provokes large scale production of sol-gel sorbent, the price of the latter will decrease, making regenerative desulphurization even more attractive. Before this can happen, however, the political decision to increase dumping costs must be made, and low attrition technology must be developed.

In the second part of this thesis (II), the new sol-gel process with in situ impregnation is examined in more detail. The objective is to improve the process control and product quality by a better understanding of the underlying physical chemistry.

The sol-gel method starts with a pseudoboehmite sol. The primary pseudoboehmite particles (II.7) have a crystal structure which causes them to be anisotropic, both in geometry and in chemistry. The platelets (diameter ≈ 25 nm, thickness ≈ 3 nm) have faces that take up protons more readily than the edges. The platelets form aggregates, in which they are packed face to face.

To obtain more details on these aggregates, rheological experiments are performed. First, a model is developed to link the geometrical and interaction properties of the flow units to the rheology of the dispersion (II.8). The model combines the results of Krieger et al. and of Stein et al. on the limiting viscosity at high shear. This parameter can be calculated from the (actual) volume fraction, axial ratio and interaction strength of the flow units in the sol. The interaction strength is an empirical parameter.

The calculations show (II.9), that the aggregates are the flow units in the sol. They are needle-like, with an axial ratio of 7 ± 3 and a width of one primary particle: 25 nm. They consist of 6-7 parallel strings of primary platelets. Due to the very regular packing inside the aggregates, the anisotropic chemistry of the primary particles is transferred to the aggregates, explaining the typical rheological behavior for varying acid concentration.

A semi-stable sol can be made at pH = 3, when the ion concentration is not too high to cause destabilization. This sol is easily dropped into the oil layer, where the droplets spherulize to minimize their surface area. Falling further into the ammonia solution, the droplets remain intact, perhaps because an oil film is formed around them (II.10). Addition of a suitable surfactant ensures that the droplets keep their advantageous spherical
shape, since they don't get a chance to deform while rapidly passing the oil-water interface.

The NH₃ causes an increase of the pH in the sol droplets, removing the stabilizing surface charge. This causes fast and strong flocculation. The total ion concentration is too high to allow reptetization at the higher pH.

During gelation, syneresis of the gel particles takes place. The osmotic imbalance across the gelated skin of the particle aids this process, which causes a loss of pore volume and consequently an increase in strength. This 'osmotic syneresis' is more important when salt is added to the ammonia solution. It can be used to control the pore volume, though care must be taken to avoid stresses and cracking. The osmotic imbalance itself is easily controlled, e.g. by adding 'indifferent' solutes to the sol.

The Ca²⁺ ions adsorb specifically onto the boehmite surface. Because they are bivalent, these ions form bridges by adsorbing on two platelets. These bridges rigidify the gel skin, and make it more sensitive to fast shrinkage. This makes it necessary to dry impregnated gels slower than nonimpregnated gels can be dried. An advantage of slow drying is that it enables the formation of a very flat concentration profile of the calcium over the particle. Together with the specific adsorption, this ensures the very good dispersion of the calcium.

After drying, the inter-aggregate pores remain as non-connected pores in a dry gel, which contains no macropores, but only the slit-shaped intra-aggregate pores. Part of the latter collapse during calcination at 850°C. This creates pores that reconnect the remaining inter-aggregate pores, so that a rather uniform pore size distribution exists in the calcined sorbent beads. The more CaO is present, the larger the resulting pores are.

The uniform pore size distribution is an important factor in determining the remarkable strength of the sol-gel sorbent beads. There are no significant local differences in the number of contacts between the aggregates. Thus, when the formation of cracks is avoided during the three shaping steps (gelation, drying and calcination), no weak spots occur in the beads. Combined with a good contact strength, due to calcium aluminate bridges, this ensures a very good particle strength.

It is concluded that in situ impregnation during sol-gel preparation enables a tailor made preparation of sorbents and of catalysts. We have the physico-chemical tools to control the particle strength and porosity, its shape, and the dispersion of the active component.
SAMENVATTING

Je ziet het bos verzuren bij het uur (.)
er zit teveel azijn in het azuur

Kees Stip


Bestaande adsorbentia kunnen echter niet gebruikt worden voor zo'n proces. De twee voornaamste problemen zijn de niet selectieve regeneratie bij 850°C en de sterke deeltjesluchtage in het wervelbed en tijdens transport van reactor naar reactor. Deze deeltjesluchtage veroorzaakt verlies van adsorbent en stofproblemen. Het doel van dit onderzoek is het ontwikkelen van een adsorbent wat wel kan worden gebruikt voor regeneratieve ontzwarend.

Het blijkt dat alleen bepaalde mengoxide in staat zijn om bij 850°C onder oxiderende omstandigheden zwavel af te vangen, en dit onder reducerende omstandigheden weer af te staan. Als rekening wordt gehouden met de beschikbaarheid en de thermische en mechanische stabiliteit, dan blijken calcium aluminaten (CaO·yAl₂O₃) het meest geschikt als regeneratief adsorbent. Als er een overmaat aan alumina (Al₂O₃) is in dergelijke adsorbentia, dan gedraagt dit alumina zich als een sterke, poreuze drager. We spreken meestal van CaO op alumina. Alumina bestaat in verschillende kristalvormen, waarvan α-Al₂O₃ en γ-Al₂O₃ het belangrijkste zijn. Tot het begin van dit onderzoek werd alleen α-Al₂O₃ toegepast voor deze doeleinden omdat het erg sterk is. Hoewel CaSO₄ op α-Al₂O₃ thermodynamisch gesproken calcialuminaat op zou moeten leveren tijdens regeneratie bij 850°C, blijkt dit pas bij 1050°C werkelijk te gebeuren. Regeneratie bij zulke hoge temperaturen is economisch gezien onaantrekkelijk en kan sinteren van het sorbent veroorzaken. De oorzaak is het kleine porieoppervlak van α-Al₂O₃. Daardoor moet het CaO, en
het daaruit gevormde CaSO₄, in tamelijk grote kristallieten verdeeld zijn over dat oppervlak. Om dan tot calciumaluminaat te kunnen regenereren, is vaste stof-diffusie noodzakelijk. Bij 850°C is dat een traag proces, zodat de vorming van calciumaluminaten traag verloopt, en de reactie tot calciumsulfide de kans krijgt om op te treden.

Dit probleem is opgelost door γ-Al₂O₃ toe te passen, wat een veel groter porieoppervlak bezit. Selektieve regeneratie kan dan ook worden bereikt door het CaO goed te verdelen over het beschikbare oppervlak. γ-Al₂O₃ is echter minder sterk dan α-alumina. Voor het maken van relatief sterke, bolvormige γ-Al₂O₃ deeltjes met een goede verdeling van het CaO over het oppervlak, bleek een sol-gel methode het meest geschikt (I.2).

Bij deze sol-gel methode (I.3) wordt een pseudoboehmiet (AlOOH.xH₂O) sol gedruipd door een olielaag in een ammoniapoplossing. In de olielaag vormen de druppeltjes om tot perfecte bollen, die vervolgens in de ammoniapoplossing 'gelopen'. Onze aanpassing van dit proces [1] behelst het oplossen van een calciumzout in de ammoniapoplossing. Tegelijkertijd met de gelering zal dan impregmatie met calciumionen plaatsvinden. We noemen dit proces in situ impregnatie. De geldeeltjes worden gedroogd en gecalcineerd bij 850°C, wat sterke, poreuze γ-alumina kralen oplevert, die voldoende CaO bevatten.

Het blijkt dat dit CaO ten gevolge van de in situ impregnatie als een mono(moleculaire) laag over het alumina oppervlak is verdeeld (I.4). Deze conclusie berust op het gedeeltelijke succes van het zogenaamde shrinking core (krimpende kern) model bij het beschrijven van de inzwaveling van sol-gel adsorbentia. Dit model houdt geen rekening met diffusielimitering door de productlaag. Als er een productlaag wordt gevormd waardoor een diffuse moet plaatsvinden, dan bepaalt dit vaste stof-diffusie de snelheid van de inzwaveling. In geval van een monolaag kan productlaagdiffusie uiteraard niet plaatsvinden. Dan wordt verwacht dat het shrinking core model de inzwaveling accuraat beschrijft. Dit blijkt correct te zijn voor sol-gel sorbents die minder calciumoxide bevatten dan in een monolaag past. Wordt er echter meer calciumoxide dan de monolaagcapaciteit van het sorbent geïmpregneerd, dan moet productlaagdiffusie optreden om al het CaO om te zetten. Zodra dat het geval is, beginnen er afwijkingen van het shrinking core model op te treden. Kennelijk is er bij lagere beladingen inderdaad sprake van een monolaag-verdeling. Ook andere argumenten wijzen in deze richting.

De monolaagverdeling besposdigt niet alleen de inzwaveling, maar ook de regeneratie, immers, ook daar is het vermijden van vaste stof-diffusie van
belang. Testen in thermogravimetrische apparatuur en in vast bed en wervelbed reactoren bewijzen dan ook dat sol-gel adsorbentia, gemaakt met in situ impregnatie, uitstekend geschikt zijn voor regeneratieve ontzwalveling, ook wat betreft hun attritiegedrag (appendix III).

Regeneratieve ontzwalveling op grotere schaal was niet haalbaar binnen dit project. Om toch uitspraken te kunnen doen over de kwaliteit van het sol-gel adsorbent, afgezet tegen andere synthetische adsorbentia en ook tegen eenmalig te gebruiken kalksteen, is ReSuLT ontwikkeld (I.5). ReSuLT is een model voor de regeneratieve ontzwalveling bij lage temperatuur. Het is gebaseerd op het shrinking core model en een simpel attritiemodel dat alleen geldig is als er technologie wordt toegepast waarbij attritie wordt gemanageerd. Met ReSuLT wordt de adsorbentkwaliteit (de hoeveelheid vers adsorbent nodig per kg steenkool voor een 100 MWe elektriciteitscentrale) berekend als functie van de sorbenteigenschappen. Zoals te verwachten was, blijken vooral de attritiesnelheidsconstante en de verdelingsgraad van het CaO van belang voor de kwaliteit van het adsorbent.

Dientengevolge zijn via het sol-gel proces met in situ impregnatie geproduceerde adsorbentia minstens een factor 6 beter dan andere adsorbentia (I.6). Maar ook het meest optimale sorbent kan, economisch gesproken, niet concurreren met kalksteen dat eenmalig wordt gebruikt. Per kWh elektriciteit zijn de sorbentkosten respectievelijk 0.64-0.68 10^{-2} Dfl en 0.23-0.34 10^{-2} Dfl. Alleen als het verbruikte sorbent als chemisch afval wordt beschouwd, en de stortkosten daardoor drastisch verhogen (ongeveer een factor 5), dan worden de sorbentkosten van beide ontzwalvingsmethoden vergelijkbaar. Als dat leidt tot een grootschalige produktie van sol-gel adsorbentia, dan zal de prijs daarvan dalen, en regeneratieve ontzwalveling nog beter concurreren. Voordat dat het geval is, moet er echter eerst de politieke beslissing genomen worden om de stortkosten te verhogen, en moet bovendien de technologie worden ontwikkeld, waarbij attritie wordt gemanageerd.

In het tweede deel van dit proefschrift (II) wordt de nieuwe sol-gel technologie met in situ impregnatie nader onderzocht. Het doel hiervan is het verbeteren van procesbeheer en van productwaliteit door een beter fysisch-chemisch begrip.

De sol-gel methode gebruikt pseudoboehmiet. Door de specifieke kristalstructuur van dit materiaal zijn de primaire kristallieten anisotropisch,
zowel wat betreft hun geometrie, als wat betreft hun chemie. De vlakken van de primaire plaatjes (diameter ≈ 25 nm, dikte ≈ 3 nm) adsorberen gemakkelijker protonen dan de randen. De plaatjes vormen aggregaten, waarin ze parallel (vlak op vlak) gestapeld zijn.

Om meer informatie betreffende deze aggregaten te verkrijgen is reologie toegespist op het sol. Allereerst is een model ontwikkeld waarin de eigenschappen van de stromende deeltjes (de ‘flow units’), wat betreft hun geometrie en hun interactiegewicht, verbonden wordt aan de reologie van de suspensies (II.8). Het model combineert de resultaten van Krieger et al. en van Stein et al. over de limiterende viscositeit bij hoge afschuifsnelheid. Deze parameter kan worden gecorrereerd aan de effectieve volume fractie, de ellipsoidaliteit en de interactiesterkte tussen de ‘flow units’. De interactiesterkte is een empirische parameter.

Berekeningen tonen aan dat de aggregaten de ‘flow units’ in het sol zijn. Deze zijn langwerpig, met een assenverhouding van 7 ± 3 en een dikte van een primair plaatje: 25 nm. Ze bestaan uit 6 tot 7 lagen van parallele primaire plaatjes. Deze regelmatige stapeling is er de oorzaak van dat de anisotropie van de primaire deeltjes wordt overgebracht op de aggregaten. Dit verklaart het merkwaardige reologische gedrag als functie van het zuurgehalte van het sol.

Een semi-stabiel sol kan worden gemaakt bij pH ≈ 3, waarbij de ionenconcentratie nog voldoende klein is om destabilisatie te voorkomen. Dit sol kan gemakkelijk worden gedruipd in een olielaag, waar de druppels omvormen tot bolletjes om hun oppervlak te verminderen. De druppels blijven intact als ze door het grensvlak olie-ammoniakoplossing heen vallen. Wellicht speelt hierbij een rol dat er een oliefilm rond de vallende druppels wordt gevormd, die die druppels voldoende tijd geeft om enigszins te gelenen, alvorens in direct contact te komen met de ammoniakoplossing. Toevoegen van een geschikte oppervlakteactieve stof bewerkstelligt dat de voordelige bolvorm blijft behouden als de druppels door het grensvlak heenvallen, omdat dat zo snel gaat dat ze geen kans krijgen te vervormen.

Het ammoniak veroorzaakt een toename van de pH in het sol en neemt daardoor de stabiliserende oppervlakkelading weg. Daardoor vlokt het sol snel en sterk uit. Bij de hoge vaste stof gehalte die worden gebruikt, levert dit een sterk geldeeltje op. De ionenconcentratie is zo hoog bij de hoogste pH’s die worden bereikt dat repeptisatie onmogelijk is.
Tijdens de gelering treedt osmotische synerese op. Er is een verschil in osmotische druk tussen het sol en de ammoniakoplossing, hetgeen leidt tot krimpen van het gel, en dus tot een kleiner porievolume en een sterker produkt. De osmotische imbalans kan worden beheerst, onder andere door het toevoegen van 'indifferenten' stoffen aan het sol. Daarmee kan het uiteindelijke porievolume worden gestuurd, onafhankelijk van het gewenste gehalte aan geimpregneerd materiaal. Dit laatste wordt beheerst met de impregnatieconcentratie en verblijftijd tijdens de geleringsstap.

De geimpregneerde (calcium)ionen adsorberen specifiek op de, in het gel, negatief geladen pseudoboehmit oppervlakken. Polyvalente ionen kunnen op die manier bruggen vormen, die het gel verstevigen. Dit heeft tot gevolg dat het langzamer moet worden gedroogd om spanningen en scheuren te vermijden. Een bijkomend voordeel van de langzame droging is dat dit de kans geeft op het ontwikkelen van een zeer uniform calciumprofiel over het drogende deeltje. Tezamen met de specifieke adsorptie veroorzaakt dit de zeer goede verdeling van het actieve materiaal over het alumina oppervlak.

Het gedroogde gel bevat twee typen poriën: spleetvormige poriën, die voortkomen uit de ruimtes in aggregaten, en inkpot-poriën die overgebleven zijn van poriën tussen de aggregaten. Tijdens calcineren bij 850 °C storten de spleetvormige poriën zodanig in, dat een tamelijk uniforme porisgroottesverdeling overblijft.

Deze uniforme verdeling is een belangrijke factor voor de sterkte van het gecalcineerde deeltje. Het houdt in dat er geen significante lokale verschillen in aantallen contactpunten bestaan. Dus bevatt het deeltje geen zwakke plekken (als het wordt vermeden dat tijdens de vormgevingsstappen haarscheyrtjes ontstaan). Omdat de calciumaluminaat bruggen bovendien ervoor zorgen dat de contactpunten erg sterk zijn, resulteren sterke, poreuze deeltjes.

De conclusie is dat met in situ impregnatie tijdens de sol-gel bereiding sorbent- (of katalysator)deeltjes kunnen worden gemaakt met een goede bolvorm, sterkte, porositeit en verdeling van het actieve materiaal. Bovendien kunnen deze eigenschappen fysisch-chemisch worden gestuurd, wat de mogelijkheid levert 'tailor-made' katalysatoren en sorbentia te maken.
CURRICULUM VITAE

At the end there was a sort of examination; as with a modern Ph.D., everyone who stayed the course seems to have passed.

But this somewhat unattractive prospect did not put students off. (...) The training was in fact vocational, and jobs lay at the end.

C.P. Snow