REGENERATIVE SULFUR CAPTURE IN FLUIDIZED BED COMBUSTION OF COAL: A FIXED BED SORPTION STUDY
REGENERATIVE SULFUR CAPTURE IN FLUIDIZED BED COMBUSTION OF COAL: A FIXED BED SORPTION STUDY

Proefschrift

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Ericus Henricus Petrus Wolff

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Dit proefschrift is goedgekeurd door de promotoren:

prof. drs. P.J. van den Berg
prof. ir. C.M. van den Bleek

Toegevoegd promotor: Dr. ir. A.W. Gerritsen
Aan mijn familie
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CURRICULUM VITAE
Summary and Main Conclusions

Fluidized bed combustion is a technique to produce energy from coal. One of the advantages is the in-situ removal of sulfur oxides by feeding sorbents like limestone or dolomite together with the coal. At the combustion temperature of 850°C, the sulfur oxides react with the sorbent and form a solid sulfate. If this spent sorbent is dumped at sea or used as a landfill, the original air pollution problem is transferred into a soil pollution problem. Multi cyclic utilization by regeneration of the sorbent would greatly reduce the quantity of solid waste to be disposed. Unfortunately, limestone and dolomite cannot meet the requirements for such a regenerative process.

At the Delft University of Technology, a low temperature regeneration process is developed, based on a synthetic sorbent which combines a relative low regeneration temperature (850°C) with a high particle strength. The main targets of the project elaborated in this thesis are:

(1) to test whether or not the sorbent is suitable with respect to the chemistry for cyclic regenerative desulfurization in the fluidized bed combustion of coal.

(2) to define the optimal process conditions for the regeneration step. Emphasis is laid on a low temperature process at 850°C and 1 bar. The sorbent is tested on its ability to produce a SO₂ rich (3-11 vol%) off-gas during the regeneration step.

(3) to define and quantify the process phenomena (mass/heat transfer and kinetics) with application of a mathematical model which describes the sulfur capture process.

(4) to test the sorbent on its resistance towards attrition.

(5) to present an economic evaluation.

The requirements for a low temperature regenerative process can be met using a sorbent (type/code SG105) consisting of CaO (8.2 wt%) on a 3.1 mm γ-Al₂O₃ support. The sorbent is prepared by the sol-gel method which enables the active compound to be highly dispersed in the sorbent. After calcination
at $850^\circ$C, the sorbent does not simply consist of CaO on the alumina support but active calcium aluminates are formed. Thermodynamics show that the sulfated synthetic sorbent can be regenerated with reducing gas at much lower temperatures ($850^\circ$C) to CaO/$\gamma$-Al$_2$O$_3$ and SO$_2$ than pure CaSO$_4$ ($1100^\circ$C).

The chemistry and kinetics of cyclic sulfation and regeneration are tested in a 12 mm ID fixed bed reactor. Both the desulfurization and regeneration steps are performed using a standard gas. At $850^\circ$C and 1 bar, the sorbent is sulfated by a gas flow containing 0.25 vol% SO$_2$ and 4 vol% O$_2$ in N$_2$ and regenerated by a gas flow containing 25 vol% H$_2$. These conditions are referred to as the standard conditions. By monitoring the outlet SO$_2$ concentration as a function of time, the so-called breakthrough curves are obtained. These curves provide the information on the sulfur capture and regeneration performance of the sorbent at the specific process conditions applied.

It is found that regeneration is a fast process and that it is less attractive to use CO than H$_2$. The addition of H$_2$O or CO$_2$ is favourable for the regeneration performance of the sorbent as it decreases the amount of a by-products; CaS. The sulfur recovery process applied after the regenerator determines whether or not an increased amount of H$_2$S or COS is profitable. A 10 cycles experiment at standard conditions shows that hardly any loss in reactivity is measured from the second cycle onward. The efficiency to SO$_2$ is approximately 65%. During regeneration, up to 15 vol% of SO$_2$ is obtained in the off-gas from the fixed bed reactor. Calcined limestone is not regenerable at the standard conditions applied.

A shrinking unreacted core model (SURE2) is proposed to describe the sulfation process. It is shown that during the sulfur capture stage SO$_3$ is formed. The rate of CaO conversion is first order with respect to SO$_3$ and proportional to the external surface area of the core. Both the shell diffusion and the chemical reaction rate are described by only one parameter each; $d_{SO_2,\text{shell}}$ and $k_S$ respectively. Experiments are performed in the fixed bed reactor at different superficial gas velocities, SO$_2$ concentrations, O$_2$ concentrations and particle diameters. The results obtained with SG105 sorbent are in good agreement with the model by using $d_{SO_2,\text{shell}} = (7.53 \pm 0.60) \times 10^{-7} \text{ m}^3 / \text{(m particle s)}$ and $k_S = (0.149 \pm 0.033) \text{ m}^3 / \text{(m$^2$ core s)}$. A reduction of the particle diameter by more than a factor of two, surpasses the kinetics of this model. The value for the effective pore diffusion coefficient is within the range, being $2.3 \times 10^{-7}$–$1.2 \times 10^{-6} \text{ m}^3 / \text{(m particle s)}$, that can be estimated from physical data of the sulfated sorbent.

Electron-Probe X-ray Microanalysis (EPMA) of the SG105 sorbent, sulfated in a thermobalance for varying time, provides an extra validation for the validity of the SURE2 model. A more or less step-wise penetration of the sulfur is observed as predicted by the model for the same value of the parameters. The SURE2 model can thus serve as an engineering tool for fluidized bed combustor design to improve sulfur capture performance.

Single-particle crushing strength tests show that the SG105 sorbent is much stronger than (calcined) limestone. The crushing strength is unaffected by the cyclic sulfur capture process. Impact tests with a gas gun show that
at 7 m/s about 31 wt% of the original SG105 sorbent fraction of 2.8–3.4 mm breaks. The amount of broken sorbent with a diameter below 1.2 mm is 1 wt%. However, at increasing impact velocity, the breakdown fraction increases up to 85 wt% at 21 m/s, 14 wt% being smaller than 1.2 mm.

Multi-particle fluidized bed tests show that a thermal shock from ambient temperature to 850°C, applied to lime or SG105, causes a negligible net mass reduction of the fraction 2.8–3.4 mm. The synthetic SG105 sorbent has a much higher resistance to attrition by fluidization than lime. Based upon the final attrition rate of SG105 at 850°C, approximately 200 cycles at an (arbitrarily chosen) sorbent residence time of 50 h per cycle are possible with respect to attrition by fluidization. The resistance of SG110 sorbent (quite similar to SG105 sorbent but prepared in another production run) towards attrition by coal combustion needs further research. Of the original 2.8–3.4 mm SG110 sorbent 25 wt% reduced in size by 3.3 h coal combustion, with 2 wt% becoming smaller than 1.4 mm. It is concluded that the texture of the sorbent is only changes a little bit by thermal shock, fluidization and coal combustion together.

An economic analysis shows that the cost of SO₂ removal using the regenerative process proposed increases about three times compared with a once-through process using conventional sorbent. The influence of cost determining factors (sorbent cost, calcium content, make-up fraction and regeneration cost) are presented. At least a threefold increase in the cost of limestone, including costs for gypsum disposal, is necessary to make the regenerative process economically feasible. Although the short term interest of many SO₂ emitting companies is focussed on once-through processes, offering an immediate solution to the emission problem, long term solutions should be found in regenerative processes with sulfur recovery.
Samenvatting en Voornaamste Conclusies

Wervelbedverbranding is een methode voor de opwekking van energie uit steenkool. Een van de voordelen is het ter plaatse afvangen van de zwaveloxiden door sorbentmaterialen, zoals kalksteen of dolomiet, samen met de steenkool toe te voegen. Bij de verbrandingstemperatuur van 850°C reageren de zwaveloxiden met het sorbent en wordt een vast sulfaat gevormd. Wanneer dit gebruikte sorbent in zee gedumpt wordt of op land gestort, is het oorspronkelijke luchtverontreinigingsprobleem verplaatst naar een bodemverontreinigingsprobleem. Meervoudig gebruik door middel van regeneratie van het sorbent zou de hoeveelheden vast afval verminderen. Helaas voldoen kalksteen en dolomiet niet aan de eisen van zo'n regeneratief proces.

Aan de Technische Universiteit Delft is een regeneratief proces ontwikkeld dat gebaseerd is op een synthetisch sorbent. Dit sorbent is te regenereren bij de relatief lage temperatuur van 850°C. Bovendien is het sorbent mechanisch sterk. De belangrijkste aandachtsgebieden van het project, uitgewerkt in dit proefschrift, zijn:
(1) Testen of het sorbent geschikt is wat betreft de chemie voor de regeneratieve ontswaveling bij de wervelbedverbranding van steenkool.
(2) De optimale procescondities van de regeneratiestap vast te stellen. Daarbij ligt de nadruk op een proces bij de lage temperatuur van 850°C en 1 bar. Het sorbent is getest op de mogelijkheid om bij regeneratie een SO₂-rijk (3-11 vol%) afgas te verkrijgen.
(3) De snelheidsbepalende stappen (stof/warmte transport en kinetiek) vast te stellen en te kwantificeren door middel van een mathematisch model dat de zwavelvangst beschrijft.
(4) Het sorbent te testen op zijn weerstand tegen attritie.
(5) Een beschouwing te geven van de economie van het proces.

De eisen voor een lage temperatuur regeneratief proces kunnen bereikt worden met behulp van een sorbent (type/code SG105) dat bestaat uit CaO (8.2 gew%) op een 3.1 mm γ-Al₂O₃ drager. Het sorbent is bereid via de sol-gel
methode waarmee het mogelijk is de actieve component zeer dispers verdeeld op de drager aan te brengen. Na calcinatie bij 850°C bestaat het sorbent dan ook niet eenvoudig uit CaO op drager, maar zijn er actieve calciumaluminaten gevormd. De thermodynamica laat zien dat het gesulfateerde synthetisch sorbent geregenerereerd kan worden met reducerend gas bij veel lagere temperaturen (850°C) naar CaO/γ-Al₂O₃ en SO₂ dan puur CaSO₄ (1100°C).

De chemie en kinetiek van cyclische sulfatatie en regeneratie zijn getest in een vast bed reactor met een inwendige diameter van 12 mm. Voor onttwisting en regeneratie werd gebruik gemaakt van standaard gassen. Het sorbent is ingezwaveld door een gas dat 0.25 vol% SO₂ en 4 vol% O₂ in N₂ bevat. Het werd geregenerereerd door middel van een gas bestaande uit 25 vol% H₂ in N₂. Deze condities worden de standaardcondities genoemd. Door de SO₂ concentratie aan de uitgang van de reactor te meten als functie van de tijd worden de zogenaamde doorbraakcurven verkregen. Deze curven leveren de informatie over het onttwisting- en regeneratiegedrag van het sorbent bij de specifieke procesomstandigheden die werden toegepast.

Gevonden werd dat de regeneratie snel is en dat het minder aantrekkelijk is om CO te gebruiken dan H₂. Het toevoegen van H₂O of CO₂ is gunstig voor het regeneratiegedrag van het sorbent omdat de hoeveelheid van een gevormd bijprodukt, CaS, afneemt. Het type proces voor de terugwinning van de zwavel na de regenerator bepaalde of een toegenomen hoeveelheid gevormde H₂S of COS aantrekkelijk is. Een 10-cyclus experiment bij standaard condities toont aan dat er nauwelijks enig verlies is in de gemeten reactiviteit na de tweede cyclus. Het regeneratierendement naar SO₂ is ongeveer 65%. Tijdens de regeneratie is maximaal 15 vol% SO₂ bereikt in het afgas van de vastbed reactor. Gecalcineerd kalksteen blijkt niet regenereerbaar bij de toegepaste standaardcondities.

Een "shrinking unreacted core" model (SURE2) wordt voorgesteld om de sulfatatie te beschrijven. Het is aangetoond dat tijdens de onttwisting SO₃ wordt gevormd. De snelheid van omzetting van CaO is eerste orde in SO₃, en evenredig met het buitenoppervlak van de ongereageerde kern. Zowel de productlaagdiffusie als de reactiesnelheid worden elk beschreven met slechts een parameter, respectievelijk $D_{SO_3}$, $k_s$. Experimenten werden verricht in een vast bed reactor bij verschillende superficie gasnennheid, SO₂-concentratie, O₂-concentratie en deeltjesdiameter. De resultaten die werden verkregen met SG105 sorbent zijn goed in overeenstemming met het model voor $D_{SO_2,shell} = (7.53 \pm 0.60) \times 10^{-7} \text{ m}^3/\text{m^2 deeltje s}$ en $k_s = (0.149 \pm 0.033) \text{ m}^2 \text{ gas/} (\text{m}^2 \text{ kern s})$. Bij een deeltjesdiameterreductie van meer dan een factor twee gaat het model niet meer op. De waarde voor de effectieve poriediffusiescoefficient ligt binnen de range $2.3 \times 10^{-7} - 1.2 \times 10^{-5} \text{ m}^3 \text{ gas/} (\text{m}^2 \text{ deeltje s})$, die op grond van fysische data van het gesulfateerde sorbent berekend wordt.

Electron-Probe X-ray Microanalysis (EPMA) van het SG105 sorbent dat voor varierende periodes gesulfatereerd is in een thermobalans, voorziet in een extra bevestiging van het SURE2 model. Een min of meer stapsgewijze penetratie van het zwavel wordt waargenomen, zoals voorspeld door het model voor dezelfde waarde van de parameters. Het SURE2 model kan dus dienen als een "engineering tool" bij het ontwerp van wervelbedinstallaties om de zwavelvangst te verbeteren.
Breeksterkte metingen van een deeltje tonen aan dat het SG105 sorbent sterker is dan (gecalcineerd) kalksteen. De breeksterkte is niet afgenomen door de regeneratieve zwavelvangst. Botsingsproeven met een pneumatisch kanon laten zien dat de originele fractie 2.8-3.4 mm SG105 sorbent ongeveer 31% breekt bij 7 m/s. De hoeveelheid gebroken sorbent met een diameter kleiner dan 1.2 mm is 1 gew%. Echter, bij een toenemende botsingssnelheid neemt de hoeveelheid gebroken materiaal toe tot 85 gew% bij 21 m/s, terwijl 14 gew% dan kleiner is dan 1.2 mm.

Wervelbed-testen tonen aan dat een "thermal shock" van kamertemperatuur naar 850°C, toegepast op gecalcineerd kalksteen of SG105, een verwaarloosbare massa reductie teweegbrengt van de fractie 2.8-3.4 mm. Het synthetische sorbent SG105 heeft een veel hogere weerstand tegen attritie door fluidisatie dan gecalcineerd kalksteen. Gebaseerd op de attritie in SG105 bij 850°C zijn ongeveer 200 cycli bij een sorbent verblijftijd van 50 h per cyclus mogelijk. De weerstand van SG110 sorbent (een zelfde soort sorbent als SG105 maar tijdens een andere produktiecyclus gemaakt) tegen attritie door steenkoolverbranding moet nader onderzocht worden. Van de originele fractie 2.8-3.4 mm SG110 was 25 gew% gereduceerd tot een kleinere diameter na 3.3 uur steenkoolverbranding, terwijl 2 gew% kleiner was dan 1.4 mm. De textuur van het sorbent veranderde slechts weinig als gevolg van thermal shock, fluidisatie en steenkoolverbranding.

Een economische evaluatie laat zien dat de kosten van SO₂ verwijdering met behulp van een regeneratief proces ongeveer een factor drie hoger is dan op basis van een eenmalig sorbent. De invloed van de kostenbepalende factoren (sorbentkosten, calcium gehalte, aan te vullen fractie en regeneratie kosten) worden gepresenteerd. Tenminste een drie-voudige verhoging in de kosten van kalksteen, inclusief gipsverwerking, is noodzakelijk om het regeneratieve proces economisch haalbaar te maken. Hoewel de korte termijn filosofie van veel SO₂-uitstotende bedrijven is gericht op eenmalige processen, als een directe oplossing voor het emissie probleem, zal de lange termijn oplossing gevonden moeten worden in een regeneratief proces met zwavelopwerking.
1.1 Coal combustion in a fluidized bed combustor

In the early 1960's, extensive research was started in England to examine fluidized bed combustion (FBC) for energy production. In this process, the fuel is burned in a chamber containing a quantity of finely-divided solid particles like sand or ash. The combustion air, which enters at the bottom of that chamber, lifts the particles until they form a turbulent "bed", which behaves like a boiling fluid, but has the heat capacity of a solid. Start-up burners heat the bed to a temperature of some 500 degrees Centigrade. The incandescent bed resembles molten lava; any combustible material fed into the combustor is ignited almost instantaneously. The heat released maintains the bed-temperature and the turbulence keeps the temperature uniform throughout the bed. The heat capacity of the solid particles gives the system "thermal inertia": even cold, wet fuel will not quench the fire. It has been shown that FBC can be used in burning low-grade fuel and even materials like colliery washings and pit spoil (FTICR, 1989). FBC operates at about 850 degrees Centigrade, several hundreds of degrees lower than conventional combustion technologies like pulverized fuel combustion (PFC). This lower temperature dramatically reduces the formation of nitrogen oxides. If the fuel contains sulfur, an appropriate amount of a calcium mineral, a "sorbent", can be fed together with the fuel to prevent the emission of sulfur oxides (sulfur dioxide and sulfur trioxide). In general, two types of limestones are used, calcitic and dolomitic
limestones. In calcitic limestones, usually simply called limestone, the main mineral is calcite with the chemical formula CaCO\textsubscript{3}. Calcitic limestones usually contain 85% or more CaCO\textsubscript{3}. The main mineral in dolomitic limestones is dolomite, a double salt of calcium and magnesium carbonate (CaCO\textsubscript{3}.MgCO\textsubscript{3}). Pure dolomite contains 54.3 wt% CaCO\textsubscript{3}. When coal is burned in this manner, the bed consists of burning coal, coal ash and the sorbent. The released sulfur oxides react with the sorbent and form a solid sulfate which can be discarded as a dry solid. In this way, an FBC unit can trap more than 90% of the sulfur present, without expensive flue gas clean-up. The chemical reaction system involved is the following:

Limestone:
calcination \( \text{CaCO}_3 \rightarrow \text{CaO (lime)} + \text{CO}_2 \quad \Delta H_r = 167 \text{kJ/mole} \) (1.1)
sulfation \( \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 \quad \Delta H_r = -482 \text{kJ/mole} \) (1.2)

Dolomite (at about 10 bar):
calcination \( \text{CaCO}_3.\text{MgCO}_3 \rightarrow \text{CaCO}_3.\text{MgO} + \text{CO}_2 \) (1.3)
sulfation \( \text{CaCO}_3.\text{MgO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4.\text{MgO} + \text{CO}_2 \) (1.4)

(Throughout this thesis the reaction enthalpies are given at 850\textdegree C and 1 bar.)

At 850\textdegree C and 1 bar pressure, the calcination reaction is usually faster than the sulfation. It creates a porous structure in the sorbent particles with a large surface area, accessible for the molecules \text{SO}_2 and \text{O}_2 to react. Under atmospheric conditions (AFBC), both \text{CaCO}_3 and \text{MgCO}_3 are calcined to their oxides.

When the combustor is at an elevated pressure (e.g. 10 bar), limestone does not easily decompose because of the thermodynamical effect of a high partial pressure of CO\textsubscript{2}. The MgCO\textsubscript{3} component in dolomite easily decomposes under these conditions and thus creates the necessary pore structure. Under the typical conditions of temperature and SO\textsubscript{2} concentration present in a
fluidized bed combustor, only the CaCO₃ component of limestone is sulfated. Even though dolomitic limestones contain about half as much CaCO₃ as calcitic limestones, the actual amount of stone needed is usually about the same. This is due to the fact that, for many dolomitic limestones, the utilization that can be achieved is often two or more times the utilization obtained by a calcitic limestone. The extent to which the CaO or CaCO₃ is converted into CaSO₄ depends on the porosity of the stone and the reactivity of CaO (or for dolomites CaCO₃) with SO₂. Gaseous SO₂ must make contact with the solid before reaction can occur. To reach the CaO, located inside the limestone particles, the gas must diffuse through the pores. Since the CaSO₄ product has a larger molar volume than calcium oxide (or CaCO₃), smaller pores will fill up. If the sulfation reaction is fast, compared with the gas transport in the pores, the mouths of the pores can become filled before extensive reaction has occurred in the inside of the particle. The overall result will be the formation of a dense layer of CaSO₄ in the outer regions of the particle with a large unsulfated core. As a result of this pore plugging, sulfations as low as 10 to 15% may be obtained for some stones (Johnson, 1980).

Variations in the technology include so-called "bubbling" FBC (BFBC) and "circulating" FBC (CFBC). In BFBC, the velocity in the air stream through the fluidized solid particles in the combustor is of the order of two meters per second. The bed, filling the lower part of the combustion chamber, has a clearly defined interface with the "freeboard" above the bed. Most of the combustion takes place within this bed; some designs have cooling tubes immersed in the bed, to take advantage of the conductive heat transfer when the turbulent incandescent bed particles strike the tubes. The hot combustion gas bursts through the surface of the bed, passes through the freeboard above the surface, emerges at the top or the side of the combustion chamber and a cyclone removes almost all the solid particles in the gas-flow. From the cyclone, the hot gases enter passages containing convective heat transfer surfaces like those in a conventional pulverized fuel boiler; then, they pass through a baghouse filter or electrostatic precipitator and are discharged through a stack.

In CFBC, the upward velocity of the fluidising air is more than eight meters per second. At this velocity, it transports the bed solids and a bed surface can not be defined. The solids fill the entire combustion chamber
with a vertical stream of incandescent particles. The hot combustion gas carries the particles right out of the top into a heavy-duty cyclone. The cyclone catches the particles, which settle into a hopper and are returned to the bottom of the main combustion chamber, to repeat their cycle. The fuel and sorbent will travel together repeatedly around the circulation loop, offering a longer "residence time" than BFBC, so improving combustion efficiency and sulfur capture. Also, CFBC is more suited to staged combustion, in which the combustion air is introduced at several heights into the combustion chamber. This limits excess oxygen and so reduces the formation of nitrogen oxides. However, CFBC requires more fan power to circulate the air, a taller combustion chamber and a heavy-duty cyclone that can cope with the impact of hot particle-loaded gases.

In general, both BFBC and CFBC are operated more or less at atmospheric pressure. Enclosing the combustor and auxiliaries inside a pressure shell, the entire process can take place at a pressure of 10 bar or more: so-called "pressurized" FBC (PFBC). The pressurized combustion air contains more oxygen per unit volume, producing a more compact combustion chamber for the same output of heat. Furthermore, the hot combustion gases emerge from the combustor under pressure; after a clean-up, they can be fed directly into a gas turbine, at an inlet temperature hundreds of degrees higher than that of a steam turbine. The gas turbine exhaust emerges still hot enough to raise steam to add to that produced by the combustor. The combined gas- and steam-turbine cycle raises the overall efficiency of electricity generation to 40% or better, compared with perhaps 35% from a modern PFBC plant with flue gas desulfurization. Except of higher combustion, power cycle and sulfur capture efficiencies and a smaller reaction vessel, also lower NOx emissions represent important system advantages (Albanese et al., 1980). However, components to operate under pressure are more complicated and costly; feeding fuel into and removing ash from a pressurized system is more difficult; further cleaning hot gases adequately so that abrasive particles do not erode gas turbine blades remains a major problem for PFBC.

After the energy crisis in 1973, a reintroduction of coal was expected. The overall energy production in the year 2000 is expected to increase so much that the use of fossil fuels will increase by almost twofold compared with current consumption. The coal resources are high and well-spread over the world. The major oil resources are concentrated in the Middle East,
which is politically an uncomfortable situation. FBC of coal was developed rapidly, mostly in the United States, England and the Federal Republic of Germany, for application in utilities, process industries and the institutional sectors with a capacity of up to about 100 MWe. Note that coal gasification is developed for converting coal into combustible synthesis gas (which can be burned to generate electric power and/or steam) on a larger scale of up to about 600 MWe. Some of the potential advantages of FBC, compared with pulverized coal firing are summarized below (Perry et al., 1984):

1. Different types of coal with varying particle sizes of up to 3 cm can be used. There is no need to pulverize coal to a small particle size.
2. Low combustion temperatures, up to about 950°C, which mean:
   a. Nearly no thermal nitrogen oxide emissions.
   b. Less problems caused by ash agglomeration. No fouling and erosion by molten or solidified slag because the bed is operated below the ash fusion temperature.
   c. Less volatilization of sodium and potassium in the coal and, consequently, less deposition on and corrosion of downstream components, such as boiler superheaters, reheaters and turbine blades in PFBC gas turbines.
3. High heat transfer coefficients between the bed and tubes immersed in the bed of 400 W/(m² °C). This is an order of three to five times higher than for conventional boilers.
4. High volumetric energy release rates of 5.2 MW/m³ as compared with 0.2 MW/m³ in a conventional pulverized coal-fired boiler.
5. In-situ desulfurization is possible, using a solid sorbent which makes the treatment of the voluminous flue gas superfluous.

Most of the early bubbling and circulating FBC units experienced major mechanical and material problems, including erosion, especially of the in-bed heat exchanger tubing in BFBC units. Also plugging of coal feed systems, undersized fans and erratic size distribution of bed-particles led to sub-optimum output. Most vendors and users have resolved these problems. Coal-fired industrial FBC boiler systems are now a fairly widespread and established technology in Western Europe and Northern America, with over 200 industrial size units in operation. These FBC units represent a wide variety of capacities, designs and applications (Thomas et al., 1986).
1.2 Regenerative desulfurization

During the combustion of coal, \( \text{SO}_2 \) is released by the oxidation of sulfur compounds in the coal. The \( \text{SO}_2 \) affects people, animals and vegetation and consequently is a matter of great importance both for government regulatory agencies and the general public. A 100 MWe combustor burning a typical coal containing 1 \( \text{wt}\% \) sulfur emits 5000 tons \( \text{SO}_2 \) a year, if no desulfurization would be included in the process. The amount of \( \text{SO}_2 \) emitted depends, of course, on the sulfur content of the coal. 1 \( \text{wt}\% \) sulfur in the coal gives about 0.07 \( \text{vol}\% \) \( \text{SO}_2 \) in the gas (Slack and Hollinden, 1975). Coals vary widely in this aspect. The bituminous types, generally used in power plants, are highest in sulfur content (up to 10 \( \text{wt}\% \)). Subbituminous coal, lignite and anthracite generally contain less than 1 \( \text{wt}\% \) sulfur. Without desulfurization, most of the sulfur in the coal would be released in the gas, although in some boiler types a small part may become combined with the ash that is removed from the bottom of the boiler. The \( \text{SO}_3 \) usually accounts for only a small part of the total sulfur oxides; the amount depends on the degree of \( \text{SO}_2 \) oxidation by oxygen, which in turn depends on boiler temperature, residence time in the boiler and catalytic effects from (metal) surfaces in the boiler and from (metal) compounds in the ash. A rough range of \( \text{SO}_3 \), concentrations is 0.5 to 5.0\% of the total sulfur present. To prevent corrosion by condensed sulfuric acid, removal of \( \text{SO}_3 \) is necessary.

At FBC the natural minerals are presently receiving most attention as sulfur capturing materials because of their high calcium content and suitable operation temperature. These materials are cheap ($2 to $5 a ton), abundant and available in most parts of the world (Münzner and Bonn, 1980; Barron et al., 1987; Couturier et al., 1987; Haji-Sulaiman and Scaroni, 1987; Hamer, 1987; Kim et al., 1987). However, because the minerals can be used only once, large amounts of only partly sulfated sorbent are being produced. If this material is not converted into a useful product, e.g. as a filler in cement and/or concrete, a waste disposal problem is created. As long as this spent sorbent is dumped at sea or used as a landfiller, the original air pollution problem is transferred into a soil contamination problem. In his opening address to the International Conference on Fluidized Bed Combustion in San Francisco in May 1989, Simbeck and Vejtasa (1989) of SFA Pacific mentioned the spent sorbent problem as one of the major reasons preventing a general introduction of fluidized bed combustion of coal. Since
much of the unsulfated limestone will convert into lime, wetting of the sorbent results in corrosive calcium hydroxide and generates heat. Multicyclic utilization by regenerating the minerals would be a potentially attractive alternative which would greatly reduce the quantity of solid waste to be disposed. The feasibility of regenerating sulfated sorbent particles depends upon:
1. The remaining reactivity of the regenerated sorbent.
2. The sorbent’s ability to resist attrition.
3. The possibility to regenerate the sorbent at a relatively low temperature.
4. The ability to produce an SO₂ rich off-gas during the regeneration of the sorbent. A percentage of 3-11 vol% makes conversion to elemental sulfur, sulfuric acid or liquid SO₂ technically and economically attractive (Slack and Hollinden, 1975; Montagna et al., 1977; Kirk-Othmer, 1983).

Of course, in a practical system design many other characteristics will be of great importance such as particle agglomeration, fluidization quality, bed mixing behaviour, heat transfer, reactor wall and tube erosion and corrosion, bed pressure drop, turbine protection, environmental impact and safety.

Limestone or dolomite can not meet these requirements. Thermal decomposition of calcium sulfate is not considered to be a viable process because of the high temperature, above 1200°C, needed to obtain a high concentration of SO₂ in the off-gas. At this temperature, ash and sulfated stone fuse and form unusable clinkers (Montagna et al., 1977a). Reductive regeneration of sulfated limestone and dolomite can still only take place at relatively high temperatures (above 1100°C). At lower temperatures and under more highly reducing conditions, the formation of CaS is favored. During cyclic sulfation and regeneration, the sulfur capture activity of limestone or dolomite decreases rapidly with the number of cycles. The resistance of the natural sorbents to attrition is poor. Finally, agglomeration can occur in the regenerator (Snyder et al., 1975; Johnson et al., 1977; Montagna et al., 1977; Albanese et al., 1980). An extra problem in using these sorbents is that SO₂ reactivity, SO₂ capacity and attrition resistance vary widely and are strongly dependent upon the geological origin of the material (Borgwardt and Harvey, 1972; Wen and Ishida, 1973; Albanese et al., 1980;
Kim et al., 1987; Hamer, 1989). This hinders a good prediction of sorbent performance in the fluidized bed system.

Due to these disadvantages, synthetic regenerable sorbents were studied as substitutes for limestone and dolomite (Snyder et al., 1975; Johnson et al., 1977; Newby and Keairns, 1977; Ruth and Varga, 1979; Yang and Shen, 1979; Albanese et al., 1980; Steinberg et al., 1981). However, the low temperature regenerable sorbents were mechanically weak and the regeneration of stronger sorbents could still only be performed at relatively high temperatures of about 1050°C. It was concluded that introducing synthetic sorbents was unattractive for economical reasons. The synthetic sorbent would be rather expensive compared with the costs of dumping the sulfated limestone or dolomite.

The U.S.A. Environmental Protection Agency (EPA) has set 0.52 kg SO₂/GJ as the emission standard and the Dutch government demands 0.23 kg SO₂/GJ (see also Chapter 7). It is expected that the emission control levels will decrease and solid waste dumping will become more and more difficult (Simbeck and Vejtas, 1989). Hence, the attention has returned to synthetic regenerable sorbents for in-situ desulfurization (Gavalas et al., 1985; Molayem and Bardakci, 1985; Noordergraaf, 1985; Wolff et al., 1989).

1.3 Research on FBC at D.U.T.

In 1979 a project was initiated at the Delft University of Technology (D.U.T.) for a contribution to the development of PFBC. At the Faculty of Mechanical Engineering (Thermal Power Laboratory) research topics like heat transfer in the fluidized bed, freeboard behaviour, process dynamics and control and dust emission control with respect to the expansion turbine, are examined. At the Faculty of Chemical Technology and Materials Science (Laboratory of Chemical Process Technology) the sulfur route during the coal combustion, sulfur capture and regeneration is investigated. This research was started by examining the sulfur capture in the fluidized bed combustion of coal with use of a (synthetic) model sorbent (Noordergraaf, 1985). This work was continued in January 1984 by describing the sulfur capture using natural sorbents with the D.U.T. SURE model (Schouten, 1988). In April 1986 a "sub"-project on the regenerative sulfur capture was started being
financially supported by the CEC (Commission of the European Communities), NOVEM (the Netherlands Agency for Energy and the Environment) and STW (the Netherlands Technology Foundation). The project is developing towards a low temperature regeneration process enabled by a new synthetic sorbent. This work will be continued by the design of a fluidized bed sorbent-regenerator and the study of NO\textsubscript{x} – SO\textsubscript{x} interaction during the sulfur capture process respectively.

1.4 Aim of the present study and outline of this thesis

1.4.1 Introduction

This thesis on the regenerative desulfurization during fluidized bed combustion of coal is written with direct application to an AFBC system. A proposed flow scheme of such an overall fluidized bed system is given in Figure 1.1.

Coal is fed continuously to the combustor where it is burned in a bed of ash and sorbent. Make-up sorbent is fed to compensate for both the attrition

![Figure 1.1 Schematic flow scheme of fluidized bed combustion with regenerative desulfurization.](image-url)
loss and the removal of deactivated sorbent. The sorbent captures the SO₂ formed and is removed together with the bottom ash from the combustor. After separation from the ash, the sorbent is transported to the regenerator. The best type of regeneration reactor is supposed to be a fluidized bed as well. Some advantages of a fluidized bed combustor mentioned in section 1.1 will then also apply for the regenerator. The transport of sorbent from regenerator to combustor is considerably simpler as the material acts like a fluid and a uniform temperature can be attained in the regenerator. In principle the fluidized bed can be used simultaneously for both the production of the reducing gases and the reduction of the sorbent. In practise the regeneration gas can be formed by:

1. The partial burning of coal for CO production (C + 1/2 O₂ → CO).
2. The gasification of coal to produce synthesis gas (C + H₂O → CO + H₂).
3. The conversion of methane with steam (CH₄ + H₂O → CO + 3 H₂).

After regeneration, the sorbent is returned to the combustor. In the regenerator the sulfur is recovered as SO₂, at a high concentration because this is necessary for an economic conversion to elemental sulfur, sulfuric acid or liquid SO₂. Compared with non-regenerative desulfurization two mayor profits are obtained. First, the production of solid waste is decreased considerably and secondly, sulfur is recovered as a useful product.

1.4.2 Main targets

In a fixed bed reactor facility the chemistry of cyclic sulfation and regeneration of the sorbent is examined. With respect to fluidized bed applications the mechanical strength is tested by single-particle and multi-particle attrition tests in a crushing strength apparatus, a gas gun and a fluidized bed. Not only the sulfur capture and regeneration experiments have been performed at atmospheric pressure but the mechanical strength tests as well. The main targets are:

1. To test whether or not the sorbent is suitable, with respect to the chemistry, for a cyclic regenerative desulfurization process during the fluidized bed combustion of coal.
2. To define the optimal process conditions for the regeneration step. Particular emphasis is placed on a low temperature regenerative process at 850°C and 1 bar.
3. To define the process phenomena (mass/heat transfer and kinetics) which determine the sulfur capture process using a simple mathematical model. A first attempt to define the process phenomena of the regeneration process is described elsewhere (Van der Laan, 1990). In future work, these results are to be included in an overall fluidized bed model which then can describe both the sulfur capture in the combustor and the sorbent regeneration in the regenerator.

4. To test the sorbent for its resistance towards attrition.

1.4.3 Outline of this thesis

The preparation method of the regenerable synthetic sorbent is described in Chapter 2. The theory about the thermodynamics and kinetics of (1) calcium aluminate formation during the sorbent preparation and (2) sulfur capture and regeneration is discussed. The fixed bed reactor equipment and the methods used to study the chemistry of the regenerative process are given in Chapter 3. The quantitative modeling of the fixed bed reactor experimental results, described in Chapter 4, to extract the process parameters of the sulfur capture process is the subject of Chapter 5. The SURE2-model for describing the sulfur capture phenomena with the synthetic sorbent is introduced. The single-particle and multi-particle tests used to study the sorbent attrition behaviour are presented in Chapter 6. Finally, a brief economic evaluation is given in Chapter 7.

References


Van der Laan, 1990, "Het meten en modelleren van de regeneratie van een synthetisch sorbent voor de zwaveldioxidevangst in een vast bed reactor", Internal Report, Department of Chemical Engineering, Delft University of Technology, Delft, The Netherlands.


2
The Regenerative D.U.T. Sol-Gel Sorbent

2.1 Introduction

At the Faculty of Chemical Technology and Materials Science (Laboratory for Physical Chemistry) of the Delft University of Technology, a new sorbent is developed based on the sol-gel production method (Van den Bleek et al., 1986–1991; Duisterwinkel, 1990). The particles are spheres of about 3 mm in diameter and consist of 8.2 wt% CaO on a γ-Al₂O₃ support. After calcination calcium aluminates are formed. Due to its typical morphology, this sorbent is able to meet the requirements mentioned in chapter 1 (see section 1.2). The principles of the preparation method, the thermodynamics and kinetics of the calcium aluminate formation and the thermodynamics of the sulphur capture and sorbent regeneration process are discussed in sections 2.2 to 2.4. The sorbent characterization is described in section 2.5. Next, the kinetics of sulphur capture and regeneration are discussed in section 2.6. Chapter 2 is concluded by a summary in section 2.7.

2.2 Principles of the sorbent preparation

In the first step of the preparation, a sol is made by dispersing very fine pseudoboehmite (A100H.xH₂O) powder in water, containing nitric acid and urea. The sol (particle size smaller than approximately 30 nm) is then dropped into a nonpolar medium e.g. kerosene (see Figure 2.1). Since the sol
is lyophobic; the drops will tend to minimize their outer surface area and become spheres. These spheres have a larger specific weight than the kerosene and sink into a second layer containing a solution of ammonia in water. Due to the ammonia, the sol gelates. This gel is a colloidal solid containing a fluid component; both the solid and the fluid component are highly dispersed. The CaO can be incorporated by adding Ca(NO₃)₂ to the ammonia solution or afterwards by wet impregnation. The advantage of the first method is the good dispersion of the CaO on the boehmite surface. This method also decreases the number of process stages. The calcium loaded gel is carefully heated to evaporate water and to decompose the Ca(NO₃)₂ to calcium oxide. The calcination step is finally carried out at a temperature of 850°C for 10 hours. After calcination, the internal surface area and pore

(1) sol supply
(2) sol pump
(3) sol dropping through four orifices
(4) kerosene
(5) kerosene container
(6) gelation column
(7) sorbent-liquid sieving
(8) gelation fluid pump
(9) overflow
(10) addition of fresh Ca²⁺/NH₃ solution
(11) Ca²⁺/NH₃ measurement
(12) purge
(13) Ca²⁺/NH₃ supply vessel

Figure 2.1 Preparation of the sol-gel sorbent (Van den Bleek et al., 1986–1991).

volume of the resulting γ-Al₂O₃ support are 100 m²/g and 0.3 ml/g respectively. The spheres are mechanically very strong (see Chapter 6). If higher temperatures are used for the calcination, the γ-Al₂O₃ is converted via two intermediates to corundum, α-Al₂O₃, the stable configuration
The regenerative D.U.T. sol-gel sorbent

(Shkrabina et al., 1981). The characteristic alumina conversion chain is given below:

\[
\text{AlOOH} \cdot x\text{H}_2\text{O} \xrightarrow{300\,^{\circ}\text{C}} \gamma \xrightarrow{900\,^{\circ}\text{C}} \delta \xrightarrow{1000\,^{\circ}\text{C}} \theta + \alpha \xrightarrow{1200\,^{\circ}\text{C}} \alpha-\text{Al}_2\text{O}_3
\]  

(pseudoboehmite)

The internal surface area reduces drastically to about 10 m²/g and the pore volume to about 0.1 ml/g which is unfavourable for the sulfur capture and the regeneration process. The preparation method described, results in a very high CaO dispersion on the support. After calcination the sorbent does not simply consist of CaO on an alumina support but products of interaction between CaO and Al₂O₃ have been formed, according to:

\[
m\text{CaO} + n\text{Al}_2\text{O}_3 \rightarrow m\text{CaO}_n\text{Al}_2\text{O}_3
\]  

Which specific calcium aluminates(s) are formed during the sorbent preparation depends on thermodynamics and kinetics as will be discussed in the next section.

2.3 Thermodynamics and kinetics of calcium aluminates formation

Because the role of calcium aluminates is of considerable importance to the chemistry of steel and cement, it has been studied extensively (Elsner et al., 1933; Coughlin, 1956; Sharma and Richardson, 1961; Rein and Chipman, 1965; Cameron et al., 1966; McEldov-Petrosjan et al., 1966; Taylor, 1967; Kor and Richardson, 1968; Edmunds and Taylor, 1972; Kubaschewski, 1972; Faulring and Ramalingam, 1980; Eliezer et al., 1981–1982). However, the temperatures (1300°C – 2100°C) in these studies were much higher than in the Delft program. In Table 2.1 are the compounds listed according to literature data. These calcium aluminates are formed during the heating of stoichiometric mixtures of CaO or CaCO₃ with Al₂O₃ at high temperature. The reaction time and temperature for total conversion of the reactants are indicated.
Table 2.1 Preparation characteristics of the water-free calcium aluminates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point °C</th>
<th>Reaction Temperature Range °C</th>
<th>Reaction Time and Temperature °C/h</th>
<th>References</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO·Al₂O₃</td>
<td>1602</td>
<td>850–1602</td>
<td>1 1300</td>
<td>3, 6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18 1490</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>168 1050</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>CaO·2Al₂O₃</td>
<td>1762</td>
<td></td>
<td>70 1450</td>
<td>2, 6</td>
<td>a, b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>168 1050</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>CaO·3Al₂O₃</td>
<td>1830</td>
<td></td>
<td>3</td>
<td>3</td>
<td>a</td>
</tr>
<tr>
<td>CaO·6Al₂O₃</td>
<td></td>
<td></td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2CaO·Al₂O₃</td>
<td></td>
<td></td>
<td>3</td>
<td>a, c</td>
<td></td>
</tr>
<tr>
<td>3CaO·Al₂O₃</td>
<td>1539</td>
<td>1350–1539</td>
<td>0.5 1425+</td>
<td>3, 6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt;2 1325</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>18 1425+</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>21 &gt;1000</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>168 1050</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>3CaO·2Al₂O₃</td>
<td></td>
<td></td>
<td>3</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>3CaO·5Al₂O₃</td>
<td>1720</td>
<td>1350–1720</td>
<td>&gt;4 1350</td>
<td>3</td>
<td>b</td>
</tr>
<tr>
<td>3CaO·16Al₂O₃</td>
<td>1860</td>
<td></td>
<td>168 1050</td>
<td>1, 5</td>
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</tr>
<tr>
<td>4CaO·Al₂O₃</td>
<td></td>
<td></td>
<td>3</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>5CaO·Al₂O₃</td>
<td></td>
<td></td>
<td>3</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>5CaO·2Al₂O₃</td>
<td></td>
<td></td>
<td>3</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>5CaO·3Al₂O₃</td>
<td>1450</td>
<td>1250–1450</td>
<td>&gt;4 1350</td>
<td>3</td>
<td>b</td>
</tr>
<tr>
<td>6CaO·5Al₂O₃</td>
<td></td>
<td></td>
<td>3</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>11CaO·10Al₂O₃</td>
<td></td>
<td></td>
<td>3</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>12CaO·7Al₂O₃</td>
<td>1392</td>
<td></td>
<td>? 1350</td>
<td>4, 6</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>21 1400+</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>27 1300</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>168 1050</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>


Notes:

a These compounds do not exist independently in the CaO-Al₂O₃ system. They can be formed by burning or melting from mixtures of CaO and Al₂O₃, with the relevant molar ratio and can usually be considered as mixtures of CaO·Al₂O₃, 3CaO·Al₂O₃, 3CaO·5Al₂O₃ and 5CaO·3Al₂O₃ (Gmelin, 1960).

b It has been established that the stoichiometry of the compounds 5CaO·3Al₂O₃ and 3CaO·5Al₂O₃ is 12CaO·7Al₂O₃ and CaO·2Al₂O₃, respectively (Nurse et al., 1965; Taylor, 1967, Budnikov and Ginstling, 1968; Imlach and Glasser, 1968). Literature is still not uniform about the nomenclature.

c No evidence was found of compounds having formulae such as 2CaO·Al₂O₃, 4CaO·3Al₂O₃ and CaO·11Al₂O₃, etc. proposed by some investigators (Nurse et al., 1965).
Snyder et al. (1975) show the formation of CaO.06Al₂O₃ and 3CaO.5Al₂O₃ beside unreacted CaO at 800°C in four hours from CaO (up to 15 wt%) on α-Al₂O₃-pellets. A temperature of 1100°C results in CaO.Al₂O₃ and CaO.2Al₂O₃. They distinguish between the compounds CaO.2Al₂O₃ and 3CaO.5Al₂O₃ in contrast with the opinion of many other authors (see note b at Table 2.1). Okutani et al. (1975) report the formation of CaO.Al₂O₃ and an unknown calcium aluminate xCaO.yAl₂O₃ in which x is smaller than y. These products were obtained during the solid state reaction of CaO with Al₂O₃ (1:1 molar ratio) in a flow of nitrogen for 1 h at 900°C. Their results indicate that a variety of aluminites is formed, the exact type formed seems to depend on the type of Al₂O₃ started with and the temperature applied (Table 2.2).

Table 2.2 Crystalline compounds formed by heating CaO-η-Al₂O₃ and CaO-α-Al₂O₃ for 1 h at various temperatures in a flow of nitrogen, 100 ml/min (Okutani et al., 1975)

<table>
<thead>
<tr>
<th>reaction temperature (°C)</th>
<th>reaction system CaO-η-Al₂O₃</th>
<th>reaction system CaO-α-Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>high XRD intensity low</td>
<td>high XRD intensity low</td>
</tr>
<tr>
<td>800</td>
<td>CaO</td>
<td>CaO, α-Al₂O₃</td>
</tr>
<tr>
<td>900</td>
<td>CaO, CA, CxAy</td>
<td>CaO, α-Al₂O₃, CA</td>
</tr>
<tr>
<td>1000</td>
<td>CaO, CA, CxAy</td>
<td>CaO, α-Al₂O₃, CA, C3A</td>
</tr>
<tr>
<td>1100</td>
<td>CxAy, CA, C3A, C3A5</td>
<td>CaO, α-Al₂O₃, CA, C3A5</td>
</tr>
<tr>
<td>1200</td>
<td>CxAy, CA, C3A5, C12A7, C3A5</td>
<td>CaO, α-Al₂O₃, CA, C3A</td>
</tr>
<tr>
<td>1300</td>
<td>CA, CxAy, C12A7, C3A5, CA</td>
<td>C12A7, CA, C3A5</td>
</tr>
</tbody>
</table>

Notes: CA = CaO.Al₂O₃; C3A = 3CaO.Al₂O₃; C3A5 = 3CaO.5Al₂O₃; C12A7 = 12CaO.7Al₂O₃; CxAy = xCaO.yAl₂O₃
The compounds were identified by X-ray diffraction.

Besides water-free calcium aluminates also water containing calcium aluminates are described by Gmelin (1960). They are noted as mCaO.nAl₂O₃.2H₂O and synthesized in an aqueous solution. Total removal of water is only possible when the samples are heated to a very high temperature. For example, 3CaO.Al₂O₃.6H₂O has to be heated up to 300°C in dry CO₂-free air to lose 75% of water under formation of a 1.5-hydrate. At higher temperatures the decomposition proceeds slowly. Total dehydration does not occur below 1100°C. Further, it is known that water-free calcium
aluminate 12CaO.7Al₂O₃ can absorb and retain water from the ambient laboratory atmosphere, even at comparatively high temperatures (Nurse et al., 1965; Imlach and Glasser, 1968; Lea, 1970). Infrared absorption shows that hydroxyl-water is present in the structure; at about 950⁰C, when sorption is maximal, the chemical structure can be represented by 11CaO.7Al₂O₃.Ca(OH)₂. Thermogravimetric studies at 930-1350⁰C show that the hydroxyl-water is gained or lost reversibly. This is not merely a surface effect because physical properties (e.g. refractive index, unit cell size, density) are all affected. It is not certain whether OH-groups are completely removed on melting and it has not been possible to prepare completely anhydrous 12CaO.7Al₂O₃.

An equilibrium phase diagram of the CaO-Al₂O₃ system is given in the Figures 2.2a, 2.2b, 2.2c and 2.2d, abstracted from Levin et al. (1969) and Lea (1970). By extrapolation, it can be concluded from these figures that in an equilibrium situation at 850⁰C a mixture up to about 8 wt% CaO in Al₂O₃ will contain CaO.2Al₂O₃ or CaO.6Al₂O₃. Note that the equilibria data are based on CaO and α-Al₂O₃, the stable phase, while the D.U.T. synthetic sorbent consists of CaO and γ-Al₂O₃. Okutani et al. (1975) found that the calcium aluminate(s) formed depend on the specific type of alumina used. Besides, according to the data provided by Table 2.1, it is doubtful whether the equilibrium situation is met at the relative low temperature of 850⁰C and the short calcination time of 10 h during the preparation of the D.U.T sorbent. The kinetics of the reaction will play an important role.

On the kinetics of the calcium aluminate formation only few literature data are known. Jagitsch (1936) reports that before CaCO₃ starts to react with Al₂O₃, the surface of the alumina crystals is seriously damaged at temperatures above 600⁰C. Because of the low diffusion rate during the solid-solid reaction, it is important to mix the components extremely well. Researchers like King (1955) suggest a process of repeatedly mixing, heating and pulverizing. With respect to this "mixing-problem", the advantage of the preparation method described in section 2.2 is obvious. By adding Ca(NO₃)₂ to the ammonia solution, a very good dispersion of CaO on the alumina surface is obtained. The reaction time of various compounds given in Table 2.1 indicates a low overall reaction rate. Nagai and Naito (1930) reported
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Figure 2.2a The system CaO-Al₂O₃ in a moisture-free atmosphere (Lea, 1970).

Figure 2.2b Congruent melting of 12CaO.7Al₂O₃ in atmosphere of ordinary humidity (Lea, 1970).
Figure 2.2c  The system CaO-Al₂O₃ (Levin et al., 1969).

Figure 2.2d  The system CaO-Al₂O₃ at high alumina portion (Levin et al., 1969). The different type of lines represent the work by various authors.
on a study of the synthesis of calcium aluminates from three mixtures: (1) a mixture of 2(CaO) and 1(Al₂O₃): 52.2 wt% CaO and 47.8 wt% Al₂O₃, (2) a mixture of 47 wt% CaO and 53 wt% Al₂O₃: the eutectic mixture of the aluminates CaO.Al₂O₃ and 5CaO.3Al₂O₃ (or 12CaO.7Al₂O₃, see comment b at Table 2.1) and (3) a mixture of 33.5 wt% CaO and 66.5 wt% Al₂O₃, the eutectic mixture of CaO.Al₂O₃ and 3CaO.5Al₂O₃ (or CaO.2Al₂O₃, see comment b at Table 2.1). The combination between calcium oxide and alumina is completed in 1 h in all cases when the mixture is molten at a temperature not lower than 1400°C. Budnikov (1968) states that at 900°C – 1000°C the compound CaO.Al₂O₃ forms intensely. The primary product of the reaction in mixtures of CaO and Al₂O₃, regardless of the original ratio between these oxides, is CaO.Al₂O₃. Complete conversion in a short time can only be obtained at the melting point of the mixture.

2.4 Thermodynamics of sulfur capture and regeneration

Not only CaO but also the calcium aluminates are able to react with SO₂ and O₂ to form CaSO₄:

\[ \text{mCaO.nAl}_2\text{O}_3 + \text{m SO}_2 + \frac{1}{2} \text{m O}_2 \rightarrow \text{m CaSO}_4 + n \text{Al}_2\text{O}_3 \]  \hspace{1cm} (2.3)

Snyder et al. (1975) report that CaO.Al₂O₃, CaO.2Al₂O₃, CaO.6Al₂O₃ and 3CaO.5Al₂O₃ are reactive, while according to Okutani et al. (1975) only the calcium aluminates with values of m/n > 1 are active. However, their figures also show reactivity of CaO.Al₂O₃, m/n = 1. It is concluded in section 2.5 (synthetic sorbent characterization) that CaO.2Al₂O₃ is the only calcium aluminate shown to be formed at 850°C. We will assume (see section 2.5) that this is the reactive compound towards SO₂, although this disagrees with the statement of Okutani et al. The reaction of the SO₂ removal is thus written as:

\[ \text{CaO.2Al}_2\text{O}_3 + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 + 2 \text{Al}_2\text{O}_3 \hspace{1cm} \Delta H_r = -461 \text{ kJ/mole} \]  \hspace{1cm} (2.4)
The regenerative D.U.T. sol-gel sorbent

The mechanism developed for the sulfation of lime has not yet been established with absolute certainty. Siriwardane (1989) proposed a reaction sequence which is also thermodynamically feasible where $\text{SO}_2$ first reacts with $\text{CaO}$ to form $\text{CaSO}_3$. The last compound is then oxidized to $\text{CaSO}_4$. However, there is good evidence that sulfur trioxide is formed first (Snyder et al., 1975; Fieldes et al., 1979; Burdett, 1980; Burdett et al., 1983; Marsh and Ulrichson, 1985; Raymant, 1989, Van den Bleek et al., 1986-1991).

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{oxidation reaction}} \text{SO}_3 \quad \Delta H_r = -97 \text{ kJ/mole} \]

\[ \text{CaO} + \text{SO}_3 \rightarrow \text{CaSO}_4 \quad \Delta H_r = -385 \text{ kJ/mole} \quad \text{(sulfation reaction)} \]

Most probably this mechanism also applies to the sulfation of calcium aluminates. It is confirmed by XRD (see section 5.5.1, Table 5.2) that $\text{CaSO}_4$ does not interact with $\text{Al}_2\text{O}_3$ in reaction (2.4). Literature data (Hanic et al., 1986) mention the formation of a calcium aluminosulphate, $\text{Ca}_4[\text{Al}_6\text{O}_{12}]\text{(SO}_4\text{)}$, from $\text{CaO.}\text{Al}_2\text{O}_3$ and $\text{CaSO}_4$. No literature data were found on a possible similar reaction with $\text{CaO.2Al}_2\text{O}_3$. Besides, conversion only proceeds above 1100°C according to:

\[ 3 \text{ CaO.}\text{Al}_2\text{O}_3 + \text{CaSO}_4 \rightarrow \text{Ca}_4[\text{Al}_6\text{O}_{12}]\text{(SO}_4\text{)} \]

The sorbent can be regenerated by thermal decomposition at a temperature higher than 850°C in the absence of a reducing medium. However, this is unattractive because of:
1. The lower regeneration rate compared to reductive regeneration.
2. The sintering of the sorbent. The internal surface area and pore volume will decrease at higher temperatures.
3. The ambition to operate isotherm with the combustor at 850°C for energetical reasons. It is pursued to maintain the sorbent temperature at 850°C during the cyclic operation.

Hence, the sorbent is to be regenerated by $\text{H}_2$ and/or $\text{CO}$:
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\[
\text{CaSO}_4 + 2 \text{Al}_2\text{O}_3 + \text{H}_2 \rightarrow \text{CaO.2Al}_2\text{O}_3 + \text{SO}_2 + \text{H}_2\text{O} \quad \Delta H_r = 212 \text{ kJ/mole} \quad (2.8)
\]

\[
\text{CaSO}_4 + 2 \text{Al}_2\text{O}_3 + \text{CO} \rightarrow \text{CaO.2Al}_2\text{O}_3 + \text{SO}_2 + \text{CO}_2 \quad \Delta H_r = 178 \text{ kJ/mole} \quad (2.9)
\]

However, during reductive regeneration, parallel reactions accompany due to the following paths:

\[
\text{CaSO}_4 + 4 \text{H}_2 \rightarrow \text{CaS} + 4 \text{H}_2\text{O} \quad \Delta H_r = -59 \text{ kJ/mole} \quad (2.10)
\]

\[
\text{CaSO}_4 + 4 \text{CO} \rightarrow \text{CaS} + 4 \text{CO}_2 \quad \Delta H_r = -191 \text{ kJ/mole} \quad (2.11)
\]

No literature data were found about the formation of calcium aluminosulfides e.g. Ca\(_2\)[Al\(_2\)O\(_3\)]S\(_2\) or Ca\(_3\)[Al\(_4\)O\(_8\)]S\(_3\) at 850°C and 1 atm. Martin (1915) reports that these compounds can only be formed by melting well mixed CaSO\(_4\), Al\(_2\)O\(_3\) and carbon in a closed furnace. Studies on the reduction of "pure" CaSO\(_4\) show that high temperatures and low partial pressures of the reducing gas prevent the formation of CaS (Wheelock and Boylan, 1960; Swift and Wheelock, 1975; Rassiwalla and Wheelock, 1977; Kostyl'kov and Nosov, 1980; Diaz-Bossio et al., 1985). Of course, the formation of CaS is undesirable because the available amount of active sorbent decreases; in the next sulfation cycle CaS will be oxidized in the combustor to CaO.2Al\(_2\)O\(_3\) and CaSO\(_4\) according to:

\[
\text{CaS} + 2 \text{Al}_2\text{O}_3 + 3/2 \text{O}_2 \rightarrow \text{CaO.2Al}_2\text{O}_3 + \text{SO}_2 \quad \Delta H_r = -478 \text{ kJ/mole} \quad (2.12)
\]

and simultaneously:

\[
\text{CaS} + 2 \text{O}_2 \rightarrow \text{CaSO}_4 \quad \Delta H_r = -938 \text{ kJ/mole} \quad (2.13)
\]

Other reactions that can occur during the regeneration are the formation of H\(_2\)S, COS and S\(_x\) according to the overall reactions:
the regenerative D.U.T. sol-gel sorbent

\[
\text{CaSO}_4 + 2 \text{Al}_2\text{O}_3 + 4 \text{H}_2 \rightarrow \text{CaO} \cdot 0.2\text{Al}_2\text{O}_3 + \text{H}_2\text{S} + 3 \text{H}_2\text{O} \quad \Delta H_r = -16 \text{ kJ/mole} \\
\text{(2.14)}
\]

\[
\text{CaSO}_4 + 2 \text{Al}_2\text{O}_3 + 4 \text{CO} \rightarrow \text{CaO} \cdot 0.2\text{Al}_2\text{O}_3 + \text{COS} + 3 \text{CO}_2 \quad \Delta H_r = -42 \text{ kJ/mole} \\
\text{(2.15)}
\]

\[
\text{CaSO}_4 + 2 \text{Al}_2\text{O}_3 + 3 \text{H}_2 \rightarrow \text{CaO} \cdot 0.2\text{Al}_2\text{O}_3 + 3 \text{H}_2\text{O} + 1/2 \text{S}_2 \quad \Delta H_r = 75 \text{ kJ/mole} \\
\text{(2.16)}
\]

\[
\text{CaSO}_4 + 2 \text{Al}_2\text{O}_3 + 3 \text{CO} \rightarrow \text{CaO} \cdot 0.2\text{Al}_2\text{O}_3 + 3 \text{CO}_2 + 1/2 \text{S}_2 \quad \Delta H_r = -24 \text{ kJ/mole} \\
\text{(2.17)}
\]

The equilibrium constant \( K_{eq,T} \) for a single reaction can be calculated as a function of temperature from the Gibbs function of reaction \( \Delta G_{r,T} \) (e.g. Atkins, 1982):

\[
\nu_1 A_1 + \nu_2 A_2 + \ldots \xrightarrow{\text{---}} \nu_1' A_1' + \nu_2' A_2' + \ldots \\
\text{(2.18)}
\]

\[
K_{eq,T}(-) \text{ is defined as:}

K_{eq,T} = \frac{(a_{A_1'})^{\nu_1'} \cdot (a_{A_2'})^{\nu_2'} \cdot \ldots}{(a_{A_1})^{\nu_1} \cdot (a_{A_2})^{\nu_2} \cdot \ldots} \\
\text{(2.19)}
\]

where \( A_i, A_i' \) = reactant i and product i respectively (-)

\( a_{A_i} \) = activity of compound \( A_i \) (-)

\( i \) = index number of compound \( A \) (-)

\( \nu_i \) = stoichiometric factor of compound \( A_i \) (-)

The Gibbs function of reaction (J/mole) can be calculated from literature data for the Gibbs function of a pure substance \( G_i \) (J/mole) according to:

- 26 -
\[ \Delta G_{r,T} = \sum (\nu_i^r G_T(A_i^r)) - \sum (\nu_i G_T(A_i)) \]  

(2.20)

while \( K_{eq,T} \) is calculated using:

\[ R_g T \ln (K_{eq,T}) = -\Delta G_{r,T} \]  

(2.21)

where \( R_g \) = gas constant; \( R_g = 8.314 \text{ (J/(mole K))} \),

\( T \) = temperature (K).

Using available thermodynamic data on CaO.2Al_2O_3 (Barin and Knacke, 1973 and Eliezer et al., 1981), the Gibbs function of its reactions can be calculated as a function of temperature. The thermodynamic equilibria for sulfation and regeneration reactions of "pure" CaO and CaO.2Al_2O_3 with H_2 or CO are shown in Figure 2.3.

![Diagram of Gibbs function reactions]

**Figure 2.3** Standard Gibbs function of reaction for sulfation and regeneration of CaO and CaO.2Al_2O_3.
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It can be seen that if the synthetic sorbent consists of a sulfated calcium aluminate, it can be easier regenerated at a relatively low temperature of 850°C than "pure" CaSO₄; CaSO₄ reacts with Al₂O₃ to form the more stable Ca₀.₂Al₂O₃ (compared to CaO) and SO₂. Of course, kinetics can play an important role in the final acceptation and regeneration performance. This will be discussed in section 2.6.

2.5 Sorbent characterization

Seven techniques have been used to characterize the composition and texture of the sorbent prepared by the technique described in section 2.2. The mechanical strength will be characterized in chapter 6.

1. Atomic Absorption Spectroscopy (AAS)
   The active metal (Ca) content of the sorbent is determined by grinding 6 g sorbent and solving 200 mg of the resulting powder in 15 ml aqua regia. The solution is then diluted with water to a suitable concentration (range 0 – 5 ppm Ca). The AAS measurements are performed with a Perkin Elmer 2380 spectroscope.

2. Phenolphthalein-test
   The presence of "free" CaO which has not interacted with Al₂O₃ is indicated by a color test. A 50 vol% water ethyl alcohol mixture containing 0.05 g phenolphthalein in 100 ml mixture is dropped on the sorbent. A purple color indicates a basic compound like free CaO. The absence of free CaO is shown if the sorbent remains colorless to this mixture (Coughlin, 1956).

3. Electron-Probe X-ray Microanalysis (EPMA)
   A Jeol JXA 733 electron probe X-ray microanalyser equipped with four wavelength dispersive spectrometers (WDS), an energy dispersive spectrometer (EDS) and a fully automated analysis system (Tracor Northern TN 5500 and TN 5600) is used to determine the distribution of Al, Ca, O and S in cross sections of sorbent spheres over a diameter of the cross section. The intensities of the Al-, Ca-, O- and S-Kα radiation excited by a focussed electron beam (10 keV and 100 nA) are measured simultaneously, using WDS at spots on a distance of 5 µm. The line scan is performed from the outer side of the particle (0 µm) to its centre (about 1500 µm). The X-ray intensities of the specimen are compared with reference material. CaSO₄ (Mineral Standard 25-53 ASTMEX Scientific Ltd,
Toronto, Canada) is used as a reference for Ca and S and Y₃Al₅O₁₂ is used as a reference for Al and O. From the corresponding intensity ratio's the values for the Al, Ca, O and S contents are determined applying the modified $\phi(\rho z)$ approach (Bastin et al., 1984).

4. X-Ray powder Diffraction (XRD)
A Guinier camera has been used at 40 kV and 20 mA during 1 h exposure. CuKα radiation is applied at vacuum and 20°C. The specific aluminas and calcium aluminates can be determined if the compounds are well crystallized and their concentration is higher than about 5 wt%.

5. N₂ physisorption
The BET technique is used with N₂ as adsorbate to determine the (internal) surface area and pore volume of the sorbent. A sample of about 0.4 g was supplied to a Micromeritics Digisorb 2600 at -196°C.

6. Hg porosimetry
In case of large pores (above 100 mm), Hg porosimetry is preferred over N₂ intrusion for the measurement of the pore volume. A Carlo Erba Strumentazione Porosimeter 2000 is used at a maximum pressure of 2000 bar and room temperature. The mass of the sample is about 0.6 g.

Table 2.3 Characterization of synthetic sorbent

| sorbent type/code | SG105 |
| shape | spherical |
| diameter (mm) | 2.8-3.4 (sieved after preparation) |
| Ca-content (wt%) | 5.83 (sample of 6 g sorbent) |
| free CaO present | yes |
| Ca-distribution | relatively uniform distribution on a scale of 5 μm (see figure 2.4) |
| other compounds detected | γ-Al₂O₃, no calcium aluminates |
| surface area $N₂$ physisorption (m²/g) | 99 ± 2 |
| Hg porosimetry (m²/g) | 80 ± 8 |
| pore volume $N₂$ physisorption (ml/g) | 0.29 ± 0.01 |
| Hg porosimetry (ml/g) | 0.22 ± 0.02 |
| solid density (skeletal) (kg/m³) | 3270 ± 15 |
| moisture 1) (wt%) | 3 ± 2 |

1) The amount of moisture was determined in a thermobalance.
2) Single measurement, i.e. "±" indicates measurement error in stead of a sample standard deviation.
7. He intrusion

The solid density has been determined with a Micromeritics Autopycnometer 1320 using He pycnometry at room temperature. The mass of the sample is about 11 g.

The results obtained are summarized in Table 2.3. Measurement of the calcium content of single sorbent particles shows a rather large variation between individual particles. The sample standard deviation of six measurements was 0.62 wt%. The EPMA-recording of the sorbent is presented in Figure 2.4; it indicates a somewhat decreasing calcium concentration from the exterior of the particle to the centre.

![Figure 2.4 Calcium and sulfur response profiles by EPMA (line scan of fresh sorbent).](image)

The distribution of the calcium is uniform on a scale of at least 5 μm, although small calcium containing crystallites seem to be present as well. This result is qualitatively supported by the phenolphthalein-test on cut particles to detect free calcium. Qualitative phase analysis using XRD shows only a poorly crystallized γ-Al₂O₃ phase (JCPDS-ASTM index number 10-425) but no calcium aluminates. This can be explained by two reasons. Either no calcium aluminates are formed or, most probably, the result is caused by the amorphous structure of the sorbent (i.e. a high calcium dispersion). An
additional test to identify the occurrence of calcium aluminates was performed by heating the sorbent SG105 for another 500 h at 850°C (see also section 4.2.1). The phenolphthalein-test still showed the presence of free CaO but a somewhat lower intensity of the purple colour was obtained. XRD clearly showed the formation of CaO.2Al₂O₃ (JCPDS-index number 23-1037) beside γ-Al₂O₃. It was discussed in section 2.3 that only a sulfated calcium aluminate can be regenerated at 850°C and atmospheric pressure; therefore a reactive calcium aluminate has to be formed according to reaction (2.2) with m/n = 1/2. In this thesis the sorbent will be symbolized as CaO/γ-Al₂O₃. The calcium aluminate will be referred to as CaO throughout this thesis, it being understood that the calcium is usually in the form of a calcium aluminate.

The adsorption and desorption curves measured by the N₂ physisorption method are presented in Figure 2.5 to provide information on the pore structure of the sorbent.

![Figure 2.5](image_url)  
*Figure 2.5* N₂ adsorption and desorption isotherm of SG105 sorbent. P₀ is the saturated vapour pressure of N₂.

The curves indicate a cylindrical shape of the pores. The internal surface area and pore volume-distribution as a function of pore diameter are given in Figures 2.6 and 2.7, respectively.
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Figure 2.6 Internal surface area distribution of SG105 sorbent, 
$S_{\text{cum}} (100\%) = 99 \text{ m}^2/\text{g}.$

Figure 2.7 Pore volume distribution of SG105 sorbent,  
$V_{\text{cum}} (100\%) = 0.29 \text{ ml/g}.$
Based on the \( \text{N}_2 \) sorption measurements, an average pore radius of 5.8 nm is calculated using:

\[
\begin{align*}
\text{r}_{\text{pore}} &= \frac{2 \ V_{\text{pore}}}{S_{\text{BET}}} \\
(2.22)
\end{align*}
\]

where \( r_{\text{pore}} \) = average radius of cylindrical pore (m),
\( V_{\text{pore}} \) = pore volume (m\(^3\)/kg),
\( S_{\text{BET}} \) = BET internal surface area (m\(^2\)/kg).

Using Hg porosimetry both the values of the surface area and pore volume are smaller. However, accurate Hg-porosimetry can only be applied on a sorbent with pores larger than about 100 nm. The calculated average pore radius of 5.8 nm thus rejects the Hg-penetration method.

2.6 Kinetics of sulfur capture and sorbent regeneration

Many workers have studied the kinetics of the sulfation of limestone in fluidized bed combustion (see section 1.2). Also the regeneration of calcium sulfate has been studied (see section 2.4). However, few data have been found on the acceptance and regeneration of calcium aluminates. Snyder et al. (1975) studied sorbents, consisting of CaO on an \( \alpha \)-Al\(_2\)O\(_3\) support, at temperatures of 800–1200°C, using thermogravimetry (TG). With this technique, the weight of a sample is recorded as a function of time or temperature while it is heated or cooled at a controlled rate. The sulfation rate of their synthetic sorbent was determined as a function of gas composition, temperature, calcium concentration and heat treatment temperature of the sorbent during preparation. A mathematical equation (shown below) was developed that predicts the sulfation rate as a function of \( \text{SO}_2 \) and CaO concentrations, temperature and the heat treatment (H.T.) temperature of the sorbent during preparation. The sorbent contains 6.6 wt% CaO and \( \text{O}_2 \) is in 5 vol% stoichiometric excess.
\[
\ln \frac{[\text{CaO}]_t}{[\text{CaO}]_0} = -\frac{Q}{2.9 \times 10^{-6}} \left[ \text{SO}_2 \right]^{0.7} t \left( 1 + \frac{1.13 \times 10^5}{R_g T} \right)
\]

where \([\text{CaO}]\) = concentration of CaO (mole/m² of surface area),
\([\text{SO}_2]\) = concentration of SO₂ (mole fraction),
t = time (s),
\(T\) = temperature (K),
\(R_g\) = gas constant; \(R_g = 8.314 \text{ J/(mole K)}\),
\(Q\) = 0.025 for 800°C H.T. sorbent (-),
\(Q\) = 0.0172 for 1100°C H.T. sorbent (-).

Regeneration experiments were performed using various reducing gases (H₂, CH₄ or CO) at 1100°C. Also the effect of temperature on the regeneration reaction was determined. The conversion of CaSO₄ to CaO can be given as a function of time:

\[
\ln \frac{[\text{CaSO}_4]_t}{[\text{CaSO}_4]_0} = -3.36 \exp \left( \frac{-62300}{R_g T} \right) [\text{H}_2 \text{ or CH}_4]^{0.8} t
\]

\[
\ln \frac{[\text{CaSO}_4]_t}{[\text{CaSO}_4]_0} = -1.08 \exp \left( \frac{-62300}{R_g T} \right) [\text{CO}]^{0.8} t
\]

where \([\text{CaSO}_4]\) = concentration of CaSO₄ (mole/m² of surface area),
\([\text{H}_2]\) = concentration of H₂ (mole/m³ at 298 K),
\([\text{CH}_4]\) = concentration of CH₄ (mole/m³ at 298 K),
\([\text{CO}]\) = concentration of CO (mole/m³ at 298 K).

From the experimental results an activation energy of 62.3 kJ/mole was obtained. XRD-results for the regenerated sorbents showed that their product was a mixture of Ca0.6Al₂O₃ and Ca0.2Al₂O₃ and that no CaS nor CaSO₄ was present. The regeneration rate was the same for H₂ and CH₄, but it was three times lower with CO as a reductant. Kinetic experiments on the regeneration
were performed over a temperature range of 800°C to 1200°C, using 1 vol% H₂ in the gas stream. The composition of the regeneration reaction product as a function of temperature is shown in Table 2.4.

<table>
<thead>
<tr>
<th>regeneration temperature °C</th>
<th>product</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>CaS</td>
</tr>
<tr>
<td>850</td>
<td>CaS</td>
</tr>
<tr>
<td>900</td>
<td>most CaS-little CaO</td>
</tr>
<tr>
<td>950</td>
<td>most CaS-little CaO</td>
</tr>
<tr>
<td>1000</td>
<td>medium CaO-medium CaS</td>
</tr>
<tr>
<td>1050</td>
<td>most CaO-little CaS</td>
</tr>
<tr>
<td>1100</td>
<td>CaO</td>
</tr>
<tr>
<td>1150</td>
<td>CaO</td>
</tr>
<tr>
<td>1200</td>
<td>CaO</td>
</tr>
</tbody>
</table>

The table shows that the regeneration efficiency increases with temperature. Complete one-step regeneration could be obtained above 1050°C. Note that the reactions (2.8) and (2.9) are endothermic and therefore favoured by higher temperatures. The reduction of sulfated calcium aluminate with low partial pressures of the reducing gas will probably prevent the formation of CaS as well (see section 2.4). Snyder et al. (1975) concluded that the rate of regeneration is fast compared with sulfation, less than five minutes being required to regenerate the sorbent at the process conditions applied. For synthetic additives of α-Al₂O₃ containing 3 to 15 percent CaO, it will take 1 to 10 hours to convert 90 percent of the CaO to CaSO₄. This rate of SO₂ capture in a fluidized bed combustor should be sufficient to meet EPA SO₂ emission standards. However, about twice as much synthetic additive is needed compared with Tymochtee dolomite. A preliminary cyclic sulfation-regeneration experiment (10 cycles) indicates no change in reactivity.
2.7 Conclusions

A new synthetic sorbent, consisting of CaO (8.2 wt%) on a 3 mm γ-alumina support, has been prepared by the sol-gel method to be used in a regenerative desulfurization process.

1. The special preparation method of the sorbent allows the active compound (CaO) to be highly dispersed in the support. After calcination at 850°C, the sorbent does not simply consist of CaO on an alumina support but interaction products between CaO and alumina are formed. It is assumed that XRD-analysis is not able to detect calcium aluminates, probably, because of the high calcium dispersion. After an additional heating period of 500 h at 850°C CaO.2Al₂O₃ is found.

2. Thermodynamics shows that a synthetic sorbent, consisting of a sulfated calcium aluminate, can be regenerated at the relatively low temperature of 850°C with reducing gases; CaSO₄ reacts with γ-Al₂O₃ to form the more stable CaO/γ-Al₂O₃ in comparison with CaO and SO₂. However, during reductive regeneration, the formation of CS₂, H₂S, COS and Sₓ is feasible. Literature data show that the formation of CaS is favoured at a lower regeneration temperature and probably at higher reducing gas concentrations as well.

In the next chapter, the fixed bed reactor system will be described which is used to study the chemistry of the (cyclic) sulfur capture and regeneration process.

References

the regenerative D.U.T. sol-gel sorbent


Edmunds, D.M. and Taylor, J., 1972, "Reaction CaO+3C=CaC_2+CO and Activity of Lime in CaO-Al_2O_3-CaF System", Journal of The Iron and Steel Institute, April, pp. 280-283.


Sirwardane, R.V., 1989, "Interaction of SO2 and O2 Mixtures with CaO (100) and Sodium Deposited on CaO (100)", Journal of Colloid and Interface Science, Vol. 132, No. 1, October, pp. 200-209.

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3

Fixed Bed Reactor Equipment and Experimental Procedures

3.1 Introduction

In literature, the kinetics of cyclic sulfur capture and regeneration processes are generally obtained using thermogravimetric balances or (laboratory scale) fluidized bed systems. However, in this work the sulfation and regeneration experiments have been performed mainly in a fixed bed reactor. Advantages of this system over thermogravimetry are:

1. A larger amount of sorbent can be used which favours the reproducibility of the experiments.
2. Less problems arise from bulk gas transfer limitation to the sorbent. In thermogravimetry such problems often occur due to the low flow rates of the gas and the bad contact between the sample in the sampleholder and the gas stream. No model is available in the literature to describe these phenomena in a thermobalance, while fixed bed reactor models are found abundantly.
3. A higher concentration of compounds in the off-gas of the reactor can be obtained and thus be determined.

Advantages of a fixed bed compared with a fluidized bed system are:

1. Safer, cheaper and faster operation. Only a limited amount of sorbent is available.
2. The hydrodynamics are better known.
3. There is no particle attrition.
3 fixed bed reactor equipment and experimental procedures

Experiments performed with a thermobalance are very useful when research is focussed on sorbent phenomena, e.g. maximum sorbent conversion. Fluidized bed experiments will match reality closest. With a fixed bed system fast screening of sorbent material and/or specific process conditions is possible.

The main targets of the study with the fixed bed reactor are:
1. To test whether or not the sorbent is suitable for cyclic regenerative desulfurization with respect to the chemistry involved.
2. To define the optimal process conditions for the regeneration step. Emphasis will be given to a low temperature regenerative process at 850°C; all tests are performed at 1 bar.
3. To define the process parameters (mass transfer and kinetics) which determine the sulfur capture process. A mathematical model is tested which describes the sulfur capture process. In future work, a regeneration model has to be developed as well. Then, these models are to be included in an overall fluidized bed model which describes both the sulfur capture in the combustor and the sulfur release in the regenerator.

This chapter describes the experimental equipment and the procedures used. In sections 3.2.1 to 3.2.3 the flowsheet of the unit is treated in detail, the procedures are explained in section 3.2.4. In section 3.3 special attention is given to the role of SO₃. Section 3.3.1 and section 3.3.2 discuss the thermodynamics and kinetics of the SO₃ formation, respectively. In section 3.3.3 various methods of SO₃ measurement are discussed. The chapter is concluded by section 3.4.

3.2 Equipment and experimental procedures

A flowsheet of the equipment is given in Figure 3.1. Cyclic retention and regeneration experiments can be performed automatically and continuously. The facility is controlled by a programmable sequence controller (Carlo Gavazzi Omron SYSMAC-P0). The installation consists of a gas feed section, a reactor section and an analysis section. Several security provisions have been made.
- 3 fixed bed reactor equipment and experimental procedures -

Figure 3.1 Simplified flowsheet of the fixed bed reactor unit.

1. The pressure regulator at the gas cylinder is protected against a too high pressure. The emergency vent at the $SO_2$-gas cylinder leads to the general blow-off vent.

2. Two contact manometers, installed on the mixing chambers (see section 3.2.4), protect the equipment against a too high pressure. In case of an emergency, the sequence controller is switched off, which generates a general shut-down. The heating is switched off, an emergency sluice is opened, the magnetic valves and mass flow controllers are closed and the gas in the reactor is blown off to the vent.

3. On top of the CO mass flow controller a CO detector is located. In case of an alarm a bell rings and the general shut-down, described above, is started.

4. The reactor is protected against over-heating. In case of an alarm a general shut-down is generated.

5. A "panic" red emergency button is provided to shut-down the equipment manually.

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3.2.1 Gas feed section

In the gas feed section not only the fluidized bed combustor off-gas can be simulated by mixing nitrogen, an oxygen/nitrogen mixture, sulfur dioxide, carbon dioxide and water, but also the feed gas to the regenerator. The latter consists of nitrogen, hydrogen, carbon monoxide, carbon dioxide and water. The model gas is obtained by mixing the gases from seven supplies:

1. $N_2$  100 vol% $N_2$
2. $O_2/N_2$  21 vol% $O_2$, 79 vol% $N_2$
3. $SO_2/N_2$  4.95 vol% $SO_2$, 95.05 vol% $N_2$
4. $CO_2$  100 vol% $CO_2$
5. $H_2$  100 vol% $H_2$
6. $CO$  100 vol% $CO$

The seventh supply consists of a motorized burette which can be used to inject liquid water to the feed. Each gas, except the $SO_2/N_2$ mixture, passes a drying column (DC, see Figure 3.1) filled with molecular sieve, type 4A. The $SO_2/N_2$ mixture cannot be dried by molsieves because $SO_2$ is absorbed too. However, it is delivered free of water (below 5 ppm) by the supplier (Air Products). The gas flows are measured and controlled by Inacom HI-TEC electronic mass flow controllers (MFC). The mass flow controller of $SO_2$ is located in a temperature controlled box (37°C) to decrease the influence of the ambient temperature. Two mixing chambers (MC) are present, one to mix gas for the retention cycle and another to mix the gas for the regeneration cycle. Water can be injected directly into the reactor with a buret (TB). The feed gas can also bypass the reactor (R) and be lead directly to the analysis section.

3.2.2 Reactor section

The reactor is situated in an electric tube furnace. The temperature is controlled by a proportional temperature controller. The reactor has been made of a ferritic stainless steel (an Al-Cr-Fe alloy) which was tested in a thermobalance on its resistance against corrosion and erosion by $SO_2/O_2/N_2$ and $H_2/N_2$ mixtures at 850°C. A detailed sketch of the reactor system and the temperature profile measured in the reactor is presented in Figure 3.2.
Figure 3.2 Diagram of the reactor tube with the fixed bed and the temperature profile.

The internal diameter (ID) is 12 mm. The lowest part of the reactor has an ID of 8 mm. On the boundary a filter is installed to support the sorbent. The temperature of the reactor is measured and controlled by a Pt-Pt10%Rh thermocouple (accuracy ±1°C) fixed to the outside of the reactor tube. The temperature gradient along the sorbent bed has to be kept as small as possible. Inert α-Al₂O₃ (2.9 mm spheres, fired 10 h at 1600°C, internal BET surface area 1 m²/g) is used to position the sorbent bed in the reactor properly and to achieve a well distributed flow across the bed. The temperature in the sorbent bed is 850 ± 3°C.

3.2.3 Analysis section

Isolation material and/or heating tape has been applied from reactor section to the analysis section. The volume between the sorbent bed in the reactor and the analysis section is about 30 ml which results in a "dead space time" of approximately 10 s at standard conditions (see next
fixed bed reactor equipment and experimental procedures

section, Table 3.3). The gas from the reactor is led into a titration vessel (TV1, see Figure 3.1) filled with a 6 wt% solution of hydrogen peroxide. Sulfur dioxide will absorb and react according to (AMS 589, 1973):

\[ \text{SO}_2(g) + \text{aq} \longrightarrow \text{SO}_2^{(aq)} \] (3.1)

\[ \text{SO}_2^{(aq)} + \text{H}_2\text{O}_2^{(aq)} + 2 \text{H}_2\text{O}(l) \longrightarrow \text{SO}_4^{2-}^{(aq)} + 2 \text{H}_3\text{O}^+^{(aq)} \] (3.2)

The hydrogen ions formed are titrated automatically by a 0.33 mole/l sodium hydroxide solution at a constant pH of 4.0. This value has been chosen for two reasons:
1. At pH = 4 the rate of decomposition of \( \text{H}_2\text{O}_2 \) is minimum (Gmelin, 1960).
2. To compromise between the optimum value for the acid base titration (pH = 5) and a lower pH to decrease the influence of CO\(_2\) absorption. A pH value of 4 decreases the sensitivity for the acid base titration only slightly.

The rate at which sodium hydroxide is consumed is proportional to the amount of sulfur dioxide leaving the reactor. The level of the buret in the titration unit generates an analog signal between 0 and 1000 mV in steps of 1 mV, which is recorded on a strip chart recorder. The noise on the signal is smaller than 0.2 mV. The signal is also sampled at a frequency of 0.71 Hz and stored by a PDP/11 preprocessor. After processing the data, the outlet \( \text{SO}_2 \) concentration can be determined as a function of time. In this way, the so-called breakthrough curves are obtained. These curves provide information on the sulfur capture and regeneration characteristics of the sorbent at the process conditions applied. By comparison of the computed breakthrough curves and measured outlet concentrations of \( \text{SO}_2 \) the mass transfer and kinetic information has been collected.

The gas from the first titration vessel enters a second vessel (TV2) filled with an aqueous solution of 14 wt% 3CdSO\(_4\).8H\(_2\)O to remove \( \text{H}_2\text{S} \). The \( \text{H}_2\text{S} \) reacts with the cadmium ion to a precipitate of cadmium sulfide and \( \text{H}_3\text{O}^+ \) (Soerawidjaja, 1985):
\[ H_2S(g) + aq \rightarrow H_2S(aq) \]  \hspace{1cm} (3.3)

\[ H_2S(aq) + Cd^{2+}(aq) + 2 H_2O(l) \rightarrow CdS(s) + 2 H_3O^+(aq) \]  \hspace{1cm} (3.4)

Similar to the SO\textsubscript{2} analysis, the H\textsubscript{3}O\textsuperscript{+} is titrated with a 0.33 mole/l sodium solution at pH = 4.0. However, the determination of H\textsubscript{2}S was performed off-line after each regeneration step. Thus only the total amount of H\textsubscript{2}S released during the regeneration step could be determined.

3.2.4 Experimental procedures

Each cycle of an experiment consists of five stages:

1. Calibration stage: during 20 minutes the feed bypasses the reactor to determine the SO\textsubscript{2} content of the FBC model gas

2. Acceptation stage: the FBC model gas is fed to the reactor at retention temperature. This stage is generally set to 25 hours.

3. N\textsubscript{2}-flush stage 1: the sorbent is flushed with nitrogen for 5 minutes at retention temperature

4. N\textsubscript{2}-flush stage 2: after heating the reactor to regeneration temperature the sorbent is flushed again with nitrogen for 5 minutes

5. Regeneration stage: during 20 minutes the sorbent is regenerated using a reducing gas

Before the calibration stage of the first cycle, an oxidation stage is inserted in which the feed gas, without SO\textsubscript{2}, is led to the reactor to bring the sorbent in the reactor in an oxidized state and to remove any sulfur compounds from previous experiments. Stage 4 is omitted when the regeneration stage is performed at the same temperature as the acceptation stage. The regeneration stage is followed by a N\textsubscript{2}-flush to remove the reducing gas. A schematic representation of the continuous titration data obtained from a complete cycle is shown in Figure 3.3.
Figure 3.3 Sketch of the continuous titration data obtained from a complete acceptance-regeneration cycle.

When measuring the feed during the calibration stage, the cumulative amount of SO₂ absorbed in the titrator vessel increases linearly with time, indicating a constant SO₂ feed rate. The slope of this line represents the molar feed rate of SO₂. When the stream of SO₂ is switched to the reactor during the acceptance stage, the effluent from the reactor is initially free of SO₂. As time proceeds, the effluent contains an increasing amount of SO₂.

Although the hydrogen peroxide solution in the titration vessel completely removes even minute amounts of SO₂ present, the lower boundary of the sensitivity of the whole titration system is about 25 ppm SO₂. Thus, during acceptance, the titration data indicate a practically zero cumulative amount of SO₂ until point A (see Figure 3.3) is reached. At this point, the outlet concentration of SO₂ is about 25 ppm.

If the acceptance stage continues sufficiently long, the outlet concentration of SO₂ finally reaches a constant value. However, there
remains a difference between the outlet and inlet concentrations of SO₂ due, at least partially, to the formation of SO₃. Since SO₃ is not titrated, the outlet readings are somewhat lower than those of the inlet gas. The formation of SO₃ will be further discussed in detail in section 3.3. Only small quantities of SO₂ are released during the N₂ flushes. In the regeneration stage the SO₂ released by the sorbent produces the peak shown in the SO₂ concentration vs. time curve of Figure 3.3. The height of the peak gives the maximum SO₂ concentration in the off-gas from the fixed bed reactor during regeneration. After the N₂-flush, without SO₂ measurement, the experiment proceeds with the calibration stage of the next cycle. The sulfur capture efficiency \( S_{\text{cap}} \) and the various regeneration efficiencies \( S_{\text{reg}} \) are defined as:

\[
S_{\text{cap}} = \frac{\text{amount of SO}_X \text{ captured during acceptation (mole)}}{\text{amount of SO}_X \text{ fed during acceptation (mole)}} \times 100\% \quad (3.5)
\]

\[
S_{\text{SO}_2,\text{reg}} = \frac{\text{amount of SO}_2 \text{ released during regeneration (mole)}}{\text{amount of CaSO}_4 \text{ present on the sorbent (mole)}} \times 100\% \quad (3.6)
\]

\[
S_{\text{H}_2\text{S,reg}} = \frac{\text{amount of H}_2\text{S released during regeneration (mole)}}{\text{amount of CaSO}_4 \text{ present on the sorbent (mole)}} \times 100\% \quad (3.7)
\]

The relative amount of elemental sulfur and CaS formed during the regeneration is defined as:

\[
S_{\text{S,reg}} = \frac{\text{amount of S formed during regeneration (mole)}}{\text{amount of CaSO}_4 \text{ present on the sorbent (mole)}} \times 100\% \quad (3.8)
\]

\[
S_{\text{CaS,reg}} = \frac{\text{amount of CaS formed during regeneration (mole)}}{\text{amount of CaSO}_4 \text{ present on the sorbent (mole)}} \times 100\% \quad (3.9)
\]

The amount of elemental sulfur formed was not measured. The amount of CaS could be quantitatively determined by chemical analysis of the sorbent; another way is by repeated oxidation of the CaS (according Eq. (2.12) and (2.13)) and reduction of the formed CaSO₄ by H₂ (according to (2.8), (2.14) and (2.16)). The decomposition of CaS proceeds by the formation of SO₂ and H₂S, which are monitored. During CO reduction, COS is formed which is not
quantitatively analysed. The definition of the sulfur capture and regeneration efficiencies provide a measure for comparison of the influence of various process conditions. Table 3.1 shows the composition of an AFBC off-gas when coal is burned with 3.7 wt% S while no desulfurization is applied.

<table>
<thead>
<tr>
<th>Table 3.1</th>
<th>Composition of stack gas produced by burning coal in an AFBC system without desulfurization at 850°C and 1 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ concentration</td>
<td>(vol%)</td>
</tr>
<tr>
<td>SO₂</td>
<td>(vol%)</td>
</tr>
<tr>
<td>CO₂</td>
<td>(vol%)</td>
</tr>
<tr>
<td>H₂O</td>
<td>(vol%)</td>
</tr>
<tr>
<td>N₂</td>
<td>(vol%)</td>
</tr>
</tbody>
</table>

The regeneration feed gas used, simulates the gas produced by a Winkler gasifier which operates at 1 bar as given in Table 3.2. Of course, other types of gasifiers can be used as well, but they usually operate at higher temperatures and pressures.

In section 4.2.1 it will be shown that CO₂ and H₂O have little influence on the acceptance performance and thus can be excluded from the standard.

<table>
<thead>
<tr>
<th>Table 3.2</th>
<th>Typical composition of the gas produced by a Winkler gasifier at 850°C and 1 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>gasification medium</td>
<td>oxygen</td>
</tr>
<tr>
<td></td>
<td>1)</td>
</tr>
<tr>
<td>H₂ concentration</td>
<td>(vol%)</td>
</tr>
<tr>
<td>CO</td>
<td>(vol%)</td>
</tr>
<tr>
<td>CO₂</td>
<td>(vol%)</td>
</tr>
<tr>
<td>H₂O</td>
<td>(vol%)</td>
</tr>
<tr>
<td>LCH₄</td>
<td>(vol%)</td>
</tr>
<tr>
<td>N₂</td>
<td>(vol%)</td>
</tr>
</tbody>
</table>

1) after drying

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fixed bed reactor equipment and experimental procedures

simulated combustor gas. To simplify the experimental procedure CO₂ and H₂O are also omitted from the gas fed in the regeneration phase of most experiments. If not mentioned otherwise, the standard conditions listed in Table 3.3 have been applied during all fixed bed experiments.

<table>
<thead>
<tr>
<th>Table 3.3 The standard process conditions of the fixed bed experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>RETENTION</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>temperature reactor (°C) 850</td>
</tr>
<tr>
<td>pressure reactor (bar) 1</td>
</tr>
<tr>
<td>superficial gas vel. (m/s) 0.2</td>
</tr>
<tr>
<td>flow gas in reactor (m³ STP/min) 335</td>
</tr>
<tr>
<td>inlet gas conc. O₂ (vol%) 4</td>
</tr>
<tr>
<td>SO₂ (vol%) 0.25</td>
</tr>
<tr>
<td>H₂ (vol%) 25</td>
</tr>
<tr>
<td>N₂ (vol%) balance</td>
</tr>
<tr>
<td>bypass feed rate SO₂ (μmole/min) 36.8 ± 0.6</td>
</tr>
<tr>
<td>weight sorbent (g) 5.5</td>
</tr>
<tr>
<td>length sorbent bed (m) 0.051</td>
</tr>
<tr>
<td>void fraction (m³ gas/m³ reactor) 0.43</td>
</tr>
<tr>
<td>gas residence time (s) 0.11</td>
</tr>
</tbody>
</table>

Using the gas flow and amount of sorbent chosen, an SO₂ outlet concentration of about 70% of the inlet value was obtained after five hours. Total conversion of calcium is obtained only after 25 hours. Under the process conditions of Table 3.3 and assuming CaO.2Al₂O₃ as the reactive compound the equilibrium concentration of SO₂, calculated by using Figure 2.3, is about 1 ppm which is low enough for adequate desulfurization.

3.3 The role of SO₃

So far, the formation of SO₃ in fluidized bed combustion has attracted relatively little attention in literature. Measurements in atmospheric and pressurized fluidized bed combustors show that SO₃ emission levels are likely to be sufficiently low in commercial units provided there is sufficient alkaline material (ash and sulfur acceptor) present to absorb SO₃ if it is produced. Theoretical considerations based on known SO₂ oxidation kinetics and temperature profiles in fluidized bed combustors show that
these systems potentially can generate large (near equilibrium) concentrations of SO₃ (Burdett et al. 1983). This species can be particularly troublesome as it condenses readily (as concentrated sulfuric acid) on "cool" surfaces. Potential problems are corrosion, fouling and acidic particulate fall out. The work of Burdett et al. shows that detailed knowledge of SO₃ production and absorption kinetics is needed. Another reason to study SO₃ formation is its influence on the sulfation mechanism.

3.3.1 Thermodynamics of the SO₃ formation

Gaseous SO₃ is formed according to the equilibrium reaction:

\[
\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{SO}_3 \quad \Delta H_r, \text{ oxidation} = -97 \text{ kJ/mole (3.10)}
\]

The equilibrium constant for this reaction can be expressed as:

\[
K_{eq,P} = \frac{P_{SO_3}}{P_0^0 \left( P_{O_2}^0 \right)^{1/2}} \quad (3.11)
\]

where \(K_{eq,P}\) = equilibrium constant of \(\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{SO}_3\) (\(\cdot\)), \(P_{SO_3}\), \(P_{SO_2}\) and \(P_{O_2}\) = partial pressure of SO₃, SO₂ and O₂ respectively (Pa), \(P_0^0\) = standard pressure, by definition 101325 (Pa).

The equilibrium constant \(K_{eq,P}\) is calculated by formula (2.21) from the thermodynamic data of Barin and Knacke (1973). A linear fit of their data provides an equation for the temperature dependency of the Gibbs function of reaction:

\[
\Delta G_{r,T} = (91.90 \pm 0.23) T - (97.59 \pm 0.26) 10^3 \text{ J/mole} \quad (T = 300-1800 \text{ K (3.12)})
\]
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A plot of the equilibrium conversion of \( \text{SO}_2 \) to \( \text{SO}_3 \) at the conditions listed in Table 3.3 is given as a function of temperature in Figure 3.4.

![Figure 3.4](image)

**Figure 3.4** Calculated equilibrium yield of \( \text{SO}_3 \) (in mole%) at standard feed composition.

3.3.2 Kinetics of the \( \text{SO}_3 \) formation

Uncertainties in the mechanism and reaction kinetics of the \( \text{SO}_3 \)-producing and converting processes makes an accurate prediction of \( \text{SO}_3 \) emission from fluidized bed combustors nearly impossible. However, some qualitative information is available which enables one to estimate the relative importance of the reactions occurring in such systems. Relevant mechanisms are (Burdett et al. 1979):

1. \( \text{SO}_2/\text{SO}_3 \) homogeneous gas phase reactions.
2. Heterogeneous catalysis of \( \text{SO}_2/\text{SO}_3 \) reactions on bed particles and reactor surfaces.
3. Reaction/adsorption of \( \text{SO}_3 \) on the alkaline ash particles in the bed and/or on elutriated material.
4. Removal of \( \text{SO}_3 \) by the sorbent.
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The first two mechanisms are discussed below and calculations are made to estimate whether or not the reactions are important during the fixed bed experiments. The third mechanism is mentioned briefly in the discussion of the second mechanism. The fourth mechanism will be described in Chapter 5.

(1) Homogeneous gas phase reactions

a. The oxidation of SO₂

SO₂ is oxidized to SO₃ by the overall reaction:

\[
SO₂ + \frac{1}{2} O₂ \rightarrow SO₃ \quad \Delta H_r = -97 \text{ kJ/mole}
\]  

(3.13)

Flint and Lindsay (1951) measured SO₃ concentrations after an air flow, containing 1400 ppm SO₂ and 8 percent water, was passed through a quartz tube, length 1.83 m and ID 0.014 m, at various temperatures. The oxidation level of sulfur dioxide at 850°C and a residence time of 0.11 s is about 0.04%. Cullis et al. (1966) found no noncatalytic oxidation of SO₂ at temperatures below 900°C. Their measurements with an equimolar mixture of 2.6 \(10^{-3}\) mole/l SO₂ and O₂ in a narrow temperature range of 900 – 1050°C (dictated by the location of the equilibrium and the consequently small maximum possible conversion to SO₃) show an activation energy of 314 kJ/mole. At 950°C the rate of formation of SO₃ is \(7.1 \times 10^{-6}\) mole/(l min). The fact that the rate depends considerably more on the concentration of SO₂ than on that of any other species present (O₂, N₂ and H₂O) suggests that the rate controlling step may well be the collisional activation of the SO₂ molecule. The resulting species react subsequently either with another molecule of sulfur dioxide or with a molecule of oxygen:

\[
SO₂ + M \xrightarrow{k_a} SO₂^*
\]  

(3.14)
where M is a general third body, SO₂, O₂ or any other molecule present acting as a chaperon for recombination.

\[
\text{SO}^* + \text{SO}_2 \longrightarrow \text{SO}_3 + \text{SO}
\]  
(3.15)

\[
\text{SO}^* + \text{O}_2 \longrightarrow \text{SO}_3 + \text{O}
\]  
(3.16)

followed by:

\[
\text{SO} + \text{O}_2 \longrightarrow \text{SO}_3
\]  
(3.17)

\[
\text{SO}_2 + \text{O} \longrightarrow \text{SO}_3
\]  
(3.18)

The rate of formation of SO₃ can now be expressed as:

\[
\frac{dC_{\text{SO}_3}}{dt} = k_a C_{\text{SO}_2}
\]  
(3.19)

The temperature dependence is given by the usual Arrhenius expression. With this assumption it is possible to write:

\[
\frac{dC_{\text{SO}_3}}{dt} = k_{a0} \exp \left( \frac{-E_a}{RT} \right) C_{\text{SO}_2}
\]  
(3.20)

Substituting above numerical data results in a value of \(6.9 \times 10^{10}\) (1/min) for \(k_{a0}\). If this result is extrapolated to the fixed bed conditions discussed in section 3.2.4 (Table 3.3), a conversion of 0.00003% SO₂ to SO₃ is calculated. Consequently, the homogeneous conversion of SO₂ to SO₃ would be negligible.
Another mechanism is proposed by Burdett et al. (1984). They investigated the extent of the homogeneous SO$_2$ oxidation occurring under well-defined conditions. A gas mixture of SO$_2$, O$_2$, N$_2$ and H$_2$O that simulated a FBC flue gas, was passed through a silica reactor tube. They proposed the following mechanism for the SO$_3$ production in combustion systems:

\[
\begin{align*}
\text{SO}_2 + O_2 & \xrightarrow{k_b} SO_3 + O \\
& \xleftarrow{k_{-b}} \text{SO}_3 + O
\end{align*}
\]  \hspace{1cm} (3.21)

and

\[
\begin{align*}
\text{SO}_2 + O + M & \xrightarrow{k_c} SO_3 + M \\
& \xleftarrow{k_{-c}} \text{SO}_3 + M
\end{align*}
\]  \hspace{1cm} (3.22)

Atomic oxygen is formed, for example, in the coalburning flames. Reaction (3.21) is dominant at temperatures below 1200 K (Squires, 1982). The rate of SO$_3$ formation can now be expressed as:

\[
\frac{dC_{SO_3}}{dt} = k_b C_{SO_2} C_{O_2}
\]  \hspace{1cm} (3.23)

According to Burdett the rate coefficient $k_b$ for this reaction is:

\[
k_b = (2.6 \pm 1.3) \times 10^{12} \exp \left[\frac{(-23000 \pm 1200)}{T}\right] \text{cm}^3\text{mole}^{-1}\text{s}^{-1}
\]  \hspace{1cm} (3.24)

If this result is extrapolated to the fixed bed conditions, a conversion of 0.02% SO$_2$ to SO$_3$ is calculated. This value is not in agreement with the results above based on Cullis et al. (1966). Both results predict a negligible homogeneous SO$_2$ oxidation in the fixed bed.
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reactor. At temperatures higher than 1200 K reaction (3.22) becomes significant since the equilibrium

\[ \text{O}_2 + M \xrightarrow{k_d} 2 \text{O} + M \]  

(3.25)

is strongly temperature dependent. Dennis and Hayhurst (1988) show that the relaxation time, i.e. the time of a system to return to equilibrium, for reaction (3.25) is given by:

\[ \tau_r = \frac{1}{k_d C_M + 4k_{-d} (C_0)^e C_M} \]  

(3.26)

where \( C_M \) = concentration of \( M \) (mole/m\(^3\)),  
\( (C_0)^e \) = equilibrium concentration of \( O \) atoms (mole/m\(^3\)).

While the rate constants \( k_d \) and \( k_{-d} \) are defined respectively by:

\[ - \frac{dC_{O_2}}{dt} = k_d C_{O_2} C_M \]  

(3.27)

\[ - \frac{dC_O}{dt} = 2k_{-d} C_O^2 C_M \]  

(3.28)

From Baulch et al. (1976):

\[ k_d = 1.8 \times 10^{-12} \frac{m^3}{\text{mole s}} \exp \left[ -59380/T \right] \]  

(3.29)

\[ k_{-d} = 19.0 \exp \left[ 900/T \right] \frac{m^6}{\text{mole}^2 \text{s}} \]  

(3.30)
At the fixed bed reactor conditions and standard thermodynamic data (Barin and Knacke, 1973), it follows that \((C_0)_e = 5.2 \times 10^{-9} \text{ mole/m}^3\) and \(C_M = 10.4 \text{ mole/m}^3\). Equation (3.26) results in a relaxation time of 31 h. This means that the uncatalyzed conversion to equilibrium of reaction (3.25) is very slow at the operating temperatures considered. A homogeneous gas-phase oxidation of \(SO_2\) by reactions (3.22) and (3.25) is most unlikely. However, materials like \(SiO_2\) or \(Al_2O_3\) can increase the speed by which \(O_2(g)\) attains equilibrium with \(O(g)\):

\[
O_2(g) \xleftrightarrow{\text{\textsuperscript{\leftrightarrow}}} 2O(g)
\]  

(3.31)

The rate coefficient \(k_c\) for reaction (3.22) is given by (Baulch et al., 1976):

\[
k_c = 3.6 \times 10^{14} \exp \left[ \frac{500}{T} \right] \frac{\text{cm}^6}{\text{mole}^2 \text{s}} \quad (T = 250-1000 \text{ K})
\]  

(3.32)

\[
k_c = (2.2 - 22) \times 10^{15} \exp \left[ \frac{-300}{T} \right] \frac{\text{cm}^6}{\text{mole}^2 \text{s}} \quad (T = 1200-1400 \text{ K})
\]  

(3.33)

The rate of formation of \(SO_3\) can thus be expressed as:

\[
\frac{dC_{SO_3}}{dt} = k_c \ C_{SO_2} \ (C_0)_e \ C_M
\]  

(3.34)

If these results are, again, extrapolated to the fixed bed conditions a conversion of 0.01% \(SO_2\) to \(SO_3\) is calculated. Despite the errors associated with the calculations above, it may be concluded that the homogeneous reaction is negligible.
b. The decomposition of SO₃

Theoretically, the rate of the reverse reaction, the homogeneous gas phase decomposition of SO₃, can be calculated at equilibrium according to

\[ K_{eq,fr} = \frac{k_f}{k_r} \]  

(3.35)

where \( k_f \) the reaction rate of the forward reaction (variable),
\( k_r \) the reaction rate of the reverse reaction (variable).

This conclusion is, however, not necessarily valid for a reaction that is the sequence of several steps. Meyer (1977) mentions that above 400°C, SO₃ decomposes without a catalyst; however, the reaction rate remains low up to 1000°C. Gmelin (1960) states that if SO₃ is heated, in the absence of catalysts, conversion is still small at 1000°C and is completed only at about 1500°C. Burdett et al. (1981) mention the cooling of a mixture of SO₂, O₂ and SO₃. As the temperature decreases, the equilibrium shifts towards SO₃ and reaction rates fall rapidly. At some temperature (around 1000–1100°C), the equilibrium situation is no longer maintained, the reaction effectively ceases and the SO₃ concentration is "frozen". In a fluidized bed combustor, the maximum (bulk) gas temperature is almost certainly below this critical value and as a result, SO₃ concentrations are usually more limited by reaction rate than by equilibrium. In a review article, Cullis and Mulcahy (1972) discuss literature data and obtain an expression for \( k_{-b} \) from (3.21):

\[ k_{-b} = 1.2 \times 10^{12} \exp \left[ -\frac{4800}{T} \right] \frac{cm^3}{mol \cdot s} \quad (T = 900–1300 \, K) \]  

(3.36)

An absolute determination of the reverse reaction (3.22) is mentioned by Baulch et al. (1976); \( k_{-c} \) (M=N₂) = \( 8 \times 10^8 \, cm^3/(mole \cdot s) \) at 1740 K. It is almost certain that this value is too high. Westenberg and De Haas (1975) measured the rate of the reaction.

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\[
\text{SO}_3 + O + M \xrightarrow{k_e} \text{SO}_2 + O_2 + M
\]  

(3.37)

with He as third body. From the data they calculated:

\[
k_e = 5.0 \times 10^{16} \exp \left[\frac{785}{T}\right] \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \quad (T = 298-507 \text{ K})
\]  

(3.38)

At 298 K the ratio \(k_e(M=\text{N}_2)/k_e(M=\text{He})\) is 1.4. Extrapolation of the calculations to 850°C is unwise.

In view of the uncertainties concerning the homogeneous decomposition of SO₃, hardly any recommendation of the reaction rate at 850°C can be made.

(2) Heterogeneous catalysis

Above calculations on the homogeneous oxidation rate of SO₂ lead to the conclusion that if there is any SO₃ production, at least at atmospheric pressure, other SO₃-producing mechanisms (i.e. heterogeneous catalysis) will be of considerable importance. SO₃ can be generated by heterogeneous catalytic oxidation of SO₂ which can take place on surfaces within the bed or downstream the combustor. The bed material may contain sufficient catalytic material, like several transition metals, V, Ni, Fe and alkaline earth metals which can enhance the formation of a significant amount of SO₃. This may, to a certain extent, be counteracted by the alkaline nature of the deposited material. The SO₃ generated reacts with, or absorbs on, the alkaline ash particles in the bed and/or on the elutriated material. Little quantitative evidence is available on the effectiveness of SO₃ removal by ash particles. Hamer (1987) reports a catalytic oxidation of SO₂ by a hot type 316 stainless steel reaction tube (ID = 53 mm) which has an equilibrium ratio of SO₃/SO₂ of 0.11 at 850°C and 5 vol% O₂. The complex nature of these heterogeneous processes towards SO₂ oxidation prevents simple calculations.

Also the decomposition of SO₃ can be catalyzed. In the presence of platinum the reaction begins at about 430°C and is completed at 900–1000°C.
3.3.3 \( \text{SO}_3 \) analysis

At room temperature and atmospheric pressure, sulfur trioxide, the anhydride of sulfuric acid, is a colourless liquid. The boiling point is 44.8°C at 1 atm and the freezing point is 16.8°C. Gaseous \( \text{SO}_3 \) is mainly monomeric (Nickless, 1968). On exposure to air, it absorbs moisture rapidly, emitting dense white fumes (The Merck Index, 1976). Three solid modifications of \( \text{SO}_3 \) have been described elsewhere (Nickless, 1968). The properties of \( \text{SO}_3 \) are described in Gmelin (1960), the Encyclopedie Des Gaz (1976) and Kirk-Othmer (1983). Sulfur trioxide that has been combined with water to sulfuric acid in a flue gas can be determined continuously using a commercially available Severn Science Ltd \( \text{SO}_3 \) monitor (Jackson et al., 1981). The principle of the method is described in an issue of the British Standards Institution (1977). A gas sample is withdrawn by a heated probe through a silica wool filter; any sulfuric acid is dissolved in a 4:1 propan-2-ol:water solution. The ratio of the flow rates of gas and solution is kept constant at a chosen value. Sulfate is determined by passing it through a static porous bed of barium chloranilate which yields an equivalent concentration of acid chloranilate ions according to:

\[
\text{SO}_4^{2-} \text{(aq)} + \text{BaC}_6\text{Cl}_2\text{O}_4^- + \text{H}_3\text{O}^+ \text{(aq)} \rightarrow \text{BaSO}_4 \downarrow + \text{HC}_6\text{Cl}_2\text{O}_4^- \text{(aq)} + \text{H}_2\text{O} \quad (3.39)
\]

This is measured photometrically at its absorption peak (535 nm). The overall time constant of the instrument is about 2 minutes. Dennis and Hayhurst (1988) measured the formation of \( \text{SO}_3 \) in a fluidized bed either by this monitor or by a mass spectrometer (a QXK 300 quadrupole instrument from V. G. Gas Analysis Ltd.). A disadvantage of the \( \text{SO}_3 \) monitor is the presence of moisture in the flue gas while the sensitivity of the mass spectrometer tends to vary from day to day. The mass spectrometer is used to measure relative concentrations, with absolute values measured by the \( \text{SO}_3 \) monitor.
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Other methods to measure the SO$_3$ concentration in flue gas are also summarized by Struschka and Baumbach (1986).

3.4 Conclusions

Using the fixed bed reactor equipment described in section 3.2 the targets mentioned in section 3.1 can be attained. Both the desulfurization and regeneration step will be performed with a model gas. It is expected that during the sulfur capture stage SO$_3$ is formed. Although the literature is not uniform about the mechanism of the homogeneous gas phase SO$_2$ oxidation, the calculations show that the contribution of this reaction is negligible. The SO$_3$ will be formed by the heterogeneous catalytic oxidation of SO$_2$ which will strongly depend on the catalytic activity of the reactor material and the sorbent. Therefore special attention will be paid to the SO$_3$ measurements as well.

The results of the experimental work are described and discussed in Chapter 4.

References

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Fixed Bed Reactor
Experimental Results

4.1 Introduction

As has been pointed out in Chapter 1 (see section 1.4), the objective of the fixed bed reactor study is to examine the chemistry of the cyclic sulfation and regeneration of the synthetic sorbent. This chapter presents and discusses the results of the experimental work performed with the fixed bed facility described in Chapter 3. Before presentation of the actual testing of the performance of the sorbent, introductory experiments concerning the applicability of the equipment and the experimental procedures are discussed in section 4.2.1. The testing of the sorbent on its suitability for cyclic regenerative desulfurization is discussed in section 4.2.2. The optimal process conditions for the regeneration step are defined in section 4.2.3. A low temperature regenerative process at 850°C is emphasized. All experiments were performed at atmospheric pressure. The conclusions are formulated in section 4.3.

4.2 Acceptation and regeneration tests

4.2.1 Introductory experiments

As mentioned in section 3.4, the formation of SO₃ during the sulfur capture stage is expected; this requires a quantitative analysis of the
extent to which this formation actually occurs. Thus, the role of SO₃ has been investigated.

Blank experiments have to be performed to determine the sulfur uptake of the support. Quantitative results are only of a limited value if no estimate is made of the experimental error. Therefore, the reproducibility of the experiments has to be determined. As the model flue gas has been simulated by mixing SO₂, O₂ and N₂ while omitting compounds such as CO₂ and H₂O, the influence of CO₂ and H₂O had to be examined separately. Finally, the thermal stability of the sorbent at 850°C was tested.

(1) SO₃ analysis

An attempt has been made to measure the SO₃ concentration in the outlet of the empty reactor, fed with the model flue gas. The method used is based on the one described by the British Standards Institution, 1977 (see also section 3.3.3). SO₃ is absorbed at room temperature in a 4:1 mixture of isopropanol and water. This enhances the formation of a sulfuric acid mist, at the same time inhibiting the oxidation of SO₂. It also reduces the solubility of BaSO₄ formed by reaction (3.39). Although some SO₂ is dissolved too, the sulfate content of the solution depends almost entirely on the SO₃ content of the gas. However, it is found that a white mist is formed as soon as the SO₃ comes in contact with (the vapour of) this mixture or water. It appears that this mist is hardly absorbed by the solution. Probably, the mist particles lack the mobility of molecules but have insufficient mass to be trapped by impingement (Nickless, 1968). Even after passing the gas through five small absorption vessels equipped with a sintered glass frit, some mist is still visible.

The sulfate concentration in the isopropanol/water mixture has been determined according to two methods:

1. Based on colorimetry, after reaction with barium chloranilate (Jackson et al., 1981).

The acid chloranilate ions yield a purple coloured solution with a broad absorption peak at a wavelength of about 535 nm. This reaction is performed in a 50% aqueous ethanol solution, slightly buffered at pH = 4.0 (Vogel, 1961). However, in our liquid mixture, the extinction
fixed bed reactor experimental results

depended stronger on the pH; this resulted in large errors at only minor pH changes.

2. Based on polarography, after stepwise addition of a lead nitrate solution (Kolthoff, 1940).
The sulfate determination is based on the following reaction:

\[ \text{Pb}^{2+} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 \downarrow \quad (4.1) \]

The Pb concentration is determined by means of DC Polarography with a dropping mercury electrode, following stepwise addition of a lead nitrate solution. The Pb concentration remains constant at a low level until the equivalent amount of Pb has been added. Subsequently, the Pb concentration increases linearly with the amount of lead nitrate added. The equivalence point can be constructed at the intersection of both lines. Although time consuming, this method showed to be satisfactory for the determination of the sulfate concentration.

Using these methods it has been shown, at least qualitatively, that SO\(_3\) is present in the exit gas of the fixed bed reactor system. Since it was not practically possible to measure the SO\(_3\) concentration in the outlet of the reactor continuously, the difference between the amount of SO\(_2\) supplied at the inlet and the amount of SO\(_2\) detected in the outlet of the reactor was taken as a measure for the amount of SO\(_3\) present in the outlet. This procedure is verified by various experiments. As the reproducibility of the SO\(_3\) analysis was rather poor, approximately ± 30%, only rough conclusions can be drawn as will be described below.

(2) SO\(_3\) experiments

A quartz tube (ID = 9 mm) was inserted concentrically in the reactor to find out whether or not the reactor wall catalyzes the SO\(_3\) formation. At standard process conditions approximately 4% SO\(_3\) (relative to the amount of SO\(_2\) fed) was formed in this situation compared with 11% in the steel tube. In another experiment about 0.06 g platinum (20 wt% on asbestos) was used in
the quartz tube to examine whether or not equilibrium conditions can be reached in the quartz tube. Such supported platinum is a well-known catalyst for the SO₂ oxidation (Gmelin, 1960). It was shown that platinum in the quartz tube indeed catalyzes the reaction. Approximately 14% SO₃ is formed. The same amount of supported platinum in the steel reactor shows that also 14% SO₃ is produced.

Further, empty reactor experiments have been carried out to investigate the influence of various process parameters on the SO₃ formation such as temperature, contact time, SO₂ concentration and O₂ concentration. The results are compared with the equilibrium concentration of the SO₂ + 1/2 O₂ ⇌ SO₃ reaction. These empty reactor experiments show that at low temperatures (below 600°C), the oxidation reaction is too slow to form any observable quantity of SO₃. The concentration of SO₃ increases from 600°C towards equilibrium at 850°C. At high temperatures (above 1000°C), the concentration of SO₃ is determined by equilibrium. The results of the experiments with different contact times, SO₂ concentration and O₂ concentration, the other conditions being standard, show a trend which agrees with thermodynamics.

The following facts support the assumption that the difference between the amount of SO₂ supplied at the inlet and the amount of SO₂ detected in the outlet of the empty reactor is due to SO₃:
1. During the experiments a dense white mist is detected in the titration vessels, indicating formation of SO₃ (Merck Index, 1976).
2. This mist, which is analyzed by absorption as sulfate in an aqueous solution of isopropanol and determined by means of DC Polarography, contains SO₃.
3. Downstream of the reactor small amounts of a colourless, strong acidic liquid is found. This is supposed to be condensed SO₃ and/or H₂SO₄.
4. At various process conditions, the measured formation of SO₃ shows a trend which agrees with the calculated equilibrium concentration of SO₃ at reactor conditions.

According to these results, it is expected that the oxidation of SO₂ is catalyzed by the reactor wall towards equilibrium at 850°C. Then, the gas is quenched and the equilibrium is assumed to be frozen at reactor conditions.
At an oxygen excess, the $SO_x$ content can be obtained by multiplying the $SO_2$ concentration by a factor $(1 + K_{eq} \frac{C_{O_2}}{C_{O_2}})^{1/2}$ since (see section 3.3.1.):

$$C_{SO_x} = C_{SO_2} + C_{SO_3}$$  \hspace{1cm} (4.2)

$$C_{SO_x} = C_{SO_2} + K_{eq} \frac{C_{O_2}}{C_{O_2}} C_{SO_2}$$  \hspace{1cm} (4.3)

$$C_{SO_x} = C_{SO_2} (1 + K_{eq} \frac{C_{O_2}}{C_{O_2}})^{1/2}$$  \hspace{1cm} (4.4)

where $C_i$ = equilibrium concentration of compound $i$ (mole/m$^3$),

$K_{eq}$ = equilibrium constant of $SO_2 + \frac{1}{2} O_2 \leftrightarrow SO_3$ (mole/m$^3$)$^{1/2}$.

$K_{eq}$ is calculated with the equations (2.21), (3.11), (3.12) while assuming ideal gas. At standard conditions, $K_{eq}$ equals 0.164 (mole/m$^3$)$^{1/2}$, the factor between brackets in (4.4) being 1.11.

(3) "Blank" sol-gel sorbent

A "blank" sorbent was prepared according to the sol-gel method by omitting

<table>
<thead>
<tr>
<th>Table 4.1 Characterization of blank sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>sorbent type/code</td>
</tr>
<tr>
<td>shape</td>
</tr>
<tr>
<td>diameter (mm)</td>
</tr>
<tr>
<td>Ca-content (wt%)</td>
</tr>
<tr>
<td>free CaO present</td>
</tr>
<tr>
<td>Ca-distribution</td>
</tr>
<tr>
<td>other compounds detected</td>
</tr>
<tr>
<td>surface area $N_2$ physisorption (m$^2$/g)</td>
</tr>
<tr>
<td>Hg porosimetry (m$^2$/g)</td>
</tr>
<tr>
<td>pore volume $N_2$ physisorption (ml/g)</td>
</tr>
<tr>
<td>Hg porosimetry (ml/g)</td>
</tr>
<tr>
<td>solid density (skeletal) (kg/m$^3$)</td>
</tr>
</tbody>
</table>
the impregnation with a calcium compound. The specifications of this sorbent are listed in Table 4.1.

In Figure 4.1, the bypass concentration can be compared with the results of (a) an "empty reactor" experiment, (b) an α-Al₂O₃ experiment in which the α-Al₂O₃, used to position the sorbent bed in the reactor tube, is tested on its inertness (see section 3.2.2), (c) a blank sorbent experiment and (d) a SG105 sorbent experiment, all at standard process conditions.

![Graph showing SO₂ breakthrough curves for some introductory experiments](image)

**Figure 4.1** SO₂ breakthrough curves for some introductory experiments (see text).

The empty reactor experiment shows a steady SO₂ analysis. Because SO₃ is formed, the SO₂ outlet concentration is approximately 11% lower than in the bypass. The sulfur uptake by the inert α-Al₂O₃ is small which justifies its use as an inert. Considerably more SO₂ is captured by the blank sorbent which can be regenerated by H₂ as well. With the SG105 sorbent, the time elapsed to observe any SO₂ in the outlet of the reactor is approximately 10 min. As the dead space time is only about 10 s, it is concluded that no channeling occurs in the bed, as will be assumed in Chapter 5.

The total amount of sulfur captured by the sorbent is calculated from the area enclosed by the breakthrough curve (after correction for the amount of
SO₃ not detected, according to Eq. (4.4)), the vertical axis and the feed. The calculated sulfur uptake is verified by a wet chemical sulfate analysis of the loaded sorbent. It is concluded that the amount of sulfur captured calculated from the breakthrough curves agrees well with the sulfate analysis afterwards. According to the sulfate analysis, the SG105 sorbent is converted for 68% in 5 h and 89% in 25 h. Measurements with smaller particles (see section 5.5.1) show that in principle a sorbent conversion of 100% can be obtained. Approximately 10% of the total amount of sulfur captured by the SG105 sorbent can be captured by the blank sorbent as well. This is due to its high surface area and large pore volume. The SO₂ is released during regeneration with H₂.

(4) Reproducibility

The reproducibility is defined as the between-run precision caused by random errors (Miller and Miller, 1984) and is tested by performing several experiments at identical conditions. Therefore, 5 one-cycle experiments are performed. A numerical indication of the reproducibility of the acceptation experiment can be given by the amount of SOₓ captured. The reproducibility, shown in Figure 4.2a, as defined here, is ± 13% (sample standard deviation).

![Figure 4.2a Reproducibility of the acceptation breakthrough curve.](image-url)
The reproducibility of the regeneration experiments is expressed by the spread in the area under the regeneration plot, see Figure 4.2b, here found to be ± 6%.

Figure 4.2b Reproducibility of the regeneration breakthrough curve.

(5) Simulation of flue gas without the presence of CO₂ and H₂O

All experiments, described so far, used a standard feed gas consisting of N₂, O₂ and SO₂. Of course, a combustor off-gas will contain, among others things, about 16 vol% CO₂ and 6 vol% H₂O as well (see Table 3.1). For thermodynamic reasons, it is not expected that these compounds influence the sulfur retention performance of the sorbent. Slack and Hollinden (1975) mention that the content of CO₂ in the gas does not have any major effect on sulfur oxide removal. However, Cullis and Mulcahy (1972) state that the conversion to SO₃ is increased by small concentrations of water vapour. This hypothesis is verified by comparison of sulfation experiments with and without these compounds. The result is presented in Figure 4.3.

It appears that CO₂ has no significant effect on the sulphur capture process. The presence of water shows an acceptance result which agrees with the statement of Cullis and Mulcahy (1972). The increased conversion to SO₃ results in a slightly better sulfur capture. However, it should be noticed
Figure 4.3 Influence of CO$_2$ and H$_2$O on the acceptance performance.

that the addition of water can increase the formation of H$_2$SO$_4$ as well. If condensed in the tubing downstream the reactor, this results in a decrease of SO$_x$ detected in the off-gas. However, the deviation from the reference curve is within the reproducibility of the experiments. This confirms that CO$_2$ and H$_2$O only slightly influence the acceptance performance of SO$_2$. The combustor off-gas can be simulated by mixing SO$_2$, O$_2$ and N$_2$ only.

(6) Pre-heating of the sorbent

The sorbent is supposed to have a lifetime of about 100 cycles with an approximate mean residence time of 50 h per cycle. The total residence time in the system is thus approximately 5000 h at 850°C. During its preparation the sorbent is calcined at 850°C for only 10 hours. To get an impression of its thermal stability, part of the SG105 sorbent was pre-heated (after the normal preparation procedure) for 500 hours at 850°C in open air. The specifications of the pre-heated sorbent are given in Table 4.2.
Table 4.2 Characterization of "500 h pre-heated sorbent"

<table>
<thead>
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<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>sorbent type/code</td>
<td>SG105-500h</td>
</tr>
<tr>
<td>shape</td>
<td>spherical</td>
</tr>
<tr>
<td>diameter (mm)</td>
<td>2.8–3.4 (sieved after preparation)</td>
</tr>
<tr>
<td>Ca-content (wt%)</td>
<td>not det., approx. 5.83 (SG105)</td>
</tr>
<tr>
<td>free CaO present</td>
<td>slightly less free CaO detected</td>
</tr>
<tr>
<td></td>
<td>compared with SG105</td>
</tr>
<tr>
<td>Ca-distribution</td>
<td>not determined</td>
</tr>
<tr>
<td>other compounds detected</td>
<td>γ-Al₂O₃, CaO₂Al₂O₃</td>
</tr>
<tr>
<td>surface area N₂ physisorption (m²/g)</td>
<td>80</td>
</tr>
<tr>
<td>Hg porosimetry (m²/g)</td>
<td>74</td>
</tr>
<tr>
<td>pore volume N₂ physisorption (ml/g)</td>
<td>0.28</td>
</tr>
<tr>
<td>Hg porosimetry (ml/g)</td>
<td>0.21</td>
</tr>
<tr>
<td>solid density (skeletal) (kg/m³)</td>
<td>3280</td>
</tr>
</tbody>
</table>

The phenolphtalein-test shows that after the 500 h heating of the sorbent some additional free CaO has reacted with the alumina support to a calcium aluminate. XRD clearly shows the formation of CaO₂Al₂O₃ (see also section 2.5). These results confirm the slow overall kinetics of the calcium aluminate formation as already mentioned in section 2.3. The internal surface area is diminished with 20%, while the pore volume is almost.

![Figure 4.4 Influence of the pre-heating treatment on the acceptation performance.](image)
unchanged. It is concluded that the micropores (2–4 nm) are affected mostly by the pre-heating treatment. Comparison of the breakthrough curves presented in Figure 4.4, shows that the activity of the sorbent is only slightly reduced after the heat-treatment period.

4.2.2 Cyclic experiments

(1) Cyclic experiment at standard conditions

A cyclic sulfation-regeneration experiment (10 cycles) was performed using SG105 sorbent. In Figure 4.5a, four five-hours acceptance breakthrough curves are given. There is only a small difference between cycle #2 and #10. It has to be noticed that these cycles start with a peak of SO₂ caused by CaS oxidation. CaS was formed in the previous regeneration step and is oxidized to both CaO/γ-Al₂O₃ (and SO₂) and CaSO₄ (see section 2.5). The amount of CaS oxidized to CaO/γ-Al₂O₃ and SO₂ can be determined by measuring the area of the SO₂-peak. It is calculated that about 10% of the CaS is oxidized to CaO/γ-Al₂O₃ (and SO₂), while 90% is oxidized to CaSO₄.

Figure 4.5a Acceptation breakthrough curves of SG105 during the cyclic experiment at standard conditions.
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Because of the relatively low regeneration temperature (850°C), deactivation mainly takes place by the formation of CaS and not e.g. by sintering. In any further step, accumulation of CaS is less. During the N2-flush after the acceptation stage, a negligible amount (about 0.4%) of the captured SO2 is released from the sorbent.

Figure 4.5b shows that the regeneration is fast compared with sulfation, less than five minutes being required to regenerate the sorbent at the process conditions applied. A good regeneration capability is maintained during these 10 cycles. The maximum SO2 outlet concentration is about 15 vol%. Note that the amount of CaSO4 present on the sorbent is too low to maintain this high concentration for a long time. After the experiment, some elemental sulfur was found in the tubing downstream from the reactor.

![Graph showing regeneration breakthrough curves of SG105 during cyclic experiment at standard conditions.](image)

*Figure 4.5b Regeneration breakthrough curves of SG105 during the cyclic experiment at standard conditions.*

The performance of the sorbent during the cyclic experiments can be characterized by its sulfur capture (S\text{cap}) and its regeneration efficiency to SO2 (S\text{SO2,reg}) which were defined in section 3.2.4. The sulfur capture efficiency of the sorbent is presented in Figure 4.6a as a function of the cycle number.
Figure 4.6a Acceptation efficiency during the cyclic experiments (cycle 8 of the standard experiment failed).

It appears that a constant value of 45% is obtained after about two cycles. The sulfur regeneration efficiency to SO₂ is shown in Figure 4.6b.

Figure 4.6b Regeneration efficiency to SO₂ during the cyclic experiments (cycle 8 of the standard experiment failed).
$S_{SO_2, reg}$ is approximately 65% and no deactivation occurs during the 10 cycles performed. The regeneration efficiency to $H_2S$ is about 12%. XRD shows the presence of $\gamma$-Al$_2$O$_3$ and CaS (JCPDS-ASTM index number 8-464) after the final regeneration step, while no CaO, CaO.2Al$_2$O$_3$ or CaSO$_4$ is found.

The main conclusion is that the sorbent is regenerable at the process conditions applied. Both during acceptance and regeneration little change in reactivity is found.

An experiment with a minimum of 100 cycles, including a longer acceptance time (e.g. 50 h), is probably needed to ascertain whether there is a (continuous) loss in reactivity as a function of the number of cycles. Note that SG105 contains 8.2 wt% CaO reacting with a maximum of 30 wt% of the support material to form CaO.2Al$_2$O$_3$ and perhaps also other aluminates. These aluminates change phase during each cycle, which may be detrimental to the reactivity and/or strength of the sorbent. Cyclic sulfation-regeneration experiments performed both in a thermobalance (50 cycles) and in a 0.05 m ID fluidized bed reactor (100 cycles) look promising (Van den Bleek et al., 1986-1990).

The texture and crushing strength (see Chapter 6) of the sorbent are measured both before and after this fixed bed experiment. The internal surface area and pore volume are diminished to 19 m$^2$/g and 0.1 ml/g respectively according to the BET analysis. Hg porosimetry shows a surface area of 31 m$^2$/g and a pore volume of 0.19 ml/g. Note that the measured reactivity is not decreased proportional. The results of the crushing strength test are presented in section 6.2.

(2) Cyclic experiment with $H_2$-regeneration at 950°C

It is expected that during regeneration at higher temperatures, e.g. 950°C, less CaS is formed (see section 2.6). Therefore, an experiment is performed with $H_2$-regeneration at 950°C. The SG105 sorbent is pre-heated (10 h at 950°C) in advance to exclude sintering and the formation of other (calcium) aluminates during the regeneration step. During the pre-heating period, sintering of the sorbent has occurred (compare Table 2.3 with Table 4.3).
Table 4.3 Characterization of 950°C pre-heated sorbent

<table>
<thead>
<tr>
<th>Property</th>
<th>Value/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>sorbent type/code</td>
<td>SG105-950C</td>
</tr>
<tr>
<td>shape</td>
<td>spherical</td>
</tr>
<tr>
<td>diameter (mm)</td>
<td>2.8-3.4 (sieved after preparation)</td>
</tr>
<tr>
<td>Ca-content (wt%)</td>
<td>not det., approx. 5.83 (SG105)</td>
</tr>
<tr>
<td>free CaO present</td>
<td>little free CaO detected compared with SG105</td>
</tr>
<tr>
<td>Ca-distribution</td>
<td>not determined</td>
</tr>
<tr>
<td>other compounds detected</td>
<td>γ-Al₂O₃, CaO.2Al₂O₃</td>
</tr>
<tr>
<td>surface area N₂ physisorption (m²/g)</td>
<td>42</td>
</tr>
<tr>
<td>Hg porosimetry (m²/g)</td>
<td>62</td>
</tr>
<tr>
<td>pore volume N₂ physisorption (ml/g)</td>
<td>0.26</td>
</tr>
<tr>
<td>Hg porosimetry (ml/g)</td>
<td>0.23</td>
</tr>
<tr>
<td>solid density (skeletal) (kg/m³)</td>
<td>not det., approx. 3270 (SG105)</td>
</tr>
</tbody>
</table>

The phenolphthalein-test shows that during heating of the sorbent at 950°C most of the CaO has reacted with the alumina support to a calcium aluminate. XRD clearly shows the formation of CaO.2Al₂O₃. These results confirm again the slow overall kinetics of the calcium aluminate formation as mentioned in section 2.3. It is demonstrated that this reaction rate is strongly dependent on the temperature. The influence of the regeneration temperature during cyclic operation with pre-heated sorbent on acceptation performance can be seen by comparing Figure 4.5a with Figure 4.7a.

![Figure 4.7a](attachment:image.png)  
*Figure 4.7a* Acceptation breakthrough curves of SG105-950C during the cyclic experiment with regeneration at 950°C.
During the \( \text{N}_2 \)-flush stage 1 (at 850°C) and stage 2 (at 950°C), a small amount (about 1\% and 5\% respectively) of the captured \( \text{SO}_2 \) is released from the sorbent. The maximum outlet \( \text{SO}_2 \) concentration during regeneration is still about 12 – 14 vol\% (Figure 4.7b).

![Figure 4.7b](image_url)  
*Figure 4.7b Regeneration breakthrough curves of SG105-950C during the cyclic experiment with regeneration at 950°C.*

Figure 4.6a shows that \( S_{\text{cap}} \) is reduced (from 40\% to 35\%) after 10 cycles. \( S_{\text{SO}_2,\text{reg}} \) is almost 80\% at higher cycle number for the SG105-950C sorbent (Figure 4.6b). The regeneration efficiency to \( \text{H}_2\text{S} \) \( (S_{\text{H}_2\text{S,reg}}) \) is approximately 10\%. Moreover, the area of the \( \text{SO}_2 \)-peak caused by CaS oxidation is small. These results confirm that the amount of CaS produced decreases at higher regeneration temperature. Further, it appears that the regeneration efficiency increases slightly as a function of the cycle number. The reason for both this phenomena and the crossing of the acceptation curves as well, is probably the formation of (other) active calcium aluminates during the cyclic experiment. Ruth and Varga (1979) noticed the same results with the sulfation and regeneration of barium titanate powders measured in a thermogravimetric analyzer. Molayem and Bardakci (1985) also found that the performance of their "SORCAT B4" sorbent improved with each regeneration cycle.
(3) Cyclic experiment with CO-regeneration at 850°C

As expected (Snyder, 1975, see section 2.6), regeneration in a cyclic process is also possible with CO, but less attractive than with H₂. From the results shown in Figure 4.5a, 4.5b, 4.8a and 4.8b it can be derived that more CaS and COS are formed during regeneration with CO than CaS and H₂S are formed during regeneration with H₂. The area of the SO₂-peak, caused by CaS oxidation, is relatively large compared with the cyclic experiment at standard conditions.

The regeneration efficiency to SO₂ is 36% compared with 65% in case of standard regeneration. The sulfur capture efficiency is 32% and is still decreasing compared with 45% during H₂-regeneration. These results are also visualized in the Figures 4.6a and 4.6b. After the experiment, more elemental sulfur was found in the tubing downstream the reactor compared with the cyclic experiment at standard conditions. XRD shows the presence of γ-Al₂O₃ and CaS in the regenerated sample.

The influence of H₂-regeneration compared with CO-regeneration is further discussed in section 4.2.3.

Figure 4.8a Acceptation breakthrough curves of SG105 during the cyclic experiment with CO-regeneration.
(4) Cyclic experiment using calcined limestone with H₂-regeneration at 850°C

To compare the synthetic sorbent with a calcined limestone (Carmeuse Engis), a cyclic experiment with the latter was performed. The calcination is started by heating the limestone at a heating rate of 2°C/min from room temperature to 850°C in air. The calcination step is subsequently carried out at a temperature of 850°C for 10 hours. A characterization of the limestone before and after calcination is given in Table 4.4.

An amount of 0.4527 g lime is used which approximately equals the amount of CaO present during a standard experiment with the synthetic sorbent. Figures 4.6a and 4.9a show a fast decrease in sulfur capture efficiency of lime during the cyclic process. After about 2 cycles the value of $S_{\text{cap}}$ is almost zero. It appears from Figure 4.6b and 4.9b that the lime can not be regenerated at the process conditions applied. The sulfate formed during the acceptation step is reduced to CaS and H₂S instead of CaO, SO₂ and H₂O. Furthermore, also the presence of unreduced CaSO₄ (JCPDS-ASTM index number 6-0226) is shown by XRD.
### Table 4.4 Characterization of Belgian Carmeuse Engis limestone

<table>
<thead>
<tr>
<th></th>
<th>before calcination</th>
<th>after calcination</th>
</tr>
</thead>
<tbody>
<tr>
<td>sorbent type/code</td>
<td>limestone</td>
<td>lime</td>
</tr>
<tr>
<td>shape</td>
<td>irregular</td>
<td>irregular</td>
</tr>
<tr>
<td>diameter</td>
<td>1.7–2.0 (mm)</td>
<td>1.7–2.0 (sieved)</td>
</tr>
<tr>
<td>(sieved)</td>
<td>38.5</td>
<td>65.4</td>
</tr>
<tr>
<td>free CaO present</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Ca distribution</td>
<td>not determined</td>
<td>not determined</td>
</tr>
<tr>
<td>compounds detected</td>
<td>1) Ca 37.2  Mg &lt;0.6  Al &lt;0.12  Fe&lt;0.04</td>
<td>1) Ca 62.6  Mg &lt;0.9  Al &lt;0.17  Fe 0.07</td>
</tr>
<tr>
<td></td>
<td>2) CO&lt;sub&gt;3&lt;/sub&gt; 47.0  others balance</td>
<td>2) CO&lt;sub&gt;3&lt;/sub&gt; 3.4  others balance</td>
</tr>
<tr>
<td>surface area N&lt;sub&gt;2&lt;/sub&gt; physisorption (m&lt;sup&gt;2&lt;/sup&gt;/g)</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Hg porosimetry (m&lt;sup&gt;2&lt;/sup&gt;/g)</td>
<td>0.1</td>
<td>3</td>
</tr>
<tr>
<td>pore volume N&lt;sub&gt;2&lt;/sub&gt; physisorption (ml/g)</td>
<td>0.004</td>
<td>0.02</td>
</tr>
<tr>
<td>Hg porosimetry (ml/g)</td>
<td>0.004</td>
<td>0.31</td>
</tr>
<tr>
<td>solid density (skeletal) (kg/m&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>2680</td>
<td>3210</td>
</tr>
</tbody>
</table>

1) The concentration of the elements is obtained by Instrumental Neutron Activation Analysis.
2) Measured by wet chemical analysis.

---

**Figure 4.9a** Acceptation breakthrough curves of lime during the cyclic experiment at standard conditions.
4.2.3. Optimization of the regeneration conditions

(1) Influence of H₂ and CO concentration

It is concluded from the cyclic experiments described in the previous section that a better regeneration performance is obtained with H₂ compared with CO. Some additional results were obtained during regeneration after 25 h of acceptance at standard conditions. These are presented in Table 4.5.

Regeneration by H₂ results in a higher regeneration efficiency to SO₂ compared with CO-regeneration. Therefore, H₂ is preferred over CO. Further, the regeneration efficiency to SO₂ increases with lower reducing gas concentration. At higher CO or H₂ concentration more CaS is formed but a smaller amount of H₂S has been measured during H₂-regeneration (Table 4.5). The amount of H₂S in the regenerator off-gas is at maximum 20% of the total amount of gaseous sulfur compounds present. Although at low reducing gas inlet concentration a relatively high SO₂ concentration is reached with respect to this inlet concentration ([SO₂]max/[H₂ or CO] up to 80 or 60%), the absolute value of the SO₂ concentration is still too low. For practical
purposes, the concentration of SO$_2$ in the off-gas of the regenerator should preferably be higher than approx. 10 vol%. Thus a reducing gas concentration of 12.5 - 25 vol% is needed. A mixture of 12.5 vol% H$_2$ and 12.5 vol% CO looks promising if the release of COS is allowed (see section (2)).

Table 4.5 Influence of H$_2$ and CO concentration and temperature on regeneration performance

<table>
<thead>
<tr>
<th>sorbent type</th>
<th>[H$_2$]</th>
<th>[CO]</th>
<th>regeneration temperature</th>
<th>S$_{SO_2}$</th>
<th>S$_{H_2S}$</th>
<th>S$_{CaS}$</th>
<th>S$_{tot}$</th>
<th>[SO$<em>2$]$</em>{max}$</th>
<th>[SO$<em>2$]$</em>{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vol%</td>
<td>vol%</td>
<td>°C</td>
<td>reg</td>
<td>reg</td>
<td>reg</td>
<td>1)</td>
<td>2)</td>
<td>3)</td>
</tr>
<tr>
<td>SG105</td>
<td>5</td>
<td>0</td>
<td>850</td>
<td>69</td>
<td>18</td>
<td>8</td>
<td>95</td>
<td>4</td>
<td>80</td>
</tr>
<tr>
<td>, ,</td>
<td>12.5</td>
<td>0</td>
<td>, ,</td>
<td>65</td>
<td>19</td>
<td>12</td>
<td>96</td>
<td>9</td>
<td>72</td>
</tr>
<tr>
<td>, ,</td>
<td>25</td>
<td>0</td>
<td>, ,</td>
<td>60</td>
<td>14</td>
<td>13</td>
<td>87</td>
<td>15</td>
<td>60</td>
</tr>
<tr>
<td>, ,</td>
<td>0</td>
<td>5</td>
<td>, ,</td>
<td>43</td>
<td>-</td>
<td>15</td>
<td>-</td>
<td>3</td>
<td>60</td>
</tr>
<tr>
<td>, ,</td>
<td>0</td>
<td>12.5</td>
<td>, ,</td>
<td>38</td>
<td>-</td>
<td>16</td>
<td>-</td>
<td>6</td>
<td>48</td>
</tr>
<tr>
<td>, ,</td>
<td>0</td>
<td>25</td>
<td>, ,</td>
<td>29</td>
<td>-</td>
<td>17</td>
<td>-</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>, ,</td>
<td>12.5</td>
<td>25</td>
<td>, ,</td>
<td>77</td>
<td>2</td>
<td>12</td>
<td>-</td>
<td>13</td>
<td>52</td>
</tr>
<tr>
<td>SG105-950C</td>
<td>25</td>
<td>0</td>
<td>950</td>
<td>67</td>
<td>6</td>
<td>2</td>
<td>75</td>
<td>15</td>
<td>60</td>
</tr>
<tr>
<td>, ,</td>
<td>0</td>
<td>25</td>
<td>, ,</td>
<td>48</td>
<td>-</td>
<td>8</td>
<td>-</td>
<td>13</td>
<td>52</td>
</tr>
</tbody>
</table>

1) During regeneration, about 19% of the total amount of H$_2$S released is absorbed in the SO$_2$ titration vessel and converted mainly to elemental sulfur and a small amount of H$_2$SO$_4$ as well. This has been included in the calculation of $S_{H_2S,reg}$.

2) According to wet chemical analysis.

3) The amount of $S_X$ and COS formed is not determined quantitatively. $S_X$ is monitored visually and the formation of COS is qualitatively shown by gas chromatography. For this reason, the total regeneration efficiency ($S_{tot,reg}$) does not equal 100%. Wet chemical analysis of a sample, after a standard acceptance and regeneration step, shows no unreduced CaSO$_4$.

However, it has to be kept in mind that these fixed bed results cannot be used directly in fluidized bed applications, because of the difference in hydrodynamics. A model which includes a description of the regeneration process and the hydrodynamics of the regenerator is needed in order to extend the quantitative conclusions reached above, especially in scale-up calculations.
(2) Influence of the regeneration temperature

The cyclic experiments performed at regeneration temperatures of 850°C and 950°C respectively, the other conditions being standard, show that the regeneration efficiency to SO₂ at higher regeneration temperatures increases. See also Table 4.5 which shows a reduced amount of H₂S and CaS formed (relative to the amount of CaSO₄ present on the sorbent) during regeneration at 950°C compared with 850°C. On the other hand, the sulfur capture efficiency decreases rapidly (see section 4.2.2). At lower regeneration temperature, the amount of CaS and H₂S or COS will also increase.

(3) Influence of the presence of H₂O or CO₂ in the regeneration feed gas

It is expected that the presence of H₂O and CO₂ in the regeneration feed gas will reduce the amount of CaS according to:

\[
\text{CaS} + \gamma\text{-Al}_2\text{O}_3 + \frac{\text{H}_2\text{O}}{\text{CO}_2} \rightarrow \text{CaO/γ-Al}_2\text{O}_3 + \frac{\text{H}_2\text{S}}{\text{COS}} \tag{4.5}
\]

Of course, a decrease of \( S_{\text{CaS,reg}} \) is favourable for the next acceptation step. However, it depends on the sulfur recovery process after the regenerator whether or not an increased amount of H₂S or COS is useful. An increase in H₂S formation can e.g. be profitable in the production of elemental sulfur according to the Claus reaction:

\[
2 \text{H}_2\text{S} + \text{SO}_2 \rightarrow 3/x \text{S}_x + 2 \text{H}_2\text{O} \tag{4.6}
\]

The formation of COS is unwanted in the Claus reaction, while both H₂S and COS are undesirable in a sulfuric acid production process.

Experiments have been performed using 3.8 vol% H₂O or 3.8 vol% CO₂ in the standard regeneration gas. The results of the experiments are summarized in Table 4.6.
Table 4.6 The influence of H₂O and CO₂ on the regeneration performance

<table>
<thead>
<tr>
<th></th>
<th>standard no H₂O or CO₂</th>
<th>standard + 3.8 vol% H₂O</th>
<th>standard + 3.8 vol% CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₅O₂,reg (%)</td>
<td>60</td>
<td>55</td>
<td>57</td>
</tr>
<tr>
<td>S₅H₂S,reg (%)</td>
<td>14</td>
<td>31</td>
<td>25</td>
</tr>
<tr>
<td>S₅CaS,reg (%)</td>
<td>13</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>S₅tot,reg 1) (%)</td>
<td>87</td>
<td>91</td>
<td>91</td>
</tr>
<tr>
<td>[SO₂]max (vol%)</td>
<td>15</td>
<td>15</td>
<td>14</td>
</tr>
</tbody>
</table>

1) see note 3) in Table 4.5.

It appears that the formation of CaS during regeneration decreases with about 60% during the addition of 3.8 vol% H₂O. A reduction of 20% was obtained with CO₂ in the regeneration feed gas. The amount of SO₂ released is only slightly reduced and the maximum SO₂ concentration remains nearly constant.

4.3 Conclusions

A synthetic sorbent consisting of Ca (5.8 wt%) on a γ-alumina support (3.1 mm spheres) prepared by the sol-gel method can be used in a regenerative cyclic process with respect to the chemistry involved. The optimal regeneration conditions are defined as the standard conditions in Table 3.3. A mixture of 12.5 vol% H₂ and 12.5 vol% CO looks promising if the release of COS is allowed. Addition of H₂O or CO₂ is favourable for the regeneration performance of the sorbent, but it depends on the sulfur recovery process whether or not an increased amount of H₂S or COS is advantageous. A regeneration feed gas with a composition as listed in Table 3.2 can thus be used. The gasification medium should be air or a mixture of air and steam.

From the introductory experiments the following conclusions can be drawn:

1) The amount of SO₃, present in the off-gas of the fixed bed reactor during the acceptation experiments, can be quantitatively estimated.
The total amount of $SO_x$ can be obtained from the measured amount of $SO_2$ by Eq. (4.4). At standard conditions a correction of 11% is applied.

(2) A blank experiment shows that approximately 10% of the total $SO_x$ uptake by the SG105 sorbent can be captured by "pure" $\gamma$-$Al_2O_3$ as well.

(3) The reproducibility of the acceptation and regeneration experiments is 13% and 6% respectively.

(4) In the sulfur capture experiments, a flue gas can be simulated by a mixture of $SO_2$, $O_2$ and $N_2$ without $CO_2$ or $H_2O$.

(5) The thermal stability of the sorbent is good. The sulfur capture performance changed only slightly. Pre-heating at 850°C for 500 h reduces the internal surface area by 20%, but the pore volume remains almost unchanged.

Cyclic experiments show that:

(6) The sulfur capture efficiency ($S_{cap}$) is stabilized at 45% after about 2 cycles at standard conditions. Hardly any loss in reactivity is measured during the remainder of the 10 cycles performed.

(7) Regeneration is fast. The sorbent can be regenerated within 5 minutes at standard conditions.

(8) The regeneration efficiency to $SO_2$ ($S_{SO_2,reg}$) of the sorbent is approximately 65% and no deactivation occurs during the 10 cycles performed.

(9) $SO_2$ concentrations up to 15 vol% are obtained in the off-gas from the fixed bed reactor during regeneration at standard conditions.

(10) Pre-heating the sorbent at 950°C decreases the sulfur capture efficiency from 40% to 35% after 10 cycles. It is noticed that the performance of the sorbent improved slightly with increasing cycle number. The regeneration efficiency to $SO_2$ is almost 80%.

(11) Regeneration with CO is less attractive than with $H_2$. $S_{cap}$ is 32% compared with 45% using $H_2$-regeneration and is still decreasing. $S_{SO_2,reg}$ is 36% compared with 65% using $H_2$ during 8 cycles.

(12) Calcined limestone (Carmeuse Engis) is not regenerable at the standard process conditions applied. The sulfur capture efficiency is almost zero after more than 2 cycles.

Experiments on the sulfur regeneration process further show that:

(13) Increasing the concentration of reducing gas results in a lower regeneration efficiency to $SO_2$. At a low inlet concentration of
Reducing gas at a relatively high SO₂ concentration is reached (Table 4.5).

(14) Using higher regeneration temperatures results in a higher regeneration efficiency to SO₂ and reduces the formation of H₂S and CaS (Table 4.5). Unfortunately, it has a negative effect on the sulfur capture efficiency as shown by the cyclic experiments.

(15) The presence of 3.8 vol% H₂O or CO₂ in the regeneration feed gas decreases the formation of CaS with about 60% and 20% respectively.

Chapter 5 will present further experiments, to support a mathematical sulfur capture model.

References


5

Modeling of the Fixed Bed Reactor Experimental Results

5.1 Introduction

In order to develop an adequate overall fluidized bed model which can sufficiently describe the sulfur route in the combustor and regenerator, it is necessary to gather a good understanding of the mass/heat transfer and (intrinsic) kinetic phenomena of the sulfur capture and regeneration processes. The effects and interrelations of the physical and chemical processes have to be evaluated. Such an insight makes it possible to decide which steps are of primary importance in the sulfur route and which steps can be neglected. In this work only the sulfur capture process is modelled (see section 1.4.2).

To determine the kinetics of the reactions a fixed bed reactor was chosen, for the reasons mentioned in section 3.1. These kinetics have to be combined with the less well-known hydrodynamics of the (slugging) fluidized bed reactor. In section 5.2, an introduction is given to the fixed bed reactor modeling study in which the fundamentals are discussed. Section 5.3 presents the conversion equation for one sorbent particle and the mass balances for the sulfur capture experiments in a fixed bed reactor. The method of solving the differential equations obtained is discussed in section 5.4 and the results are treated in section 5.5. The conclusions are summarized in section 5.6.
5.2 Theoretical and experimental evaluation of the fundamentals

Reactors design involves all basic principles of chemical engineering and includes fluid flow (hydrodynamics), mass transfer, heat transfer and chemical kinetics. It all starts with the material and energy balances:

\[
\text{accumulation = in - out - conversion} \quad \text{(5.1)}
\]

For any reactor, the balances have to be set up over a certain element of volume and over a certain element of time. If the composition varies with the position in the reactor, as is the case in a fixed bed reactor, a differential element with volume \(dV\) must be used and the equations integrated. Likewise, if the composition changes with time, the balance must also be made over a differential element of time. Generally, the mass and heat balances of a fixed bed reactor result in a set of differential equations which must be solved simultaneously. For an heterogeneous gas solid system in a fixed bed reactor, these balances include effects of fluid dynamics, transfer of mass and heat and the chemistry of the system. A combination of these physical and chemical rate processes determines the overall rate of the process. Sometimes a rate determining step can be found, thus excluding the effect of the other steps on the overall rate of the process.

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

1. Mode of operation: steady or nonsteady
2. Hydrodynamics of the reactor system
3. Mass/energy production and transfer inside the porous solid
4. Mass/energy production and transfer outside the porous solid
- 5 modeling of the fixed bed reactor experimental results -

Rules of thumb will be given in this section for a fixed bed reactor system with a gas-solid reaction in order to determine the influence of the topics described above. The numerical values used in the calculations are collected from Table 2.3, Table 3.3 and literature data. A review of these data is given in Table 5.1.

| reactor: | temperature | T | 1123 | K |
| pressure | P | 1 | bar |
| bed diameter | d_b | 0.012 | m |
| bed length | L_b | 0.051 | m |
| bed porosity | e_b | 0.43 | m^3 gas/m^3 reactor |
| sorbent: (SG105) | average particle diameter | d_p | 3.1 10^{-3} | m |
| particle apparent density | \rho_p | 1680 | kg/m^3 particle |
| internal surface area | S_{BET} | 99 10^{-3} | m^2/kg |
| pore volume | V_{pore} | 0.29 10^{-3} | m^3/kg |
| feed gas: (at reactor conditions) | flow | \phi_F | 2.26 10^{-5} | m^3/s |
| density | \rho_F | 0.31 | kg/m^3 |
| thermal conductivity | \lambda_F | 0.072 | W/(m K) |
| specific heat | C_F | 1140 | J/(kg K) |
| viscosity | \eta_F | 4.6 10^{-5} | Pa.s |
| SO_2 concentration | C_F | 0.027 | mole/m^3 |

The calculations will be presented for the sulfation reaction only. As a first approximation, it is assumed that the reaction is comparable to the sulfation of "pure" CaO. The sulfation is assumed to be first order in SO_2 and zero order in O_2 (Marsh and Ulrichson, 1985). The calculations for the regeneration step are similar. The reductive decomposition of calcium sulfate is assumed to be first order with respect to the gaseous reactant with either H_2 or CO (Diaz-Bossio et al., 1985). The conclusions drawn are the same.

(1) Mode of operation: steady or nonsteady

The gas-solid SO_2 retention and regeneration reactions are in a nonsteady state. However, in some calculations, a pseudo steady state
- 5 modeling of the fixed bed reactor experimental results -

approximation will be used to simplify the mathematical equations involved.

(2) Hydrodynamics of the reactor system

The fluid hydrodynamics of the reactor system are to be considered.

a. The pressure drop in the reactor.

Leva (1949) gives a formula to calculate the pressure drop for a flow of a fluid through a bed of granular solids:

\[ \Delta P = \frac{2 f_m G^2 l_b (1-\epsilon_b)^3-\eta}{d_p g_c \rho_f \phi_{sh}^3 \epsilon_b^3} \]  

(5.2)

with \( G = U_f \rho_f \) (5.3) and \( U_f = \frac{\phi_f}{4 \pi d_b^2} \) (5.4)

where \( \Delta P \) = pressure drop (Pa),
\( f_m \) = friction factor; see Leva (1949) (-),
\( G \) = fluid superficial mass velocity (kg gas/(m² reactor s)),
\( q \) = exponent (-),
\( g_c \) = dimensional constant; \( g_c = 1.0 \) (kg m/(N s²)),
\( \phi_{sh} \) = shape factor of solid; perfect sphere: \( \phi_{sh} = 1.0 \) (-),
\( U_f \) = superficial gas velocity (m³ gas/(m² reactor s)).

Substituting the values from Table 5.1, the value for the friction factor \( f_m = 24 \) and unity for the exponent \( q \) results in:

(5.4): \( U_f = 0.2 \) m/s  
(5.3): \( G = 0.062 \) kg/(m² s)

(5.2): \( \Delta P = 40 \) Pa

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This pressure drop is very low. Measurements at the standard conditions applied also show no significant pressure drop across the total content of the reactor consisting of the sorbent bed embedded in the inert material. The influence of the pressure drop can therefore be neglected in the modeling work.

b. Axial gradients

The existence of axial dispersion is negligible (error less than approx. 10%) if:

\[
Bo = Pe_{ax} \frac{L_b}{d_p} > 20
\]  \hspace{1cm} (5.5)

and (Kulkarni and Doraiswamy, 1980)

\[
\frac{1}{Pe_{ax}} = \frac{0.5}{1 + \frac{3.8}{Re_p Sc}} + \frac{0.3}{Re_p Sc} \quad 0.008 < Re_p < 400
\]  \hspace{1cm} (5.6)

with

\[
Pe_{ax} = \frac{d_p V_f}{D_{ax}} \quad (5.7) \quad Re_p = \frac{\rho_f U_f d_p}{\eta_f} \quad (5.8)
\]

\[
Sc = \frac{\eta_f}{\rho_f D_{a/b}} \quad (5.9) \quad V_f = \frac{U_f}{c_b} \quad (5.10)
\]

where

\[
Bo \quad = \quad \text{Bodenstein number} \ (-),
\]
\[
D_{ax} \quad = \quad \text{axial dispersion coefficient} \ (m^3 \text{ gas/(m reactor s)}),
\]
\[
Pe_{ax} \quad = \quad \text{axial Peclet number} \ (-),
\]
\[
Re_p \quad = \quad \text{Reynolds number on particle} \ (-),
\]
\[
Sc \quad = \quad \text{Schmidt number} \ (-),
\]
\[
V_f \quad = \quad \text{interstitial gas velocity} \ (m/s),
\]
\[
D_{a/b} \quad = \quad \text{diffusion coefficient in fluid phase} \ (m^2/s).
\]
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The diffusivity, $D_{a/b}$, for a binary mixture consisting of component $a$ (SO$_2$) diffusing into component $b$ (N$_2$) can be calculated according to Reid et al. (1977):

$$D_{a/b} = \frac{10^{-7} \, T^{1.75} \, ((M_a + M_b)/(M_a \, M_b))^{1/2}}{P \, (V_a^{1/3} + V_b^{1/3})^2}$$  \hspace{1cm} (5.11)

where $M_a$ = molar weight component $a$ (g/mole),
$M_b$ = molar weight component $b$ (g/mole),
$V_a$ = atomic diffusion volume component $a$; $V_a$ SO$_2$ = 41.1;
$V_b$ = atomic diffusion volume component $b$; $V_b$ N$_2$ = 17.9 (cm$^3$/mole).

Substituting this in the equations gives:

(5.8): $Re_p = 4.2$ \hspace{1cm} (5.11): $D_{a/b} = 1.3 \times 10^{-4}$ m$^2$/s

(5.9): $Sc = 1.1$ \hspace{1cm} (5.6): $\frac{1}{Pe_{ax}} = 0.34$

(5.5): $Bo = 48$

According to these results, there is no significant dispersion of SO$_2$ in the axial direction.

c. Radial gradients

To ensure proper radial mass distribution in large units, it is sufficient to use a well-designed multi-point distributor (Gierman, 1988). Normally, a single-point distributor is sufficient in a laboratory unit. The calculated length required to achieve an equilibrated condition is usually a few centimeters (of inert material).

Also, the reactor diameter may not be too small, because then the gas flow along the wall becomes significantly larger than the flow through
the bed due to the higher local porosity. Schwartz and Smith (1953) studied the flow distribution of air through a packed bed of cylindrical and spherical pellets at room temperature. Their data, obtained in pipe sizes corresponding to a range of pipe diameter to pellet diameter from 5 to 32, showed that the peak velocity is at approximately one pellet diameter away from the pipe wall. The profile differs less than 20% from the assumed uniform profile for \( \frac{d_b}{d_p} \) ratios of more than 30. It is generally assumed that the tube diameter should be at least 20 particle diameters wide (e.g. Kramers and Westerterp, 1963). In the tubular reactor used in this work we obtain:

\[
\frac{d_b}{d_p} = 4
\]  

(5.12)

Consequently, for a flat profile the reactor diameter should be increased and/or the particle size diminished. However, the aim is towards a small reactor diameter in the laboratory as it is safer, cheaper and faster. Moreover, there is also a limited amount of sorbent available. As will be shown later, the particle size influences the overall rate of reaction because the sorbent effectiveness factor may be much smaller than 1. Thus, the particle size should be kept close to reality. Besides, if external mass and heat transfer (film diffusion) are not rate limiting, the velocity profile is of no importance. The resulting nonflat velocity profile is therefore accepted. Including the shape of the velocity profile into a model is mathematically complex and will thus be neglected.

Criteria for estimation of the significance of the thermal gradient have been developed, but no reliable correlation exists for calculating the heat transfer coefficient at the wall of the laboratory reactor. Gierman (1988) recommends for a trickle bed that temperatures both at the wall and at the centre of the bed should always be measured if the diameter of the bed is more than 3 cm. The diameter of the fixed bed reactor used was only 1.2 cm. It will be shown later that during the fixed bed experiments heat effects are negligible.
(3) Mass/energy production and transfer inside the porous solid

a. Mass production and transfer inside the porous solid

A substantial part of the reaction takes place within the particle itself, because the particle contains much more internal surface area than external. Therefore reactants move through the pores to the surface. Fluid products diffuse back, out of the particle. In the present section, a brief analysis is given of mass and heat transport within a porous sorbent. Sections (3) and (4) are complementary in that they both deal with the effects of finite transport rates on the kinetic behaviour of a system. When reaction occurs simultaneously with mass transfer within a porous structure, a concentration gradient is established and the internal surface is exposed to lower reactant concentrations than the surface near the exterior of the particle. Satterfield (1970) gives a correlation for the effectiveness factor for a first-order irreversible reaction in a catalyst sphere using the generalized Thiele modulus $h_s$ (Thiele, 1939). The effectiveness factor $E$ is defined as the ratio of the rate at which reaction actually occurs in a pellet to the rate at which reaction would occur if the temperature and concentrations throughout the pellet were the same and equal to their respective values at the external surface of the pellet. The correlation is employed on the gas-solid reaction:

$$E = \frac{3}{h_s} \left( \frac{1}{\tanh h_s} - \frac{1}{h_s} \right)$$

(5.13)

$$h_s = \frac{d_p}{z} \left( \frac{S_{BET} \rho_p k_1}{D_{pore}} \right)^{1/2}$$

(5.14)

$k_1$ is the intrinsic first order reaction rate constant for surface reaction in $m^3$ gas/(m$^2$ internal surface s) which is unknown. $D_{pore}$ is the effective pore diffusivity which is calculated by the relation (Perry et al., 1984):
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\[ D_{\text{pore}} = \frac{X}{\tau} \left( \frac{1}{D_{\text{Knu}}} + \frac{1}{D_{\text{a/b}}} \right)^{-1} \]  \hspace{1cm} (5.15)

with \( X = \rho_p V_{\text{pore}} \)  \hspace{1cm} (5.16)

and \( D_{\text{Knu}} = \frac{4}{3} \frac{r_{\text{pore}}^2}{\frac{2}{\pi} \frac{R_g T}{M}} \)  \hspace{1cm} (5.17)

where \( D_{\text{pore}} \) = effective pore diffusion coefficient (m³ gas/(m particle s)),
\( X \) = internal porosity of the particle (m³ gas/m³ particle),
\( \tau \) = tortuosity; Satterfield (1970), see section 5.3.1:
\( \tau = 3 \) (m² gas/m² particle),
\( D_{\text{Knu}} \) = Knudsen diffusion coefficient (m²/s),
\( r_{\text{pore}} \) = average pore radius calculated according eq. (2.5) (m),
\( R_g \) = gas constant; \( R_g = 8.314 \) (J/(mole K)),
\( M \) = molar weight (kg/mole).

There is no limitation by pore diffusion if (Van den Bleek and Gerritsen, 1988):

\[ \phi_m = h_s^2 \frac{L}{E} < 0.15 \]  \hspace{1cm} (5.18)

with \( \phi_m = \frac{(-Ra) \exp(n+1) \frac{V_p^2}{\mu}}{C_f \left(1-\epsilon_b\right) 2 D_{\text{pore}} A_p^2} \)  \hspace{1cm} (5.19)

where \( \phi_m \) = a dimensionless number (-),
\( (-Ra)_{\text{exp}} \) = experimental overall rate (moie/(m³ reactor s)),
\( n \) = reaction order (-),
\( V_p \) = volume of one sorbent particle; \( V_p = 1.56 \times 10^{-8} \) (m³),
\( A_p \) = external surface area of one sorbent particle;
\( A_p = 3.02 \times 10^{-5} \) (m²).
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The experimental overall rate is a function of time and is unknown. The molar feed gas is totally consumed by the amount of sorbent in the reactor because, initially, the reactor off-gas does not contain any SO\textsubscript{2} for about ten minutes. A low estimate of (-Ra)\textsubscript{exp} is thus:

\[
(-Ra)_{\text{exp}} = \frac{\phi_f C_f}{\frac{1}{4} \pi d_b^2 L_b} = 0.11 \text{ mole/(m}^3 \text{ reactor s)}
\]  
(5.20)

If only part of the sorbent in the reactor is already able to consume the SO\textsubscript{2} fed, the value of the overall conversion is correspondingly higher. A high estimate for (-Ra)\textsubscript{exp} is obtained by supposing that this part has a length of only one particle diameter. Then the experimental overall rate is 1.74 mole/(m\textsuperscript{3} reactor s).

If it is assumed that the texture of the sorbent does not change dramatically during reaction, the effective pore diffusion coefficient can be calculated with:

\[
(2.5): r_{\text{pore}} = \frac{2 V_{\text{pore}}}{S_{\text{BET}}} = 5.9 \times 10^{-9} \text{ m} \quad (5.16): \chi = 0.49 \text{ m}^3 \text{ gas/m}^3 \text{ particle}
\]

\[
(5.17): D_{\text{Knu}} = 2.4 \times 10^{-6} \text{ m}^2/\text{s} \quad (5.15): D_{\text{pore}} = 3.8 \times 10^{-7} \text{ m}^3 \text{ gas/(m particle s)}
\]

\[
(5.19): 5 \leq \phi_m \leq 80
\]

Thus, a rate limiting effect of pore diffusion is expected. Experiments at standard conditions with varying particle diameter indeed show a strong influence of pore diffusion (see section 5.5).

b. Energy production and transfer inside the porous solid

For fast reactions accompanied by a large heat effect, the flow of heat into or out of the reaction zone may not be fast enough to keep the particle isothermal. If this happens the particle will cool or heat, strongly affecting the rate of conversion. Thus the heat transfer
resistance within the particle or across the surrounding gas film could influence the rate of reaction. There is no temperature gradient in the particle if (Petersen, 1965):

$$\delta_T = \frac{E_a D_{pore} C_f \left| (-\Delta H_r) \right|}{\lambda_{eff} R_g T_p^2} < 0.3 \quad (5.21)$$

where \( \delta_T \) = a dimensionless number (-),
\( E_a \) = activation energy (J/mole),
\( \Delta H_r \) = enthalpy of reaction (J/mole),
\( \lambda_{eff} \) = effective thermal conductivity of a particle (W/(m K)),
\( T_p \) = particle temperature (K).

A rough estimation of the activation energy (80 kJ/mole) for the sulfation reaction is obtained from Marsh and Ulrichson (1985). The activation energies for the reductive decomposition of calcium sulfate are 288 and 242 kJ/mole for \( H_2 \) and \( CO \) respectively (Diaz-Bossio et al., 1985). The value of the effective thermal conductivity of the porous material is not exactly known. However, an indication, \( \lambda_{eff} = 0.2 \) W/(m K), is given for alumina pellets where the fluid in the pores is air at 50\(^\circ\)C (Satterfield, 1970). The thermal conductivity of the gas under reaction conditions is greater than at 50\(^\circ\)C. The value reported represents thus the minimum value to be expected during reaction. Temperature gradients within a sorbent particle calculated by these numbers would thus represent probable maximum values. Assuming that \( T_p \) equals \( T \) and substituting in equation (5.21) gives:

$$\delta_T = 2 \times 10^{-4}$$

The result shows that the temperature gradient in the particle can be neglected.

(4) Mass/energy production and transfer outside the porous solid

Reactants diffuse from the main body of the fluid to the outer surface
of the particle through a stagnant boundary layer. This phenomenon is commonly expressed as film diffusion. Fluid products move from the mouth of the pores into the main body of the gas. Under certain circumstances it may be necessary to account for the influence of transport resistances external to the catalyst pellet in order to determine the overall kinetic behaviour of a system. An estimation of the concentration and temperature difference between gas stream and the sorbent is calculated below.

a. Concentration gradient in film

The concentration gradient in the film is given by:

$$C_f - C_s = \frac{\phi_S^\prime}{k_{SO_2, film}}$$  \hspace{1cm} (5.22)

with

$$\phi_S^\prime = \frac{(-Ra) \exp \left( \frac{1}{4} \pi d_b^2 L_b \right)}{S_0}$$ \hspace{1cm} (5.23)
$$S_0 = \frac{3\pi (1-\epsilon_b)}{2 d_p^2 L_b}$$ \hspace{1cm} (5.24)

and the mass transport coefficient ($k_{SO_2, film}$) can be estimated by the correlations (Perry et al., 1984):

$$St \; Sc^{2/3} = (0.81 \pm 0.05) \; Re_p^{-0.5} \quad 5 < Re_p < 500$$  \hspace{1cm} (5.25)

$$St \; Sc^{2/3} = (0.60 \pm 0.1) \; Re_p^{-0.43} \quad 50 < Re_p < 2000$$  \hspace{1cm} (5.26)

with

$$St = \frac{k_{SO_2, film} \; \epsilon_b}{U_f}$$ \hspace{1cm} (5.27)

where $C_s$ = SO$_2$ concentration at core surface (mole/m$^3$)

$\phi_S^\prime$ = sulfur flux to one particle (mole/(m$^2$ s)),

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\[ k_{SO_2,\text{film}} = \text{SO}_2 \text{ film mass transport coefficient (m/s)}, \]
\[ S_o = \text{total external surface area of particles in the reactor (m}^2\text{)}. \]

From equation (5.25), while neglecting that Re_p is smaller than 5, the mass transport coefficient \( k_{SO_2,\text{film}} \) is 0.17 m/s.

(5.24): \( S_o = 0.0064 \text{ m}^2 \)  
(5.23): \( \phi_s'' = 9.9 \times 10^{-5} \text{ mole/(m}^2\text{ s)} \)

(5.22): \( 0.02 \leq \frac{C_f - C_s}{C_f} \leq 0.32 \)

Thus (only) the low estimate \((-Ra)_{\text{exp}}\) results in a small concentration gradient in the film.

b. Temperature gradient in film

There is a negligible temperature gradient in the film, i.e. \((T_p - T)/T\) is smaller than 1%, if (Van den Bleek and Gerritsen, 1988):

\[
\psi_T = \frac{E_a \phi_m A_p D_{\text{pore}} C_f (-\Delta H_r)}{R T^2 V_p h} < 0.1 \quad (5.28)
\]

where \( \psi_T \) = a dimensionless number (-),
\( h \) = heat transfer coefficient (W/(m\(^2\) K)).

\( h \) is to be calculated from:

\[
Nu = \frac{h d_p}{\lambda_f} \quad (5.29)
\]

where \( Nu \) = Nusselt number (-).
The Nusselt number is predicted by (Beek and Muttzall, 1975):

$$\text{Nu} = 0.75 \frac{1}{\varepsilon_b} \left( \frac{3}{2} (1 - \varepsilon_b) \right)^{1/2} \text{Re}_p^{1/2} \text{Pr}^{1/3} \quad 30 < \frac{2}{3 (1 - \varepsilon_b)} \text{Re}_p < 10^3 \quad (5.30)$$

with \( \text{Pr} = \frac{\eta_f C_p}{\lambda_f} \) \hspace{1cm} (5.31)

(5.31): \( \text{Pr} = 0.73 \)

Neglecting that \( \frac{2}{3 (1 - \varepsilon_b)} \text{Re}_p \) is much smaller than 30:

(5.30): \( \text{Nu} = 3 \)

(5.29): \( h = \frac{\text{Nu} \lambda_f}{d_p} = 70 \text{ W/(m}^2 \text{ K)} \)

(5.28): \( 0.005 \leq \psi_T \leq 0.08 \)

Measurements at standard conditions showed no temperature changes of the gas phase during the sulfation experiments. It is therefore concluded that heat effects do not have to be included in the modeling work and thus the energy balance can be omitted.

In principle, the following mass transfer resistances can be distinguished as well:

a. Product-layer diffusion resistance. If a nonporous solid product-layer is formed during reaction the reactant has to diffuse through this layer to reach the fresh reactant. There are little data available on product-layer diffusion in literature. Estimates of the solid state diffusivity of SO$_2$ through CaSO$_4$ were obtained by Marsh and Ulrichson, 1985. A value of about 1.5 $10^{-12}$ m$^2$/s was found at 841°C. Values in modeling efforts range from 6 $10^{-13}$ to 2.5 $10^{-10}$ m$^2$/s (Daniell et al., 1988).

b. Surface phenomena resistance. The reactant molecules associate with the surface of the particle and give the products. A description of the
surface phenomenon resistance is given in Levenspiel (1972) and Coulson & Richardson (1979). Here it is included in the chemical rate constant.

c. Chemical reaction rate resistance. This rate is determined by the intrinsic kinetics of the reaction. Burdett (1983) showed that the CaO/SO₃ kinetics are rapid. The chemical step is usually much more temperature-sensitive than the physical steps as caused by the temperature dependency from Arrhenius’ Law. This also means that at higher temperatures the reaction rate will be less rate limiting (Coulson & Richardson, 1979).

From the calculations and fixed bed reactor experimental results described in this section, it is concluded that the pressure drop, the axial dispersion, the heat produced and heat transfer effects do not have to be included as a first approximation in the modeling work. Also all radial reactor gradients will be omitted. Film diffusion, pore diffusion and/or product-layer diffusion are to be included. Surface phenomena like adsorption and the chemical reaction rate are combined in one overall reaction rate constant.

5.3 Selection of a sulfur capture model and the mass balances for the fixed bed reactor: the SURE2 model

5.3.1 Introduction

A mathematical model is needed to extract the necessary kinetic information of the experiments. In any such model, a rate equation for the progress of reaction has to be defined. The reaction of a nonporous particle surrounded by a fluid is described by the simple and idealized "shrinking unreacted core model", as developed by Yagi and Kunii (1955). The model assumes that reaction occurs first at the outer skin of the particle. The reaction zone moves into the nonporous solid particle while a "shell" of completely converted and inert, porous solid material is produced.

The shrinking core model is not necessarily limited to solids of which the core is nonporous. With a fast reaction in the porous solid, diffusion into the core and chemical reaction occur in parallel. Such a combination gives
Figure 5.1 Representation of the concentrations of reactants during sulfur retention with a combination of resistances according to the SURE2 model.

rise to a thin diffuse reaction zone which advances to the center at a certain rate. While the shell grows in thickness, the unreacted core of porous material shrinks during reaction (Figure 5.1). The overall size of the particle remains unchanged.

The model generally considers five reaction steps, which together define the overall rate of the process.

Step 1. Diffusion of gaseous reactant through the film, surrounding the particle, to the outer surface of the particle. Although calculations and experimental results show that film diffusion is generally not rate-controlling, it will be included in the model to simplify the mathematical start of the calculations. The corresponding transport parameters \( k_{SO_2, \text{film}} \) and \( D_{SO_2, \text{film}} \) are obtained from literature data.
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Step 2. Diffusion of the reactant through the shell to the surface of the unreacted core. This transport is described with a single parameter, $D_{SO_2, \text{shell}}$.

Step 3. Reaction of gaseous reactants with solid at the core surface. It is supposed that the conversion rate of CaO is first order in SO$_3$ and proportional to the external surface area of the core.

Step 4. Diffusion of gaseous products through the shell to the exterior surface of the solid. During the sulfur capture stage no gaseous products are formed.

Step 5. Diffusion of gaseous products through the gas film into the main bulk of the fluid. This step does not apply for the retention process either.

The resulting model, which combines both the conversion equation and the reactor hydrodynamics, is called the SURE2 (Sulfur Retention) model. The digit "2" is added to distinguish this model from another model developed at the Delft University of Technology (Schouten and Van den Bleek, 1987; Schouten, 1988). The conversion equation for one sorbent particle is developed in next section.

5.3.2 Conversion equation for one sorbent particle

The development of the conversion equation, an expression between time and core radius $r_C$, requires a two step analysis. First, a single typical partially reacted particle is examined, writing the flux relationships for this situation. Then this relationship is applied for all values of $r_C$; in other words, $r_C$ is integrated between R and 0. Consider a partially reacted particle as shown in Figure 5.1. The reactants diffuse through a stationary film layer after which both the reactants and the boundary of the unreacted core move inward towards the center of the particle. The shrinkage of the unreacted core is slower than the linear velocity of reactants towards the unreacted core by a factor of about 1000, which is roughly the ratio of densities of the solid to gas (Bischof, 1963; Bischof, 1965; Bowen, 1965; Luss, 1968). Because of this, it is reasonable to assume that the unreacted core has a quasi-stationary radius. The concentration gradient in film and shell can be calculated assuming a pseudo-stationary process. The molar balance (5.1) will be elaborated for the gaseous sulfur components SO$_2$ and
SO\textsubscript{3} in the sulfur balance. Oxygen is present in such an excess that its concentration (C\textsubscript{O\textsubscript{2}}) can be assumed to be constant at any time and place. The sulfur balance according Eq. (5.1) for both film layer and shell reads:

\[ 0 = [4\pi r^2 \phi^r_S]_{\text{in}} - [4\pi r^2 \phi^r_S]_{\text{out}} - 0 \]  \hspace{1cm} (5.29)

where \( r \) = radius; \( 0 \leq r \leq R + \delta \) (m),
\( R \) = particle radius (m),
\( \delta \) = thickness of film layer around particle (m),
\( \phi^r_S \) = sulfur flux towards (centre of) particle (mole/(m\text sup\(2\) s)).

Let the flux of SO\textsubscript{2} and SO\textsubscript{3} within the film and shell be expressed by Fick's law for stationary equimolar counter diffusion. The reacting components are highly diluted with inert N\textsubscript{2} and the net diffusion flux may be neglected (other forms of this diffusion equation will give the same result; Levenspiel, 1972). Then, noting that both \( \phi'' \) and \( \frac{dC}{dr} \) are positive, we have

\[ \phi'' = D \frac{dC}{dr} \]  \hspace{1cm} (5.30)

where \( \phi'' \) = flux of SO\textsubscript{2} or SO\textsubscript{3} towards (centre of) particle (mole/(m\text sup\(2\) s)),
\( D \) = diffusion coefficient; \( r_{c<R} \leq D_{\text{shell}} \); \( r_{R<R+\delta} \leq D_{\text{film}} \) (m\text sup\(3\)/(m s)),
\( r_c \) = radius of core (m),
\( C \) = concentration; \( C_{SO_2} \) or \( C_{SO_3} \) (mole/m\textsup\(3\)).

In Eq. (5.30) is \( D_{\text{film}} \) the film layer diffusion coefficient and \( D_{\text{shell}} \) the effective diffusion coefficient of the gaseous component in the shell. Substitution of Eq. (5.30) in Eq. (5.29) results in:
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\[
\left[4\pi r^2 \left( D_{SO_2} \frac{dC_{SO_2}}{dr} + D_{SO_3} \frac{dC_{SO_3}}{dr} \right) \right]_{r+\Delta r} = \left[4\pi r^2 \left( D_{SO_2} \frac{dC_{SO_2}}{dr} + D_{SO_3} \frac{dC_{SO_3}}{dr} \right) \right]_r
\]

Taylor expansion and integrating once results in:

\[
\left[4\pi r^2 \left( D_{SO_2} \frac{dC_{SO_2}}{dr} + D_{SO_3} \frac{dC_{SO_3}}{dr} \right) \right]_r = \phi_r
\]

(5.32)

The integration constant \( \phi_r \) has the dimension of mole/s. It is assumed (and verified in section 5.5.1) that \( SO_2, O_2 \) and \( SO_3 \) are in equilibrium at every time and place in the sorbent bed. Therefore, \( C_{SO_3} \) can be expressed in \( C_{SO_2} \) by using the equilibrium constant:

\[
K_{eq} = \frac{C_{SO_3}}{C_{SO_2} C_{O_2}^{1/2}} \quad \text{or} \quad C_{SO_3} = K_{eq} C_{O_2}^{1/2} C_{SO_2}
\]

(5.33)

where \( K_{eq} = \) equilibrium constant of \( SO_2 + 1/2 O_2 \rightleftharpoons SO_3 \) \((m^3/mole)^{1/2})\), \( C_{O_2} = \) oxygen concentration in feed \((mole/m^3)\).

Thus:

\[
4\pi r^2 \left( D_{SO_2} \frac{dC_{SO_2}}{dr} + D_{SO_3} K_{eq} C_{O_2}^{1/2} \frac{dC_{SO_2}}{dr} \right) = \phi_r
\]

(5.34)

\[
dC_{SO_2} = \frac{\phi_r}{4\pi r^2 \left( D_{SO_2} + D_{SO_3} K_{eq} C_{O_2}^{1/2} \right)} dr
\]

(5.35)

Integrating over the gas film (see Figure 5.1):

\[
\int_{C_{SO_2}, R}^{C_{SO_2}, R+\delta} dC_{SO_2} = \int_{R}^{R+\delta} \frac{\phi_r}{4\pi r^2 \left( D_{SO_2, \text{film}} + D_{SO_3, \text{film}} K_{eq} C_{O_2}^{1/2} \right)} dr
\]

(5.36)
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where \( D_{SO_2,\text{film}} \) = diffusion coefficient of \( SO_2 \) in film (m\(^2\)/s),
\( D_{SO_3,\text{film}} \) = diffusion coefficient of \( SO_3 \) in film (m\(^2\)/s).

results in:

\[
C_{SO_2,R+\delta} - C_{SO_2,R} = \frac{\phi_r}{4\pi \left( D_{SO_2,\text{film}} + D_{SO_3,\text{film}} k_{eq} C_{O_2}^{1/2} \right)} \left( \frac{1}{R} - \frac{1}{R+\delta} \right) \tag{5.37}
\]

and in an analogous way for the shell:

\[
C_{SO_2,R} - C_{SO_2,r_c} = \frac{\phi_r}{4\pi \left( D_{SO_2,\text{shell}} + D_{SO_3,\text{shell}} k_{eq} C_{O_2}^{1/2} \right)} \left( \frac{1}{r_c} - \frac{1}{R} \right) \tag{5.38}
\]

where \( D_{SO_2,\text{shell}} \) = effective diffusion coefficient of \( SO_2 \) in the shell
(m\(^3\) gas/(m particle s)),
\( D_{SO_3,\text{shell}} \) = effective diffusion coefficient of \( SO_3 \) in the shell
(m\(^3\) gas/(m particle s)).

Summation of (5.37) and (5.38) results in:

\[
C_{SO_2,R+\delta} - C_{SO_2,r_c} = \frac{\phi_r}{4\pi \left( D_{SO_2,\text{film}} + D_{SO_3,\text{film}} k_{eq} C_{O_2}^{1/2} \right)} \left( \frac{1}{R} - \frac{1}{R+\delta} \right) + \frac{\phi_r}{4\pi \left( D_{SO_2,\text{shell}} + D_{SO_3,\text{shell}} k_{eq} C_{O_2}^{1/2} \right)} \left( \frac{1}{r_c} - \frac{1}{R} \right) \tag{5.39}
\]

This expression is rewritten as:
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\[ C_{SO_2, r+6} - C_{SO_2, r_c} = \frac{\phi_r}{4\pi} (\alpha_{SO_X, \text{film}} + \alpha_{SO_X, \text{shell}}) \]  \hspace{1cm} (5.40)

with

\[ \alpha_{SO_X, \text{film}} = \frac{1}{D_{SO_2, \text{film}} + D_{SO_3, \text{film}} K_{eq} C_{O_2}^{1/2}} \left( \frac{1}{R} - \frac{1}{R+6} \right) \]  \hspace{1cm} (5.41)

\[ \alpha_{SO_X, \text{shell}} = \frac{1}{D_{SO_2, \text{shell}} + D_{SO_3, \text{shell}} K_{eq} C_{O_2}^{1/2}} \left( \frac{1}{r_c} - \frac{1}{R} \right) \]  \hspace{1cm} (5.42)

The integration constant \( \phi_r \) must equal the pseudo steady state reaction rate. This rate is supposed to be first order in the \( SO_3 \) concentration and proportional to the core outer surface. The reaction rate constant is expressed by \( k_s \) (m³ gas/(m² core s)):

\[ \phi_r = k_s 4\pi r_c^2 C_{SO_3, r_c} = k_s 4\pi r_c^2 K_{eq} C_{O_2}^{1/2} C_{SO_2, r_c} \]  \hspace{1cm} (5.43)

Combining (5.40) and (5.43), it follows:

\[ C_{SO_2, r_c} = \frac{C_{SO_2, r+6}}{1 + K_{eq} C_{O_2}^{1/2} k_s r_c^2 (\alpha_{SO_X, \text{film}} + \alpha_{SO_X, \text{shell}})} \]  \hspace{1cm} (5.44)

In the second part of the analysis, the size of the unreacted core changes with time. As the core shrinks, the shell becomes thicker, lowering the rate of diffusion. The outer surface area of the core decreases. Consequently, it can be written:

\[ \frac{dN_{CaO}}{dt} = - \Gamma k_s 4\pi r_c^2 K_{eq} C_{O_2}^{1/2} C_{SO_2, r_c} \]  \hspace{1cm} (5.45)
where \( N_{CaO} \) = amount of CaO in the core of one particle (mole),
\( t \) = time (s),
\( \Gamma \) = stoichiometric coefficient; \( \Gamma = 1 \) (mole CaO/mole SO\(_3\)).

Substitution of (5.44) into (5.45) gives:

\[
\frac{dN_{CaO}}{dt} = -\Gamma k_s \frac{4\pi r_c^2 K_{eq} C_{O_2}^{1/2}}{1 + K_{eq} C_{O_2}^{1/2} k_s r_c^2 (\alpha_{SO_x, film} + \alpha_{SO_x, shell})} \cdot \frac{C_{SO_2,R+\delta}}{C_{SO_2,R}}
\]

(5.46)

Let \( N_{CaO} = \frac{4}{3} \pi r_c^3 C_{CaO} \)  

(5.47)

and \( C_{CaO} \) = calcium oxide concentration in a fresh sorbent particle (mole CaO/m\(^3\) particle).

After substitution of (5.47) in (5.46), the conversion equation is finally obtained as:

\[
\frac{dr_c}{dt} = -\frac{\Gamma/C_{CaO} C_{SO_2,R+\delta}}{k_s k_{eq} C_{O_2}^{1/2} r_c^2 (\alpha_{SO_x, film} + \alpha_{SO_x, shell})}
\]

(5.48)

Initial condition: \( t = 0 \longrightarrow r_c,0 = R \)

5.3.3 Mass balances for the sulfur capture experiments in the fixed bed reactor

We define the mass balance for sulfur (S) and calcium oxide (CaO) across an elementary section of the reactor as shown in Figure 5.2.
Figure 5.2 One dimensional fixed bed reactor. The reaction zone extends from $z = 0$ to $z = L_b$.

Fluid phase S balance fixed bed:

\[
\frac{\partial (\epsilon_b A \Delta z C_S)}{\partial t} = [\phi_f C_S]_z - [\phi_f C_S]_{z+\Delta z} - [\phi_{SGS}]_z N_{part} A \Delta z
\]  

(5.49)

where

- $\epsilon_b$ = bed porosity (m$^3$ gas/m$^3$ reactor),
- $A$ = cross-section area of empty reactor (m$^2$),
- $z$ = length coordinate (m),
- $C_S$ = $C_{SO_2} + C_{SO_3}$ (mole/m$^3$),
- $\phi_f$ = gas flow (m$^3$/s),
- $\phi_{SGS}$ = sulfur flow to one particle from gas to solid (mole/s),
- $N_{part}$ = concentration of particles in reactor (#/m$^3$ reactor).

(5.50)

As $\epsilon_b$, $A$, $\Delta z$ and $\phi_f$ are constants.
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\[ \varepsilon_b A \Delta z \left( \frac{\partial C_s}{\partial t} \right)_z = \phi_f [C_s]_z - (\phi_f [C_s]_z + \phi_f [\frac{\partial C_s}{\partial z}]_z \Delta z) - [\phi_{s-g-s}]_z N_{part} A \Delta z \]  

(5.51)

\[ \frac{\partial [\phi_s g-s]}{\partial z}_z = - \frac{\phi_f}{\varepsilon_b A} \frac{\partial [\theta_s]}{\partial z}_z - \frac{1}{\varepsilon_b} [\phi_{s-g-s}]_z N_{part} \]  

(5.52)

The term \( [\phi_{s-g-s}]_z \) is directly obtained from Eq. (5.43):

\[ [\phi_{s-g-s}]_z = k_s 4\pi [r_c^2 k_{eq} C_o^{1/2} C_{SO_2},r_c]_z \]  

(5.53)

in which \( C_{SO_2},r_c \) is obtained from the analysis of a single particle (see Eq. (5.44)):

\[ [C_{SO_2},r_c]_z = \left[ \frac{C_{SO_2}}{1 + k_{eq} C_o^{1/2} k_s r_c^2 (\alpha_{SO_2,film} + \alpha_{SO_2,shell})} \right]_z \]  

(5.54)

The initial conditions are at \( t = 0; 0 \leq z \leq L_b \rightleftharpoons C_s = 0 \)

and the boundary condition is at \( z = 0; C_s = 1 \)

The boundary condition for \( C_{SO_2},z \) is calculated using (4.4) according to:

\[ C_{SO_2},z = \left[ \frac{C_s}{1 + k_{eq} C_o^{1/2}} \right]_z \]  

(5.55)

Solid phase CaO balance fixed bed:

\[ [N_{part} A \Delta z \frac{\partial (N_{CaO})}{\partial t}]_z = - \Gamma [\phi_{s-g-s}]_z N_{part} A \Delta z \]  

(5.56)
- 5 modeling of the fixed bed reactor experimental results -

\[
\frac{\partial (N_{CaO})}{\partial t}_z = - \Gamma \phi_{s g} \cdot s_z \tag{5.57}
\]

which results in (see section 5.3.2):

\[
\frac{\partial r_c}{\partial t}_z = - \left[ \frac{\Gamma/C_{CaO} \cdot C_{SO_2}}{k_s \cdot K_{eq} \cdot C_{O_2}^{1/2} + r_c^2 (\alpha_{SO_x,film} + \alpha_{SO_x,shell})} \right]_z \tag{5.58}
\]

The initial conditions are at \( t = 0 \): \( 0 \leq z \leq L_b \rightarrow r_c, z, 0 = R \)

Two partial differential equations, (5.52) and (5.58), are obtained which have to be solved simultaneously by a numerical procedure.

The method used here is to divide the sorbent bed into \( N_{tanks} \) volumetric sections (ideally mixed tanks), each having a volume \( V_{r,i} \). In Figure 5.3 is the approximation by the so-called \( N \)-Tanks-in-Series model visualized.

![Figure 5.3 Approximation of the sorbent bed by the \( N \)-Tanks-in-Series model.](image)

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The S- and CaO-balance for tank $i$ are:

**Fluid phase S balance tank:**

$$
V_g,i \left[ \frac{dC_S}{dt} \right]_i = \phi_f [C_S]_{i-1} - \phi_f [C_S]_i - [\phi_s g-s]_i N_{\text{part}} V_r,i
$$

(5.59)

where $V_g,i$ = gas volume in one tank (m$^3$),

$V_r,i$ = volume of one tank (m$^3$),

$i$ = tank index number; $1 \leq i \leq N_{\text{tanks}}$ (-),

$N_{\text{tanks}}$ = total number of tanks = $V_r/V_r,i$ (-),

$V_r$ = volume of reactor (m$^3$).

with $[\phi_s g-s]_i = k_s 4\pi \left[ r_c^2 K_{eq} C_{O_2}^{1/2} C_{SO_2},r_c \right]_i$

(5.60)

and $[C_{SO_2},r_c]_i = \frac{C_{SO_2}}{1 + K_{eq} C_{O_2}^{1/2} k_s r_c^2 (x_{SO_x,\text{film}} + x_{SO_x,\text{shell}})}$

(5.61)

$$
\left[ \frac{d(C_{SO_2} + C_{SO_3})}{dt} \right]_i = \frac{\phi_f}{V_g,i} [C_{SO_2} + C_{SO_3}]_{i-1} - \frac{\phi_f}{V_g,i} [C_{SO_2} + C_{SO_3}]_i - \\
\frac{1}{V_g,i} \frac{4\pi r_c^2 C_{SO_2} N_{\text{part}} V_r}{k_s K_{eq} C_{O_2}^{1/2} + r_c^2 (x_{SO_x,\text{film}} + x_{SO_x,\text{shell}})}
$$

(5.62)

$$
\left[ \frac{dC_{SO_2}}{dt} \right]_i = \frac{\phi_f}{V_g,i} ([C_{SO_2}]_{i-1} - [C_{SO_2}]_i) - \ldots
$$
- 5 modeling of the fixed bed reactor experimental results -

\[- \frac{1}{V_{g,i} (1 + K_{eq} C_{O_2}^{1/2})} \left( \frac{1}{k_s K_{eq} C_{O_2}^{1/2} + r_c^2 (\alpha_{SO_x}^{film} + \alpha_{SO_x}^{shell})} \right) \frac{4\pi r_c^2 C_{SO_2}}{N_{part} V_r} \right]_i \]  

(5.63)

The initial conditions are at \( t = 0 \): \( 1 \leq i \leq N_{tanks} \) \( \longrightarrow \) \( C_{SO_2,i} = 0 \)

Solid phase CaO balance tank:

\[ [N_{part} V_r, i] \left( \frac{d(N_{CaO})}{dt} \right)_i = - \Gamma \left[ \phi_{s-g-s} \right]_i N_{part} V_r, i \]  

(5.64)

\[ \frac{d(N_{CaO})}{dt} \right)_i = - \Gamma \left[ \phi_{s-g-s} \right]_i \]  

(5.65)

which results in (see section 5.3.2):

\[ \frac{dr_c}{dt} \right)_i = - \left[ \frac{\Gamma / C_{CaO} C_{SO_2}}{k_s K_{eq} C_{O_2}^{1/2} + r_c^2 (\alpha_{SO_x}^{film} + \alpha_{SO_x}^{shell})} \right]_i \]  

(5.66)

Initial conditions at \( t = 0 \): \( 1 \leq i \leq N_{tanks} \) \( \longrightarrow \) \( r_{c,i,0} = R \)

The following dimensionless quantities are now defined:

\[ X_i = \frac{C_{SO_2,i,t/C_{SO_x}^{feed}}}{1 \leq i \leq N_{tanks}} \]  

(5.67)

\[ \theta = \frac{t}{t_{stoich}} \]  

(5.68)

\[ Y_i = \frac{r_{c,i,t/R}} {1 \leq i \leq N_{tanks}} \]  

(5.69)
where \( X \) = dimensionless \( \text{SO}_2 \) concentration (-),
\( C_{\text{SO}_x, \text{feed}} \) = sulfur oxide concentration in feed (mole/m³),
\( \Theta \) = dimensionless time (-),
\( t_{\text{stoich}} \) = stoichiometric breakthrough time (s),
\( Y \) = dimensionless core radius (-).

The stoichiometric breakthrough time is defined as the total amount (mole) of calcium oxide present in the reactor divided by the sulfur flux (mole/s) entering the reactor. The equations (5.63) and (5.66) can now be rewritten in dimensionless form:

\[
\frac{C_{\text{SO}_x, \text{feed}}}{t_{\text{stoich}}} \frac{dX}{d\Theta} = \frac{\phi_f}{V_{g,i}} C_{\text{SO}_x, \text{feed}} (X_{i-1} - X_i)
\]

\[
\frac{K_{eq} C_{O_2}^{1/2}}{V_{g,i} (1 + K_{eq} C_{O_2}^{1/2})} \left[ \frac{4\pi (Y R)^2 C_{\text{SO}_x, \text{feed}} X N_{\text{part}} V_r}{k_s + (Y R)^2 (\beta_{\text{SO}_x, \text{film}} + \beta_{\text{SO}_x, \text{shell}})} \right]_i
\]

\[
\beta_{\text{SO}_x, \text{film}} = \frac{K_{eq} C_{O_2}^{1/2}}{D_{\text{SO}_2, \text{film}} + D_{\text{SO}_3, \text{film}} K_{eq} C_{O_2}^{1/2}} \left( \frac{1}{R} - \frac{1}{R+\delta} \right)
\]

\[
\beta_{\text{SO}_x, \text{shell}} = \frac{K_{eq} C_{O_2}^{1/2}}{D_{\text{SO}_2, \text{shell}} + D_{\text{SO}_3, \text{shell}} K_{eq} C_{O_2}^{1/2}} \left( \frac{1}{R_1 R} - \frac{1}{R} \right)
\]

\[
\frac{dX}{d\Theta} = \frac{\phi_f t_{\text{stoich}}}{V_{g,i}} (X_{i-1} - X_i)
\]

\[
\frac{K_{eq} C_{O_2}^{1/2}}{V_{g,i} (1 + K_{eq} C_{O_2}^{1/2})} \left[ \frac{4\pi (Y R)^2 t_{\text{stoich}} X N_{\text{part}} V_r}{k_s + (Y R)^2 (\beta_{\text{SO}_x, \text{film}} + \beta_{\text{SO}_x, \text{shell}})} \right]_i
\]
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\[
\frac{R}{t_{\text{stoich}}} \frac{dY}{d\Theta}_i = - \left[ \frac{\Gamma}{C_{\text{CaO}} K_{\text{eq}} C_{\text{O}_2}^{1/2} C_{\text{SO}_X,\text{feed}} X}{\left[ \frac{1}{k_s} + (Y R)^2 (\beta_{\text{SO}_X,\text{film}} + \beta_{\text{SO}_X,\text{shell}}) \right]} \right]_i
\]

\[
\frac{dY}{d\Theta}_i = - \frac{1}{C_{\text{CaO}} R} \left[ \frac{\Gamma K_{\text{eq}} C_{\text{O}_2}^{1/2} C_{\text{SO}_X,\text{feed}} t_{\text{stoich}} X}{\left[ \frac{1}{k_s} + (Y R)^2 (\beta_{\text{SO}_X,\text{film}} + \beta_{\text{SO}_X,\text{shell}}) \right]} \right]_i
\]

Initial conditions: \( \Theta = 0 \)
\( 1 \leq i \leq N_{\text{tanks}} \)
\( \rightarrow X_{i,0} = 0 \)
\( Y_{i,0} = 1 \)

Boundary condition: \( i = 0 \)
\( \rightarrow X_{0,\Theta} = X_{\text{feed}} \)

The required numerical value for \( \delta \) can be estimated from the film theory according to:

\[
\delta = \frac{1}{k_{\text{SO}_2,\text{film}}} \frac{1}{D_{\text{SO}_2,\text{film}} - \frac{1}{R}}
\]

The diffusion coefficient of \( \text{SO}_2 \) in the film layer \((D_{\text{SO}_2,\text{film}})\) is calculated by Eq. (5.11) and the film mass transport coefficient \((k_{\text{SO}_2,\text{film}})\) is given by the correlations (5.25) to (5.27). The diffusion coefficients of \( \text{SO}_2 \) \((D_{\text{SO}_2,\text{shell}})\) and \( \text{SO}_3 \) \((D_{\text{SO}_3,\text{shell}})\) in the shell and the reaction rate constant \((k_s)\) are unknown. It is supposed that \( D_{\text{SO}_3,\text{shell}} = 0.9 \ D_{\text{SO}_2,\text{shell}} \) because that is approximately true for both free gas phase- and Knudsen diffusivity. The differential equations (5.73) and (5.75) of the SURE2 model have to be solved for \( N_{\text{tanks}} \) simultaneously. From the experimental results the parameters \( D_{\text{SO}_2,\text{shell}} \) and \( k_s \) are estimated.
5.4 Computation method

The differential equations (5.73) and (5.75) of the SURE2 model have been solved with the RGRK-package which can solve sets of stiff and/or nonstiff first order differential equations simultaneously. It uses an IBM-PC or compatible computer and TURBO PASCAL (a registered trademark of Borland International, Inc.). The package, distributed by the Reactor Research Foundation (Delft, The Netherlands), is developed and described by Gerritsen and Soerawidjaja (1989).

A short summary of the principles of the solution method used in the package is:
1. The equations may be stiff or nonstiff, or even vary in stiffness during the course of integration, but must have the same independent variable.
2. Embedded integration codes are used. This means that the code not only determines the value of the dependent variable(s) at the end of a step but also provides an estimation of the local error in the result obtained.
3. The nonstiff code (or nonstiff integrator) uses an embedded explicit Runge Kutta method of order 4, according to Merson (1957) and May (1984). The error is estimated by comparing with an order 3 result.
4. The stiff integrator uses an embedded implicit "W-method" of order 3, according to Shintani (1982). The error is estimated by comparing with an order 2 result.
5. At the start of each step an estimation is made of the maximum stepsize that will give a stable solution using the nonstiff integrator. The value of this stepsize is called "stable stepsize".
6. At the end of each step the estimated local error is compared with a tolerance specified by the user. If the estimated local error is larger the step is rejected and a smaller stepsize chosen, otherwise the step is accepted.
7. If the step is accepted, the stepsize proposed for the next step is obtained by multiplying the current stepsize with a factor ranging from 1 to 5, depending upon the ratio of tolerated and estimated error in the last step(s) and the current value of the stable stepsize.
8. The first step will always be calculated with the nonstiff integrator. The first stepsize tried is the stable stepsize.
9. Before all subsequent steps, the new proposed stepsize is compared with the stable stepsize. If the proposed stepsize is less than 2 times the stable stepsize the nonstiff integrator and stable stepsize are chosen. If the proposed stepsize is more than 2 times the stable stepsize the stiff integrator is used with the proposed stepsize.

Above RRGRK-package is included in a program which solves the differential equations and simultaneously optimizes the estimated values for the two parameters $D_{SO_2, shell}$ and $k_s$ by comparing the calculated and the experimental results. The optimization procedure used is a Simplex routine, while the best-fit is obtained using the least-squares method. This work is documented by Hultermans, 1990.

<table>
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<tr>
<th>Superficial</th>
<th>$SO_2$ conc.</th>
<th>$O_2$ conc.</th>
<th>Particle diameter</th>
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<td>vol%</td>
<td>vol%</td>
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<tr>
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<td>2.8–3.4</td>
</tr>
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<td>0.25</td>
<td>4</td>
<td>2.8–3.4</td>
</tr>
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<td>2.8–3.4</td>
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</table>
5.5 Modeling results

5.5.1 Fixed bed reactor breakthrough curves

A series of experiments has been conducted using SG105 to test the proposed model. Details of the experimental conditions are given in Table 5.1. The sulfation experiments were performed in the fixed bed reactor using different superficial gas velocities, $SO_2$ concentrations, $O_2$ concentrations and particle diameters. The unknown parameters $D_{SO_2,\text{shell}}$ and $k_s$ have been estimated. The influence of the reactivity of "pure" $\gamma$-$Al_2O_3$ as described in section 4.2.1 was neglected. Besides, the incorporation of the calcium compound perhaps reduces the contribution of the reactivity of the pure support. The results are presented in the Figures 5.4a to 5.4d.

![Figure 5.4a SURE2 model prediction at various superficial gas velocities.](image)

Figure 5.4a shows a comparison between the predicted and experimental breakthrough curves for different superficial gas velocities, the other conditions being maintained standard. It is established that the SURE2 model is able to describe the experiments accurately with:

$$D_{SO_2,\text{shell}} = (7.53 \pm 0.60) \times 10^{-7} \text{ m}^3\text{ gas/(m particle s)}$$
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\[ k_s = (0.149 \pm 0.033) \text{ m}^3 \text{ gas/(m}^2 \text{ core s)} \]. The residual sum of squares for one point is \((4.19 \pm 3.30) \times 10^{-4}\).

The influence of the \( \text{SO}_2 \) concentration is shown in Figure 5.4b. Using the very same values of \( D_{\text{SO}_2, \text{shell}} \) and \( k_s \), the SURE2 model is able to describe these experimental results as well.

![Figure 5.4b SURE2 model prediction at various SO\(_2\) concentrations.](image)

In Figure 5.4c, the computed plots are presented at varying \( \text{O}_2 \) concentration. It is seen that the calculated results are still good with the same estimated values for the parameters.

Finally, Figure 5.4d shows data giving the effect of changing the particle size from 3.1 mm to 0.225 mm diameter. The particle diameter was reduced by grinding standard (3.1 mm) particles. The results of the experiments are not well in agreement with the model. The model predicts a better sulfur capture than obtained experimentally and errors become larger if conditions are used progressively further away from the standard. It is probably unrealistic to expect the sulfation kinetics of different sized particles to be identical. The reason can be the role of diffusion of reactants into the unreacted core. In large particles, the diffusion of reactants into the unreacted core can be neglected by assuming that the concentration drops infinitely rapid
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at the core surface. In other words, the reacting zone is negligibly small. In small particles, however, the thickness of such a zone can not be neglected anymore and should be included in the model.

Figure 5.4c SURE2 model prediction at various O₂ concentrations.

Figure 5.4d SURE2 model prediction at various particle diameters.

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This can be verified by calculating the Thiele modulus, $h_S$, for both the large and small unreacted particles. In the SURE2 model the rate of conversion is expressed by:

$$ (\phi)_{SURE2} = k_s 4\pi R^2 C_{SO_3,R} \text{ (mole/s)} $$

(5.77)

while in the Thiele concept the rate expression is:

$$ (\phi)_{Thiele} = k_{1} S_{BET} \rho_d \frac{4}{3} \pi R^3 E C_{SO_3,R} \text{ (mole/s)} $$

(5.78)

Combining both equations and substituting Eq. (5.13) and (5.14) results in:

$$ \frac{h_S}{R} \left( \frac{1}{\tanh h_S} - \frac{1}{h_S} \right) - \frac{k_S}{D_pore} = 0 $$

(5.79)

For the original particles ($d_p = 3.1$ mm, $k_s = 0.149$ m$^3$ gas/(m$^2$ core s) and $D_{pore} = 5.6 \times 10^{-7}$ m$^3$ gas/(m particle s)) this results in $h_S = 413$ and $E = 0.007$. The small value of $E$ indicates a sharp concentration profile in the particle which agrees with the shrinking unreacted core assumption.

Repeating the calculation for the small particles ($d_p = 0.225$ mm) gives $h_S = 31$ and $E = 0.09$. Carberry and Gorring (1966) show that for a sharp concentration drop, thus establishing the shell-core interface, $h_S$ must be greater than 200. Therefore, the shrinking core assumption is not valid in the case of the smaller particles. These calculations are made for a steady state assumption at time zero ($r_C = R$). When $r_C$ is smaller than $R$, the value of $E$ increases resulting in a less sharp concentration profile in the particle. In that case the shrinking unreacted core assumption will be more and more affected. A mathematical evaluation is given by Luss (1968).

An additional test run is performed to verify the hypothesis described above using a sorbent with an average particle diameter larger than original (3.1 mm). The sorbent used has an average diameter of 3.9 mm and the calcium
content is determined being 5.25 wt%. The SURE2 model should be able to predict the measured breakthrough curve because the diffusion of reactants into the unreacted core should be negligible. The result is presented in Figure 5.5 and a reasonable agreement is obtained. The first part of the curve up to 500 min is well predicted but at longer times some divergence appears.

![Graph showing SO2 out/SO2 feed](image)

**Figure 5.5** SURE2 model prediction of standard 3.1 mm sorbent and large particle diameter (3.9 mm) sorbent.

In section 5.3.2, it was assumed that SO2, O2 and SO3 are in equilibrium at every time and place in the sorbent bed. To verify whether SO3 formation is rate limiting, an experiment has been performed with an impregnated sorbent (0.1 wt% Pt). The platinum surface area is determined using CO adsorption (Quantasorb Corporation System, Quantachrome Corporation): 0.098 m² Pt/g sorbent. Platinum catalyzes the SO3 formation towards equilibrium and should lead to an increased reactivity of the sorbent. Figure 5.6 shows that no significant change in reactivity is observed which supports the assumed equilibrium situation (section 5.3.2).

Further, the catalytic influence of the reactor material is tested by performing an acception experiment in a quartz reactor (ID = 9 mm). The gas residence time in the sorbent bed is kept the same as under standard
- 5 modeling of the fixed bed reactor experimental results -

conditions by using about 3.9 g sorbent. The experimental and modeling results are presented in Figure 5.7. The SURE2 model still successfully describes the breakthrough curve with the same set of parameters.

![Graph](image1)

Figure 5.6 SURE2 model prediction of standard sorbent and Pt impregnated (0.1 wt%) sorbent.

![Graph](image2)

Figure 5.7 SURE2 model prediction of a standard experiment (steel reactor) and an experiment performed in a quartz reactor.
modeling of the fixed bed reactor experimental results

The value for the effective shell diffusion coefficient can be compared with the effective pore diffusion coefficient \( D_{pore} \), estimated from physical data of the totally sulfated sorbent (Eq. (5.15)). The completely sulfated sorbent is characterized in Table 5.2.

<table>
<thead>
<tr>
<th>Table 5.2 Characterization of sulfated sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>sorbent type/code</td>
</tr>
<tr>
<td>shape</td>
</tr>
<tr>
<td>diameter (mm)</td>
</tr>
<tr>
<td>Ca-content (wt%)</td>
</tr>
<tr>
<td>free CaO compounds</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>surface area ( N₂ ) physisorption (m²/g)</td>
</tr>
<tr>
<td>pore volume ( N₂ ) physisorption (m³/g)</td>
</tr>
<tr>
<td>Hg porosimetry (m³/g)</td>
</tr>
<tr>
<td>solid density (skeletal) (kg/m³)</td>
</tr>
</tbody>
</table>

For a binary mixture states (see section 5.2):

\[
D_{pore} = \frac{X}{\tau} \left( \frac{1}{D_{knu}} + \frac{1}{D_{a/b}} \right)^{-1}
\]  

(5.15)

Satterfield (1970) showed that the tortuosity \( \tau \) is in the range of 1 to 5. For diffusion through a randomly oriented system of long cylindrical pores the tortuosity is 3. The calculated effective pore diffusion coefficient of \( SO₂ \) in this range is between \( 2.3 \times 10^{-7} \) and \( 1.2 \times 10^{-6} \text{ m}^3\text{gas/(m particle s)} \). This matches the value obtained with the model for \( D_{SO₂, shell} \) of \( 7.53 \times 10^{-7} \text{ m}^3\text{gas/(m particle s)} \).

A simplified model can be obtained by omitting the film diffusion and the chemical reaction rate as rate determining steps. If both \( k_{SO₂, film} \) and \( k_s \) are assumed infinite, the model has only one parameter: \( D_{SO₂, shell} \). The optimized value is \( (5.58 \pm 0.57) \times 10^{-7} \text{ m}^3\text{gas/(m particle s)} \). The residual sum of squares for one point is \( (9.46 \pm 3.36) \times 10^{-4} \).
5.5.2 Thermobalance sulfation experiments

This section presents results of sorbent sulfation in a thermobalance with EPMA-WDS analysis on partially reacted particles to provide proof for the validity of the SURE2 model. Unlike the modeling of the fixed bed experimental results, the solid conversion is modelled as well. SG105 sorbent is sulfated in a thermobalance, which is described in detail elsewhere (Van den Bleek et al., 1986-1991), for varying times up to 36 h. The sulfation conditions are summarized in Table 5.3.

<table>
<thead>
<tr>
<th>Sulfation conditions in the thermobalance</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature reactor: 850 °C</td>
</tr>
<tr>
<td>pressure reactor: 1 bar</td>
</tr>
<tr>
<td>superficial gas velocity: 0.01 m/s</td>
</tr>
<tr>
<td>flow gas: 92 ml STP/min</td>
</tr>
<tr>
<td>inlet gas concentration:</td>
</tr>
<tr>
<td>O₂: 2.5 (vol%)</td>
</tr>
<tr>
<td>SO₂: 0.25 (vol%)</td>
</tr>
<tr>
<td>N₂: balance (vol%)</td>
</tr>
<tr>
<td>number of sorbent particles sulfated: 4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SG105 sample #</th>
<th>calcium concentration wt%</th>
<th>particle diameter mm</th>
<th>sulfation time min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.2</td>
<td>3.2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>6.3</td>
<td>3.1</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>6.3</td>
<td>3.4</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>5.9</td>
<td>3.4</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>5.8</td>
<td>3.2</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
<td>4.8</td>
<td>3.3</td>
<td>420</td>
</tr>
<tr>
<td>7</td>
<td>5.2</td>
<td>3.2</td>
<td>2160</td>
</tr>
</tbody>
</table>

1) The calcium concentration of the fresh sorbent is known to be inhomogeneous from particle to particle (see section 2.4). As only a few particles are used in these experiments, the initial calcium concentration of a sorbent particle is estimated from the EPMA graph.

To obtain the equation which describes the conversion of a particle in a thermobalance as a function of time, equation (5.48) is integrated. This results in:
- 5 modeling of the fixed bed reactor experimental results -

\[ t = \frac{1}{C_1} \left[ C_2 (1 - Y) + \frac{C_3}{2} (1 - Y^2) + \frac{C_4 - C_3}{3} (1 - Y^3) \right] \quad (5.80) \]

with (the symbols used are defined in the Notation)

\[ C_1 = \frac{r C_{SO_2, \text{feed}}}{C_{CaO}} \quad (5.81) \]
\[ C_2 = \frac{R}{k_s k_{eq} C_{O_2}^{1/2}} \quad (5.82) \]
\[ C_3 = \frac{R^2}{D_{SO_x, \text{shell}}} \quad (5.83) \]
\[ C_4 = \frac{R^3}{D_{SO_x, \text{film}}} \left( \frac{1}{R} - \frac{1}{R + \delta} \right) \quad (5.84) \]

For low superficial gas velocities (creeping flow) the thickness of the film layer around the particle can be calculated according to Eq. (5.76) with the mass transfer coefficient predicted by Sherwood et al., 1975:

\[ k_{SO_2, \text{film}} = \frac{D_{SO_2, \text{film}}}{2 R} \left( 4.0 + 1.21 \text{Pe}^{2/3} \right)^{1/2} \quad \text{Pe} = \text{Re}_p \text{Sc} < 10^4 \quad (5.85) \]

The results are presented in the Figures 5.8a to 5.8g, in which only the Ca- and S-profiles are shown. In the fresh sorbent, as can be seen in Figure 5.8a, the calculated sulfur concentration is not exactly zero, due to instrumental and data processing errors. In the other figures, a more or less step-wise penetration of the sulfur into the sorbent is observed as predicted by the SURE2 model with \( D_{SO_2, \text{shell}} = 7.53 \times 10^{-7} \) m³ gas/(m particle s) and \( k_s = 0.149 \) m³ gas/(m² core s).

The sulfur concentration in the converted layer of the sorbent particles differs quite considerably between particles. This is due to a large inhomogeneity of the calcium content of single sorbent particles (see section 2.4). Therefore, the Ca concentration used to calculate the model curves is taken from the EPMA graphs. Note that an increase in the local sulfur concentration results in a decrease of the calcium concentration because the total amount of the elements still equals 100 wt%.

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Figure 5.8a Calcium and sulfur response profiles by EPMA (line scan of fresh sorbent).

Figure 5.8b Calcium and sulfur response profiles by EPMA (line scan after 10 minutes sulfation in a thermobalance).
Figure 5.8c Calcium and sulfur response profiles by EPMA (line scan after 30 minutes sulfation in a thermobalance).

Figure 5.8d Calcium and sulfur response profiles by EPMA (line scan after 150 minutes sulfation in a thermobalance).
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Figure 5.8e Calcium and sulfur response profiles by EPMA (line scan after 300 minutes sulfation in a thermobalance).

Figure 5.8f Calcium and sulfur response profiles by EPMA (line scan after 420 minutes sulfation in a thermobalance).
Figure 5.8g Calcium and sulfur response profiles by EPMA (line scan after 2160 minutes sulfation in a thermobalance).

The observation in Figure 5.8e, that the sulfur concentration equals the calcium concentration, whereas it should be only about 80% as is seen in the other figures (Figure 5.8d, 5.8f and 5.8g), is not understood. It appears that the sulfur is able to penetrate more easily beyond the predicted reaction interface after about 150 minutes. It can be suggested that the pore size distribution in the interior of the sorbent might be more open than near the particle surface. Additional measurements have been done on the pore size distribution of both original particles (2.8–3.4 mm) and crushed original particles (0.15–0.30 mm). It appears that the difference between both distributions is small.

At this place it should be mentioned that preliminary sulfur capture experiments are performed in a 0.05 m ID fluidized bed reactor. Also with this type of reactor, the predictive results of the SURE2 model look very promising (Van den Bleek et al., 1986–1991).
5.6 Conclusions

A shrinking unreacted core model (SURE2) is proposed, to describe the sulfation process which is examined in a fixed bed reactor. The model visualizes that reaction occurs first at the outer skin of the particle. The reaction zone moves into the solid particle producing an inert solid (referred to as "shell") of completely converted material. While the shell grows in thickness, the unreacted core of material shrinks during reaction. The overall size of the particle remains unchanged. The rate of CaO conversion is first order with respect to SO₂ and is proportional to the external surface area of the core. Both the shell diffusion and the chemical reaction rate are described by one parameter only, \( D_{SO_2,shell} \) and \( k_s \) respectively. Experiments are performed with different superficial gas velocities, SO₂ concentrations, O₂ concentrations and particle diameters. The results obtained with SG105 sorbent are in good agreement with the model by using \( D_{SO_2,shell} = (7.53 \pm 0.60) \times 10^{-7} \text{ m}^2\text{ gas/(m particle s)} \) and \( k_s = (0.149 \pm 0.033) \text{ m}^3\text{ gas/(m}^2\text{ core s)} \). However, when the particle diameter is reduced by more than a factor of two, the experimental results are poorly described by these values. The value for the effective shell diffusion coefficient is quite close to the calculated effective pore diffusion coefficient which can be estimated from physical data of the sulfated sorbent. The effective pore diffusion coefficient of SO₂ in this range is \( (7.2 \pm 4.9) \times 10^{-7} \text{ m}^3\text{ gas/(m particle s)} \).

Electron-Probe X-ray Microanalysis (EPMA) of SG105 sorbent which is sulfated in a thermobalance for varying times, provides proof for the validity of the SURE2 model. A more or less step-wise penetration of the sulfur is observed as predicted by the model for the same value of the parameters.

The SURE2 model can thus serve as an engineering tool for FBC reactor design to improve sulfur capture performance.

References

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Hultermans, R.J., 1990, "Het meten en modelleren van de zwavelzoutenretentie in een vast bed reactor", Internal Report, Department of Chemical Engineering, Delft University of Technology, Delft, The Netherlands.


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6

Single-Particle and Multi-Particle Attrition Tests

6.1 Introduction

In the previous chapters, it was shown that the synthetic sorbent is chemically suitable for a regenerative sulfur capture process at 850°C and 1 bar. However, as mentioned in section 1.4, the mechanical aspects are important as well. Because the sorbent will be used in a fluidized bed it should withstand "attrition". This phenomenon is defined by Vaux and Keairns (1980) as (unwanted) particle size reduction by any process. As defined by these authors, attrition includes wear, fracture, decrepitation, abrasion, crushing, splitting, shattering, chipping and disintegration. An understanding of attrition is important for process operability, e.g. bed-loss during start-up, changes in particle size distribution and fluidisation properties. Moreover, the control of fines production to minimize downstream deposits and erosion needs to be considered. A decrease in sorbent reactivity or environmental regulations, e.g. minimization of fine particle emission, represent also additional process costs.

Attrition of solids in a fluidized bed is caused by several mechanisms. The most important are:

1. thermal stress; this phenomenon occurs if particles are being heated or cooled where unequal temperatures in the particles cause uneven expansion, intraparticle stress and decrepitation (breakdown of
- 6 single-particle and multi-particle attrition tests -

particles due to internal forces, generally induced by heating).

(2) kinetic stress; slow-moving particles suffer surface abrasion upon collision or fast-moving particles may shatter completely, e.g. in cyclones or high velocity (grid) jets.

(3) static mechanical stress; a bed particle is pressed at its surface. This is caused by the hydrostatic pressure of a fixed bed of particles. Another possibility is that the particle is pressed from within e.g. by the formation of gas by vaporization of hydrated water.

(4) chemical stress; a reaction produces discontinuities between chemical compounds in the particle which causes stress by their structural difference.

A fluidized bed facility provides many sources of attrition described by these four mechanisms. The main sources are summarized in Table 6.1.

Table 6.1 Sources of attrition in a fluidized bed system with limestone or dolomite desulfurization (Vaux and Keairns, 1980)

<table>
<thead>
<tr>
<th>source of attrition in a fluidized bed combustion facility</th>
<th>thermal stress</th>
<th>kinetic stress</th>
<th>static mechanical stress</th>
<th>chemical stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>pneumatic conveying</td>
<td></td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>solids feed (including dispersion devices, screen feeders, etc.)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>particle heating</td>
<td>+</td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>calcination</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>chemical reaction (sulfation)</td>
<td></td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>particle internal gas pressure</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>reactor bubbling</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>jetting at grid holes</td>
<td></td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>reactor/freeboard internals</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e.g. heat transfer surface)</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>surface splashing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>falling in downcomers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclones</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) s = slow, m = moderate and f = fast
single-particle and multi-particle attrition tests

In case of a regenerative desulfurization process using the D.U.T. SG105 sorbent, this table can be extended by sources like sorbent-ash separation (medium kinetic stress) and chemical reactions during regeneration (chemical stress). The calcination process does not apply to the SG105 sorbent.

A number of screening tests is available to measure the attrition tendency of fluidizable solids. Many of these assign a number based on a practical engineering measure. For example, the percentage of particles reduced to less than a certain size in a specified time within a specified test apparatus. Such an approach, which will also be used here, is useful for quality and process control, but does not really represent the complexity of the attrition process and extrapolation beyond the regime of the tests is not allowed. The mechanical tests fall into two categories, viz. single-particle and multi-particle tests. The single-particle tests enhance the understanding of particle breakdown but can hardly be applied to attrition phenomenon observed in practice; the multi-particle tests are primarily empirical in nature. An extensive review of attrition and attrition test methods is given by Bemrose and Bridgwater (1987).

In this chapter, three techniques are presented for testing the susceptibility of limestone, lime and SG105 sorbent to attrition. Two single-particle tests are discussed in section 6.2 (a crushing test) and section 6.3 (an impact test). Section 6.4 reports on results of multi-particle fluidized bed tests. An estimation of the sorbent lifetime is made. This chapter is concluded in section 6.5. The results can be used to make a further prediction of reactor and/or operating parameter conditions to minimize the overall attrition rate.

6.2 Single-particle crushing test

Testing of single particles mainly gives rise to particle breakage or fragmentation due to crack propagation; there is only a negligible amount of surface wear or abrasion. Breakage is the process whereby a particle splits into a small number of pieces while at fragmentation a particle splits into smaller parts, usually large in number and with a broad size distribution. Wear is the progressive removal of small pieces of material, usually from one surface of a solid body and often caused by the relative motion of two
- 6 single-particle and multi-particle attrition tests -

bodies. Abrasion is the removal of material from a particle such that the material removed is very much smaller than the particle itself.

In principle, single particle crushing tests are useful for investigating the role of breakage caused by static mechanical stress. The test described in this section considers a single-particle test where the breakage is induced by the application of a slowly increasing crushing force. The experiments are performed with a Schleuniger-2E/205 instrument (Dr. K. Schleuniger & Co, Switzerland). One particle is placed between two smooth and parallel compression surfaces made of steel. According to American ASTM standard D4179 (1982), one of the surfaces moves horizontally and the force is increased at a uniform rate of 44 N/s. At the end of the test the particle crushes or collapses and a pointer indicates the crushing strength applied in Newton. Each test sample contains 100 individual particles randomly chosen from the bulk. Table 6.2 lists the results of tests performed with limestone (Carmeuse Engis, see Table 4.4), calcined limestone and SG105 (characterized in Table 2.3). The influence of cyclic sulfation and regeneration reactions (chemical stress) on the SG105 sorbent is tested as well. The result of a sample of this sorbent, used in a 10 cycles sulfation/regeneration experiment at standard conditions (described in section 4.2.2), is included.

<table>
<thead>
<tr>
<th>sorbent</th>
<th>crushing strength N</th>
</tr>
</thead>
<tbody>
<tr>
<td>limestone</td>
<td>57 ± 24</td>
</tr>
<tr>
<td>lime</td>
<td>&lt;10</td>
</tr>
<tr>
<td>SG105</td>
<td>91 ± 47</td>
</tr>
<tr>
<td>SG105 after 10 cycles in a fixed bed</td>
<td>89 ± 50</td>
</tr>
</tbody>
</table>

It is concluded that the crushing strength of the synthetic sorbent is significantly higher in comparison with the (calcined) limestone and thus more suitable for regenerative fluidized bed operation. Less attrition due to solids feed, particle heating and the particle internal gas pressure may
also be expected. Note that the crushing strength of the sorbent is
unaffected by the chemical reactions during 10 cycles of the sulfur capture
process.

6.3 Single-particle impact test

Another mechanism causing attrition is kinetic stress which may cause
major problems during transport in pneumatic conveying systems. In Table
6.3, details are listed for four categories of factors that determine the
extent of degradation in such systems.

Table 6.3 Factors that affect degradation in pneumatic and hydraulic
conveying systems (British Materials Handling Board, 1987)

category                              factors that influence attrition

particle properties                   (i) hardness, strength or friability
                                      (ii) size, size distribution and shape
                                      (iii) particle velocity
                                      (iv) phase density of the conveying suspension
                                      or particle concentration
                                      (v) direction of impact relative to a surface

materials of construction            (i) hardness, resilience or ductility of the
                                      material
                                      (ii) roughness and condition of the surface

gonmetry of the system                (i) size and shape of the pipe
                                      (ii) overall length of the conveying system
                                      (iii) number of diverter valves and branches
                                      (iv) number and design of bends-variables
                                      associated with pipe bends include (a)
                                      bend radius, (b) angle of the bend and (c)
                                      orientation of the bend.

carrier gas                           (i) type of gas
                                      (ii) temperature and pressure of system
                                      (iii) pressure gradient

Relative little work has been carried out on the attrition problems
associated with these types of conveying systems. Two of the most important
factors are the conveying air velocity and the geometry of the system
(Vervoorn et al., 1984; Vervoorn et al., 1987). In this work, the influence
of particle velocity will be examined.
A gas gun is used to propel a sorbent particle to velocities from 7 to 21 m/s, representative for pneumatic conveyors. A sketch of the apparatus is given in Figure 6.1.

![Schematic presentation of the gas gun](image)

**Figure 6.1 Schematic presentation of the gas gun (Hoeksma, 1984).**

One particle is placed in a sample holder which is inserted in the barrel. The sample holder is accelerated by compressed nitrogen and is stopped at the end of the barrel. The particle is fired and its velocity is measured by a light detector. This velocity is controlled by the pressure on the sample holder. The particle strikes a flat-faced steel plane, placed in a catcher tank to collect the fragments. By choosing the strike of the particle at a normal angle to the plate, the worst case of an impact is tested. Such impacts are to be prevented as much as possible in a conveying system.

At each velocity 50 shots are fired; a sieve analysis (with U.S.A. ASTM E11-70 or U.K. BS 410:1969 specified sieves) is carried out on the fragments. The test is only performed with SG105 sorbent. In Figure 6.2 the particle size distribution is given for various impact velocities.

Although the reproducibility of the experiments is not very high, it appears that a velocity of 7 m/s results in 31 wt% breakdown of the original (100 wt%) 2.8–3.4 mm fraction. The amount of sorbent with a
diameter smaller than 1.2 mm is 1 wt%. At increasing impact velocity, the breakdown increases up to 85 wt% at 21 m/s, of which 14 wt% is smaller than 1.2 mm.

Figure 6.2 Mass particle size distribution of SG105 sorbent after one strike for various impact velocities.

Figure 6.3 Probability of SG105 sorbent passing through a sieve with a mesh size of 1.2 mm and 2.8 mm respectively based on mass after one impact. At each velocity 50 particles are fired.
1.2 mm. The poor accuracy is probably caused by the wide distribution of strength of the particles, some being much stronger than others (see Table 6.2). Secondly, the force which is exerted on the particle is dependent not only upon the velocity, but also upon the chance inclination of the particle when it strikes the target. Besides, the mass of the particle has a distribution too. In this context, the results of particle breakdown at each velocity are plotted in the form of a probability graph in Figure 6.3.

It is obvious that these results may influence the design of the pneumatic conveying system. During the last few years, a number of companies that specialises in pneumatic conveying systems has developed low-velocity dense phase conveyors which operate at less than five metres per second. Claims are made for systems that achieve velocities as low as one or two metres per second (British Materials Handling Board, 1987). In general, dense phase pneumatic systems would tend to cause less damage than lean phase systems, because of the lower velocities applied and the "cushion" effect. An high bulk density (stick-slip) flow of sorbent in transfer lines is described by Hoke et al. (1978).

To avoid the impact of sorbent at high particle velocities (10–20 m/s) in the tubing and the sorbent/ash separator, an Interconnected Fluidized Bed system (IFB) is being proposed (Van den Bleek et al., 1986–1991, Korbee et al., 1990). Such a system uses fluidized bed properties to induce a circulating solids flow through a set of four fluidized beds with different fluidizing velocities. The circulating solids flow over a weir and through an orifice at the bottom. One bed is regarded as the combustion section, a second bed as the regeneration section, while the others serves as e.g. sorbent/ash separation section. The main advantages are: low particle breakdown, a simple way of sorbent transport and a relatively easy ash/sorbent separation. Because the different beds are connected either by a weir in the freeboard or by an orifice, an important source of kinetic stress has been removed.

6.4 Multi-particle fluidized bed tests

The most widely reported attrition tests are those using fluidized beds (Bemrose and Bridgwater, 1987). There is still no universal procedure to
assess attrition for high-temperature operations with reactive particles, due to the many attrition mechanisms involved. Separate investigations are necessary to determine which attrition mechanism dominates. Literature on attrition caused by thermal and chemical stress is sparse (Chraibi and Flamant, 1989). In order to analyze the dominant attrition mechanism for reactive gas-solid systems such as CaO/γ-Al₂O₃/SO₂/O₂/SO₃ in the present work, experimental procedures have been established to estimate thermal, kinetic and chemical attrition rates independently. When fresh (make-up) sorbent is fed to the reactor, its temperature increases from room temperature to reactor temperature in a relatively short period of time (about 10 s). During the fluidization process, attrition occurs by interaction between the sorbent particles, the bed material and the reactor system. The combustion of coal causes local hot spots up to 300°C higher than the average bed temperature of 850°C. The sulfur dioxide released from the coal is captured by the sorbent which results in a structural molecular volume change of its calcium compound.

Experiments were carried out in a 0.05 m ID atmospheric fluidized bed, schematically shown in Figure 6.4. The quartz reactor is 1.2 m high. The lower section of 0.5 m is heated to 850°C by an electric element, while the upper section is isolated. The windbox is heated by four radiation heating

Figure 6.4 Schematic presentation of the 0.05 m ID fluidized bed reactor.
units. The temperature of the bed is measured by a Pt-Pt10%Rh thermocouple which can be moved along the axis of the bed. The gas distributor is a stainless steel plate with 53 holes (1 mm ID) on an equilateral triangle pitch of 6.5 mm; its free cross section is 2.1%. By using such a gas distribution device, the fluidization is relatively uniform and attrition due to gas jet effects is reduced (see Blinichev et al., 1968). The reactor is connected with an air circuit, the flow is measured by a rotameter. A pre-heater raises the air temperature to 550°C. The materials tested were lime and synthetic sorbent. The process conditions are listed in Table 6.4.

Table 6.4  Process conditions of the 0.05 m fluidized bed during the thermal shock, fluidization and coal combustion experiments

<table>
<thead>
<tr>
<th>process</th>
<th>temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>thermal shock</td>
<td></td>
</tr>
<tr>
<td>lime</td>
<td>850</td>
</tr>
<tr>
<td>SG105</td>
<td>850</td>
</tr>
<tr>
<td>fluidization</td>
<td></td>
</tr>
<tr>
<td>lime</td>
<td>20</td>
</tr>
<tr>
<td>lime</td>
<td>850</td>
</tr>
<tr>
<td>SG105</td>
<td>20</td>
</tr>
<tr>
<td>SG105</td>
<td>850</td>
</tr>
<tr>
<td>coal combustion</td>
<td></td>
</tr>
<tr>
<td>lime</td>
<td>850</td>
</tr>
<tr>
<td>SG105</td>
<td>850</td>
</tr>
</tbody>
</table>

1) Another type of synthetic sorbent is used during the coal combustion experiment. It is quite similar to the SG105 sorbent but prepared in another production run (Ca content = 6.2 wt%, \( \rho_d = 1760 \) kg/m\(^3\); the texture is given in Table 6.11).

During the experiments, the sorbent, ash and sand were removed from the reactor by means of a vacuum system and analysed by sieving. Tests showed that this results in some attrition as well; the reported sorbent loss is corrected for this by performing blanks.
(1) Thermal shock attrition test

In a thermal shock attrition test, about 300 g sand (representing the coal ash) is fluidized at 850°C. A total amount of 75 g sorbent particles at room temperature is injected in portions of 10 g each, every two minutes (this procedure prevents a temperature decrease of the reactor bed). After all sorbent is added the heating is switched off. The bed is cooled down in 3.5 h at fluidizing conditions to prevent thermal stress in the reactor tube. The bed is removed from the reactor and analysed by sieving.

A blank is performed by fluidizing 300 g sand at room temperature. A total amount of 75 g sorbent is added in portions of 10 g each, every two minutes, followed by relatively slow heating of the mixture to 850°C in approximately 1 h. Then, the bed is cooled in 3.5 h to room temperature.

The particle size distribution is determined both before and after the thermal shock and blank. Sorbent with a particle diameter below 1.4 mm is considered as attrition waste (although the sulfur capture capability of these small particles is quite high according to section 5.5.1, a sorbent/ash separation would become difficult in a commercial system). The diameter at which a particle is elutriated by the rising stream of gas is approx. 0.3 mm.

Table 6.5 Attrition of lime and SG105 by thermal shock

<table>
<thead>
<tr>
<th>sorbent</th>
<th>temperature shock</th>
<th>original particle size</th>
<th>reduction original size</th>
<th>mass fraction above 1.4 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0°C (C)</td>
<td>mm</td>
<td>wt%</td>
<td>wt%</td>
</tr>
<tr>
<td>lime</td>
<td>blank</td>
<td>1.7-2.0</td>
<td>62</td>
<td>80</td>
</tr>
<tr>
<td>lime</td>
<td>25-850</td>
<td>1.7-2.0</td>
<td>62</td>
<td>77</td>
</tr>
<tr>
<td>SG105</td>
<td>blank</td>
<td>2.8-3.4</td>
<td>26</td>
<td>100</td>
</tr>
<tr>
<td>SG105</td>
<td>25-850</td>
<td>2.8-3.4</td>
<td>27</td>
<td>99</td>
</tr>
</tbody>
</table>
Figure 6.5a  Mass particle size distribution before and after the thermal shock experiment with lime.

Figure 6.5b  Mass particle size distribution before and after the thermal shock experiment with SG105 sorbent.
Due to the sieve method applied, a small fraction (generally < 5 wt%) of the sorbent can stick in a sieve is found larger than 3.4 mm after the experiments. The accuracy of the experiments is approximately ± 5 wt%. The blank shows an almost equal mass reduction as the original experiments. So, it is concluded that thermal shock has a negligible effect on lime and SG105.

(2) Fluidization attrition test

During the fluidization experiments, a mixture of 150 g sand and 150 g sorbent is fluidized for approximately 200 h. It is observed visually that no segregation occurs. The fluidized bed seems to be well-mixed during all experiments. The minimum fluidization velocity measured during the SG105 experiments at 20°C and 850°C is 0.7 m/s and 1.3 m/s, respectively. At minimum fluidization, the bed height is 0.12 m at 20°C and 0.15 m at 850°C.

The decrease of the amount of sorbent with a particle diameter above 1.4 mm is measured (off-line) several times during the experiment. A blank is performed by repeatedly introducing solids into the reactor, removing and sieving the solids at room temperature for equal times.

![Graph showing attrition weight loss](image)

**Figure 6.6** Attrition weight loss (particle diameter < 1.4 mm) during fluidization of lime and SG105 sorbent at 20°C and 850°C.
From Figure 6.6 it is concluded that the SG105 sorbent has a high resistance towards attrition by fluidization in comparison with lime. The results are summarized in Table 6.6.

<table>
<thead>
<tr>
<th>sorbent</th>
<th>temperature</th>
<th>original particle size</th>
<th>initial rate wt%/h</th>
<th>final rate wt%/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>lime</td>
<td>20</td>
<td>1.7-2.0</td>
<td>3.44</td>
<td>0.004 1)</td>
</tr>
<tr>
<td>lime</td>
<td>850</td>
<td>1.7-2.0</td>
<td>1.15</td>
<td>0.06</td>
</tr>
<tr>
<td>SG105</td>
<td>20</td>
<td>2.8-3.4</td>
<td>0.31</td>
<td>0.01 2)</td>
</tr>
<tr>
<td>SG105</td>
<td>850</td>
<td>2.8-3.4</td>
<td>0.16</td>
<td>0.01</td>
</tr>
</tbody>
</table>

1) the amount of lime still present in the bed is almost negligible.
2) the final attrition rate is constant up to at least 1200 h after start-up.

Figure 6.6 shows that the attrition rate decreases with time, tending to some constant value. The relatively fast initial attrition rate is probably related to the preferential detachment of asperities from the sorbent surface and/or breakdown of weak material. Further decrease is much slower, indicated by the long time required to change the particle size significantly by fluidization only. During the fluidization experiment with lime, the originally irregular shaped particles became well rounded.

The attrition rate depends on the reactor temperature. The measured initial attrition rate at 850°C is lower compared with 20°C. This can be explained by the difference in minimum fluidization velocity \( U_{mf} \) at both temperatures. Many workers (Merrick and Highley, 1974; Vaux and Keairns, 1980; Arena et al., 1983; Chironi et al., 1985; Salataino and Massimilla, 1985; Ray et al., 1987; Basu and Halder, 1989; Chandran and Duqu, 1989; Son et al., 1989; Shamlow et al., 1990) report that the attrition rate \( R_a \) is proportional to \( U_{mf} \) according to:

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- 6 single-particle and multi-particle attrition tests -

\[ R_a = (U_f - U_{mf}) \] (6.1)

Substituting the values for \( U_{mf} \) for SG105 sorbent at 20° C (0.7 m/s) and 850° C (1.3 m/s), while the superficial gas velocity \( U_f \) is fixed at 2 m/s, shows that the attrition rate at 20° C is about twice the attrition rate at 850° C. This result is in agreement with the measured initial attrition rate listed in Table 6.6. A similar agreement is obtained with lime.

The final attrition rate of SG105 at 850° C indicates that approximately 200 cycles at a (rather arbitrarily chosen) sorbent residence time of 50 h seem to be possible.

After the experiments the particle size distribution is measured and compared with the original distribution. In the Figures 6.7a to 6.7d the results are presented. Some important values are summarized in Table 6.7.

![Figure 6.7a Mass particle size distribution before and after the fluidization experiment with lime at 20° C.](image)
- 6 single-particle and multi-particle attrition tests -

Figure 6.7b Mass particle size distribution before and after the fluidization experiment with lime at 850°C.

Figure 6.7c Mass particle size distribution before and after the fluidization experiment with SG105 at 20°C.
Figure 6.7d Mass particle size distribution before and after the fluidization experiment with SG105 at 850°C.

Table 6.7 Attrition of lime and SG105 by fluidization

<table>
<thead>
<tr>
<th>sorbent</th>
<th>temperature</th>
<th>original particle size</th>
<th>fluidization time</th>
<th>reduction original size</th>
<th>mass fraction above 1.4 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>lime (blank)</td>
<td>20</td>
<td>1.7-2.0</td>
<td>-</td>
<td>20</td>
<td>97</td>
</tr>
<tr>
<td>lime</td>
<td>20</td>
<td>1.7-2.0</td>
<td>164</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>lime</td>
<td>850</td>
<td>1.7-2.0</td>
<td>191</td>
<td>92</td>
<td>27</td>
</tr>
<tr>
<td>SG105 (blank)</td>
<td>20</td>
<td>2.8-3.4</td>
<td>-</td>
<td>25</td>
<td>98</td>
</tr>
<tr>
<td>SG105</td>
<td>20</td>
<td>2.8-3.4</td>
<td>250</td>
<td>69</td>
<td>88</td>
</tr>
<tr>
<td>SG105</td>
<td>850</td>
<td>2.8-3.4</td>
<td>211</td>
<td>55</td>
<td>90</td>
</tr>
</tbody>
</table>

The results show that at 850°C about 30 wt% of the original (100 wt%) 2.8-3.4 mm fraction of SG105 has been reduced in size due to fluidization only. However, 90 wt% of the original fraction of SG105 has a particle diameter above 1.4 mm and can still be used easily for sulfur capture purposes compared with only 27 wt% of the lime.
The experimental work described above indicates that attrition occurs in two steps. The first step is virtually instantaneous and the second one occurs continuously. Attrition is accordingly partitioned into two rate terms. The total weight decrease of the sorbent in a fluidized bed can be defined by an empirical equation which correlates the data, presented in Figure 6.6:

\[
\frac{W}{W_0} = 100 \left( f_w \exp \left[-g_1 t\right] + (1-f_w) \exp \left[-g_2 t\right] \right) \quad \text{\%} \quad (6.2)
\]

where \( W \) = the weight of the sorbent (diameter > 1.4 mm) in the bed (kg),
\( W_0 \) = initial weight of the sorbent in the bed (kg),
\( f_w \) = fraction of weak material (-),
\( g_1 \) = rate constant total fines (diameter < 1.4 mm) generation by breakdown of weak material during fluidization (1/h),
\( g_2 \) = rate constant total fines (diameter < 1.4 mm) generation by fluidization (1/h),
\( t \) = exposure time of solids in the bed (h).

The values of the parameters obtained are listed in Table 6.8. The parameters \( g_1 \) and \( g_2 \) may depend on particle properties, materials of construction, the geometry of the system and the operating conditions (see Table 6.3). However, no attempt is made to further interpret and validate this model equation.

<table>
<thead>
<tr>
<th>sorbent</th>
<th>temperature (°C)</th>
<th>( f_w )</th>
<th>( g_1 )</th>
<th>( g_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>lime</td>
<td>20</td>
<td>0.9966 ± 0.0023</td>
<td>0.0769 ± 0.0011</td>
<td>0</td>
</tr>
<tr>
<td>lime</td>
<td>850</td>
<td>0.5853 ± 0.0061</td>
<td>0.0461 ± 0.0012</td>
<td>0.002337 ± 0.000092</td>
</tr>
<tr>
<td>SG105</td>
<td>20</td>
<td>0.0724 ± 0.0026</td>
<td>0.0763 ± 0.0081</td>
<td>0.000202 ± 0.000017</td>
</tr>
<tr>
<td>SG105</td>
<td>850</td>
<td>0.0573 ± 0.0062</td>
<td>0.0347 ± 0.0070</td>
<td>0.000208 ± 0.000036</td>
</tr>
</tbody>
</table>
- 6 single-particle and multi-particle attrition tests -

(3) Coal combustion test

In the coal combustion tests, a mixture of 150 g sand and 150 g sorbent is fluidized at 850°C. Then, 500 g coal is fed over the top of the reactor in portions of 5 g, every 2 minutes. The average coal content in the reactor is thus about 1 wt%, which matches the typical coal content of an industrial fluidized bed combustor. The temperature of the bed is kept at approximately 850 ± 50°C. A blank is performed by fluidizing the sorbent and sand for 3.3 h at 850°C, the total time for a coal combustion experiment. Then, heating is switched off and the bed is cooled down in 3.5 h. The coal used is specified in Table 6.9.

Table 6.9 Characterization of the coal

<table>
<thead>
<tr>
<th>coal sample 1)</th>
<th>I31US30</th>
</tr>
</thead>
<tbody>
<tr>
<td>mine</td>
<td>Thurston Property</td>
</tr>
<tr>
<td>country</td>
<td>United States</td>
</tr>
<tr>
<td>layer</td>
<td>upper freeport</td>
</tr>
<tr>
<td>type</td>
<td>channel</td>
</tr>
</tbody>
</table>

| proximate analysis | ash (dry) (wt%) | 12.55 |
|                   | volatile matter (daf) | 30.36 |
|                   | fixed carbon (daf)  | 69.64 |
|                   | calorific value (daf) (MJ/kg) | 36.28 |

| ultimate analysis (daf) | C (wt%) | 88.00 |
|                         | H       | 5.09  |
|                         | N       | 1.72  |
|                         | S       | 2.13  |
|                         | Cl      | 0.16  |
|                         | O-dif   | 2.90  |

| sulfur forms (daf) | pyrite (wt%) | 1.23 |
|                   | sulfate     | 0.06 |
|                   | organic     | 0.83 |
|                   | total       | 2.13 |

| diameter (sieved after receipt) (mm) | 1.4–2.4 |
| solid density (skeletal) (kg/m³)    | 1570    |

1) The coal is obtained from the European Centre for Coal Specimens SBN, Egyelsheven, The Netherlands.
daf dry and ash free

The particle size distribution of lime and SG110 is determined both before and after each experiment. The results are presented in Figure 6.8a, Figure 6.8b and Table 6.10.
- 6 single-particle and multi-particle attrition tests -

Figure 6.8a  Mass particle size distribution before and after the coal combustion experiment with lime.

Figure 6.8b  Mass particle size distribution before and after the coal combustion experiment with SG105.
Table 6.10 Attrition of lime and SG110 by coal combustion

<table>
<thead>
<tr>
<th>sorbent</th>
<th>temperature</th>
<th>original particle size</th>
<th>reduction original size</th>
<th>mass fraction above 1.4 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>lime</td>
<td>(blank)</td>
<td>1.7-2.0 mm</td>
<td>65</td>
<td>72</td>
</tr>
<tr>
<td>lime</td>
<td>850°C</td>
<td>1.7-2.0 mm</td>
<td>65</td>
<td>78</td>
</tr>
<tr>
<td>SG110</td>
<td>(blank)</td>
<td>2.8-3.4 mm</td>
<td>42</td>
<td>97</td>
</tr>
<tr>
<td>SG110</td>
<td>850°C</td>
<td>2.8-3.4 mm</td>
<td>65</td>
<td>95</td>
</tr>
</tbody>
</table>

It can be concluded that coal combustion applied to a 1.7-2.0 mm fraction of lime causes no net mass reduction. The resistance to attrition by coal combustion of SG110 sorbent is less good. A net mass fraction reduction of the original sorbent (2.8-3.4 mm) of 23 wt% is obtained. The net amount of SG110 sorbent reduced in size to below 1.4 mm is 2 wt%. The effect of coal combustion on SG110 sorbent needs further research. A long term experiment with a minimum of 5000 h (about 100 cycles) is needed to ascertain whether or not there is an acceptable continuous loss in strength and/or reactivity.

Wet chemical analysis afterwards showed that the lime was capable to capture 42% of the sulfur supplied to the combustor, while the SG110 sorbent captured 10% sulfur. However, the amount of CaO initially present in the case of lime was about 11 times higher compared with the SG110 sorbent. The synthetic sorbent thus seems to have a meritorious sulfur capture behaviour during the fluidized bed combustion conditions.

Further, the texture of the sorbent is determined both before and after the thermal shock, fluidization and coal combustion experiments performed at 850°C; the results are presented in Table 6.11. It is concluded that only small changes occur in the texture of the sorbent.

At this point, it is difficult to make an accurate estimation of the sorbent lifetime in a commercial system. The design of the transport system is unknown yet and the influence of the coal combustion on attrition is to be quantified by long term experiments. Also the regenerative sulfation and
Table 6.11 Texture of the sorbent before (original) and after the thermal shock, fluidization and coal combustion experiments

<table>
<thead>
<tr>
<th>experiment</th>
<th>temperature °C</th>
<th>particle size mm</th>
<th>surface area m²/g</th>
<th>pore volume ml/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>original lime</td>
<td>20</td>
<td>1.7–2.0</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>SG105</td>
<td>20</td>
<td>2.8–3.4</td>
<td>99</td>
<td>80</td>
</tr>
<tr>
<td>SG110</td>
<td>20</td>
<td>2.8–3.4</td>
<td>67</td>
<td>74</td>
</tr>
<tr>
<td>thermal shock lime</td>
<td>850</td>
<td>1.7–2.0</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>SG105</td>
<td>850</td>
<td>2.8–3.4</td>
<td>98</td>
<td>87</td>
</tr>
<tr>
<td>fluidization lime</td>
<td>850</td>
<td>1.7–2.0</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>SG105</td>
<td>850</td>
<td>2.8–3.4</td>
<td>102</td>
<td>84</td>
</tr>
<tr>
<td>coal combustion lime</td>
<td>850</td>
<td>1.7–2.0</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>SG110</td>
<td>850</td>
<td>2.8–3.4</td>
<td>77</td>
<td>77</td>
</tr>
</tbody>
</table>

of the sorbent should be included in those experiments. Only if the attrition by fluidization is the rate determining step, a sorbent residence time of about 10000 h can be expected.

6.5 Conclusions

The synthetic sorbent SG105 is chemically as well as mechanically suitable for a regenerative cyclic sulfur capture process at 850°C and 1 bar.

The single-particle crushing strength test shows qualitatively that the SG105 sorbent is stronger compared with (calcined) limestone. The sorbent seems to be unaffected by the chemical reactions during the cyclic sulfur capture process. The impact test with a gas gun showed that at 7 m/s about 31 wt% of the original SG105 sorbent fraction of 2.8–3.4 mm breaks. The amount of sorbent with a diameter below 1.2 mm is 1 wt%. However, at increasing impact velocity the breakdown increases up to 85 wt% at 21 m/s of which 14 wt% becomes smaller than 1.2 mm.
The multi-particle fluidized bed tests showed that:

1. A thermal shock applied at 850°C to both a 1.7-2.0 mm fraction of lime or a 2.8-3.4 mm fraction of SG105 causes a negligible net mass reduction.

2. SG105 sorbent has a high resistance towards attrition by fluidization if compared with lime. The values are summarized in Table 6.6 and Table 6.7. Based upon the final attrition rate of SG105 at 850°C, approximately 200 cycles seem to be possible at a sorbent residence time of 50 h per cycle.

3. A coal combustion experiment, applied at 850°C on a 1.7-2.0 mm fraction of lime, causes no net mass reduction. The resistance towards attrition by coal combustion of SG110 sorbent needs further research. A net mass fraction reduction of 23 wt% (with 2 wt% below 1.4 mm) of the original 2.8-3.4 mm SG110 sorbent is obtained.

4. It is concluded that the texture of the sorbent only changes a little by thermal shock, fluidization and coal combustion experiments.

References


7.1 Introduction

It is obviously preferable to recover the sulfur oxides in stack gas rather than to convert them into a solid waste. In the previous chapters it is concluded that the synthetic sorbent SG105 is suitable for a regenerative sulfur capture process at 850°C and 1 bar. This sorbent has been successfully tested on the chemistry involved and on its mechanical strength.

Beside these technical points, the economic characteristics now needs to be explored. All recovery processes developed so far appear to have a higher production cost than the throwaway type (Slack and Hollinden, 1975). Beside the lack of proven technology, one of the major problems is the uncertainty regarding sale of the sulfur-containing by-product. Hence, the producers involved, prefer a once-through process unless the recovery approach shows the promise of a considerable economic advantage. It is unlikely that SO2 recovery from dilute gas will ever be a profit-making operation in the usual commercial sense. However, the recovery route is still preferable if it costs less than a throwaway operation with regard to the costs of solid waste dumping. Besides, the throwaway process operation is considered politically unacceptable in the near future.
In this chapter a preliminary economic analysis is made. The cost of the once-through system, using a natural limestone, are compared with the cost of using the synthetic sorbent in a cyclic regenerative process. The results are presented in the sections 7.2 and 7.3 respectively. The conclusions are drawn in section 7.4.

7.2 The total cost of SO₂ removal using limestone

The total cost of SO₂ emission control may be computed using a method proposed by Snyder et al., 1977. They use:

\[
C_{\text{tot}} = \frac{R_{\text{Ca/S}} S_{\text{gen}}}{C_{\text{sorb}}} (f_n C_{\text{sorb}} + (1-f_n) C_{\text{reg}})
\]

(7.1)

where \(C_{\text{tot}}\) = total cost of SO₂ removal (DFl./kWhe),
\(R_{\text{Ca/S}}\) = Ca/S ratio needed to achieve the governmental SO₂ emission level (mole Ca/mole S),
\(S_{\text{gen}}\) = sulfur released (mole S/kWhe),
\(C_{\text{sorb}}\) = calcium content of sorbent (mole Ca/kg sorbent),
\(f_n\) = fraction of new sorbent which must be fed to make up deactivated and attrited sorbent material (-),
\(C_{\text{sorb}}\) = cost of new sorbent, including gypsum disposal (DFl./kg sorbent),
\(C_{\text{reg}}\) = regeneration cost (DFl./kg sorbent).

It is assumed that the variables in Eq. (7.1) are independent of each other; for example, the calcium content of the sorbent does not influence the cost of new sorbent.

The SO₂ emission allowed by several countries is shown in Table 7.1. If limestone is used in an AFBC system at 850°C, a value of \(R_{\text{Ca/S}}\) of about 2 is needed for 85% SO₂ removal (see e.g. Slack and Hollinden, 1975). The generation of 1 kWhe of power requires about 0.35 kg coal based upon a heating value of 27 MJ/kg. If this coal contains 1 wt% of sulfur, the value for \(S_{\text{gen}}\) is 0.11. The natural limestone contains about 39 wt% Ca and hence
the value of \( C_{S\text{orb}} \) is 9.73. There is no recycle, thus \( f_n \) equals 1 in this case. The cost of the sorbent \( C_{S\text{orb}} \) (including gypsum disposal) is estimated to be DFL 0.16/kg, but is expected to increase in the near future due to an increase in the gypsum disposal cost.

### Table 7.1

<table>
<thead>
<tr>
<th>MWth</th>
<th>emission standards</th>
<th>FRG</th>
<th>Belgium</th>
<th>The Netherlands</th>
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<td>50 - 100</td>
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<td>&gt;500</td>
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1) linear decline from 2000 mg/m³ at 100 MWth to 400 mg/m³ at 500 MWth.
2) and 60% removal; for FBC 400 mg/m³ or 75% removal.
3) and 85% removal.
4) after 1995.
5) an emission maximum is applied.

Based upon Eq. (7.1) the total cost \( C_{\text{tot}} \) for this once-through system can be calculated as a function of the sorbent cost \( C_{S\text{orb}} \). The result is shown in Figure 7.1, line 1.

### 7.3 The total cost of \( \text{SO}_2 \) removal using SG105

The \( \text{Ca/S} \) ratio needed for the SG105 sorbent must be estimated from the fixed bed results for the synthetic sorbent by comparing these with a similar experiment for calcined limestone. It can be estimated from the results described in section 4.2.2 and section 6.4 that again a \( R_{\text{Ca/S}} \) value of about 2 will be required to achieve 85% sulfur removal. Since the SG105 sorbent contains 8.2 wt% \( \text{CaO} \), the value of \( C_{S\text{orb}} \) is 1.46. The attrition rate measurements on fluidization for the SG105 sorbent indicate that over 100 cycles would be possible, hence, \( f_n \) is fixed at 0.01.
Figure 7.1 Cost comparison limestone once-through process [1] and regenerative sorbent process [2].

Although no production method for large quantities of the synthetic sorbents has been tested yet, a sorbent cost $C_{sorb} \approx \text{DFL.} \, 6/\text{kg}$ seems realistic for (only) large scale production (Van den Bleek et al., 1991). The $C_{reg}$-factor depends on the size of the regeneration plant, which in turn depends on the recycle rate and the size of the FBC system. An estimation made by Voet (1990) indicates a value of $C_{reg} = \text{DFL.} \, 0.012/\text{kg}$. This value is in the range calculated from the reports of Kamphuis and Spitsbergen, 1986 (DFL. 0.007/kg) and Snyder et al., 1977 (DFL. 0.014/kg). Further, it is assumed that the cost for $\text{SO}_2$ recovery from the regenerator off-gas equals the profits of the $\text{H}_2\text{SO}_4$ or $\text{S}$ produced. The total cost $C_{tot}$ for the regenerative sorbent SG105 is given in Figure 7.1 as well (line 2). When synthetic sorbent is used instead of limestone, the cost for sulfur removal is about 0.011 DFL./kWh, approximately three times higher than limestone.

Examination of Eq. (7.1) shows where future work on the synthetic sorbent development work should be focussed. Four factors appear amenable to improvement: the sorbent calcium content $C_{sorb}$, the make-up fraction $f_n$, the sorbent cost $C_{sorb}$ and the regeneration cost $C_{reg}$. The lines in Figure
7.2 show the results for the regenerative sorbent if \( C_{a_{\text{sorb}}} \) is varied from 1 to 2 mole Ca/kg sorbent (5.6 – 11.2 wt% CaO on \( \gamma-Al_2O_3 \)).

![Diagram showing the influence of calcium content of sorbent on total cost of SO₂ removal.](image)

**Figure 7.2 Influence of the calcium content of sorbent \( C_{a_{\text{sorb}}} \) on the total cost of SO₂ removal.**

If the price of limestone and SG105 is fixed at DFL. 0.16/kg and DFL. 6/kg respectively, at least a calcium content of 25 wt% CaO is necessary to equal the cost of the limestone process. It is unlikely that such a high CaO concentration is possible with a homogeneous distribution of the calcium compound, necessary for the formation of the calcium aluminates (see section 2.2 and 2.3).

Figure 7.3 describes the effect of using SG105 50 – 200 cycles instead of 100 as assumed originally \((f_n = 0.02 – 0.005)\). The synthetic sorbent can compete with the once-through process only if \( f_n < 0.002 \) (sorbent usage > 500 cycles).

Finally, the influence of a variation in the regeneration cost in the range 0.006 – 0.018 DFL./kg is presented in Figure 7.4.
Figure 7.3 Influence of the fraction of new sorbent $f_n$ on the total cost of $SO_2$ removal.

Figure 7.4 Influence of the regeneration cost $C_{reg}$ on the total cost of $SO_2$ removal.
- 7 economic evaluation -

Even if the regeneration cost approaches zero, the total cost of SO₂ removal using SG105 is about 2.5 times higher than with the throwaway type. Comparing the influence of the calcium content, make-up fraction and regeneration cost on the total cost of SO₂ removal shows that the make-up fraction of new sorbent \( f_n \) is the most influential parameter.

7.4 Conclusions

It is concluded that the total cost of SO₂ removal using the regenerative process increases about three times if compared with the once-through process (as shown in Figure 7.1). The influence of the several cost determining factors (sorbent cost, calcium content, make-up fraction and regeneration cost) are presented in Figures 7.2 to 7.4. At least a threefold increase in the cost of limestone, including gypsum disposal, is necessary to make the regenerative process economically feasible.

Although the short term interest of many SO₂ emitting companies is focussed on once-through processes, being an immediate solution to the emission problem, long term solutions should be found in regenerative processes with sulfur recovery.

References


Notation

$A$ = cross section area of empty reactor (m$^2$ reactor)

$A_i$, $A'_i$ = reactant i and product i respectively in Eq. (2.18) to (2.20) (m$^2$)

$A_p$ = external surface area of one sorbent particle (m$^2$ particle)

$a_{A_i}$ = activity of component $A_i$ in Eq. (2.19) (-)

AAS = atomic absorption spectroscopy

AFBC = atmospheric fluidized bed combustion

BET = sorption theory of Brunauer, Emmett and Teller

BFBC = bubbling fluidized bed combustion

$B_0$ = Bodenstein number defined by Eq. (5.5) (-)

$C$ = concentration (mole/m$^3$)

$C_{CaO}$ = calcium concentration in a fresh sorbent particle (mole CaO/m$^3$ particle)

$C_f$ = SO$_2$ concentration in feed gas (mole/m$^3$ gas)

$C_{feed}$ = concentration of a compound entering the sorbent bed (mole/m$^3$)

$C_i$ = (equilibrium) concentration of compound i (mole/m$^3$gas)

$(C_i)_e$ = equilibrium concentration of compound i (mole/m$^3$gas)

$C_{O_2}$ = oxygen concentration in feed (mole/m$^3$gas)

$C_{out}$ = concentration of a compound leaving the sorbent bed (mole/m$^3$)

$C_p$ = specific heat of fluid (J/(kg K))

$C_S$ = SO$_2$ concentration at core surface (mole/m$^3$)

$C_S$ = sulfur concentration, $C_{SO_2} + C_{SO_3}$ (mole/m$^3$ gas)
\( C_{SO_2,feed} \) = \( SO_2 \) concentration in feed in equilibrium with \( SO_3 \) and \( O_2 \) (mole/m\(^3\)gas)

\( C_{SO_x,feed} \) = sulfur concentration in feed (mole/m\(^3\) gas)

\( C_{\text{reg}} \) = regeneration cost (DFl./kg sorbent)

\( C_{\text{sorb}} \) = cost of new sorbent, including gypsum disposal (DFl./kg sorbent)

\( C_{SO_3} \) = \( SO_3 \) concentration at particle outer surface (mole/m\(^3\))

\( C_{\text{tot}} \) = total cost of \( SO_2 \) removal (DFl./kWhe)

\( C_{a_{\text{sorb}}} \) = calcium content of sorbent (mole Ca/kg sorbent)

CEC = Commission of the European Communities

CFBC = circulating fluidized bed combustion

\( C_{x,A_y} \), \( C_{x,A_y} \) = \( xCaO.yAl_2O_3 \)

\( C_{1..C4} \) = constants defined by Eq. (5.81) .. Eq. (5.84) (variable)

\( D \) = diffusion coefficient in film (\( D_{\text{film}} \)) or shell (\( D_{\text{shell}} \)) (m\(^3\)/m s)

\( D_{a/b} \) = diffusion coefficient in fluid phase (m\(^2\)/s)

\( D_{ax} \) = axial dispersion coefficient (m\(^3\) gas/(m reactor s))

\( d_b \) = bed diameter (m bed)

\( D_{\text{Knu}} \) = Knudsen diffusion coefficient (m/s)

\( d_p \) = average particle diameter (m particle)

\( D_{\text{pore}} \) = effective pore diffusion coefficient (m\(^3\) gas/(m particle s))

\( d_r \) = reactor diameter (m reactor)

\( D_r \) = radial dispersion coefficient (m\(^3\) gas/(m reactor s))

\( D_{SO_2,film} \) = diffusion coefficient of \( SO_2 \) in film (m/s)

\( D_{SO_3,film} \) = diffusion coefficient of \( SO_3 \) in film (m/s)

\( D_{SO_2,shell} \) = effective diffusion coefficient of \( SO_2 \) in shell (m\(^3\) gas/(m particle s))

\( D_{SO_3,shell} \) = effective diffusion coefficient of \( SO_3 \) in shell (m\(^3\) gas/(m particle s))

\( D_{SO_x,film} \) = \( D_{SO_2,film} + D_{SO_3,film} K_{eq} \frac{1}{2} \) (m/s)

\( D_{SO_x,shell} \) = \( D_{SO_2,shell} + D_{SO_3,shell} K_{eq} \frac{1}{2} \) (m\(^3\) gas/(m particle s))

\( d_{af} \) = dry and ash free

DFl. = Dutch Florin, DFl. 1 = US$ 0.55 (November 1990)

D.U.T. = Delft University of Technology

E = effectiveness factor (-)

\( E_a \) = activation energy (J/mole)

EDS = energy dispersive spectrometry
EPA = Environmental Protection Agency
EPMA = electron-probe X-ray microanalysis
FBC = fluidized bed combustion
f_m = friction factor defined by Eq. (5.2) (-)
f_n = fraction of new sorbent which must be fed to make up deactivated and attrited material (-)
f_w = fraction of weak material (-)
G = fluid superficial mass velocity (kg gas/(m² reactor s))
q_c = dimensional constant in Eq. (5.2); q_c = 1.0 (kg m/(N s²))
G_T = Gibbs function of a pure substance (J/mole)
\Delta G_{r,T} = Gibbs function of reaction (J/mole)
g_1 = attrition rate constant defined by Eq. (6.2) (1/h)
g_2 = attrition rate constant defined by Eq. (6.2) (1/h)
h = heat transfer coefficient (W/(m² K))
\Delta H_r = reaction enthalpy at 850°C and 1 bar (J/mole)
h_s = Thiele modulus defined by Eq. (5.14) (-)
H.T. = heat treatment
i = index number of compound A in Eq. (2.18) to (2.20) (-)
      = index of a compound (-)
      = tank index number, 1 ≤ i ≤ N_tanks (Chapter 5) (-)
ID = internal diameter (mm)
IFB = interconnected fluidized bed
K_{eq} = equilibrium constant of SO₂ + 1/2 O₂ ⇌ SO₃ ((mole/m³)⁻¹/²)
K_{eq,fr} = equilibrium constant, defined in Eq. (3.35) (-)
K_{eq,P} = equilibrium constant, defined in Eq. (3.11) (-)
K_{eq,T} = equilibrium constant, defined in Eq. (2.19) (-)
k_j = rate constant for reaction j, defined in Chapter 3, section 3.3.2 and Eq. (5.14) (variable)
k_s = reaction rate constant (m³ gas/(m² core s))
k_{SO₂,film} = SO₂ film mass transport coefficient (m²/s)
L_b = bed length (m reactor)
M = molar weight (kg/mole)
M_a = molar weight component a (g/mole)
M_b = molar weight component b (g/mole)
n = reaction order (-)
N_{CaO} = amount of CaO in the core of one particle (mole CaO)
N_{part} = concentration of particles in reactor (#/m³ reactor)
N_{tanks} = total number of tanks (-)
NOVEM = the Netherlands Agency for Energy and the Environment

Nu = Nusselt number defined by Eq. (5.29) (-)

P = pressure (bar)

\( P^0 \) = standard pressure, by definition 101325 (Pa)

\( \Delta P \) = pressure drop (Pa)

\( P_0 \) = saturated vapour pressure of \( N_2 \) (bar)

\( P_{i} \) = partial pressure of compound \( i \) (Pa)

Pe = Peclet number defined by Eq. (5.85) (-)

\( P_{e_{ax}} \) = Peclet number (axial) defined by Eq. (5.7) (-)

PFBC = pressurized fluidized bed combustion

PFC = pulverized fuel combustion

Pr = Prandtl number defined by Eq. (5.31) (-)

q = exponent in Eq. (5.2) (-)

Q = constant defined in Eq. (2.23) (-)

r = radius, \( 0 \leq r \leq R+\delta \) (m)

R = particle radius (m)

\( R_a \) = attrition rate (wt%/h)

\( r_c \) = core radius (m)

\( R_{Ca/S} \) = Ca/S ratio needed to achieve the governmental \( SO_2 \) emission level (mole \( Ca/mole\) \( S \))

\( R_g \) = gas constant; \( R_g = 8.314 \) (J/(mole K))

\( r_{pore} \) = average radius of cylindrical pore according Eq. (2.22) (m)

\( (-Ra)_{exp} \) = experimental overall conversion rate (mole/(m³ reactor s))

\( Re_p \) = Reynolds number on particle defined by Eq. (5.8) (-)

\( S_{BET} \) = BET internal surface area (m²/kg)

\( S_{cap} \) = sulfur capture efficiency defined by Eq. (3.5) (%)

\( S_{CaS,reg} \) = regeneration efficiency to CaS defined by Eq. (3.9) (%)

\( S_{cum} \) = cumulative BET internal surface area (m²/kg)

\( S_{gen} \) = sulfur released (mole S/kWhe)

\( S_{H_2S,reg} \) = regeneration efficiency to \( H_2S \) defined by Eq. (3.7) (%)

\( S_o \) = total external surface area of particles in the reactor (m²)

\( S_{S,reg} \) = regeneration efficiency to \( S \) defined by Eq. (3.8) (%)

\( S_{SO_2,reg} \) = regeneration efficiency to \( SO_2 \) defined by Eq. (3.6) (%)

\( S_{tot,reg} \) = total regeneration efficiency (%)

\( S_{tot,reg} = S_{CaS,reg} + S_{H_2S,reg} + S_{S,reg} + S_{SO_2,reg} \)

Sc = Schmidt number defined by Eq. (5.9) (-)

SG105 = synthetic sorbent prepared by the sol-gel method

\( SO_x \) = \( SO_2 + SO_3 \)
St  = Stanton number defined by Eq. (5.27) (-)
STP  = Standard Temperature and Pressure, defined at 273.15 K and 100kPa
STW  = the Netherlands Technology Foundation
SURE2  = Sulfur Retention model version 2 (developed at D.U.T.)
t  = time (s)
T  = temperature (K)
Tg  = gas temperature (K)
Tp  = particle temperature (K)
tstoich  = stoichiometric breakthrough time (s)
TG  = thermogravimetry
Uf  = superficial gas velocity (m³ gas/(m² reactor s))
Umf  = minimum superficial gas velocity (m³ gas/(m² reactor s))
Va  = atomic diffusion volume component a in Eq. (5.11) (cm³/mole)
Vb  = atomic diffusion volume component b in Eq. (5.11) (cm³/mole)
Vcum  = cumulative pore volume (m³/kg)
Vf  = interstitial gas velocity (m gas/s)
Vg,i  = gas volume in one tank (m³ gas)
Vp  = volume of one sorbent particle (m³ particle)
Vpore  = pore volume (m³/kg)
Vr  = volume of reactor (m³)
Vr,i  = volume of one tank (m³ tank)
W  = weight of the sorbent defined by Eq. (6.2) (kg)
W0  = initial weight of the sorbent defined by Eq. (6.2) (kg)
WDS  = wavelength dispersive spectrometry
X  = dimensionless SO₂ concentration, CSO₂/C₅SO₅,feed (-)
Xfeed  = dimensionless SO₂ concentration in feed in equilibrium with SO₂ and O₂ (-)
XRD  = X-ray powder diffraction
Y  = dimensionless core radius, r_C/R (-)
z  = length coordinate (m reactor)
Δz  = slice of thickness (m reactor)
[CaO]  = concentration of CaO in Eq. (2.23) (mole/m² of surface area)
[CaSO₄]  = concentration of CaSO₄ in Eq. (2.24, 2.25)
                      (mole/m² of surface area)
[CH₄]  = concentration of CH₄ in Eq. (2.24) (mole/m³ at 298 K)
[CO]  = concentration of CO in Eq. (2.25) (mole/m³ at 298 K)
[H₂]  = concentration of H₂ in Eq. (2.24) (mole/m³ at 298 K)
\[ [\text{SO}_2] = \text{concentration of SO}_2 \text{ in Eq. (2.23) (mole fraction)} \]

**Greek symbols**

\[ \alpha_{SO_x, \text{film}} = \frac{1}{D_{SO_2, \text{film}} + D_{SO_3, \text{film}} K_{eq} C_{O_2}^{1/2} (\frac{1}{R} - \frac{1}{R+\delta}) (s/m^3)} \]

\[ \alpha_{SO_x, \text{shell}} = \frac{1}{D_{SO_2, \text{shell}} + D_{SO_3, \text{shell}} K_{eq} C_{O_2}^{1/2} (\frac{1}{R} - \frac{1}{R+\delta}) (s/m^3)} \]

\[ \beta_{SO_x, \text{film}} = \frac{K_{eq} C_{O_2}^{1/2}}{D_{SO_2, \text{film}} + D_{SO_3, \text{film}} K_{eq} C_{O_2}^{1/2} (\frac{1}{R} - \frac{1}{R+\delta}) (s/m^3)} \]

\[ \beta_{SO_x, \text{shell}} = \frac{K_{eq} C_{O_2}^{1/2}}{D_{SO_2, \text{shell}} + D_{SO_3, \text{shell}} K_{eq} C_{O_2}^{1/2} (\frac{1}{R} - \frac{1}{R+\delta}) (s/m^3)} \]

\( \Gamma \) = stoichiometric coefficient; \( \Gamma = 1 \) (mole CaO/mole SO\(_3\))

\( \delta \) = thickness of film layer around particle (m)

\( \delta_t \) = dimensionless number defined by Eq. (5.21) (-)

\( \varepsilon_b \) = bed porosity (m\(^3\) gas/m\(^3\) reactor)

\( \eta_f \) = fluid viscosity (Pa s)

\( \Theta \) = dimensionless time, \( t/t_{stoich} \) (-)

\( \lambda_{\text{eff}} \) = effective thermal conductivity of a sorbent particle (W/(m K))

\( \lambda_f \) = thermal conductivity of fluid (W/(m K))

\( \nu_i \) = stoichiometric factor of component A\(_i\) in Eq. (2.18) to (2.20) (-)

\( \rho_b \) = bed density (kg particle/m\(^3\) reactor)

\( \rho_p \) = particle density (kg particle/m\(^3\) particle)

\( \rho_f \) = fluid density (kg gas/m\(^3\) gas)

\( \tau \) = tortuosity (m\(^2\) gas/m\(^2\) particle)

\( \tau_r \) = relaxation time, defined in Eq. (3.26) (s)

\( \phi'' \) = flux of SO\(_2\) or SO\(_3\) towards (centre of) particle (mole/(m\(^2\) s))

\( \phi_f \) = volumetric fluid flow (m\(^3\) gas/s)

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\( \phi_m \) = dimensionless number according Eq. (5.18) (-)

\( \phi_r \) = pseudo steady state reaction rate defined by Eq. (5.32) and (5.43) (mole/s)

\( \phi_s \) = sulfur flux towards (centre of) one particle (mole/(m² s))

\( \phi_{sh} \) = shape factor of solid in Eq. (5.2) (-)

\( \phi_{Sg-s} \) = sulfur flow to one particle from gas to solid (mole/s)

\( X \) = internal porosity of the particle (m³ gas/m³ particle)

\( \psi_T \) = dimensionless number defined by Eq. (5.28) (-)
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Curriculum Vitae


