

Åbo Akademi University

**Experiments and Modeling of Gasification Gas
Desulfurization Reactors with Regenerable Zinc Titanate
Sorbents**

Jukka Konttinen



Academic Dissertation

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PREFACE

The work in this thesis has been performed as part of my main work with Carbona Inc. (in 1996-1998) and its predecessor Enviropower Inc. (in 1994-1995) at Tampere. The sponsors and co-operation partners of this work are gratefully acknowledged: Nearly all the appendices were prepared in cooperation with the Combustion Chemistry Research Group at Åbo Akademi University. The work on the development and testing of regenerable sulfur removal sorbents and the involved processes has been carried out as part of Combustion and Gasification Research Program LIEKKI and Energy and Environmental Technology Program SIHTI, both of which are partly financed by the Technology Development Centre of Finland (TEKES). The pilot-scale testing of zinc titanate sorbents, during 1994-1995, was part of the Cooperative Research and Development Agreement (CRADA) between Enviropower Inc. and the U.S. Department of Energy, USA. The grant received in 1996 from the Imatran Voima Foundation helped me essentially to start with the development of the reactor models.

I wish to express my gratitude to the managing director of Carbona Inc., Mr. Kari Salo, for his flexibility in allowing me to prepare this thesis alongside my other duties in the company. Because of his positive attitude, there has always been room for me to apply scientific know-how in supporting the design projects of our company. During the years I have worked with him, I have always felt more like a friend to him than just an employee. I am grateful to my supervisor, the leader of the Combustion Chemistry Research Group, Professor Mikko Hupa for his never-ending enthusiastic attitude towards this work which has largely encouraged me to complete this thesis. The preparation of the journal articles (included as appendices) was originally Professor Hupa's idea. Submitting and revising the manuscripts has been very rewarding: the new ideas evolved in the process of modeling, analyzing the results and reporting them have been directly applied in the design projects at Carbona Inc.

The publication of some essential laboratory, and pilot-scale experimental results as part of this thesis would have not been possible without the kind permission granted by the board of Enviropower Inc. in 1995. For this, I would like to express my gratitude to Mr. Lauri Virkkunen, the former managing director of Enviropower Inc.

I would like to thank all my co-authors. Dr. Ron Zevenhoven of Åbo Akademi University helped me countless times to process the most recent manuscripts of this thesis into readable portions. He also reviewed the models and parameter estimation with great care. Dr. Patrik Yrjas of Åbo Akademi University, now working at ABB Carbon, Sweden, was responsible for the coordination of the PTGA tests and reporting the obtained results. Dr. Wahab Mojtahedi of Carbona Inc. provided valuable comments about the thesis

manuscript. Dr. Javad Abbasian of the Institute of Gas Technology, Des Plaines, IL, USA, arranged the HTHP bench-scale fluidized bed reactor test data and related sorbent laboratory analysis data that are applied in many parts of this thesis.

I am grateful to Professor Dr. Maria Flytzani-Stephanopoulos of Tufts University, MA, USA, who provided many invaluable comments during the evaluation of sulfidation reaction modeling results. The discussions with her started in Kusadasi, Turkey in 1996, in the NATO Advanced Study Institute (ASI) meeting which I participated on the grant by the *Acta Chemica Scandinavica*. Mr. Thomas Dorchak of the Federal Energy Technology Center, WV, USA is gratefully acknowledged for his contribution for coordinating the CRADA-project and for providing useful comments to the manuscripts of regeneration reactor modeling. I also would like to thank Dr. Santosh Gangwal of the Research Triangle Institute, NC, USA, for producing the laboratory-scale ambient-pressure sulfidation and regeneration kinetic data used in this thesis. Mr. Peter Backman of Åbo Akademi University deserves thanks for carrying out the actual experiments with the PTGA.

I wish to thank my colleagues and other personnel at Carbona Inc. and Enviropower Inc. They have contributed to this work and created a pleasant working atmosphere. Mr. Andras Horvath carefully reviewed the parts dealing with IGCC in this thesis, of which I am grateful. Mr. Markku Liukkonen, Mr. Mika Raassina, and Ms. Anja Tanni deserve special thanks for helping me to produce the high quality graphs in this thesis.

And finally, my warmest thanks to my children Mikko and Leena and to my parents and for their love and support. Thank you, Marja-Liisa, for your love and encouragement. These people have always helped me to keep in mind what the most important things in life are.

Tampere/Tammerfors, June 1998


Jukka Kontinen

ABSTRACT

Regenerable mixed metal oxide sorbents are the prime candidates for the removal of hydrogen sulfide (the main pollutant) from the hot gasifier gas in the simplified integrated gasification combined cycle (IGCC) process. This is primarily due to problems associated with disposal of large amounts of solid wastes generated with non-regenerable sorbents. The addition of TiO_2 to zinc oxide (ZnO), to form the mixed metal oxide zinc titanate ($\text{ZnO}\cdot x\text{TiO}_2$), stabilizes the zinc and permits the use of the sorbent in continuous regenerable sulfur capture at temperatures up to 800°C .

As part of the regenerative sulfur removal process development, Carbona Inc. is developing reactor models for scale-up. It is essential for this work to apply a reliable and simple correlation for the conversion rate of zinc titanate or gaseous reactants (H_2S , O_2) in the sulfidation and regeneration reactions. For (fluidized bed) reactor modeling purposes, it is desirable to have a gas-solid reaction model with the following properties: 1) the model should describe the rate of gas-solid reaction with a minimum of numerical iteration and still take the sorbent's physical properties into account; 2) it has to have a minimum number of adjustable parameters; 3) the adjustable parameters should have a logical dependence on process variables such as temperature and pressure.

The experimental results of some laboratory-scale tests made in order to determine rate parameters for the zinc titanate sulfidation and regeneration rate models are presented. Two different models, the unreacted shrinking core (USC) and the overlapping grain (OG) models, are applied to the modeling of zinc titanate sulfidation. All the experimental data in sulfidation can be fitted with two parameters, reaction rate constant and product layer diffusion coefficient. The values of the parameters agree reasonably well with the corresponding values obtained from the literature.

In ZnS regeneration, the experimental data of atmospheric thermogravimetric analyzer (ATGA) at different temperatures could be fitted by assuming uniform conversion of ZnS in the solid particles. The results indicate that the rate of the ZnS regeneration reaction is strongly temperature-dependent, with an activation energy of about 140 kJ/mol for the rate constant. The results of pressurized thermogravimetric apparatus (PTGA) indicate that the rate of ZnSO_4 formation at high temperature and pressure is negligible, in comparison with the rate of SO_2 release.

A method of applying the solid conversion rate models to bench- and pilot-scale fluidized bed reactor modeling is presented in this thesis. It is assumed that the possible mass transfer limitation effects due to fluidized bed hydrodynamics are not significant. As a result of the parameter fit into pilot-scale ZnS regeneration data, a value of the apparent

activation energy for the global reaction rate constant of 200-210 kJ/mol is found, which is higher than that obtained with laboratory-scale results.

The solid conversion rate models with parameter values determined in this thesis, together with fluidized bed mass and energy balances, can be used to predict the performance of large-scale zinc titanate sulfidation and regeneration reactors. Steady-state kinetic reactor models are needed for reactor sizing, and dynamic models can be used for process control design. Due to differences in regeneration reaction rate parameter values, a sensitivity analysis of a large-scale steady-state regeneration reactor model is performed using rate constants from pilot-scale in comparison with constants from laboratory-scale. Significant differences in the model performance can be observed at low regeneration temperatures of 550-650°C, but under these conditions the model and its parameters give a performance window which can be used as guideline information.

The validity of some simplifying assumptions of the large-scale fluidized bed reactor models are checked in a separate study. Hydrodynamic modeling equations for dense fluidized bed and freeboard (above the dense bed) are applied for the prediction of the performance of a large-scale regeneration reactor. These equations can partly explain the differences observed with the simpler model (in the determination of regeneration reaction rate constants from pilot-scale fluidized bed in comparison with constants from laboratory-scale). It is shown that the sensitivity of the fluidized bed hydrodynamic models towards its main parameters is significant; thus more experimental data of large-scale reactors is required to support the application of such models. In the circulation of the sulfur removal sorbent between large-scale sulfidation and regeneration fluidized beds, a residence time distribution (RTD) is created. The effect of RTD on the modeling results is also checked and found not to be significant in sulfidation reactor modeling, where sorbent fractional conversions below 50 mol % are common. In regeneration reactor modeling, a maximum error of about 25 % in gas-solid mass balances can take place when not taking RTD into account. But since this error takes place at sorbent fractional conversions of 0.7-0.9 only, it is stated that the results with no RTD effect in regeneration reactor modeling can be used as guideline information.

The successful pilot-scale test run results of the side-by-side sulfur removal fluidized bed reactor arrangement, in connection with a 15 MW_{th} gasifier pilot, are presented. The results show that a high sulfidation efficiency as well as continuous production of SO₂-containing regeneration reactor off-gas at design temperatures and pressures could be achieved. The pilot-scale test results prove that the preliminary sizing model results, based on the principles presented in this thesis, were in good agreement with test data.

TABLE OF CONTENTS

PREFACE	2
ABSTRACT	4
NOTATION	8
1. INTRODUCTION	12
2. PRESSURIZED POWER PRODUCTION PROCESSES	15
3. INTEGRATED GASIFICATION COMBINED CYCLE PROCESS	17
3.1 LARGE-SCALE IGCC PROJECTS.....	17
3.2 IGCC PROCESS BASED ON AIR-BLOWN FLUIDIZED BED GASIFICATION.....	19
4. SULFUR CAPTURE IN CONNECTION WITH IGCC PROCESSES	22
4.1 CA-BASED SORBENTS	22
4.2 REGENERABLE METAL OXIDE SORBENTS	23
4.3 ZINC-BASED SORBENTS	27
4.4 REGENERATION REACTOR OFF-GAS TREATMENT	29
5. EXPERIMENTAL TESTING AND DESIGN OF SULFUR REMOVAL PROCESSES WITH ZINC-BASED SORBENTS	30
5.1 LABORATORY-SCALE TESTS	31
5.1.1 Sulfidation.....	31
5.1.2 Regeneration	33
5.2 PILOT-SCALE TESTS	36
6. DESIGN AND MODELING OF THE SULFUR REMOVAL AND SORBENT REGENERATION REACTORS	41
6.1 SOLID CONVERSION MODELS	41
6.2 FLUIDIZED BED REACTOR MODELS.....	48
6.2.1 Simplified models	48
6.2.2 Some specific issues in large-scale reactor modeling	54
7. EXPERIMENTAL APPARATUS USED IN THIS THESIS	62
8. SUMMARIES OF PAPERS IN THIS THESIS	65
9. CONCLUDING REMARKS	72
9.1 CONCLUSIONS ON THIS WORK.....	72
9.2 IMPLICATIONS	74
10. LITERATURE CITED	76

Appendices

- I. Konttinen, J.; Mojtahedi, W.: Gasifier Gas Desulfurization at High Temperature and Pressure. *Kemia-Kemi (Finnish Chemistry)* 1993, 20 (9-10), pp. 847-851.
- II. Konttinen, J.; Zevenhoven, C.A.P.; Hupa M.M.: Hot Gas Desulfurization with Zinc Titanate Sorbents in a Fluidized Bed. 1. Determination of Sorbent Particle Conversion Rate Model Parameters. *Ind. Eng. Chem. Res.* 1997, 36 (6), pp. 2332-2339.
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- VI. Konttinen, J.; Zevenhoven, C.A.P.; Hupa, M.M.: Modeling of Sulfided Zinc Titanate Regeneration in a Fluidized Bed Reactor. 2. Scale-Up of the Solid Conversion Model. *Ind. Eng. Chem. Res.* 1997, 36 (12), pp. 5439-5446.
- VII. Konttinen, J.; Mojtahedi, W.; Abbasian J.: Coal Gas Desulfurization at the 15 MW_{th} Pressurized Gasification Pilot Plant. In: *High Temperature Gas Cleaning*; Schmidt, E., Gäng, P., Dittler A., Eds.; G. Braun Printconsult GmbH: Karlsruhe, Germany, September 1996; pp. 756-766.
- VIII. Konttinen, J.: Large-scale fluidized bed reactor modeling. To be published.

NOTATION

a, a'	decay constants (1/m)
A, B	constants defined by equation 27
b	stoichiometric factor
C	concentration (mol/cm ³)
D	diffusion coefficient (m ² /s)
d_p	particle diameter (m)
ΔH_{298}	reaction enthalpy at 298 K (kJ/mol)
$E(t)$	residence time distribution function
F	flow of gaseous or solid reactant (mol/s)
F_g	grain shape factor
k, k_f	reaction rate constant according to uniform conversion model (cm ³ /(mol s)) and global reaction rate constant (defined in Paper VI) (cm ³ /(mol s))
k_i	reaction rate constant in equation 33 (cm ³ /(g s))
k_{OG}, k_{USC}	reaction rate constants of overlapping grain and unreacted shrinking core models (m/s)
k' (1/s)	intrinsic reaction rate constant defined by equations 29 and 30
k_1, k_2	reaction rate constants in equations 31 and 32, (1/s) and (mol/(g min) respectively
K_{bc}, K_{ce}	coefficients of gas interchange between bubble and cloud (1/s) and cloud and emulsion phases (1/s), respectively
K, K_1	equilibrium constants, (-) and (cm ³ /mol), respectively
K_r	reaction rate constant according to catalytic plug-flow reactor model (in equation 45) (1/s)
K_f	reaction rate parameter defined by equation 45 (1/s)
L	height (m)
m_{sorb}	sorbent circulation rate (g/s)
M	parameter defined by equations 37 and 40
n_S	flow of reactant sulfur gas (mol/s)
$n(r)$	grain size distribution
n_{Zn}, n_{ZnS}	total amount of zinc and zinc sulfide in a fluidized bed (mol)
N	total number of vertical slices in series
p	pressure (bar)
r	grain radius (m)
r_1	reaction rate (1/s)
$rate_{Zn}$	reaction rate parameter defined by equation 36 (1/s)
R	ideal gas constant (8.314 J/(mol K))

R_0	initial surface reaction rate (mol/(cm ² s))
R_p	particle radius (m)
R_s	reaction rate defined by equation 13 (mol/cm ³ s)
S	particle surface area per unit volume of solid (m ² /m ³)
t	time (s)
T	Temperature (°C or K)
u_0	gas superficial velocity (m/s)
V	volume (m ³)
V_{gas}	gas volumetric flow (cm ³ /s)
W	weight (g or kg)
x	stoichiometric coefficient in equations 8 and 10
X	fractional conversion (-)
X_{max}	fitting parameter in equation 14 (-)
\bar{X}_s	mean fractional conversion of solid (-)
y	volume fraction of gas (-), also as stoichiometric coefficient in equations 8 and 10
y_e^*	parameter defined by equation 33
Z	stoichiometric volume ratio of solid product to solid reactant (-)
z_{FB}	freeboard height (m)

Greek symbols

α	reaction rate group parameter defined by equations 36, 37, 42 and 43 (-)
β	parameter defined by equations 38 and 41
δ	bubble fraction in a fluidized bed (-)
ε	void fraction or porosity (-)
$\gamma_b, \gamma_c, \gamma_e$	volume of solids dispersed in the bubble-, cloud- and emulsion phases, respectively, divided by the volume of bubbles (-)
η	efficiency factor (-)
ρ	density (kg/m ³)
τ	time scale or residence time parameter (s)
τ_0	gas residence time parameter independent of bed voidage (s)
τ_{bed}	mean residence time solid in a fluidized bed (s)

Subscripts

A	gaseous reactant A
b	bulk
bed	fluidized bed

dif	intraparticle diffusion
DB	dense fluidized bed
e	electric, also at fluidized bed exit (in equation 46)
eff	effective
eq	equilibrium
f	complete fluidization conditions
FB	freeboard
g	gas
j	order number of the vertical slice
kin	kinetics
m	mean
max	maximum
min	minimum
mol	molecular
o	at exit of a dense fluidized bed
OG	overlapping grain model
p	product surface
pl	product layer
r	reaction surface
s	solid
th	thermal
tot	total
USC	unreacted shrinking core
v	internal
x	without correction for grain overlap
0	initial

Superscripts

n	reaction order parameter
---	--------------------------

Abbreviations

HTHP	high-temperature high-pressure
IGCC	integrated gasification combined cycle
OG	overlapping grain
ppmv	parts per million by volume
PFBC	pressurized fluidized bed combustion
PTGA	pressurized thermogravimetric apparatus
RTD	residence time distribution

SEM	scanning electron microscopy	SEM
USc	cent	USc
USC	unreacted shrinking core	USC
USD	dollar	USD
vol %	volume percent	vol %

1. INTRODUCTION

Solid fuels have and will retain an important role in the world's thermal power and electricity generation. Energy demand will continue to increase with increasing population and as the economies of the less developed countries mature. Besides being more efficient and economic, the future energy generation processes have to be environmentally acceptable. Moreover, a characteristic of the growth of energy consumption is that electric power consumption increases more than heat consumption. For these reasons, development work is focused on new power plant concepts which are thought to replace the techniques now in use. Promising new technologies under commercialization include pressurized combustion and gasification of solid fuels and the application of those technologies in integrated gasification combined cycle (IGCC) processes. In the IGCC, solid fuel is first gasified under pressure to form a combustible gas with carbon monoxide (CO), hydrogen (H₂), methane (CH₄), and inert gases. A combination of the gas and steam turbine processes (combined cycle technology) is then utilized in generating electricity from the gasifier gas.

The combustion and gasification processes of solid fuels in combined heat and power generation generate gaseous emissions such as carbon dioxide (CO₂), nitrogen oxides (NO₂, NO), and sulfur dioxide (SO₂). Lately, CO₂ has received attention because of its contribution to the enhanced greenhouse effect. One way to reduce the total CO₂ emissions is to increase the efficiencies of the power plants. Increased efficiency demands less fuel to produce an equivalent amount of electricity. Another way is to develop methods of combustion and gasification of biomass. The released CO₂ will be rebonded by the regrowth of the vegetation and thus the net CO₂ in the atmosphere is not increased. Both methods of reducing CO₂ emissions can be combined with the use of advanced power plant processes, such as the IGCC processes, using biomass fuels.

Sulfur dioxide (SO₂) is the primary source of the acid rain problem (and of NO_x to a lesser extent). Most of the acid rain originates in sulfur emissions deriving from power generation processes based on solid fossil fuels. Gaseous sulfur compounds (produced by fuel combustion or gasification) can be captured with Ca-based compounds in wet scrubbers, spray dry scrubbers, or by sorbent injection at high temperature in the combustion or gasification chamber. In connection with the IGCC process, the use of regenerable sorbents instead of once-through Ca-based sorbents (limestone, dolomite) for sulfur retention has recently received more attention, primarily due to problems associated with disposal of large amounts of solid wastes generated with non-regenerable sorbents. With the use of regenerable sorbents, the amount of solid waste produced is minimized and the fuel-bound sulfur can be recovered as a commercial product, such as elemental sulfur (Portzer et al., 1995, Salo et al., 1995). In addition, very low sulfur emission levels (5-20 ppmv)

after the sulfur capture reactor can be achieved under reducing conditions, with metal oxide-based regenerable sorbents, whereas minimum sulfur emission levels of 80-150 ppmv are possible with Ca-based sorbents.

A number of metal oxides, mixed metal oxides, and supported metal oxides can be used for high temperature regenerative sulfur removal. The oxides of Ba, Ca, Co, Cu, Fe, Mn, Mo, Sr, W, V, and Zn are thermodynamically feasible candidates (Westmoreland and Harrison, 1976). Under favorable conditions, two metal oxides can react to form a mixed-metal oxide. In the United States, zinc oxide-based sorbents have been under investigation since the late 1970's (Cicero, 1994; Harrison, 1995). Zinc titanate appears to be the leading regenerable sorbent for high-temperature high-pressure (HTHP) sulfur removal in fluidized bed reactors (Harrison, 1995; Paper VII). The complex combination of zinc oxide and titanium dioxide reduces the tendency of zinc oxide reduction and subsequent volatilization of metallic zinc, thereby increasing the maximum sorbent operating temperature from 650°C to about 760°C.

In this thesis, the experimental and modeling results related with HTHP sulfur capture and regeneration with zinc titanate sorbents are presented and discussed. This work forms an essential part of the regenerative sulfur removal process development by Carbona Inc. (successor to Enviropower Inc.). An overview of the IGCC demonstration projects and related sulfur removal technologies is also given, with the main emphasis on pilot- and demonstration-scale projects. In the scale-up of the regenerable sulfur removal process, fluidized bed reactor models are needed. The application of the experimental data from laboratory- and pilot-scale reactors into zinc titanate sulfidation/regeneration solid conversion models is presented. A validated solid conversion model, together with fluidized bed mass and energy balances, can be used to predict the performance of large-scale sulfidation and regeneration reactors. In addition to this steady-state scale-up design, a dynamic reactor model (based on the same elements) can be used for process control system design and operator training.

Besides this introductory part, this thesis consists of the following eight appendices:

- I. Kontinen, J. T.; Mojtahedi, W.: Gasifier Gas Desulfurization at High Temperature and Pressure. *Kemia-Kemi (Finnish Chemistry)* 1993, 20 (9-10), pp. 847-851.
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- VIII. Konttinen, J.: Large-scale fluidized bed reactor modeling. To be published.

2. PRESSURIZED POWER PRODUCTION PROCESSES

Figure 2.1 shows schematic diagrams of the advanced power generation technologies based on pressurized fluidized bed combustion (PFBC) and gasification (IGCC) of solid fossil fuels or biomasses. In the combustion reactor of a PFBC process, solid fuel reacts with air under pressure (10-15 bar), to produce a flue gas (CO_2 , H_2O , N_2). In the gasification reactor of an IGCC process, solid fuel reacts with a mixture of steam and air (or oxygen) at pressures of 15-25 bar, to form a combustible gas with carbon monoxide (CO), hydrogen (H_2), methane (CH_4), and inert gases. If oxygen is used as a gasification reactant (oxygen-blown gasifier), an additional air separation plant is required. The resulting flue/gasification gases are cleaned from solid ash particulates and sulfur compounds at system pressure and at temperatures of 500-1000°C (hot gas clean-up) or at below 100°C (cold gas clean-up, IGCC plants only). The gases are then directed into a gas turbine, where electricity is generated. Additional power is generated in the steam cycle, which consists of a steam turbine and heat recovery systems. In the PFBC, the pressurized flue gas is expanded in an expansion turbine, and in the IGCC, the gasification gas is burned in the gas turbine combustion chamber.

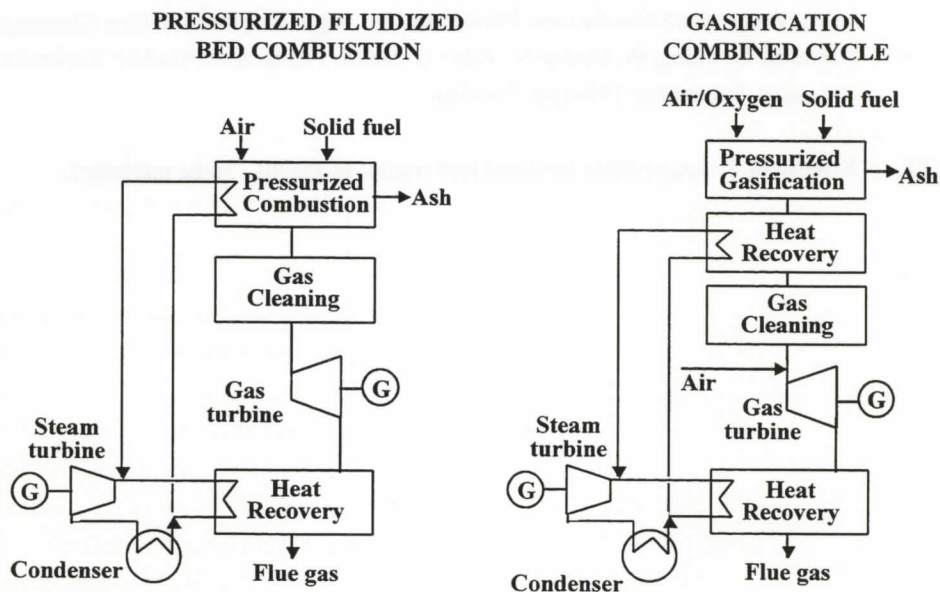


Figure 2.1 The schematic process flow diagrams of the advanced power generation technologies of solid fuels (according to Hupa, 1994).

The advantage of the pressurized combined-cycle processes (PFBC, IGCC) is that the electricity generation efficiency can be increased to 43-47 %, as compared to the efficiency achieved with the conventional boiler technologies (38-43 %, steam turbine only). Furthermore, when increasing the gas turbine inlet temperature, there is a possibility of reaching efficiencies of over 50 % (Pruschek et al., 1997). The effect of the gas turbine inlet temperature in large 600 MW_e class power plants is illustrated in Figure 2.2. The fact that the gas turbine inlet temperature can be increased when using gasifier gas while it is limited with PFBC (i.e., IGCC has the potential for higher efficiency) makes the IGCC process concept more attractive than PFBC.

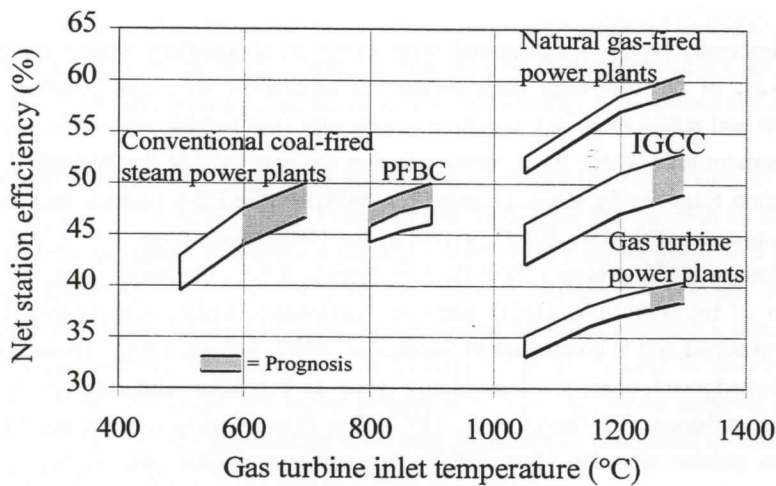


Figure 2.2 Thermal performance of different 600 MW_e class power plants (according to Pruschek et al., 1997).

One of the latest advanced power generation processes under development, the so-called "topping cycle", combines the technologies of pressurized gasification and combustion together with gas cleaning systems. The fuel is only partly gasified (70-80 wt %) in the gasifier, after which the fuel gases are led to a combustion chamber of a gas turbine, like in the IGCC process. The residue from gasification, the char, is fed to a combustor, where it is burned. An advantage of this process is that the partial gasification of fuel can be performed with air, eliminating the need for an expensive oxygen plant. More information on the development and demonstration of PFBC and topping cycle power plant technologies can be found in the literature (Preto, 1997).

desulfurization and reduction of nitrogen oxides will be required for conventional type plants. It is plain that the cost of electricity produced with IGCC will have to decrease further in the future, in order to compete with the conventional type processes, which means that further development of IGCC is still needed. The cost comparisons between IGCC and other types of processes include several uncertainties, simply due to the fact that at the moment only a few commercial-scale IGCC plants are in operation. More information will be obtained on this subject towards the end of this decade.

3.2 IGCC process based on air-blown fluidized bed gasification

The IGCC process developed by Carbona Inc., for power production, is shown in Figure 3.1. It incorporates three main parts: 1) the gasification plant, including fuel preparation and feeding, air-blown fluidized bed gasifier, gas cooling to 550-650°C, and hot gas clean-up; 2) the gas turbine plant, including gas turbine and the booster compressor/heat exchanger system for the gasifier air supply; and 3) the steam cycle, including heat recovery steam generator, steam turbine, and the conventional parts of a steam cycle.

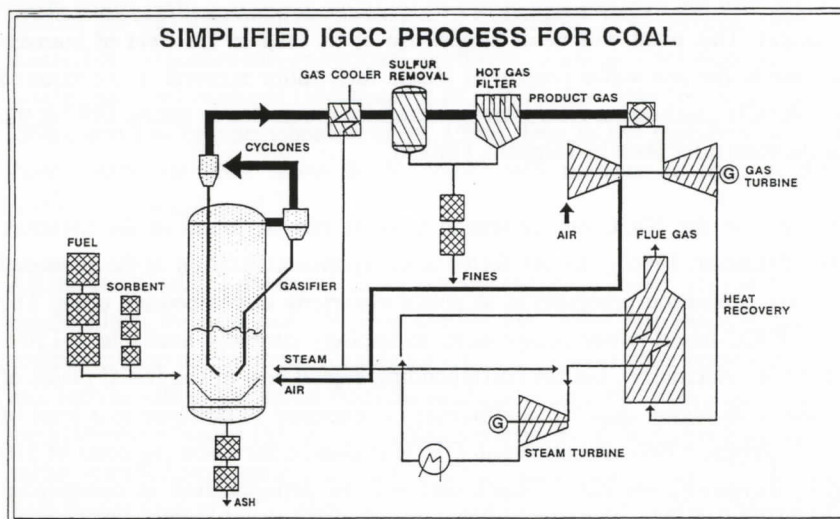


Figure 3.1 The IGCC process scheme.

A solid fossil fuel, such as coal or biomass, is pressurized and fed into the gasifier by a lock-hopper system. The sorbent required for in-bed desulfurization and/or fluidization is introduced in the same way. The gasification air is supplied by a gas turbine (air extraction after compressor) through a booster compressor/heat exchanger system. This is to increase

the air pressure from the post-compressor pressure to the gasifier pressure, 15 to 25 bar, depending on the gas turbine requirements. The gasification steam is extracted from the steam turbine or produced by the gas cooler and fed into the gasifier through the gasifier distributor plate.

The gasification system is the U-Gas process, a fluidized bed type gasifier. In the gasifier, the fuel reacts with air and steam (air-blown gasifier) in the fluidized bed at temperatures of 800°C to 1100°C, thus producing the combustible gasifier gas. Typical gas compositions for different fuels are presented in Table 3.1. The key features of the patented U-Gas process are the ash removal system and a hot oxidation zone in the gasifier fluidized bed to burn the small size fuel char particles (that have a low gasification reactivity) and this way to increase the overall fuel conversion to gases. The coal ash is removed from the gasifier in the form of agglomerates. Due to the ash removal system, the gasifier achieves a low level of carbon losses, which enables a very high overall carbon conversion, above 97 %. The elutriated fines from the gasifier are partly separated from the product gas and recycled into the gasifier through a two-stage cyclone system. The product gas leaving the gasifier is cooled to 650-550°C in the fire tube gas cooler. The gas cooler produces saturated steam and is connected to the high-pressure steam cycle of the heat recovery steam generator.

Table 3.1 Typical product gas compositions of the U-gas fluidized bed gasifier (Air/Steam gasification at 20 bar) (Salo and Hokajärvi, 1994).

FUEL	COAL	COAL	LIGNITE	WOOD
Moisture (%)	5	25	20	20
Gas composition				
CO (vol %)	24	18	17	16
CO ₂ (vol %)	5	8	9	12
CH ₄ (vol %)	2	2	3	7
H ₂ (vol %)	14	12	12	12
H ₂ O (vol %)	5	11	10	14
N ₂ (vol %)	50	49	49	39
Gas lower heating value (LHV, MJ/m ³)	5.0 - 5.5	4.0 - 5.0	4.0 - 5.0	5.0 - 6.0

The principal gaseous sulfur compound formed in the highly reducing gasifier atmosphere is hydrogen sulfide, H₂S, with some other compounds, such as carbonyl sulfide, COS (Iisa, 1992; Yrjas, 1996). In air-blown fluidized bed gasification of solid fuels with high sulfur content, with about 90 % sulfur capture by dolomite, the remaining high H₂S concentration in the product gas can be reduced further in a two-reactor sulfur removal unit, which is the

subject of this thesis. The sorbent used in this unit is regenerated by air and steam, taken from the gas turbine extraction air and from the high-pressure extraction steam, respectively. The SO₂-rich gas stream produced by regeneration can be recycled back to the gasifier or can be processed further to produce elemental sulfur or sulfuric acid. The remainder of the fine particles, elutriated from the gasifier and from the sulfur removal system, is removed from the sulfur-free product gas in a HTHP filtration unit employing porous rigid ceramic candle filters. The filter elements are cleaned periodically by a rapid pulse of high-pressure nitrogen or steam in the opposite direction of the flow of gasifier gas.

The clean product gas is burnt in the combustion chamber of the gas turbine, and the fuel gas generated is expanded through the expansion turbine. The heat of the gas turbine exhaust gas is utilized in the steam cycle part of the IGCC process, which includes the heat recovery steam generator (HRSG), steam turbine, and other sections of a steam generating process.

In order to make the process thermally more efficient and to reduce the total capital requirements associated with cooling and reheating of the fuel gas stream, IGCC fuel gas should be cleaned at or near the temperatures and pressures prevailing at the outlet of the gasifier (hot gas clean-up). IGCC systems with hot gas clean-up may have efficiencies of about 5 percentage points higher than those achieved with cold gas clean-up (Kurkela, 1988).

Cold gas clean-up combined with oxygen-blown gasification has been used widely in the chemical industry where the main interest is to get as high as possible yields of carbon monoxide (CO) and hydrogen (H₂) for chemicals (like methanol) production. In the oxygen-blown gasification plants (such as presented in the previous chapter), gasifier gas is quenched or cooled and scrubbed for low temperature removal of sulfur compounds. The air separation unit adds the capital cost and internal power consumption of the IGCC plants. Air-blown gasification with hot gas clean-up (simplified IGCC) eliminates the need for air separation unit and minimizes the need for gas cooling and waste water processing. However, the operability of the simplified IGCC at commercial-scale is yet to be demonstrated.

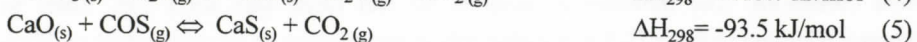
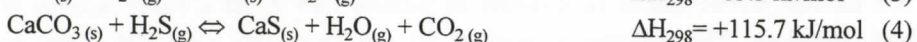
4. SULFUR CAPTURE IN CONNECTION WITH IGCC PROCESSES

4.1 Ca-based sorbents

Limestone (CaCO_3) or dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) is typically used for sulfur capture in combustion or gasifier fluidized beds. Both materials are cheap, naturally occurring minerals. Depending on the carbon dioxide (CO_2) partial pressure and the temperature, the sorbents may calcine according to the following reactions (Iisa, 1992; Yrjas, 1996):



In fluidized bed gasifiers, the temperature is too high for MgCO_3 to be stable. As a result, it will always calcine to MgO , but will not react with sulfur compounds, due to unfavourable thermodynamics. Abbasian (1991) and Iisa (1992) found dolomite to be more reactive than limestone at sulfur removal under pressurized gasifier gas conditions. In reducing atmosphere of the gasifier, the gaseous sulfur compounds are mainly in the form of H_2S (Iisa, 1992; Yrjas, 1996), and the principal sulfur capture reactions are:



In addition to the solid sulfur-containing product, gaseous reaction products (H_2O , CO_2) will be formed, which is not the case for sulfur capture in oxidizing conditions (only CO_2). The gaseous products of calcination reaction (2) and sulfur capture reactions (3), (4), and (5) will set thermodynamical limitations, especially at high partial pressures of CO_2 and H_2O . To illustrate this, Figure 4.1 shows the calculated equilibrium concentrations for H_2S with CaCO_3 -containing sorbent under typical air-blown U-gas gasifier fluidized bed conditions.

In the case of gas mixtures produced by an air-blown fluidized bed gasifier at 20 bar, Figure 4.1 shows that with the use of CaCO_3 at about 860°C and with low volume fractions of CO_2 and H_2O , a minimum of about 80 ppmv H_2S remains in the gasifier gas. The H_2S content cannot fall below that due to thermodynamic limitation under these gasifier gas conditions. The temperature where the lowest equilibrium H_2S content in the gas can be achieved is the same as that where the calcination of CaCO_3 occurs according to reaction 2.

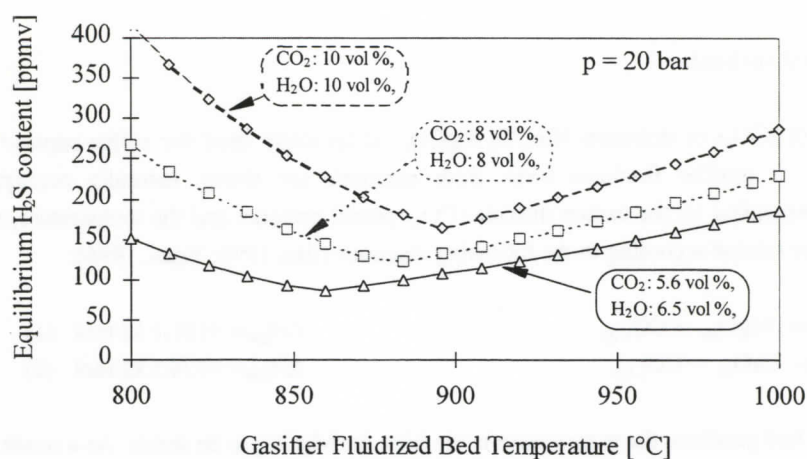


Figure 4.1 Equilibrium H₂S content as a result of reaction with a Ca-based sorbent in typical U-gas type gasifier gas atmospheres (with CO₂ and H₂O).

In pressurized gasification, the calcium sulfide formed in sulfur capture reactions is removed from the bottom of the gasifier together with inert ash originating in coal. This mixture of ash and calcium sulfide cannot be disposed of because CaS is not a stable material at ambient conditions. The moisture in ambient air can cause this solid CaS waste to decompose releasing gaseous H₂S to the atmosphere and causing an environmental problem (Abbasian, 1991). Therefore, before disposal, CaS has to be oxidized to calcium sulfate (CaSO₄), which is a stable, environmentally acceptable material (Abbasian, 1991; Yrjas, 1996), according to the reaction:



The oxidation of CaS in the solid discharge to environmentally acceptable levels, and related oxidation reactor design issues, have been studied elsewhere (Rehmat et al. 1987; Abbasian et al., 1991).

4.2 Regenerable metal oxide sorbents

The use of regenerable sorbents instead of once-through Ca-based sorbents for sulfur retention has recently received more attention. This is primarily due to problems associated with disposal of large amounts of solid wastes generated with non-regenerable sorbents, such as dolomite, where the magnesium oxide and ash components are practically inert. With the use of regenerable sorbents, the amount of solid waste produced is minimized and the fuel-bound sulfur can be recovered as a commercial product, such as

elemental sulfur (Portzer et al, 1995). In addition, very high (over 99 %) sulfur capture efficiencies can be achieved in reducing conditions with regenerable sorbents based on metal oxides, which is not possible with Ca-based sorbents (Figure 4.1)

A number of metal oxides, mixed metal oxides, and supported metal oxides can be used for high-temperature regenerative sulfur removal. The oxides of Ba, Ca, Co, Cu, Fe, Mn, Mo, Sr, W, V, and Zn are thermodynamically feasible candidates. The results obtained by thermodynamic screening on the high temperature metal sorbents (mainly oxides) by Westmoreland and Harrison (1976) are shown in Figure 4.2.

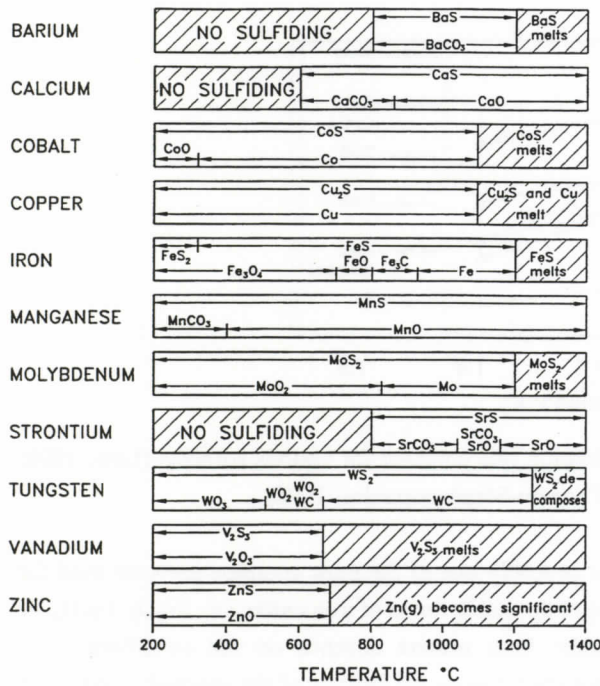


Figure 4.2 Sorbents selected by Westmoreland and Harrison (1976) for high temperature desulfurization as a function of their operational temperature window.

In addition to a high removal efficiency, the sorbent must be stable in the coal gas atmosphere, have acceptable sulfur uptake capacity, be regenerable, and maintain high activity through a large number of sulfidation/regeneration cycles. The possible thermal and mechanical problems that can occur in continuous use of the sorbents include sintering, loss of porosity and contact area, attrition, and cracking (Gupta and Gangwal, 1992; Harrison,

1995). Compromises are necessary since none of the metal oxides mentioned satisfy all the requirements.

The selection of a regenerable metal oxide sorbent for gasifier gas desulfurization is strongly dependent on the sulfidation temperature and the relative amounts of reducing CO and H₂ and inert H₂O and CO₂ gases. The dispersion with inert support materials has to be applied in order to prevent the reduction of the active metal oxide. The sulfidation equilibria with single metal oxides favours zinc and copper at temperatures of 500-800°C for gasifier gases produced by an air-blown gasifier. Figure 4.3 shows a comparison of the sulfidation reaction rate constants obtained under laboratory conditions with several metal oxides.

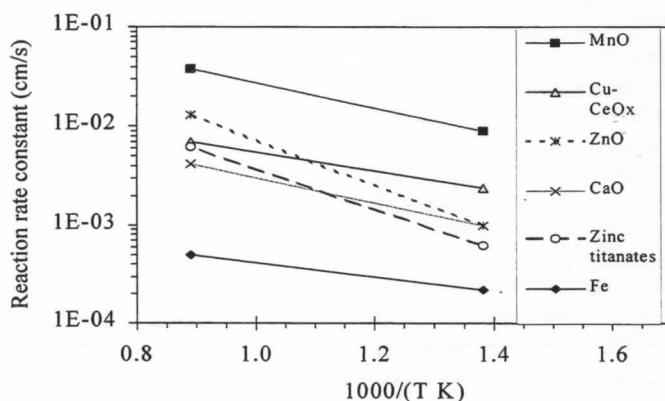
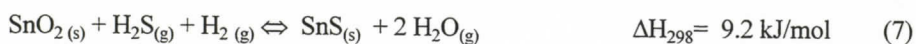


Figure 4.3 Arrhenius plot of sulfidation rate constant for various sorbents (Lew, 1990; Lew et al., 1992 a, b; Flytzani-Stephanopoulos, 1996).

Besides calcium oxide, iron oxide is probably one of the most common sorbents used for H₂S removal. In the H₂S capture, one of the stable forms of iron oxide, i.e., Fe₂O₃, Fe₃O₄, or FeO, reacts to form FeS. The oxidic form present depends on the conditions (e.g., temperature, pressure, gas composition) but also on the kinetics of the successive reduction reactions. Equilibrium calculations indicate that the maximum operating temperature of sulfidation should not exceed 450°C, for a better performance than with calcium-based sorbents (Wakker, 1992). Iron oxide is, without binding agents, insufficiently durable in several successive sulfidation and regeneration cycles at high temperature. By mixing the iron compound with, for example, aluminium oxide or silicon dioxide or by adding small amounts of certain additives, the durability of the sorbent can be improved (Wakker, 1992). The commercialization and demonstration work on iron oxide-based sorbents and processes have been reported by Japanese companies such as Ishikawajima Heavy industries in fluidized bed reactors (IHI brochure, 1991), Kawasaki Heavy industries in moving-bed

reactors (Ishikawa, 1993), and Mitsubishi Heavy Industries in fixed-bed reactors (Suehiro and Fujishima, 1993).

Nielsen and Sigurdardottir (1993) have investigated sorbents based on tin oxide. The sulfidation of tin oxide in the temperature range of 350-500°C takes place according to the reaction:



The sorbent can be regenerated with steam, which yields a 2-3 vol % H₂S containing gas stream, which can be concentrated by steam condensation. In laboratory-scale tests, the sorbent's mechanical durability could be maintained at its initial level in repeated sulfidation and regeneration up to 30 cycles. Recently Nielsen and Sigurdardottir (1995) reported the development of a "sandwich"-type (fixed-bed) sulfidation-regeneration reactor configuration. The reactor includes a SnO₂ layer to take care of bulk desulfurization, and a layer of ZnO is used to reduce the H₂S level at the reactor exit to a few ppmv. Regeneration is conducted at 450-550°C with steam containing a limited amount of oxygen. The system has been tested in laboratory and bench-scale, with simulated gasifier gases.

Wakker (1992) and Moulijn (1996) have tested manganese oxide-based sorbents for hot gas desulfurization. They propose to regenerate this sorbent with steam. The reduction and sulfur capture of different manganese oxides in different support materials (Al₂O₃, WO₃) has been tested with a laboratory-scale test arrangement. Generally the stability of the sorbents and their reactivity in sulfur capture has proven to be good at temperatures up to 525°C. Based on thermodynamics, manganese oxides are also active in the capture of HCl and HF compounds that can be present in gasifier gas in smaller fractions, depending on the Cl/F content of the fuel gasified. Moulijn (1996) presented a "rotating monolith"-type reactor, in which the manganese-based sorbent rotates in between sulfidation and regeneration gas streams, thus enabling continuous regeneration. The process has only been tested at ambient pressure; the pressure sealing between pressurized sulfidation and regeneration gas streams should be demonstrated.

Copper oxide-based sorbents have been developed as alternatives for zinc-based sorbents. Copper oxide is generally reduced to metallic copper in reducing gasifier gas. The thermodynamics of Cu sulfidation are not as favourable as of CuO, thus resulting in an insufficient level of desulfurization. According to Abbasian et al. (1995), the stability upon reduction and, therefore, the desulfurization performance of copper oxide sorbents can be significantly improved by combining CuO with other oxides in a supported form as bulk-mixed metal oxides. The results of Abbasian et al. (1995) indicate that mixed binary oxides of copper with chromium are the most promising sorbents. The sorbent shows an excellent

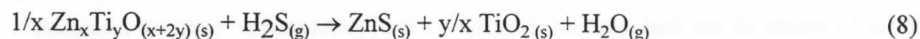
desulfurization efficiency (<10 ppmv) at 750°C in a bench-scale fluidized bed. However, the sulfur removal capacity decreases gradually in the cyclic process, and therefore further testing in the temperature range of 650-750°C is necessary.

Recent literature reviews on regenerable sulfur removal sorbents and process configurations are given by Takematsu et al. (1991), Harrison (1995), van der Ham (1996), and Abbasian (1997).

4.3 Zinc-based sorbents

Much of the recent research has focused upon zinc-based sorbents (Cicero, 1994; Harrison, 1995). ZnO is capable of reducing the H₂S concentration to low levels and is more stable than copper oxide. However, in strongly reducing atmospheres at temperatures above 600°C (Figure 4.2), ZnO is slowly reduced to metallic zinc (Gupta and Gangwal, 1992; Lew et al., 1992 b). The addition of TiO₂ to form the mixed oxide ZnO·xTiO₂ stabilizes the zinc and permits its use at temperatures about 100°C higher than would be possible with pure ZnO (Harrison, 1995). While the addition of TiO₂ does not change the H₂S capture thermodynamics much, it does reduce the sorbent sulfur uptake capacity since TiO₂ will not react with H₂S. In spite of the reduced capacity, most recent pilot-scale studies have used either ZnO·xTiO₂ or the commercial sorbent with the name Z-sorb[®]. Z-sorb[®] consists of ZnO on a porous matrix with nickel oxide promoter, but other details of its composition are proprietary (Gangwal et al., 1994).

The sulfidation reaction of zinc titanate was represented by Lew (1990) and Lew et al. (1992 a) with:



The reactive solid can be Zn, ZnO, or some crystal form of zinc titanate, as used by Lew et al. (1992 a) in equation (8), accounted for by the stoichiometry constant 1/x. During the cyclic sulfidation/regeneration tests, Mojtahedi and Abbasian (1995 a, b) reported the possible formation of different crystalline structures of the zinc titanate, in which case Zn or ZnO can be assumed as the solid reactant. The comparison of the initial sulfidation rates with different mixtures of zinc and titanium oxides is shown in Figure 4.4 (Lew et al., 1992 b).

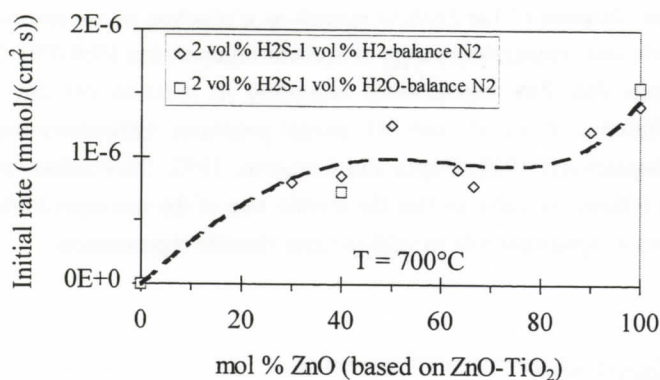


Figure 4.4 Comparison of initial sulfidation rates with zinc oxide and different zinc titanates (according to Lew et al., 1992 b).

In Figure 4.4, the rates are normalized on the basis of sorbent surface area. Generally the sulfidation rates and sulfur capacity of mixed metal oxide materials including inert additives are lower than with single metal oxides, but the stability at high-temperature reducing atmosphere is significantly higher. The sulfidation of zinc oxides and zinc titanates was tested at 800°C by Lew et al. (1992 b) by varying the reducing hydrogen content of the gas from 1 to 20 vol %. Some evidence of the reduction to zinc was found with zinc oxide but the structural effects were minor if the TiO₂ content in the sorbent was high (> 30 wt %).

After sulfidation of the sorbent to a certain level, the sorbent is regenerated. The desirable reaction in zinc titanate regeneration is:



The individual oxides of the sorbent are then assumed (Woods et al, 1989) to produce the original zinc titanium oxide starting material as follows:



At regeneration conditions, undesired zinc sulfate can, however, be formed via the following side reactions (Woods et al, 1989; Siriwardane and Woodruff, 1995):



Figure 4.5 shows the phase diagram of the Zn-S-O system as a function of O_2 and SO_2 partial pressures. At the relevant temperature range of sorbent regeneration (500-750°C), the phase diagram suggests that ZnS regeneration according to reaction (9) can be achieved by using a combination of low O_2 and SO_2 partial pressures. Laboratory-scale results reported earlier (Bagajewicz, 1988; Gupta and Gangwal, 1992; Siriwardane and Woodruff, 1995; Paper IV), however, indicate that the kinetic rate of the reactions (rather than thermodynamics) plays a significant role in sulfided zinc titanate regeneration.

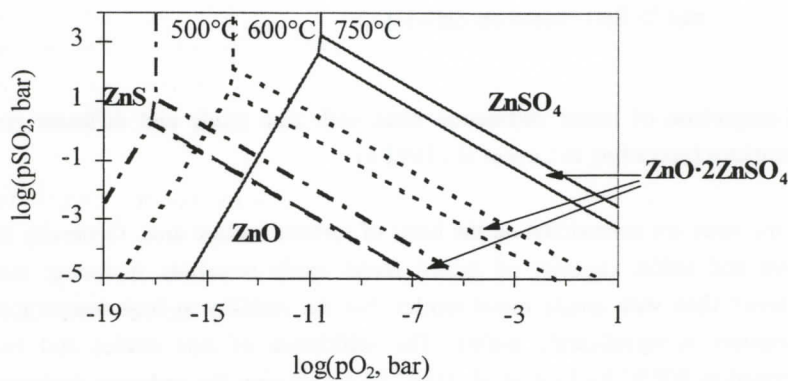


Figure 4.5 Zn-O-S phase diagram (Paper V).

4.4 Regeneration reactor off-gas treatment

As a result of regeneration of a sulfided metal oxide sorbent, a SO_2 - or H_2S -containing gas stream is produced. For further treatment of H_2S , commercially available processes based on Claus reaction may be used. However, for air-blown IGCC plants firing fossil fuels, Claus plants are not economically attractive because of the relatively small amounts of sulfur (below 1 vol %) in the gasifier gas. The methods of treating SO_2 in connection with IGCC processes include (Paper I): 1) recycling to gasifier, which is applicable in cases where a Ca-based sorbent is used for bulk sulfur capture in the gasifier bed, 2) sulfuric acid production and 3) reduction to elemental sulfur. A process for reducing SO_2 to elemental sulfur called the "Direct Sulfur Recovery Process" (DSRP) is developed specially for IGCC applications and is currently being demonstrated at pilot-scale, with promising results (Portzer et al., 1995).

5. EXPERIMENTAL TESTING AND DESIGN OF SULFUR REMOVAL PROCESSES WITH ZINC-BASED SORBENTS

Zinc-based sorbents, such as zinc titanates have been developed and tested in fixed, moving, and fluidized bed type reactor configurations at different scales (Cicero, 1994; Harrison, 1995; van der Ham, 1996). Fluidized bed reactors offer significant potential advantages in IGCC systems over other reactor types because of their ability to control the highly exothermic regeneration involved. A comparison of different reactor configurations for HTHP regenerative sulfur removal is given in Table 5.1. The inherent problems that have lead to the rejection of the idea of using fixed beds are described in detail later in this chapter. Zinc titanate sorbent particle sizes of 50-300 μm are suitable for fluidized bed operation. The manufacture of such sorbents is described in detail by Gupta and Gangwal (1992).

Table 5.1 A comparison of different reactor configurations for HTHP regenerative sulfur removal (Paper I).

	Fixed bed with pellets	Moving bed	Fluidized bed
Heat transfer	poor, resulting in temperature gradients ("hot spots"), sintering, and undesirable reactions	temperature gradients, resulting in sintering and undesirable reactions	efficient; the bed can be assumed as isothermal
Mass transfer	poor due to large particles, results in poor solid utilization, slow reaction rates due to pore diffusion	limitations due to large particles; resulting in poor sorbent utilization, slow reaction rates	efficient mass transfer results in good gas-solid contact, fast reactions
Throughput	low		high
Scale-up	easy	includes uncertainties	includes uncertainties
Steady-state operation	difficult due to sulfidation/regeneration cycling	operation at pilot-scale has been reported (Ayala et al., 1995)	continuous, steady-state operation possible due to sorbent circulation
Exit gas filtering	not needed	might be needed	filtering required due to sorbent elutriation
Valve requirement	many high temperature and pressure (HTHP) mechanical parts required	requires HTHP valves	number of moving mechanical parts can be minimized
Demonstration	long-term pilot-scale operation has not been demonstrated	commercial-scale demonstration under work (Mc Daniel et al., 1997)	demonstrated at pilot-scale in Finland (Salo et al., 1995) and in Japan (van der Ham, 1996)

Figure 5.1 shows clearly that, even at the relatively high temperature, the sorbent consistently reduces the H₂S content of simulated gasifier gas from 11400 ppmv to below 20 ppmv before breakthrough. The sulfur capacity of the sorbent at a breakthrough of 500 ppmv H₂S in reactor exit ranged from 12.6 wt % in cycle 1 to 5.8 wt % in cycle 100. Most of the decline in sulfur capacity occurred during the first 50 cycles and stabilized somewhat thereafter. The drop in sulfur capacity was found to correlate with a decrease in sorbent internal surface area and pore volume, which is in agreement with the results of Mojtahedi and Abbasian (1995 a,b). The analysis of Zn and Ti contents did not show any zinc loss. The reason for some of the sorbent reactivity loss in cycling was believed to have come from the formation of zinc silicate due to the contact with the fluidization grid (distributor) material with 15 % silica. Since the sorbent properties seem to change in continuous sulfidation-regeneration cycling, an important question in the design of the large-scale sulfidation reactor is, what are the stabilized properties (reactivity and capacity) that should be considered in long-term continuous use. This question will be discussed in the next chapter.

Khare et al. (1995) tested their Z-sorb[®] sorbent in the bench-scale fluidized bed reactor with the same sulfidation-regeneration cycling procedure as used earlier by Gupta and Gangwal (1993). Z-sorb[®] consists of ZnO on a porous matrix with nickel oxide promoter, but other details of its composition are proprietary (Gangwal et al., 1994). The sulfidation temperature used was 540°C at 20 bar with 5000 ppmv H₂S in the incoming simulated gasifier gas. The total number of cycles accomplished was 50. Almost complete removal of H₂S (to nearly zero ppmv) was achieved in each sulfidation cycle before sulfur breakthrough. The estimation of the sorbent utilization indicated that essentially 100 percent of the sorbent theoretical sulfur loading capacity was utilized over the first 10 cycles. This capacity then decreased gradually to 50 percent after 50 cycles. Even though these results are better than those obtained at corresponding temperature with zinc titanates (Mojtahedi and Abbasian, 1995 a), the decline of sorbent properties in cycling indicates that there is still room for improvement for both zinc titanate and Z-sorb[®] sorbents.

5.1.2 Regeneration

Bagajewicz (1988) studied the regeneration of high-surface-area ZnO particles ($d_p \approx 600\mu\text{m}$), using pure ZnS (99.9 wt-%) in an atmospheric thermogravimetric apparatus, at temperatures 650-700°C. It was concluded that the oxidation of ZnS to ZnO follows the direct route according to reaction (9), with no intermediate compounds. Bagajewicz suggested that the ZnS regeneration rate (as a function of solid conversion) passes through a maximum, as a result of increasing available reactive surface area of the solid. Zinc sulfate or oxysulfate formation was found to be caused by secondary reactions with freshly formed ZnO. The experiments yielded very low reaction rates for these secondary

reactions, but some differences were found between fresh and regenerated ZnO, which were attributed to a changing intra-particle morphology of the ZnO particles.

Woods et al. (1989) studied the regeneration of zinc titanate pellets ($d_p \approx 4.8$ mm) containing ZnS at temperatures 680-760°C, mainly at ambient pressure. The rate of ZnS regeneration was found to increase with increased temperature, and the test data showed that regeneration kinetics are more sensitive to temperature than sulfidation kinetics are, which agrees with the findings of Bagejevicz (1988). An increase in O₂ from 1 to 8 vol % concentration increased the rate of regeneration, with no sign of ZnSO₄ formation. It was stated that part of the concentration effect may have been due to an increase in temperature as a result of the exothermic reaction in a large pellet. Although the regeneration reaction rate was shown to be dependent on gas temperature and O₂ concentration, no kinetic parameters nor the order of O₂ were reported. An increase in total pressure from 1.013 bar to 20 bar (with increasing O₂ partial pressure) decreased the regeneration rate, which was attributed to the decrease of mass transfer coefficients with pressure for the gas. No evidence of ZnSO₄ formation was found in any of the tests. The change in regeneration reactivity of the ZnS-containing sorbent was found to be negligible after 4 consecutive sulfidation/regeneration cycles.

Siriwardane and Woodruff (1995) studied the interaction of oxygen with zinc sulfide samples by FTIR. They suggest that, at 550-650°C, the reactions in regeneration follow paths (9) or (12), which is in agreement with the findings of Bagajewicz (1988). At temperatures 550-650°C they found that gaseous SO₂ according to reaction (9) was the initial product, which was then adsorbed by ZnO to form sulfate in the presence of oxygen (reaction (12)) at oxygen partial pressures above 0.05 mbar. Several forms of adsorbed SO₂ on the solid surface were detected at temperatures 600°C and 650°C. Zinc sulfate started to form after longer exposures, which, in agreement with Bagajewicz (1988), indicates that the overall rate of reaction (12) is much lower than that of reaction (9). After evacuation of the oxygen from the sample, the sulfate started to decompose. The effect of elevated total pressure was not studied.

Sofekun et al. (1996) performed an analysis of the oxidation of sulfided ZnO particles in a TGA between 548 and 630°C with different oxygen concentrations. It was found that, in the presence of external mass transfer effects, an oxysulfate intermediate ($2\text{ZnSO}_4 \cdot \text{ZnO}$) was formed (see Figure 4.5). No zinc sulfates were formed when the flow rate was chosen such that the mass transfer effect was eliminated. On the basis of the ZnS regeneration data, different forms of reaction rate equations were determined, which will be studied in detail later in this text.

Mojtahedi et al. (1996) performed regeneration tests with sulfided zinc titanate samples in a TGA. The inlet gas consisted of SO_2 , O_2 , and N_2 at compositions relevant for a large-scale regeneration reactor. In each TGA test run, the 50 mg zinc titanate samples were first sulfided in gasifier gas at 550°C containing 1.2 vol % H_2S for 60 min. Regeneration of the sulfided samples was then started at a low temperature ($400\text{--}475^\circ\text{C}$), and the temperature was increased stepwise up to 775°C . The results of these testing are used directly in the regeneration reaction rate constant parameter determination in Paper V of this thesis.

Yrjas et al. (1996, Paper IV) performed regeneration of sulfided zinc titanate samples at 20 bar pressure and $700\text{--}750^\circ\text{C}$ using different partial pressures of O_2 in the inlet gas. The formation of sulfate could be observed on the basis of the changes in weight decrease rate during regeneration with different O_2 partial pressures. When plotting the conversion of zinc sulfide (in sulfided zinc titanate) to zinc oxide, with different O_2 partial pressures, peculiar forms of "s-shaped" curves were obtained, shown in Figure 5.2

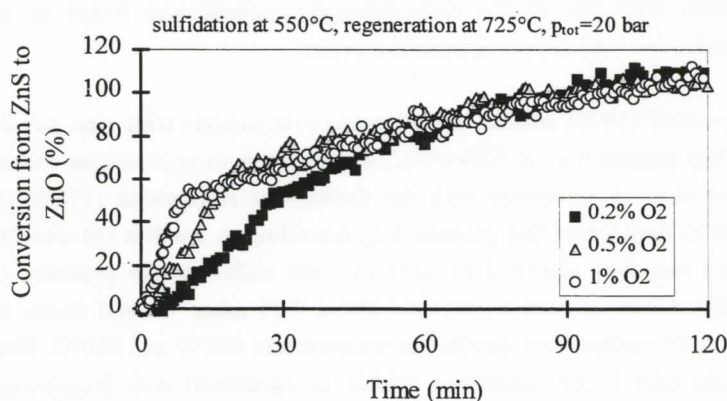


Figure 5.2 Regeneration of sulfided zinc titanate to zinc oxide at 725°C , 20 bar, in the PTGA, with O_2 partial pressure as a parameter (Paper IV).

As the most probable explanation to the form of the curves it was thought that the concentration of SO_2 in the sulfided zinc titanate sample changes locally, thus making the formation of ZnSO_4 possible. At lower regeneration conversions (0-30 mol %), ZnO and some ZnSO_4 are formed simultaneously. At higher molar conversions ZnO is formed as a result of both SO_2 release (from ZnS) and ZnSO_4 decomposition: the combined rate of these two reactions are significantly lower than the ZnO formation rate at lower conversions. The results of the PTGA tests are reported and analyzed in more detail in Papers IV and V.

In the determination of the kinetic parameters of sulfided zinc titanate regeneration (Paper V) the formation of sulfate could be observed from the weight increase of the ATGA sample when exposing the sulfided sample to O_2 and SO_2 gases. The experimental results with probable sulfate formation were omitted from further analysis. The PTGA results of Paper IV indicate that when SO_2 is removed, the sulfate formed via reaction 12 starts to decompose. This observation, in connection with the observations of Siriwardane and Woodruff (1995), indicates that, if either of the gaseous reactants SO_2 and O_2 , necessary for sulfate formation are not present, sulfate formation is not possible. This conclusion will be used in connection with the evaluation of sulfate formation in pilot-scale tests in Paper VI.

5.2 Pilot-scale tests

Figure 5.3 shows a flow diagram of the moving bed concept, as developed by General Electric (Ayala et al, 1995), for high temperature gasifier gas desulfurization.

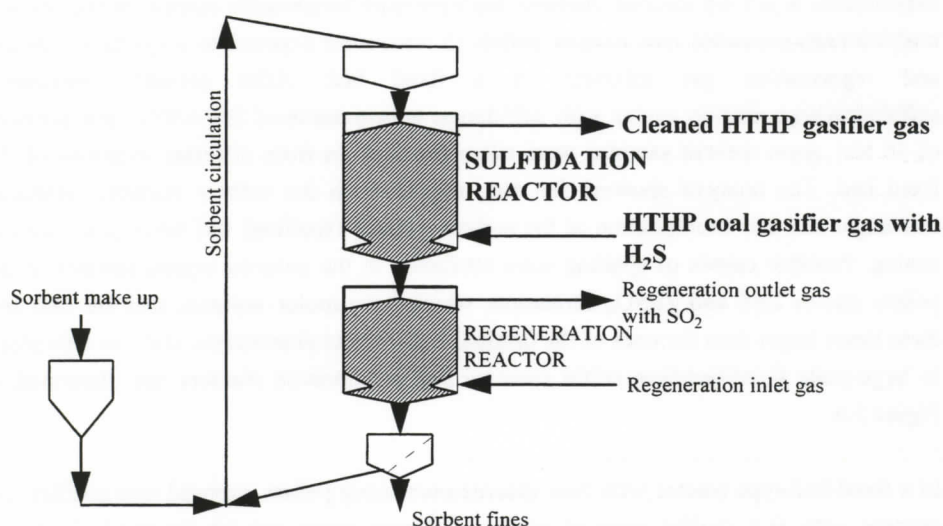


Figure 5.3 Simplified drawing of the GE moving-bed, high-temperature desulfurization process (according to Ayala et al., 1995).

In the GE's moving-bed sulfidation reactor, the zinc-based sorbent moves slowly downwards by gravity, countercurrently to the fuel gas flowing upwards. Sulfided sorbent material is removed from the absorber and fed to the top of the regeneration reactor, which is also a slowly-moving bed. Regenerated sorbent is recycled to the top of the absorber. In the moving-bed regeneration reactor, due to poor mixing of gases and solids, the

temperature control of exothermic reactions has been difficult, and therefore a significant amount of zinc sulfate has been formed, making a part of the sorbent inaccessible for sulfur capture (Gal et al., 1994). Also, because of high levels of SO_2 and steam, large amounts of sulfuric acid have formed causing corrosion in the low-temperature parts of the process. Much improvement to the mechanical and control system performance has been made in order to achieve stable operation with the process in continuous mode (Gal et al., 1994, Ayala et al., 1995). Reusable zinc-based mixed metal oxide sorbents, such as zinc titanate and Z-sorb[®], have been developed and tested for this process. Z-sorb[®] (Version III) lost more than 50 % of its reactivity and sulfur absorption capacity in about 200 hours of pilot plant testing. Better results have recently been obtained with zinc titanates in test runs lasting several hundred hours of continuous operation, with low levels of H_2S (below 20 ppmv) in the purified gas at reactor exit (Ayala et al., 1995).

In connection with the Pinon Pine Power IGCC project, the M. W. Kellogg company was developing a regenerable sulfur removal process based on fixed-bed reactors (Mei et al., 1993). To select suitable sorbents for this application, Mei et al. (1993) conducted experiments in a 5 cm internal diameter high-pressure bench-scale reactor. In the reactor, molybdenum-promoted zinc titanate pellets (5 mm) were exposed to a synthetic gasifier and regeneration gas mixtures in a fixed bed. After several consecutive sulfidation/regeneration cycles with sulfidation temperatures of 550-650°C and pressure of 10 bar, spent sorbent samples were taken for analysis from different locations of the fixed bed. The analysis showed that zinc migration to the sorbent surface, elemental rearrangement and decrepitation at the sorbent surface (spalling) had taken place during testing. Possible causes of spalling were attributed to the induced crystal stresses in the pellets due to ZnS and ZnSO_4 formation, which have molar volumes that are two and three times larger than the ones of the original ZnO . These phenomena, that can take place in large-scale fixed-bed-type sulfur removal and regeneration reactors, are illustrated in Figure 5.4.

In a fixed-bed-type reactor with zinc titanate-containing pellets exposed into gasifier gas mixture with H_2S (sulfur removal mode), different zones can be observed (Flytzani-Stephanopoulos, 1996). The sorbent pellets that are closest to the gasifier gas inlet are totally reacted, and a zone where sulfur capture takes place comes after that. The sorbent pellets located towards the gasifier gas exit are not exposed to H_2S at all. Instead, zinc oxide in the zinc titanate pellets can reduce to elemental zinc, which migrates to the sorbent surface, thus causing elemental rearrangement (decrepitation) (Mei et al., 1993). In regeneration mode, in the part of the bed which contains sorbent pellets with structural changes, dense ZnS and ZnSO_4 formation (Mei et al., 1993) can take place, which leads into cracking and spalling of the sorbent particles.

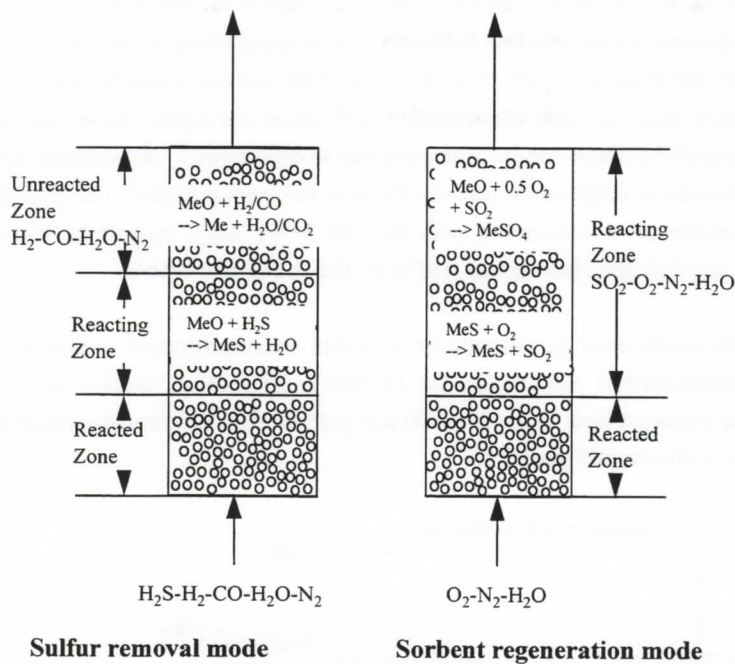


Figure 5.4 The phenomena that can take place in fixed-bed-type sulfur removal and sorbent regeneration reactors (according to Flytzani-Stephanopoulos, 1996).

Since a moving-bed-type reactor is actually a fixed-bed reactor with slow downward motion of the sorbent pellets by gravity (Ayala et al., 1995), the phenomena reported above for fixed beds may explain, at least partly, the problems reported in testing of moving beds.

Due to the inherent problems observed with fixed beds, M.W Kellogg Company started to develop a hot gas desulfurization system based on transport-type fluidized bed sulfidation and regeneration reactors (Campbell and Henningsen, 1995). The transport reactor uses sorbent particles with mean particle size below 100 μm and operates at velocities 10-20 times higher than bubbling fluidized beds, such as presented in Papers VI and VII. The authors claim that very high sulfur removal efficiencies have been achieved with simulated gasifier gas in bench-scale tests. The use of undiluted air for regeneration has resulted in regeneration off-gas with 4-7 times higher SO_2 content than that reported in Paper VII.

The use of zinc-based sorbents with relatively low reaction rate (Figure 4.3) in transport-type reactors can be a matter of concern. Due to the high voidage in a transport-type reactor (about 95 %), the sorbent bed inventory in sulfidation is extremely low. Therefore, the regeneration of the sorbent has to be almost perfect in order to keep the sorbent sulfur

content at low levels in the sulfidation reactor, which then makes the sulfur removal rate high enough to compensate for the low bed inventory. Mechanical issues to be resolved in terms of operation of the process as part of an IGCC process include pressure sealing of sorbent circulation pipe lines between high-pressure sulfidation and regeneration reactors and elimination of possible sorbent escape (attrition) due to high-velocity fluidization and circulation. No pilot-scale or larger-scale test results have yet been reported. The process is about to be demonstrated in connection with the 100 MW_e IGCC project by Sierra Pacific Company (Campbell and Henningsen, 1995) by the end of this decade.

Enviropower Inc. (the predecessor of Carbona Inc.) carried out experimental testing with two side by side fluidized-bed reactors at the 15 MW_{th} pilot plant, employing two different zinc titanate sorbents, both in the 100-300 μm particle size. A schematic diagram of the reactor system is shown in Figure 5.5.

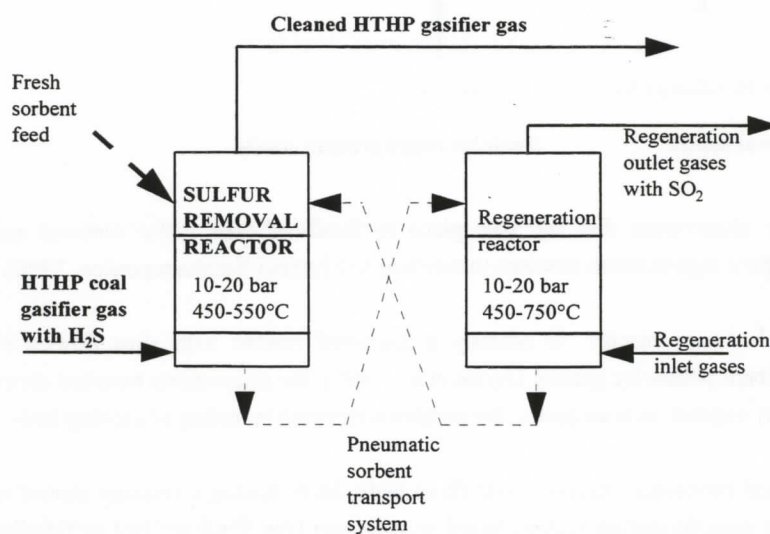


Figure 5.5 Schematic diagram of the pilot-scale fluidized bed sulfur removal and sorbent regeneration test rig (Paper VI).

In the beginning of pilot-scale test runs, a batch of fresh zinc titanate sorbent was fed into the sulfur removal reactor chamber. The H₂S-containing coal gasifier gas then fluidized the sorbent bed, causing sulfur removal (according to reaction 8) to take place at 450-550°C and 10-20 bar. During continuous operation, the ZnS-containing sorbent (as a result of reaction 8) was transported pneumatically from the sulfur removal reactor to the regeneration reactor and regenerated at 600-750°C and 10-20 bar, thus releasing gaseous SO₂ (via reaction 9). The regenerated sorbent was then transported back to the sulfur removal reactor.

Figure 5.6 shows examples of the operation performance of the sulfur removal and sorbent regeneration reactors at high temperature and pressure. The detailed results of these pilot-scale tests are presented in Paper VII. The test results showed that very high sulfur removal efficiency (up to 99 %) can be achieved with the bubbling fluidized-bed-type sulfidation reactor. In a bubbling fluidized bed, the voidage and bed inventory are significantly different from those in a transport-reactor-type fluidized bed, thus making it possible for a sorbent with moderate sulfur removal rate to produce high sulfur removal efficiency. In the pilot-scale tests, the gas from coal gasification contained impurities such as dust, alkali and trace metals, hydrogen chloride, ammonia, and others. The contact with this gasifier gas for 5-6 days of continuous operation had no detrimental effect on the sorbents' physical or chemical properties. Upon regeneration, a gas stream containing SO₂ was produced, with no formation of undesirable zinc sulfate.

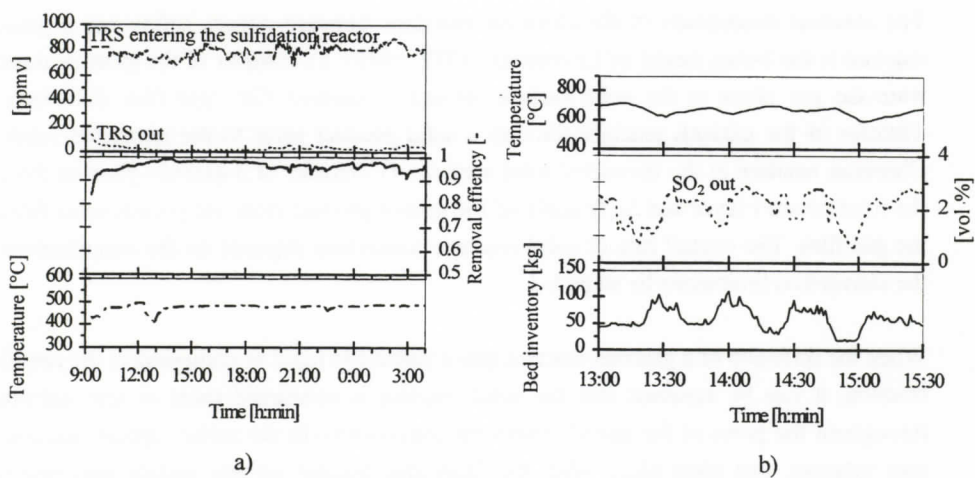


Figure 5.6 Examples of the operation performance values of the pilot-scale a) sulfur removal and b) regeneration fluidized bed reactors with zinc titanate sorbent (D) at 12-14 bar (Paper VII). (TRS = Total Reduced Sulfur: mainly H₂S with some COS).

6. DESIGN AND MODELING OF THE SULFUR REMOVAL AND SORBENT REGENERATION REACTORS

6.1 Solid conversion models

A reliable solid conversion model for the gas-solid reaction, together with reactor mass and energy balances, can be used to predict the performance of large-scale sulfidation and regeneration reactors. For fluidized bed sulfidation reactor modeling purposes, it is desirable to have a gas-solid reaction model with the following properties: 1) the model should be able to describe the rate of gas-solid reaction with a minimum of numerical iteration and still take the sorbent's physical properties into account; 2) it has to have a minimum number of adjustable parameters; 3) the adjustable parameters should have a logical dependence on process variables like temperature and pressure.

The classical description of the chemical reactions between porous solids and a gaseous reactant is the 5-step model of Levenspiel (1972, 1989): 1) Transfer of the gaseous reactant from the gas phase to the solid surface through a stagnant film (gas film diffusion); 2) Transfer of the gaseous reactant through a solid product layer to the unreacted solid; 3) Chemical reaction at the unreacted solid surface; 4) Transfer of a gaseous product through the solid product layer and 5) Transfer of the gaseous product from the porous solid through the gas film. The overall rate of solid reactant conversion depends on the contributions of the conversion limitations by steps 1-5.

When the diffusion of a gaseous reactant into a particle is rapid as compared to the chemical reaction, it can be assumed that the solid reactant is consumed more or less uniformly throughout the pores of the particle (uniform conversion). In the sulfur capture reaction by zinc titanates, this takes place when the fresh zinc titanate sorbent surface gets into first contact with gaseous H_2S (reaction 8). The same can be assumed to take place with sulfided zinc titanate in reaction with gaseous O_2 (reaction 9). The following expression of the uniform conversion model was used to describe the conversion rate of the solid zinc sulfide in reaction (8) (Gupta and Gangwal, 1992), and zinc oxide, in reaction (9) (Mojtahedi et al., 1996):

$$R_s = - \frac{dC_s}{dt} = k C_g C_s \quad (13)$$

where R_s is the molar rate of the conversion of solid reactant (ZnO, ZnS) to solid product (ZnS, ZnO) (mol solid/(cm³ solid s)), C_s , the concentration of solid reactant (mol solid/(cm³ sorbent)), C_g , the concentration of gaseous reactant (H_2S , O_2) (mol gas/(cm³ gas)), and k , the reaction rate constant (cm³ gas/(mol gas s)). The activation energy determined for the sulfur

capture reaction by several zinc titanates (Gupta and Gangwal, 1992) was 58 - 71 kJ/mol, which, according to Gupta and Gangwal, indicated that the sulfidation reaction is controlled by intrinsic reaction kinetics rather than external or pore diffusion. This data is, however, not in agreement with the other data used in this thesis. Lew (1990) reported an activation energy of 38.9 kJ/mol for the initial sulfidation reaction rate, and Yrjas et al. (1996), 33 kJ/mol. The activation energy on the basis of the ATGA sulfidation data in Paper II is about 25 kJ/mol. The data of Lew (1990) is applied in the reactor modeling, Paper III of this thesis.

An essential characteristic of gas-solid reactions like sorbent sulfidation, where a solid product is produced, is the changing internal structure of the particle. During conversion, a product layer gradually builds up, separating the solid reactant from the gas phase (Zevenhoven et al, 1996). Due to this, intra-particle mass transport is strongly affected by the progress of conversion. Several models to describe the combined effect of chemical kinetics and formation of solid product layer on rate of gas-solid reaction have been developed (Zevenhoven, 1994; Zevenhoven et al, 1996; Lew, 1990; Fenouil and Lynn, 1995). However, the computational complexity can become a problem when these models are implemented into a reactor model. Mojtahedi and Abbasian (1995 b) found that a simple first order rate expression such as presented in equation (13) cannot adequately describe the sulfidation reaction rate with zinc titanates, which is in agreement with the results of Lew (1990) and Lew et al. (1992 a). They used a two-parameter rate expression for fitting the experimental data:

$$\frac{dX_s}{dt} = k(X_{\max} - X_s)C_{H_2S} \quad (14)$$

where the parameter X_{\max} represents the maximum extent of conversion of the solid zinc titanate in sulfidation and X_s is a fractional conversion of the solid reactant. It should be noted that, in the absence of diffusion limitations inside the solid reactant, the value of X_{\max} is 1 and equation 14 can be directly derived from equation 13. Mojtahedi and Abbasian (1995 b) determined the values of X_{\max} (lower than 1) by empirical fitting of the two-parameter model in equation 14 into test results. The parameter values were used as a tool for describing and predicting possible effects of the sulfur capacity loss on fresh zinc titanate replacement rate in consecutive sulfidation/regeneration cycling.

Although equations 13 and 14 are simple and easy to use, they do not satisfy the model selection criteria of taking the sorbent physical properties into account, which should be the case in sulfidation with zinc titanates, in order to compare parameter values with sorbents of different quality. Lew (1990) and Lew et al. (1992 a) found that, under conditions free of mass-transfer and pore diffusion limitations, the resistances in sulfidation reaction with zinc

oxides and titanates were due to intrinsic sulfidation kinetics and diffusion through the product layer. The rate of H₂S capture with zinc oxides and titanates in surface reaction (8) was expressed with the following:

$$R_0 = k_{OG} C_{H_2S}^n \quad (15)$$

where R_0 is the initial molar rate of ZnS formation per unit surface area of the solid reactant (mol/(cm² s)) and n is the reaction order, which was found to be 1. In equation 15, the reaction rate is normalized on the basis of the internal surface area of the sorbent. The Arrhenius expressions for the reaction rate constant k_{OG} were found to be $0.013 \cdot \exp(-43.1 \text{ kJ/mol}/(RT))$ (m/s) for ZnO and $0.004 \cdot \exp(-38.9 \text{ kJ/mol}/(RT))$ (m/s) for several zinc titanates in sulfidation (plotted in Figure 4.3). The initial sulfidation reaction rate constants determined in Paper II (based on the ATGA data) appear to be 1.6-2.5 times lower at temperatures of 400-500°C than those presented above. Since the reported values of Lew et al. (1992 b) are measured intrinsic solid phase reactivities, it is suspected in Paper II that the lower values could have been caused by some external diffusional effects in the ATGA tests. In order to minimize the number of adjustable parameters, the values of Lew et al. (1992 b) are applied in reactor modeling of Paper III.

In addition to chemical reaction, the formation of the solid product layer as a function of the zinc titanate conversion in sulfidation reaction was simulated by Lew (1990) and Lew et al. (1992 a), with the overlapping grain (OG) model. In the model, the porous solid is simulated as an assemblage of grains randomly distributed in space with overlapping of the grains permitted. In the case where the solid product occupies more volume than the stoichiometrically equal volume of reactant (as in sulfidation with zinc titanates), i.e., $Z > 1$, pore closure is possible.

The grain size distribution $n(r)$ of the solid zinc titanate reactant was determined with the help of SEM micrographs (Lew, 1990, Lew et al, 1992 a). The internal surface per unit volume ($S_{v,0}$) and porosity (ε_0) of the particle (corrected for overlapping of grains) is determined with the following equations:

$$-\ln(\varepsilon_0) = \varepsilon_{0,x} = \frac{4\pi}{3} \int_{r_{\min}}^{r_{\max}} r^3 n(r) dr \quad (16)$$

$$S_{v,0} = \varepsilon_{0,x} S_{0,x} = \varepsilon_0 4\pi \int_{r_{\min}}^{r_{\max}} r^2 n(r) dr \quad (17)$$

where ε_0 and $S_{v,0}$ are the initial internal porosity (-) and surface area (m^2/g) of the solid from standard laboratory analysis, $\varepsilon_{0,x}$ and $S_{0,x}$ are the corresponding porosity (-) and surface area (m^2/m^3) without correction of overlapping and r_{min} and r_{max} are the minimum and maximum size of grains (m) with grain size distribution $n(r)$. When a uniform grain size distribution is assumed (n_0 grains with diameter r_0), the above equations can be combined to give the initial grain radius (r_0) based on randomly overlapping spherical grains:

$$-\ln(\varepsilon_0) = \frac{4}{3} \pi r_0^3 n_0 \quad S_{v,0} = 4 \pi \varepsilon_0 r_0^2 n_0 \quad (18)$$

$$\rightarrow r_0 = \frac{-3\varepsilon_0 \ln \varepsilon_0}{S_{v,0}} \quad (19)$$

The basic equations of the model are the following:

$$\frac{dr_r}{dt} = \frac{-b k_{OG} C_{Ab}}{1 - \frac{k_{OG}}{D_{pl}} \varepsilon_r r_r^{F_g-1} I} \quad \text{where: } I = \int_{r_p}^{r_r} \frac{dr}{\varepsilon(t') r^{F_g-1}} \quad (20)$$

$$\frac{dr_p}{dt} = -\frac{dr_r}{dt} \left((Z-1) \frac{\varepsilon_r r_r^{F_g-1}}{\varepsilon_p r_p^{F_g-1}} \right) \quad (21)$$

where r_p is the radius of a grain at the surface of the product layer (m) and r_r , the radius at the surface where chemical reaction takes place (these are found with integration over time t) (m), b , the stoichiometry constant, ε_p , the porosity of the grain outer surface (reactant + product), ε_r , the porosity at the reaction surface, F_g , the grain shape factor (1 for plates, 2 for cylinders, and 3 for spheres) and Z , the stoichiometric molar volume ratio of solid product to solid reactant. Thus the solid product layer thickness equals $r_p - r_r$.

The porosity of the solid (product + reactant) is found by:

$$\varepsilon_p = \varepsilon_0 - (Z-1)(\varepsilon_r - \varepsilon_0) \quad (22)$$

and the fractional conversion of the solid reactant to product is:

$$X = \frac{\varepsilon_0 - \varepsilon_p}{(Z-1)(1 - \varepsilon_0)} \quad (23)$$

Lew (1990) and Lew et al. (1992 a) modeled the test data of sulfidation with zinc oxide with the model by assuming the solid particles to consist of spherical overlapping grains. For different zinc titanates (mixtures of zinc oxide and titanium dioxide) a discrete bimodal grain size distribution was used, in which 50 % of the grains in the solid particle were assumed as spherical and 50 % as plate-like grains. In addition, two different porosities had to be included, which were evaluated from SEM analysis.

Another model to describe this phenomenon is the unreacted shrinking core model (USC) with variable effective diffusivity (Zevenhoven, 1994; Zevenhoven et al., 1996). In order to account for the changing internal structure of the particle, a more general version of the USC model is used, where the effective diffusivity is defined as a function of overall particle conversion. In the model, pore diffusion and product layer diffusion are separated. The model has been successfully used for the modeling of sulfidation and sulfation with limestone and dolomite particles (Zevenhoven et al. 1994, 1996).

The USC time-conversion equations for the combination of reaction kinetics and intra-particle diffusion (under negligible external mass transfer limitations) give the following relation between time and overall sorbent conversion:

$$t = \tau_{kin} f_{kin}(X) + \tau_{dif,0} \frac{1+BX}{1+AX} f_{dif}(X) \quad (24)$$

where:

$$f_{kin}(X) = 1 - (1-X)^{\frac{1}{3}} \quad (25)$$

$$f_{dif}(X) = 3 \left(\frac{Z - (1+ZX - X)^{\frac{2}{3}}}{Z-1} - (1-X)^{\frac{2}{3}} \right) \quad (26)$$

$$A = \frac{(1-\varepsilon_0)}{\varepsilon_0} \quad B = \frac{A D_{eff,0} Z}{D_{pl}} \quad Z = \frac{V_{mol, solid product}}{V_{mol, solid product}} \quad (27)$$

$$\tau_{dif,0} = \frac{R_p^2 \rho_{mol,s}}{6 D_{eff,0} C_{Ab}} \quad \tau_{kin} = \frac{R_p \rho_{mol,s}}{k_{USC} C_{Ab}} \quad (28)$$

In equations 25-28 V_{mol} is molar volume (m^3/mol), τ_{kin} , the time-scale parameter for chemical reaction control (s) and $\tau_{dif,0}$, the initial time-scale parameter for diffusion control (s), $D_{eff,0}$, the initial effective diffusivity (m^2/s), D_{pl} , product layer diffusivity

(m²/s), and k_{USC} , reaction rate constant (m/s). More details of this model are given in Zevenhoven et al. (1994, 1996).

The activation energies obtained from ambient pressure TGA tests (Paper II) for the reaction rate constant (26 kJ/mol for k_{OG} or k_{USC}) and for the product layer diffusion coefficient D_{pl} (110 kJ/mol), using the USC and OG models, agree reasonably well with previously reported data (Lew, 1990; Lew et al., 1992). The values found for the reaction rate constant for the USC and OG models differ by more than 2 orders of magnitude due to the fact that the OG model takes into account the internal surface area for the reaction while the USC mode does not. In fact, the USC model approach implies a thick product layer deposited on little surface while the OG model implies a much thinner product layer on a much larger surface. Therefore, it is reasonable to compare the intrinsic reaction rate constants, i.e., based on the reaction per unit surface. In Paper II, the relations between the intrinsic reaction rate constant k' (1/s) and the reaction rate constant k_{OG} or k_{USC} (m/s) are given and related to the reaction surface (m²/m³) by

$$k'_{\text{USC}} = bk_{\text{USC}}S_{\text{USC}} = k_{\text{USC}} \frac{3}{R_p} \quad (29)$$

$$k'_{\text{OG}} = k_{\text{OG}}S_{\text{OG}} \quad (30)$$

where k_{USC} and k_{OG} are the reaction rate constants (m/s) of the USC and OG models and b is a stoichiometry coefficient. The values of the initial reactive surface areas (S_{USC} and S_{OG}) for different zinc titanate sorbents are shown in Table 2 of Paper II. Figure 4 of Paper II shows that the values of intrinsic reaction rate constants obtained from USC and OG models are reasonably close to each other.

The application of the intrinsic reaction rate constant (k') proves that the different approach of USC and OG models on reactive surfaces is the reason for the difference in the model parameters in Paper II. Since, in the OG model, the sulfidation rate is proportional to the reactive internal surface area of the porous particles, it follows the real physical behavior of the sorbent in sulfidation more closely than the USC model. Therefore, the OG model can be preferred in the modeling of the laboratory-scale solid conversion rate data. The USC model with changing effective diffusivity is included because of the possibility of obtaining analytical results without numerical integration, this matching the requirements of a desirable gas-solid reaction model as part of the sulfidation reactor model better than the OG model. As the results of Paper III show, both models can be used for the modeling of a batch fluidized bed reactor, but, because of the advantages of the USC model mentioned, it may be preferred in industrial-scale sulfidation reactor modeling applications.

In order to describe the regeneration reaction of sulfided zinc oxide, Bagajewicz (1988) determined the kinetic parameters for a Langmuir-Hinshelwood-type expression in which the reaction of adsorbed oxygen with the solid is the rate-limiting step:

$$r_1 = k_1 \frac{K_1 C_{O_2}}{1 + K_1 C_{O_2}} \quad (31)$$

where K_1 is the equilibrium constant for the adsorption process (cm^3/mol) and k_1 is the kinetic rate constant ($1/\text{s}$) with the activation energy of 270 kJ/mol . The order of the partial pressure of O_2 in the rate expression was found to be close to 1.

The expression of equation 31 was also applied by Sofekun and Doraiswamy (1996), on the basis of some experimental TGA results and a comprehensive literature survey on the kinetic regimes and controlling regimes in zinc sulfide oxidation at different temperatures. They reported the following correlations for the reaction rate constant k_2 and adsorption equilibrium constant K_1 :

$$k_2 = 4.089 \times 10^{20} \exp(-46110/T) \text{ and } \ln K_1 = 29300/T - 23.54 \quad (32)$$

where the unit of k_2 according to Sofekun and Doraiswamy (1996) is (mol of ZnS/(g of ZnS min)) and K_1 is (cm^3/mol). When applying k_2 , the unit of the reaction rate r_1 in equation (31) is then (mol of ZnS/(g of ZnS min)), respectively. Sofekun and Doraiswamy (1996) found that equation 32 accurately describes the true kinetics of the reaction up to 609°C . For higher temperatures, a simplified power law reaction rate model was applied.

The uniform conversion model (equation 14 with $X_{\max} = 1$) is used in Papers V and VI to describe ZnS reaction with O_2 . The values of the reaction rate constant at laboratory-scale were determined based on the ATGA data. Figure 6.1 shows the laboratory-scale reaction rate data by Sofekun and Doraiswamy (1996), of sulfided zinc oxide, in comparison with corresponding data of sulfided zinc titanate presented in Paper V.

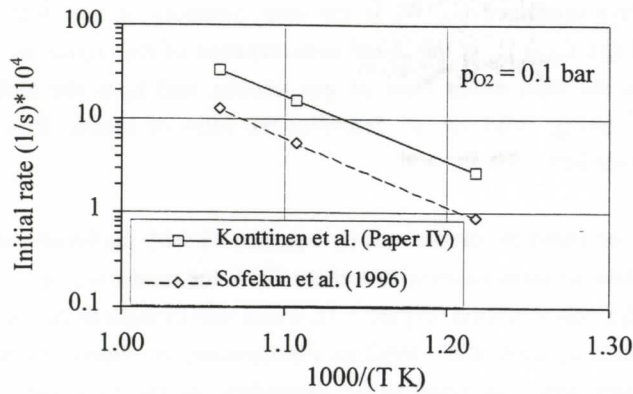


Figure 6.1 The regeneration reaction rate data of sulfided zinc oxide by Sofekun and Doraiswamy (1996) in comparison with the regeneration reaction rate data of sulfided zinc titanate presented in Paper V.

Figure 6.1 shows that, despite the high surface area of 8.5 m²/g of the sulfided zinc oxide (Sofekun and Doraiswamy, 1996), the reaction rates obtained are slightly lower than those obtained with sulfided zinc titanate (2.5 m²/g, Paper V). Mojtahedi et al. (1996) determined an activation energy of approximately 200 kJ/mol for the first order rate constant in sulfided zinc titanate regeneration reaction with O₂. In Paper V, an activation energy of 140 kJ/mol is obtained.

6.2 Fluidized bed reactor models

6.2.1 Simplified models

The basic approach towards the modeling of the chemical performance of fluidized bed reactors is to describe the flow of gas and solids by separate "phases". Usually the reactive gas in its bulk concentration is one "phase", as well as the reactive solid has its own "phase" (Froment and Bischoff, 1990; Kunii and Levenspiel, 1991). Gupta and Gangwal (1992) derived a simple model to describe the sulfidation reaction with zinc titanates in a bench-scale fluidized bed. The basic assumptions behind the model are that gas ("phase") in the reactor follows plug-flow behavior, and solids in the fluidized bed are well mixed. The external mass transfer between gas ("phase") and solid ("phase") is neglected. As a result, the following equation was obtained:

$$y_e^* = \exp(-\alpha_i (1 - X_s)) \quad \text{where} \quad \alpha_i = \frac{W_0 k_i C_{ZnO, t=0}}{G} \quad (33)$$

and y_e^* is the fraction of H_2S unreacted (-), W_0 is the total inventory of zinc titanate sorbent in the fluidized bed (g), $C_{ZnO, t=0}$ is the initial concentration of zinc oxide in the bed (mol/cm^3 solid), G is the total molar flow of gas (mol/s), and k_i is the global reaction rate constant (cm^3 gas/(g solid s)). α_i describes the ratio of kinetic flux to momentum flux in the fluidized bed.

Gupta and Gangwal (1992) compared the predictions by equation 33 with the bench-scale fluidized bed experimental data. In some cases with sorbent ZT-4, the model was not able to predict the sharp rise of H_2S concentration (Figure 5.1), which was thought to be due to diffusional effects (as discussed by Lew et al., 1992 a). Furthermore, the global reaction rate constant k_i in the model was concluded to be dependent on the fluidized bed hydrodynamics (gas-solid contacting). These external and internal diffusional effects were not included in the model.

Mojtahedi and Abbasian (1995 b) used a fluidized bed reactor model based on equation 14 and the same basic assumptions as Gupta and Gangwal (1992). The external diffusional mass transfer effects between gas and solid "phases" in the fluidized bed were lumped into one additional parameter. The results of model predictions with the model were able to explain the experimental results satisfactorily. However, due to the empirical nature of the values for external mass transfer parameter, X_{max} and k' (equation 14) obtained, they cannot be used in other sulfidation reactor design cases.

In Paper III of this thesis, a model is presented where the intra-particle diffusional effects, in addition to sulfidation chemical reaction, can be taken into account as part of a bench-scale fluidized bed sulfidation reactor model. The reactor model is based on the assumption that the concentration and temperature of the zinc titanate particles are uniform at any position of the fluidized bed, but the nonideal flow of gas is modeled as several perfectly mixed tanks in series (Levenspiel, 1972; Levenspiel, 1989; Froment and Bischoff, 1990). The possible effect of the bench-scale fluidized bed hydrodynamics on the mass transfer between gas and solid is assumed not to be significant. The division into N identical horizontal tanks or slices is shown graphically in Figure 1 of Paper III. For each individual slice, the following mass balance should be satisfied (one mole of sulfur gas (H_2S) reacts with one mole of solid zinc (in zinc titanate particle)):

$$\left(\frac{\text{mols of S in}}{\text{time}} \right) \times \text{gas conversion} = \text{mols of Zn} \times \left(\frac{\text{solid conversion}}{\text{time}} \right) \quad (34)$$

By using the symbols presented in Figure 1 of Paper III, this can be rewritten for j :th slice:

$$n_{S,0}(1 - X_{S,1})(1 - X_{S,2}) \dots (1 - X_{S,j})X_{S,j} = \frac{n_{Zn}}{N} \frac{dX}{dt} \quad (35)$$

where $n_{S,0}$ is the sulfur inlet flow (mol/s), $X_{S,j}$; the conversion of sulfur in j :th slice, n_{Zn} , the total amount of zinc in the fluidized bed (mol), X , the overall conversion of solid (zinc) in bed, t , time (s), and N , the number of horizontal slices in series. In equations 34 and 35, the rate of solid conversion can be obtained from the USC and OG models (equations (16)-(28)) by discretizing (producing values of $\Delta X/\Delta t$ as functions of solid conversion). In Paper III, equation 35 is shown to reduce to:

$$\alpha = \frac{X_{S,j}}{1 - X_{S,j}}, \quad \text{where} \quad \alpha = \frac{n_{Zn} \text{ rate}_{Zn}}{N n_{S,0}} \quad \text{and} \quad \text{rate}_{Zn} = \frac{dX}{dt} \quad (36)$$

This form is analogous to the performance equation of the first-order irreversible reaction in a perfectly mixed reactor (Levenspiel, 1972, 1989; Froment and Bischoff, 1990). For the parameter fitting using fluidized bed data at sufficiently high temperatures, the equilibrium limitation of the sulfidation reaction of zinc titanate should be taken into account. For the conversion of gas in reversible reaction in slice j , an equation presented by Levenspiel (1972, 1989) can be applied:

$$\alpha = \frac{M_j + X_{S,eq_j}}{M_j + 1} \left(\frac{X_{S,j}}{X_{S,eq_j} - X_{S,j}} \right), \quad \text{where} \quad M_j = \frac{y_{H_2O,j-1}}{y_{H_2S,j-1}} = \left(\frac{y_{H_2O,0} + y_{H_2S,0}}{y_{H_2S,0} \prod_{i=1}^{j-1} (1 - X_{S,i})} - 1 \right) \quad (37)$$

where X_{S,eq_j} is the conversion gas when at equilibrium concentration and $y_{H_2O,j-1}$ and $y_{H_2S,j-1}$ are the fractional H_2O and H_2S contents entering slice j . $y_{H_2S,0}$ and $y_{H_2O,0}$ are the fractional H_2S and H_2O contents at the bed inlet (-). Equation 37 can be modified to give the conversion of gas in slice j in the reversible sulfidation reaction:

$$X_{S,j} = \frac{\alpha X_{S,eq_j}}{\beta + \alpha}, \quad \text{where} \quad X_{S,eq_j} = 1 - \frac{M_j}{K} \quad \text{and} \quad \beta = \frac{M_j + X_{S,eq_j}}{M_j + 1} \approx 1 \quad (38)$$

In equation 38 K is the equilibrium constant of the sulfidation reaction (-). Because at the test conditions of interest the volume fraction of steam is more than 60 times higher than the volume fraction of H_2S , the term β is assumed to be 1. The volume fraction of H_2S at the bed exit is:

$$y_{H_2S,e} = y_{H_2S,0}(1 - X_{S,1})(1 - X_{S,2}) \dots (1 - X_{S,N}) = y_{H_2S,0} \prod_{i=1}^N (1 - X_{S,i}) \quad (39)$$

Paper III shows that the best results with equation 39 in modeling the experimental fluidized bed data are obtained when N is larger than 3. Thus, a plug-flow model is used instead. An equation that describes first-order reversible reaction in plug-flow reactor (Levenspiel 1972, 1989) is directly applied:

$$\frac{n_{Zn} \text{ rate}_{Zn}}{n_{S,0}} = \frac{M + X_{S,eq}}{M + 1} \ln \left(\frac{X_{S,eq}}{X_{S,eq} - X_{S,e}} \right), \quad \text{where } M = \frac{y_{H_2O,0}}{y_{H_2S,0}} \text{ and } X_{S,eq} = 1 - \frac{M}{K} \quad (40)$$

where $X_{S,e}$ is the total fractional conversion of H_2S at the bed exit and $X_{S,eq}$ the conversion of H_2S when reaching equilibrium concentration. By rearranging equation 40, the volume fraction of H_2S at the bed exit is:

$$y_{H_2S,e} = y_{H_2S,0} \left(1 - X_{S,eq} \left(1 - \exp \left(\frac{-n_{Zn} \text{ rate}_{Zn}}{n_{S,0} \beta} \right) \right) \right) \quad \text{where } \beta = \frac{M + X_{S,eq}}{M + 1} \approx 1 \quad (41)$$

Figure 6.2 b) shows an example of the fit of equation 41 into high pressure fluidized bed sulfidation test results, with the application of USC and OG models in producing the solid conversion rate data (values of parameter rate_{Zn}). Figure 6.2 a) shows the fit of the USC and OG models into high-pressure kinetic test data, with the same kinetic parameters as in Figure 6.2 b). The bench-scale fluidized bed reactor modeling results together with related kinetic parameter values for different zinc titanate sorbents are reported in detail in Paper III.

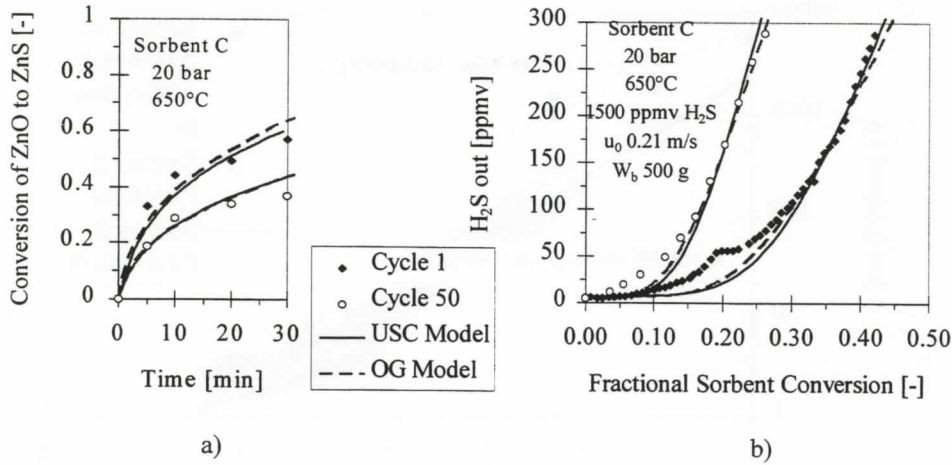


Figure 6.2 USC and OG model fits into a) kinetic test experimental data with 5 g sorbent sample and into b) cyclic test data (500 g sample) in a bench-scale fluidized bed reactor. Data shown for both fresh sorbent "C" (Cycle 1) and used sorbent "C" (Cycle 50) samples (Papers II and III).

An analogical equation to equation 41, the volume fraction of sulfur dioxide (SO_2) at the regeneration reactor fluidized bed exit, is presented in Paper VI:

$$y_{\text{SO}_2, e} = \frac{y_{\text{O}_2, 0}}{1.5} (1 - \exp(-\alpha)), \quad \text{where} \quad \alpha = \left(\frac{1.5 n_{\text{ZnS}} k_f (1 - X_{\text{ZnS}})}{V_{\text{gas}}} \right) \quad (42)$$

where $y_{\text{O}_2, 0}$ is the initial volume fraction of oxygen (-) and $y_{\text{SO}_2, e}$, the volume fraction of SO_2 at the regeneration reactor exit (-), n_{ZnS} , the total molar amount of sulfur in the regeneration reactor (mol), k_f , the global reaction rate parameter according to the uniform conversion model ($\text{cm}^3/(\text{mol s})$) including chemical reaction and possible mass transfer effects, X_{ZnS} , fractional conversion of zinc sulfide, and V_{gas} , regeneration inlet gas volumetric flow (cm^3/s). The illustration of the symbols used in equation 42 can be found in Figure 2 of Paper VI.

In Paper VI, equation 42 is applied to the determination of regeneration reaction rate constant parameter values directly from the experimental pilot-scale regeneration reactor data. Parameters $y_{\text{O}_2, 0}$, $y_{\text{SO}_2, e}$, n_{ZnS} , X_{ZnS} , and V_{gas} are determined from the measurements, and equation 42 is rearranged to give the global reaction rate constant k_f at different temperatures. Figure 6.3 gives a comparison of the regeneration reaction rate constant data obtained from high pressure pilot-scale fluidized bed reactor tests (Paper VI) and laboratory-scale ATGA tests (Paper V).

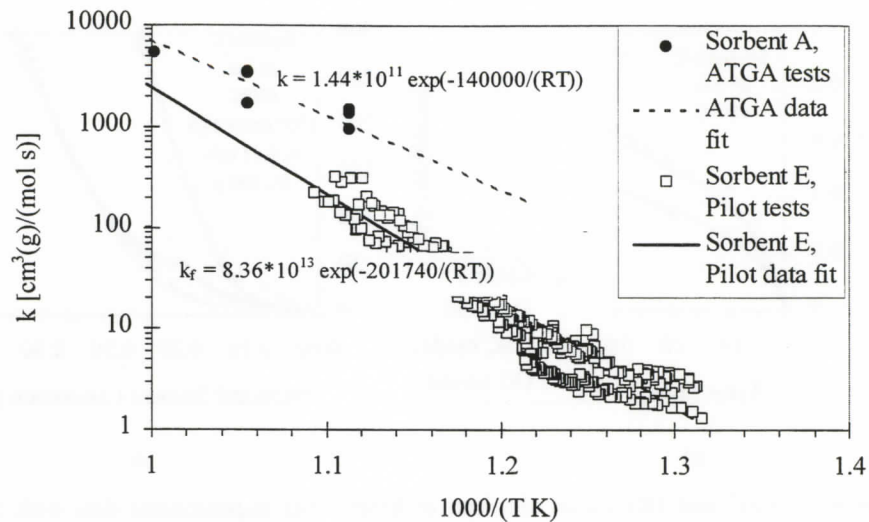


Figure 6.3 Arrhenius plot of the regeneration reaction rate constant data obtained from laboratory-scale ATGA tests (Paper V) and pilot-scale fluidized bed regeneration reactor tests (Paper VI).

The apparent activation energy for the pilot-scale global reaction rate constant (k_f) is 200-210 kJ/mol for two different sulfided zinc titanate sorbents, which is higher than that obtained from laboratory-scale results (Paper V): 140 kJ/mol. As Figure 6.3 shows, the values of the reaction rate constants from pilot-scale are about one order of magnitude lower than those from laboratory-scale. Because of the difference in the reaction rate parameters, a sensitivity analysis of a large-scale steady-state regeneration reactor model is performed in Paper VI, using rate constants obtained from pilot-scale in comparison with constants from laboratory-scale. The equation for the large-scale steady-state regeneration reactor model is:

$$X_{ZnS} = \frac{F_{O_2,0}(1 - \exp(-\alpha))}{1.5 F_{ZnS,0}} \quad \text{where} \quad \alpha = \left(\frac{1.5 F_{ZnS,0} (1 - X_{ZnS}) \tau_{bed} k_f (1 - X_{ZnS})}{V_{gas}} \right) \quad (43)$$

where $F_{O_2,0}$ and $F_{ZnS,0}$ are the initial molar flows of O_2 and ZnS (mol/s) and τ_{bed} is the regeneration reactor fluidized bed residence time parameter (s). Figure 6.4 shows an example of the results of the regeneration reactor model sensitivity analysis. More results are shown in Paper VI.

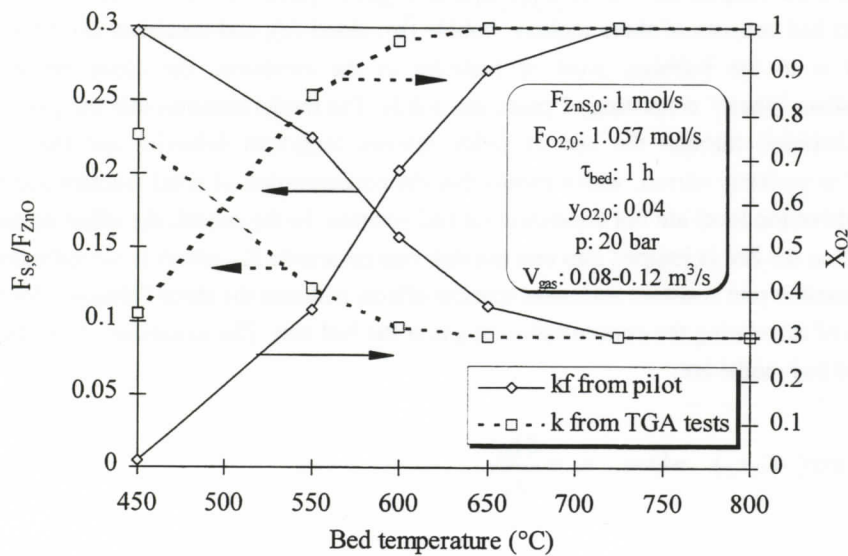


Figure 6.4 The results of a sensitivity analysis of a large-scale continuously-operated fluidized bed reactor model in sulfided zinc titanate regeneration. The regeneration level ($F_{S,e}/F_{ZnO}$) and fractional conversion of O_2 (X_{O_2}) are plotted as a function of reactor bed temperature (Paper VI).

The results in Figure 6.4 show that differences in the large-scale regeneration reactor model performance with different reaction rate parameters can be observed at temperatures below 700°C . At practical steady-state operation temperatures of 700 - 800°C , these appear not to be significant since the rate of sulfided zinc titanate regeneration is not controlled by reaction kinetics. With respect to the scale-up factor of 10^6 between laboratory- and pilot-scale results, the model (equation 43) and its parameters at temperatures 550 - 650°C give a performance window of a large-scale regeneration reactor that can be used as guideline information.

6.2.2 Some specific issues in large-scale reactor modeling

In the modeling of large-scale fluidized bed reactors, there are some specific phenomena whose effect in the models of Papers III and VI are assumed not to be significant. These phenomena include the possible mass transfer limitations due to nonideal flow patterns of gas and solids and the residence time distribution (RTD) of solid particles in a large-scale fluidized bed (Froment and Bischoff, 1990; Kunii and Levenspiel, 1991). Appendix VIII of this thesis presents a detailed study of evaluating the significance of these phenomena in large-scale sulfidation and regeneration fluidized-bed reactor modeling. This study is briefly reviewed below.

Kunii and Levenspiel (1991) have introduced a three-”phase” model, where the dense fluidized bed consists of three regions: bubble (b), cloud (c), and emulsion (e). Most of the gas is in the bubbles, most of particles in the emulsion, the cloud being an intermediate ”phase” consisting of gases and solids. The model assumes that the gas flow (all in bubbles) through the bed of solids follows plug-flow behavior and the solid ”phase” is perfectly stirred, which means that the concentration of solid reactant and the solid conversion level are not dependent on bed position. In the model, the effect of three ”phases” in the bed is lumped into one reaction rate parameter K_f , which is a combination of the reaction rate constant and mass transfer effects between the three ”phases”, for the purpose of calculating the concentration of gas at the bed exit. The equations of the dense fluidized bed model are:

$$\frac{y_{A,o}}{y_{A,0}} = \exp(-K_f \tau_f) \quad \text{where} \quad \tau_f = \frac{\delta L_f}{u_0} \quad (44)$$

$$\text{and } K_f = \left(\gamma_b K_r + \frac{1}{\frac{1}{K_{bc}} + \frac{1}{\gamma_c K_r + \frac{1}{\frac{1}{K_{ce}} + \frac{1}{\gamma_e K_r}}}} \right) \quad (45)$$

where $y_{A,0}$ is the initial fraction of the reactant gas A and $y_{A,o}$, the corresponding fraction at dense fluidized bed exit; L_f is the height of the fluidized bed (m), u_0 is the gas superficial velocity (m/s), δ is the fraction of bed in gas bubbles (-), τ_f is the gas residence time parameter (s), and γ_b is the ratio of volume of solids in bubble per total bubble volume, γ_c in cloud and γ_e in emulsion, respectively. K_r is the reaction rate constant (1/s), K_{ce} is the mass transfer constant from cloud to emulsion (1/s), and K_{bc} , the mass transfer constant between bubble and cloud ”phases” (1/s). The procedure for the determination of the parameters in equations 44 and 45 is given in the literature (Levenspiel, 1989; Kunii and Levenspiel, 1991) and is presented in more detail in Appendix VIII.

Another model for the freeboard zone (above the dense fluidized bed) is applied in Appendix VIII with the following equations (Kunii and Levenspiel, 1991):

$$\ln \frac{y_{A,o}}{y_{A,e}} \cong \frac{(1 - \varepsilon_f) K_r}{u_0 a} \left((1 - \exp(-a z_{FB})) - \frac{1 - \eta_{DB}}{1 + \frac{a'}{a}} (1 - \exp(-(a + a') z_{FB})) \right) \quad (46 \text{ a,b})$$

$$\rightarrow X_{A,FB} = 1 - \exp\left(-\ln \frac{y_{A,o}}{y_{A,e}}\right)$$

where z_{FB} is the height of the freeboard (m), ε_f , voidage of the dense fluidized bed (-), a and a' , hydrodynamic decay constants (1/m), η_{DB} , contact efficiency parameter between reactant gas and solids in the dense fluidized bed (-); $y_{A,o}$ is the volume fraction of gas at the top of the dense fluidized bed (-) and $y_{A,e}$ at the exit of the freeboard, respectively. $X_{A,FB}$ is the fractional conversion of gas A (-) in the freeboard. The total conversion of gas A over dense fluidized bed and freeboard is then:

$$X_{A,tot} = 1 - (1 - X_{A,DB})(1 - X_{A,FB}) \quad (47)$$

where the conversion of gas in the dense bed ($X_{A,DB}$) can be obtained from equation 44. The equations 44-46 were first developed for modeling of a catalytic fluidized (Kunii and Levenspiel, 1991). In the modeling of the non-catalytic regeneration reaction in a large-scale fluidized bed, the reaction rate parameter K_r is determined in Appendix VIII with the following conversion:

$$1 - X_{O_2} = \exp(-K_r \tau_0) = \exp(-\alpha) \rightarrow K_r = \frac{\alpha}{\tau_0} \quad (48)$$

where τ_0 is the gas residence time parameter (s) determined at plug-flow conditions independent of bed voidage and particle physical properties when particle internal diffusion effects do not intrude (Kunii and Levenspiel, 1991). X_{O_2} is the fractional conversion of oxygen in regeneration reaction (-). α is the dimensionless reaction rate group parameter determined in Paper VI.

A comparison of the modeling results with different versions of large-scale fluidized bed models (using equations 47 and 48) is presented in Figure 6.5.

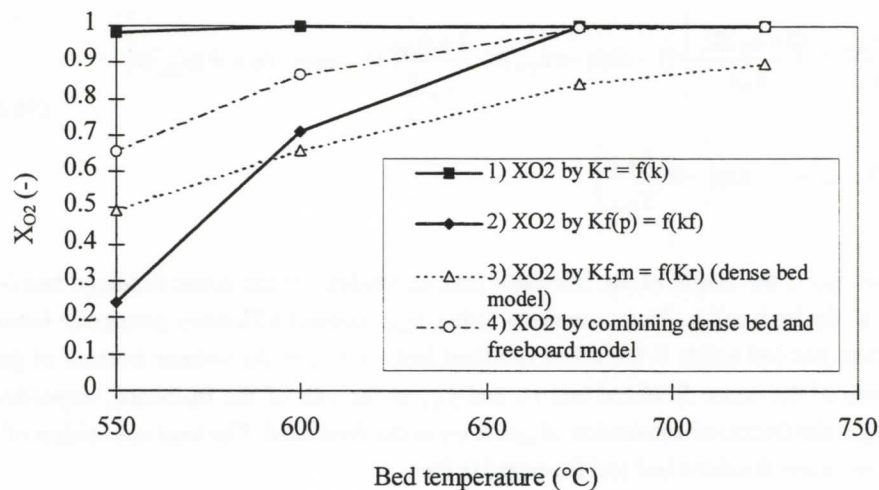


Figure 6.5 The fractional conversions of oxygen in a pilot-scale regeneration reactor at different temperatures, using different versions of fluidized bed models (Appendix VIII).

In Figure 6.5 the solid lines 1) and 2) represent the data obtained from equation 48 with parameters 1) $K_r = f(k)$ and 2) $K_{f(p)} = f(k_f)$, respectively. The reaction rate parameters k and k_f are obtained from Papers V and VI. The dashed line 3) represents the data of the dense fluidized bed model with parameter $K_{f,m} = f(K_r)$ (equation 45) for the pilot-scale reactor ($W_{bed} = 50$ kg), and line 4), the data with combined dense fluidized bed and freeboard hydrodynamic models (equation 47). The Kunii-Levenspiel model assuming dense bed alone (line 3) seems in comparison with results of lines 1) and 2) to underpredict the conversion of O_2 at reactor temperatures 675-725°C, which is not in agreement with the pilot-scale measurements. The results of the combined dense bed and freeboard model (line 4) seem to be in good agreement with the results described by lines 1) and 2) at these temperatures, but at temperatures below 675°C, significant differences can be observed.

A disadvantage of the Kunii-Levenspiel model is the large number of empirical input parameters that, for best results, should be specified experimentally for the material to be fluidized at the design operation conditions (pressure, temperature, reactor geometry) in question. The most sensitive parameters include the average size of gas bubbles (as a function of bed height) and the minimum fluidization velocity of the solid particles. Jensen (1996) found out that in his version of the hydrodynamic fluidized bed model the results are most sensitive to the dense-bed model parameters bubble diameter, minimum fluidization velocity, bubble rise velocity, and combined mass-transfer rate constant from bubble phase to emulsion. The sensitivity of his model towards the freeboard parameters,

the same as those used in this study, was found not to be significant. A sensitivity analysis is performed in Appendix VIII for large-scale fluidized bed regeneration reactor modeling, using equations 47-48. The model outcomes are reported in the form of parameter η_{tot} :

$$\eta_{\text{tot}} = \frac{\alpha_{\text{tot}}}{\alpha} \quad \text{where} \quad \alpha_{\text{tot}} = -\ln(1 - X_{\text{O}_2, \text{tot}}) \quad (49)$$

where the parameter $X_{\text{O}_2, \text{tot}}$, the total conversion of O_2 in regeneration reaction in the fluidized reactor, is determined by equation 47. Parameter α_{tot} is a reaction rate group parameter taking the mass transfer effects (predicted by equations 44-46) into account. By rearranging equation 49, the total conversion of gas in a large-scale regeneration fluidized bed reactor can be obtained with:

$$X_{\text{O}_2, \text{tot}} = 1 - \exp(-\eta_{\text{tot}} \alpha) \quad (50)$$

By varying the values of the most sensitive modeling input parameters (Appendix VIII, Table VII-5), the model outcome changes. The resulting values of η_{tot} are presented in Figure 6.6 in the form of probability density functions at two different temperatures. The good feature of this form of analysis is that the effect of all the different input parameter combinations can be studied.

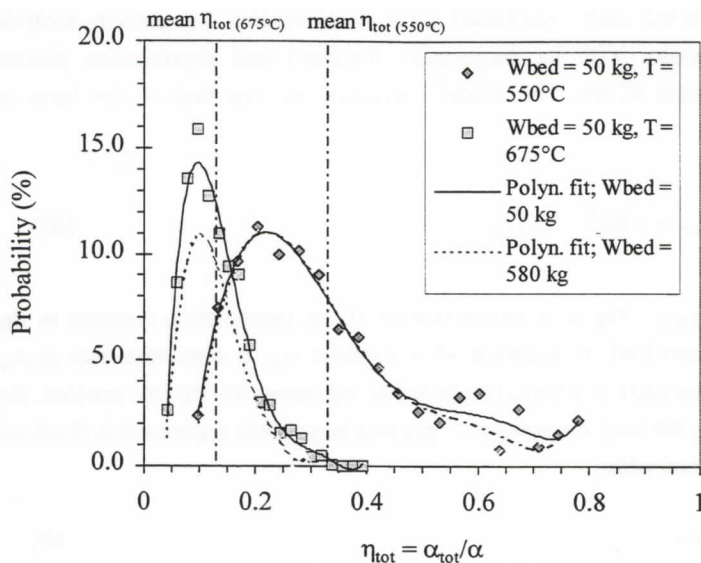


Figure 6.6 The probability density functions of the parameter η_{tot} as results of the sensitivity analysis of the pilot- and large-scale regeneration reactor fluidized bed models at temperatures 550°C and 675°C (Appendix VIII).

Figure 6.6 shows that significant variations in the parameter η_{tot} can be obtained by varying the most sensitive input parameters, especially at 550°C. The values of parameter η_{tot} seem to decrease as the reactor temperature increases: the mass transfer limiting effect is more pronounced when the values of parameter α (regeneration reaction rates) are higher. On the basis of the arithmetic mean values of parameter η_{tot} , the values of the parameter $X_{O_2,tot}$ by equation 50 for the 50 kg pilot-scale reactor are 0.77 (with $\eta_{tot} = 0.335$; $\alpha = 4.43$) at 550°C and 0.999 (with $\eta_{tot} = 0.131$; $\alpha = 53.01$) at 675°C. These values of $X_{O_2,tot}$ are in reasonable agreement with the values in Figure 6.5. However, by taking the distribution of the parameter η_{tot} into account, the values of $X_{O_2,tot}$ can vary between 0.44 - 0.96 at 550°C and between 0.93 - 1 at 675°C.

The results of the large-scale hydrodynamic fluidized bed reactor modeling (Appendix VIII) indicate that the application of the equations for dense fluidized bed and freeboard can explain only partially the differences observed in large-scale regeneration reactor modeling of Paper VI. In Paper VI, any hydrodynamic effects of the pilot-scale fluidized bed are lumped into the global reaction rate constant k_f . It is stated that either the simpler modeling approach of Paper VI or the approach presented in Appendix VIII can be used for large-scale regeneration reactor modeling, to give qualitative guideline information. Figure 6.6 shows that the sensitivity of the fluidized bed hydrodynamic models towards its main parameters is significant. Therefore, the application of any of the fluidized bed

models will require more experimental data of large-scale reactors for support. Those data can be obtained at any future test run of a large-scale regeneration and sulfidation fluidized bed reactor.

In large-scale sulfur removal and regeneration reactors, solid zinc titanate particles are continuously circulated in between the reactors. As a result of this circulation, different particles spend different times in the reactor, and thus their degree of conversion is different, depending on the total residence time. The exit age distribution or residence time distribution (RTD) of solids in a perfectly stirred reactor (Froment and Bischoff, 1990; Kunii and Levenspiel, 1991) can be described with:

$$E(t) = \frac{1}{\tau_{bed}} e^{-\frac{t}{\tau_{bed}}} \quad \text{where} \quad \tau_{bed} = \frac{W_{bed}}{m_{sorb}} \quad (51)$$

where τ_{bed} is the mean residence time of solids in the fluidized bed (s), W_{bed} is the bed inventory (kg) and m_{sorb} is the sorbent circulation rate (kg/s) between sulfidation and regeneration reactors.

In Appendix VIII the solid conversion rate models are presented as functions of time:

$$1 - X_s = f(t) \quad (52)$$

where X_s is the fractional conversion of solid reactant (zinc titanate, sulfided zinc titanate) in sulfidation (equation 8) and regeneration (equation 9) reactions. The mean conversion of solid reactant \bar{X}_s in large-scale fluidized bed sulfidation and regeneration reactors, as a result of solid circulation, is obtained in Appendix VIII by integrating:

$$\bar{X}_s = 1 - \int_0^{\infty} \left((1 - X_s) \frac{1}{\tau_{bed}} \exp\left(-\frac{t}{\tau_{bed}}\right) \right) dt \quad (53)$$

Figure 6.7 (Appendix VIII) summarizes the results of the application of equation 53 in the modeling of large-scale sulfidation and regeneration reactors.

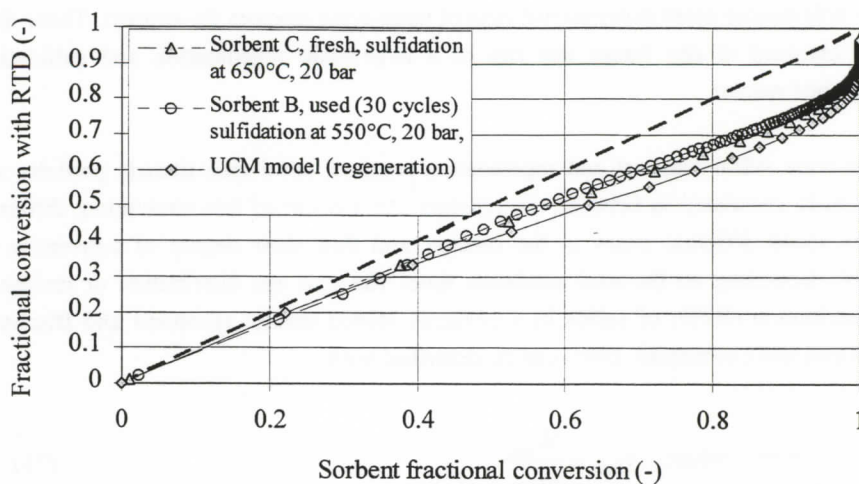


Figure 6.7 The RTD-affected fractional conversion of reactive solid (zinc titanate, sulfided zinc titanate) in large-scale sulfidation and regeneration reactors, in comparison with corresponding conversion of no RTD effect (Appendix VIII).

The results of Figure 6.7 indicate that the difference between the "RTD-affected" and original (no RTD effect) sorbent conversion results in the modeling of large-scale reactors is largest at fractional conversions of 0.7-0.9. Since the relevant conversions in sulfidation are 0-0.5, the effect of RTD is not significant in sulfidation reactor modeling. In regeneration reactor modeling, a maximum error of about 25 % can take place. But since this error takes place at fractional conversions of 0.7-0.9 only, it is stated that results with no RTD effect (such as in Paper VI) can be used as guideline information.

7. EXPERIMENTAL APPARATUS USED IN THIS THESIS

The kinetics of sulfidation and regeneration of zinc titanate sorbent A (UCI-3) was evaluated in a thermogravimetric analyzer (TGA) DuPont 951, designed to handle corrosive gases (Gupta and Gangwal, 1992; Mojtahedi et al., 1996), shown in Figure 7.1. In a TGA, the progress of a gas-solid reaction can be monitored by determining the change in mass of the solid. The sulfidation of zinc titanate (reaction 8) will result in an increase in mass, since zinc sulfide has a higher molecular weight than zinc oxide. Obviously, the regeneration reaction of zinc sulfide (reaction 9) will lead to a decrease in mass. When the exact stoichiometry of the reaction is known, the change in sample mass can be directly related to the extent of conversion. The inlet gas used in the atmospheric TGA (ATGA) experiments with zinc titanate sorbents consisted of H_2S , CO , H_2 , and N_2 (sulfidation) and O_2 , SO_2 , and N_2 (regeneration) at compositions representative for large-scale sulfidation and regeneration reactors (Mojtahedi et al., 1996). Approximately 50 mg of the sorbent in the 100- 300 μm size range was used in each experiment. The technical details of the ATGA are described by Gupta and Gangwal (1992).

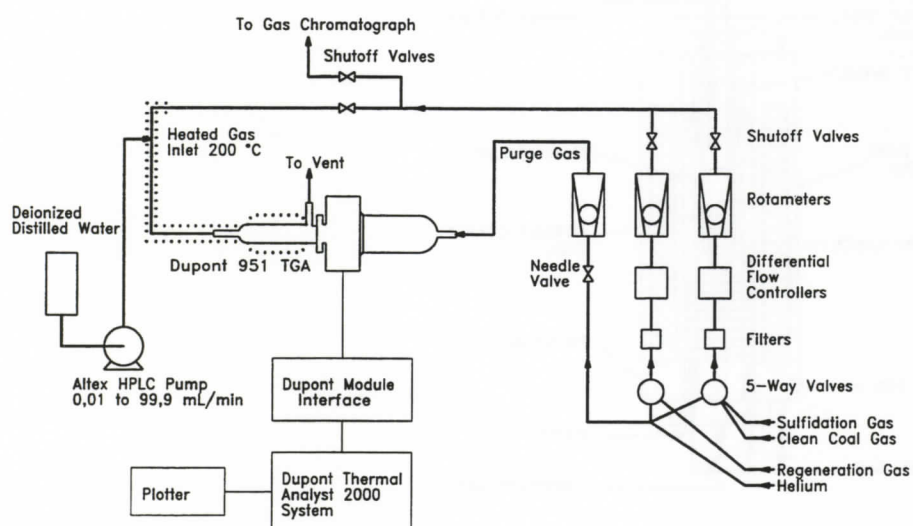


Figure 7.1 Ambient pressure thermogravimetric analyzer (according to Gupta and Gangwal, 1992).

Pressurized thermogravimetric apparatus (PTGA) was also used for testing of sulfidation and regeneration with a zinc titanate sorbent (Yrjas, 1996). The principles of determining the extent of sorbent conversion are the same as those with the ATGA. The maximum

operating pressure of the PTGA is 100 bar and the maximum operating temperature is 1100°C. The pressure in the electrically heated reactor was obtained by using the pressure of the gas bottles. The heated reactor was lined with a quartz tube, for protection from corrosive gases. The sample holder used was cylindrical and made of platinum. The zinc titanate sorbent sample was placed between an inner core and an outer net. The apparatus was recently described in more detail by Yrjas (1996).

A high-temperature high-pressure (HTHP) reactor system has been used to evaluate candidate sorbents in cyclic sulfidation/regeneration tests (Abbasian et al., 1994; Mojtahedi and Abbasian, 1995 a, b). The test unit includes feed systems for creating simulated hot gasifier gas, a 7.5 cm diameter fluidized bed reactor with associated process instrumentation and control devices. A schematic diagram of the HTHP fluidized bed reactor assembly is shown in Figure 7.2.

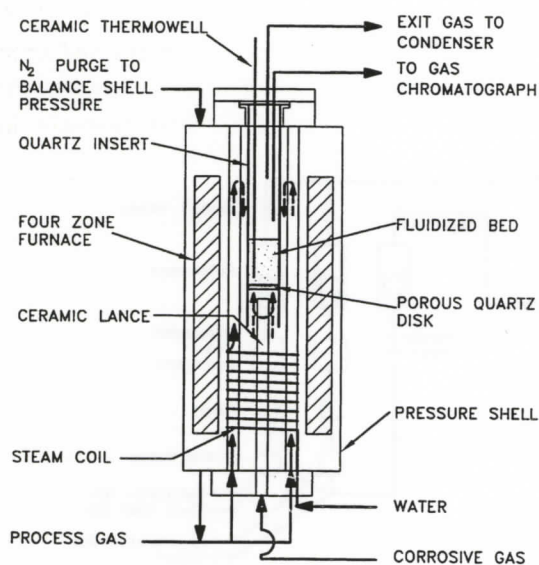


Figure 7.2 The high-temperature high-pressure fluidized bed reactor assembly (according to Abbasian et al., 1994).

The cyclic sulfidation/regeneration tests were conducted in this test unit in the temperature range of 550-650°C at 20 bar, using a simulated coal gas mixture containing 1500 ppmv of hydrogen sulfide. A detailed description of the reactor system and

operating procedure in cyclic tests has been reported elsewhere (Abbasian et al, 1994, Mojtahedi and Abbasian 1995 a, b).

Figure 7.3 shows a schematic diagram of the unique pilot-scale sulfidation and regeneration reactor system. The regenerative sulfur removal pilot plant consists of high-temperature and -pressure (HTHP) fluidized-bed-type sulfidation (sulfider) and regeneration (regenerator) reactors and systems for fresh sorbent feeding, sorbent circulation between the reactors, and gas preheating/cooling for the regenerator. In the sulfidation reactor, 200-500 kg of fresh sorbent is injected to the bed, which is then fluidized by the sulfur-containing gasifier gas at 500-600°C and 10-20 bar. The gas fluidization velocity in the bubbling fluidized-bed-type reactors is 0.15-0.3 m/s. The sorbent containing zinc sulfide is transported pneumatically from the sulfidation reactor to the regeneration reactor, where it is regenerated with a gas mixture of air and steam or nitrogen at 600-800°C and 10-20 bar, thus releasing gaseous SO₂. The regenerated sorbent is then transported back to the sulfidation reactor. In 1994, two different zinc titanate sorbents were tested in the system (Salo et al., 1995; Lehtovaara and Kontinen, 1995; Paper VII). Both sorbents were in contact with real coal gasifier gas, which contained impurities such as elutriated particulates from the gasifier, alkali and trace metals, HCl, and ammonia, among others. The zinc titanate sorbents were tested in connection with coal gasification test runs during 5-6 days of continuous operation in each test. More results are given in Paper VII.

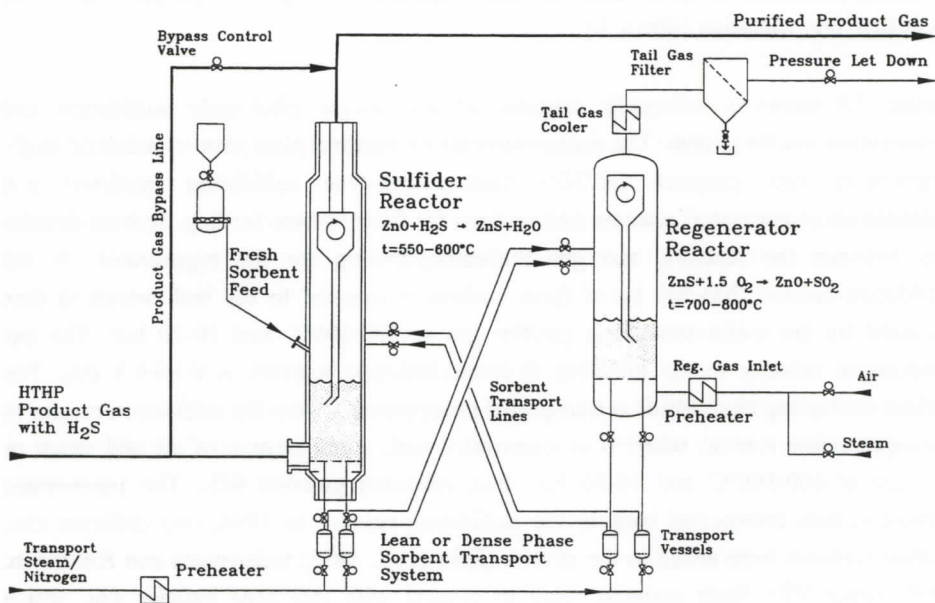


Figure 7.3 The high temperature high pressure pilot scale sulfur removal reactor system.

8. SUMMARIES OF PAPERS IN THIS THESIS

Paper I: Gasifier Gas Desulfurization at High Temperature and Pressure

This paper was published during the regenerative sulfur removal process development program of Enviropower Inc. (predecessor of Carbona Inc.) in 1993. In this thesis it is included as an introduction to the work presented in other papers. The possible options of sulfur removal with solid non-regenerable and regenerable sorbents in connection with air-blown IGCC processes are presented. The selection criteria of the sorbents and processes used further in the laboratory- and pilot-scale experimental testing are described. Some examples of the laboratory- and bench-scale results are presented.

Paper II: Hot Gas Desulfurization with Zinc Titanate Sorbents in a Fluidized Bed. 1. Determination of Sorbent Particle Conversion Rate Model Parameters.

A solid conversion model, together with fluidized bed mass and energy balances, can be used to predict the performance of a large-scale sulfidation reactor. This paper concentrates on the experimental results of some laboratory-scale tests in order to determine rate parameters for the zinc titanate sulfidation rate models. Two different models, the unreacted shrinking core with variable effective diffusivity (USC) and the overlapping grain (OG) models, were applied to the modeling of zinc titanate sulfidation. All the experimental data can be fitted with two parameters, a reaction rate constant and a product layer diffusion coefficient. The activation energies obtained from ambient pressure TGA tests for the reaction rate constant (26 kJ/mol) and for the product layer diffusion coefficient (110 kJ/mol) agree reasonably with previously reported data, although the initial sulfidation rates seem to be significantly lower than those obtained earlier by Lew et al. (1992 a). Potential reasons for this difference are discussed. The Arrhenius expression for reaction rate constant by Lew et al. (1992 a) was used to fit the experimental data at high pressure, leaving the product layer diffusion coefficient as a fitting parameter. The solid conversion rate model and its parameters obtained were used further as part of the fluidized bed reactor model in Paper III.

In the OG model, the sulfidation rate is proportional to the internal surface area of the porous particles; thus it follows the real physical behavior of the sorbent in sulfidation more closely than the USC model. However, for best results with the OG model, the grain shapes and porosities of the zinc titanate sorbent samples should be determined, which in practice increases the number of adjustable parameters. The USC model with variable effective diffusivity is included because of the possibility of obtaining analytical results without numerical integration, thus matching the requirements of a desirable gas-solid reaction model better as part of the sulfidation reactor model than the OG model. The OG

model can be preferred for the modeling of solid conversion rate data produced at laboratory-scale experiments, since, as the results show, the parameter values obtained have logical dependence on both process temperature and pressure.

Paper III: Hot Gas Desulfurization with Zinc Titanate Sorbents in a Fluidized Bed.
2. Reactor Model.

This paper concentrates on a method of applying the solid conversion rate model (unreacted shrinking core (USC) and the overlapping grain (OG) models) for bench-scale fluidized bed reactor modeling. The results presented show that the models generally used for fitting time versus solid conversion data (presented in Paper II) can be applied directly to model fluidized bed results with gas conversion versus solid conversion data. All the experimental data can be fitted with two parameters, the reaction rate constant and the product layer diffusion coefficient. In order to minimize the number of adjustable parameters, the reaction rate constant was obtained from the literature data on zinc titanates (Lew, 1990; Lew et al., 1992 a), thus leaving the product layer diffusion coefficient as a fitting parameter. The assumptions that are made for the batch fluidized bed modeling are first-order reversible sulfidation reaction, plug-flow of reactant gas through the fluidized bed, and perfectly mixed flow of solid reactant in the bed. The method provides a simple way to apply laboratory-scale rate data to a real-scale fluidized bed reactor for modeling purposes. In addition to steady-state scale-up design, a dynamic sulfidation reactor model (based on the same principles) can be used for process control system design and operator training.

As the results show, both the USC and OG models can be used for modeling of a batch fluidized bed reactor. However, in industrial-scale sulfidation reactor modeling applications, the computational complexity can become a concern. Because in such cases the pressure and temperature and sorbent physical properties are very close to the values in the experimental data of this article, the use of the USC model is preferable due to the possibility of obtaining analytical results without numerical integration.

Paper IV: Regeneration of Sulfided Zn-Titanate by Oxidation under Pressure.

In this paper, the results from pressurized regeneration of sulfided Zn-titanate are presented and discussed. The fact that regeneration is pressurized (20 bar) is essential, since the formation of $ZnSO_4$ is dependent on the partial pressures of SO_2 and O_2 . Thus, the possibility of $ZnSO_4$ formation is significantly more plausible under pressurized conditions than under atmospheric conditions.

The experiments were made with the PTGA in two consecutive steps. The sorbent was first sulfided at a certain temperature for about 2.5 hours after which the gas was changed to that of regeneration. The degree of sulfidation was calculated from the weight change (+16.1 g/mol) and the initial sample mass. The regeneration degree was calculated based on the weight change (-16.1 g/mol) and the total ZnS available after sulfidation.

The results showed that all ZnO could be regenerated within 2 hours at elevated pressure and a temperature between 700°C and 750°C. However, even when lowering the O₂ fraction to as low as 0.2 vol % it was found that ZnO could not be regenerated without the formation of ZnSO₄. This ZnSO₄ was then further decomposed when the partial pressures of O₂ and SO₂ apparently became sufficiently low. According to the weight-time curves, it was calculated that about 10 mol % of the ZnS formed ZnSO₄ and the rest, 90 mol %, formed ZnO. It was also shown that the decomposition rate of ZnSO₄ to ZnO was significantly slower than the formation of ZnO from ZnS.

Paper V: Modeling of Sulfided Zinc Titanate Regeneration in a Fluidized Bed Reactor.

1. Determination of the Solid Conversion Rate Model Parameters.

This paper concentrates on the experimental results of some laboratory-scale tests, in order to determine kinetic parameters for a zinc titanate regeneration rate model. Some of the results reported in Paper IV are analyzed in connection with the other experimental data used in this paper. The solid conversion rate data from the ambient pressure thermogravimetric analyzer (ATGA) were used for model-parameter fitting. The ATGA data at different temperatures could be fitted by assuming uniform conversion of ZnS in the solid particles.

The results indicate that the rate of ZnS regeneration reaction is strongly temperature-dependent, with an activation energy of about 140 kJ/mol for the rate constant. The PTGA data on regeneration (Paper IV) could not be directly used for model-parameter fitting, due to sample bed diffusion limitations, but these results indicate that the rate of ZnSO₄ formation at high temperature and pressure is negligible in comparison with the rate of SO₂ release. The results obtained will be used further as part of a regeneration reactor model.

reactor. These equations can partly explain the differences observed with the simpler model in the determination of regeneration reaction rate constants in Paper VI. It is shown that the sensitivity of the fluidized bed hydrodynamic models towards its main parameters is significant; thus more experimental data of large-scale reactors is required to support the application of such models.

In the circulation of the sulfur removal sorbent between large-scale sulfidation and regeneration fluidized beds, a residence time distribution (RTD) is created. The effect of RTD on the modeling results is also checked and found not to be significant in sulfidation reactor modeling, where sorbent fractional conversions below 50 mol % are common. In regeneration reactor modeling, a maximum error of about 25 % in gas-solid mass balances can take place when not taking RTD into account. But since this error takes place at sorbent fractional conversions of 0.7-0.9 only, it is stated that the results with no RTD effect considered can be used as guideline information at regeneration reactor modeling.

9. CONCLUDING REMARKS

9.1 Conclusions on this work

This thesis consists of some essential parts of the research and development work for the high-temperature high-pressure regenerative sulfur removal process by Enviropower Inc. and its successor Carbona Inc. The sulfur removal process forms an essential part of the hot gas clean-up section of an integrated gasification combined cycle process (IGCC) for energy production from sulfur-containing solid fuels, such as coal. The advantages of the advanced pressurized power generation processes like IGCC, over the conventional type of combustion plants, are the use of a gas turbine, which increases the electricity generation efficiency, and the possibility to minimize the amount of harmful emissions like SO_2 , NO_x , and dust. The IGCC process is in a commercial demonstration phase, which is to be finalized by the end of this decade. An overview of the IGCC demonstration projects and related sulfur removal technologies is given, with the main emphasis on pilot- and demonstration-scale projects.

In connection with IGCC processes, the use of regenerable sorbents instead of once-through Ca-based sorbents for sulfur retention has recently received more attention, primarily due to problems associated with the disposal of large amounts of solid waste generated with non-regenerable sorbents. With the use of regenerable sorbents, the amount of solid waste produced is minimized and the fuel-bound sulfur can be recovered as a commercial product, such as elemental sulfur. In addition, very high (over 99 %) sulfur capture efficiencies can be achieved under reducing conditions with metal oxide-based regenerable sorbents, which is not possible with Ca-based sorbents.

Several metal oxides and their combinations have been developed and tested, mainly on laboratory scale, for H_2S capture in a gasifier gas. The H_2S capture equilibria with single metal oxides favors zinc and copper at temperatures of 500-800°C with gasifier gases produced by an air-blown gasifier. The addition of TiO_2 with zinc oxide (ZnO) forms the mixed metal oxide zinc titanate ($\text{ZnO}\cdot x\text{TiO}_2$), stabilizes the zinc oxide, and permits the use of the sorbent in continuous sulfur capture at temperatures up to 800°C. The sorbent can be regenerated with O_2 to form gaseous SO_2 , which can be treated further. Fluidized bed reactors offer potential advantages in IGCC systems over other reactor types for HTHP sulfur capture and sorbent regeneration because of their ability to control the highly exothermic regeneration reaction.

Reactor models are needed for the scale up of the regenerative sulfur removal process. A reliable solid conversion model, together with fluidized bed mass and energy balances, can be used to predict the performance of a large-scale sulfidation and regeneration

reactor. For fluidized bed reactor modeling purposes it is desirable to have a gas-solid reaction model with the following properties: 1) the model should be able to describe the rate of gas-solid reaction with a minimum of numerical iteration and still take the sorbent's physical properties into account 2) it has to have a minimum number of adjustable parameters 3) the adjustable parameters should have a logical dependence on process variables, such as temperature and pressure.

The experimental results of some laboratory-scale tests in order to determine kinetic parameters for the zinc titanate sulfidation and regeneration rate models are presented. Two different models, the unreacted shrinking core model (USC) with variable effective diffusivity and the overlapping grain (OG) model are applied to the modeling of zinc titanate sulfidation. The OG model follows the real physical behavior of the sorbent in sulfidation more closely than the USC model. The latter is included because of the possibility of obtaining analytical results without numerical integration, thus matching the requirements of a desirable gas-solid reaction model as part of the sulfidation reactor model better than the OG model. All the experimental data in sulfidation can be fitted with two parameters, i.e., the reaction rate constant and the product layer diffusion coefficient. The values of the parameters agree reasonably well with the corresponding values obtained from the literature. In ZnS regeneration, the experimental data from an atmospheric thermogravimetric analyzer (ATGA) at different temperatures could be modeled by assuming uniform conversion of ZnS in the solid particles. The results indicate that the rate of the ZnS regeneration reaction is strongly temperature-dependent, with an activation energy of about 140 kJ/mol for the rate constant. The high-pressure PTGA data on regeneration could not be directly used for model-parameter fitting, due to sample bed diffusion limitations, but these results show that the rate of ZnSO₄ formation at high temperature and pressure is negligible in comparison with the rate of SO₂ release.

A method of applying the solid conversion rate models for bench- and pilot-scale fluidized bed reactor modeling is presented in this thesis. The results show that the models used generally for the modeling of time versus solid conversion data can be applied directly to model fluidized bed results with gas conversion versus solid conversion data. As a result of the parameter fit into pilot-scale ZnS regeneration experimental data, the apparent activation energy for the global reaction rate constant equals 200-210 kJ/mol. When using these regeneration reaction rate constants as inputs of a sensitivity analysis for a large-scale reactor model, in comparison with the rate constants obtained on laboratory scale, some differences can be observed. Based on the experimental and modeling results, it is found that the reason for negligible zinc sulfate formation in regeneration in a pilot scale fluidized bed is that, at sufficiently high temperatures, the partial pressure of oxygen (required for sulfate formation) at the exit of

the bed is practically zero, so any sulfate that may be formed at lower temperatures will decompose.

The large-scale regeneration reactor model of Paper VI includes some simplifying assumptions: the possible contributions by hydrodynamic mass transfer limitation and solid residence time distribution should not have significance to the modeling results. The validity of these assumptions in large-scale fluidized bed reactor modeling are checked in a separate study. Hydrodynamic modeling equations for dense fluidized bed and freeboard (above the dense bed) are applied for the prediction of the performance of a large-scale regeneration reactor. These equations can partly explain the differences observed with the simpler model in the determination of regeneration reaction rate constants from a pilot-scale fluidized bed, in comparison with constants obtained on laboratory scale. It is shown that the sensitivity of the fluidized bed hydrodynamic models towards their main parameters is significant; thus more experimental data of large-scale reactors is required to support the application of such models. In the circulation of the sulfur removal sorbent between large-scale sulfidation and regeneration fluidized beds, a residence time distribution (RTD) is created. The effect of RTD on the modeling results is also checked and found not to be significant in sulfidation reactor modeling, where sorbent fractional conversions below 50 mol % are common. In regeneration reactor modeling, a maximum error of about 25 % in gas-solid mass balances can take place by not taking RTD into account. But since this error takes place at sorbent fractional conversions of 0.7-0.9 only, it is stated that the results with no RTD effect considered can be used as guideline information in regeneration reactor modeling.

The pilot-scale test run results of a side-by-side sulfur removal fluidized bed reactor arrangement, in connection with 15 MW_{th} gasifier pilot, are presented. Three test runs were accomplished with two different zinc titanate sorbents in the HTHP fluidized bed sulfur removal pilot; each of them with 5-6 days of continuous operation. The results showed that high sulfidation efficiency as well as continuous production of SO₂-containing regeneration reactor off-gas at design temperatures and pressures could be achieved. The successful pilot-scale test results proved that the preliminary steady-state reactor dimensioning model results based on the principles presented in this thesis were in good agreement with the test data.

9.2 Implications

As stated in this thesis, fluidized bed reactor models are needed in the scale-up design of the regenerable sulfur removal process in connection with IGCC. The results of this thesis show that the factors affecting the rate of sulfur removal reaction with regenerable zinc titanate sorbents under laboratory- and bench-scale conditions are sufficiently well

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