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Optimisation of Experimental Conditions for Ex-Bed Desulfurization

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Optimisation of Experimental Conditions for Ex-Bed Desulfurization

Sánchez Hervás, J. M.; Ruiz Martínez, E.; Otero Ruiz, J.

45 pp. 20 figs. 36 refs. 18 Tables

Abstract:

This report compiles the results of the work conducted by CIEMAT for Task 6.3 “Sulfur and Nitrogen Compounds Abatement” of the FLEXGAS project “Near Zero Emission Advanced Fluidised Bed Gasification”, which has been carried out with financial support from the Research Fund for Coal and Steel, RFCR-CT-2007-00005. The assignment of CIEMAT in Task 6.3 has dealt with the experimental study of ex-bed desulfurization at high temperature and high pressure. Based on a review of the state of the art, a zinc oxide sorbent was chosen as a promising candidate for bulk sulfur removal in highly reducing gases such as those from coal and waste oxygen gasification or for a polishing stage in low sulfur content gases, which is typically the case in biomass gasification gases. The work accomplished has included the study of the sulfidation and regeneration stages in order to determine successful operating conditions and the assessment of the long term performance of the sorbent over subsequent sulfidation and regeneration cycles.

Optimización de las Condiciones de Operación para Desulfuración en Lecho Externo

Sánchez Hervás, J. M.; Ruiz Martínez, E.; Otero Ruiz, J.

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Resumen:

Este informe recoge los resultados del trabajo realizado por CIEMAT en la tarea 6.3 “Eliminación de compuestos de azufre y nitrógeno” del Proyecto FLEXGAS “Near Zero Emission Advanced Fluidised Bed Gasification”, el cual se ha realizado bajo financión de los Fondos para la Investigación del Carbón y del Acero, RFCR-CT-2007-00005. CIEMAT ha explorado la viabilidad técnica posibilidad de la desulfuración a alta temperatura y alta presión en lecho externo al gasificador. A partir de la revisión del estado del arte se seleccionó un óxido de zinc como candidato potencial para el proceso de desulfuración tanto en gases con un elevado contenido en sulfuro de hidrógeno como por ejemplo la gasificación con oxígeno de carbón y residuos, como en gases con bajo contenido, como por ejemplo la gasificación de biomasa. La investigación realizada ha incluido el estudio de las etapas de sulfidación y regeneración para definir condiciones exitosas de operación y la evaluación del adsorbente a largo plazo al someterlo a sucesivos ciclos de sulfidación y regeneración.

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SUMMARY

This report compiles the results of the work conducted by CIEMAT for Task 6.3 "Sulfur and Nitrogen Compounds Abatement" of the FLEXGAS project "Near Zero Emission Advanced Fluidised Bed Gasification", which has been carried out with financial support from the Research Fund for Coal and Steel, RFCR-CT-2007-00005. The assignment of CIEMAT in Task 6.3 has dealt with the experimental study of ex-bed desulfurization at high temperature and high pressure.

Ex-bed desulfurization is usually accomplished with the use of regenerable sorbents. The review of the state of the art shows that the external adsorption bed processes which are in the most advanced stage are those based on the zinc titanate or zinc oxide sorbents [1]. For this project, desulfurization studies have been conducted using a commercial zinc oxide-nickel oxide sorbent. The sorbent has been shaped as extrudates in cylindrical form. The pellets are 0.32 cm in diameter by 0.64-0.95 cm in length. They are suitable therefore to be used in fixed beds. The performance of the sorbent for desulfurization of synthetic gases representative of an oxygen-blown gasifier has been studied, that is for a syngas with a high content of CO (>50% v/v) and H_2 (>20%v/v), which was in perfect agreement with the objectives of the FLEXGAS project.

The work accomplished has included:

- Review of the state of the art on removal of sulfur compounds from gasification gases
- Design of the experimental plan to study at bench scale level, selective hydrogen sulfide removal from oxy-gasification gases
- Adaptation of the experimental facility to carry out the tests
- Sulfidation tests under simplified atmosphere
  - Effect of gas components using binary and ternary mixtures (H_2S/N_2, $H_2S/H_2/N_2$, $H_2S/CO/N_2$, $H_2S/H_2O/N_2$)
  - Effect of temperature (250-600ºC),
  - Effect of gas space velocity, (3500-10.000 h^{-1})

    - Effect of sulfidation pressure (2-20 atm)
    - Effect of H_2S concentration (1-5%v/v)
- Regeneration tests: Evaluation of the regenerability of the sorbent
    - Regeneration agent: Steam, Oxygen in Nitrogen
    - Regeneration agent content (steam or oxygen to nitrogen ratio)
- Multicycle sulfidation-regeneration tests: Assessment of the performance of the sorbent over subsequent sulfidation and regeneration stages.

Desulfurization tests conducted show that the zinc oxide sorbent used is suitable for hot gas desulfurization. The sorbent is effective for H_2S removal in a wide range of gas compositions. The presence of H_2, CO, H_2O do not have deleterious effect on sorbent performance. It is operational in a wide range of temperature (250-650ºC), pressure (2-20 atm) and gas velocity (3500-10000 h^{-1}) with very low H_2S leakage and sharp breakthrough characteristics. Dry diluted-oxygen regeneration schemes are deemed as appropriate to return the sorbent to its original state so that it can be reused in the absorber.

The sorbent has demonstrated high desulfurization capacity either in bulk sulfur removal in highly reducing gases such as those from coal and waste oxygen gasification or for a polishing stage in low sulfur content gases, which is typically the case in biomass gasification gases. The multi-cycle fixed bed tests show promise to withstand successive cycles of sulfidation regeneration.

1 OVERVIEW OF THE FLEXGAS PROJECT

In the 1970's and 1980's the development of fluidised bed gasification technologies stopped at pilot/demonstration scale for economic reasons but the interest in its use with biomass grew for several reasons (fuel flexibility, wide range operation scales suitability, etc.).

In the FLEXGAS project the way to overcoming the potential disadvantages of fluidised bed gasification and its use to process biomass/waste together with coal (at different operation scales and applications) and the technology for CO_2 capture/reduction are investigated. The effects of different fuels, composition and gasification medium on the quality of the producer gas are also evaluated. Particular focus is on novel technologies for gasification coupled with CO_2 sequestration and for producing hydrogen rich syngas from coal and biomass/waste.

The FLEXGAS project "Near Zero Emission Advanced Fluidised Bed Gasification", funded by the Research Fund for Coal and Steel (project No. RFCR-CT-2007-00005) is intended to contribute to sustainable coal development by improving the potential for the application of fluidised bed technology to coal gasification and co-gasification with biomass/wastes under near zero emissions. From the onset the project aimed to achieve the following targets:

- Adapting the concept of oxy-fuel firing for PF combustion to fluidised bed gasification

- Considering the potential of fluidised bed technology to produce H_2 rich gas and CH_4

- Investigating the co-gasification of coal with biomass and/or waste in fluidised beds and to consider the impact of scale of operation

- Considering the impact of the above developments on the release of tar, fuel N and S

- Investigating alternative gas cleaning/separation options (e.g. for CO_2 sequestration)

- Promoting the exploitation and utilisation of energy source that are available within EU

- Promoting the project findings with potential developers

- Supporting the European and local policy on energy concerns

To fulfil the above, the project was organized in seven work packages that were mutually interconnected

- Work Package 1 (WP1): Coordination and management

- Work Package 2 (WP2): Selection and characterization of materials for co-gasification
- Work Package 3 (WP3): To adapt and test the concept of ‘oxy-fuel firing’ to fluidised bed gasification
- Work Package 4 (WP4): Fundamental research and system analysis on co-gasification of coal with biomass/waste in a fluidised
- Work Package 5 (WP5): Experimental investigations and scale up of ICFB gasification process with coal/biomass mixtures
- Work Package 6 (WP6): Optimisation of gas composition, gas cleaning and shift conversion
- Work Package 7 (WP7): Data collection and dissemination of results.

Workpackage 6 has dealt with different approaches to optimise gas composition, gas cleaning and upgrading. One of the tasks in WP6 has been experimental studies of sulfur removal at high temperature in an external bed downstream the gasifier. CIEMAT was responsible for that task and the outcome of the study is presented in this report.

2 SULFUR REMOVAL: BACKGROUND & STATE OF THE ART

During gasification, sulfur present in the solid fuel - let it be coal, biomass or wastes- is converted primarily to H_2S and to some extent to COS and CS_2. During combustion of the fuel gas in a turbine, H_2S oxidizes to SO_2, which is a precursor of the acid rain. In addition to its toxicity to the environment, high H_2S concentrations are also detrimental to process units. The gas is corrosive to downstream equipment e.g. process instruments, and turbine blades, and it can deactivate for instance sweet shift catalysts or adversely affect the performance of MFCs, etc. due to sulfur poisoning of the electrodes. Thus, if the gas is going to be used as raw material for other products or uses, it becomes necessary to clean the gas from sulfur to the order of a few ppm or less. In a gasification process the sulfur removal step can be integrated in a variety of configurations (Figure 1). The choice of a particular configuration will depend on the quality of the gas to be treated, in particular regarding its content of tars and water, and also the characteristics of the chosen sulfur removal concept.

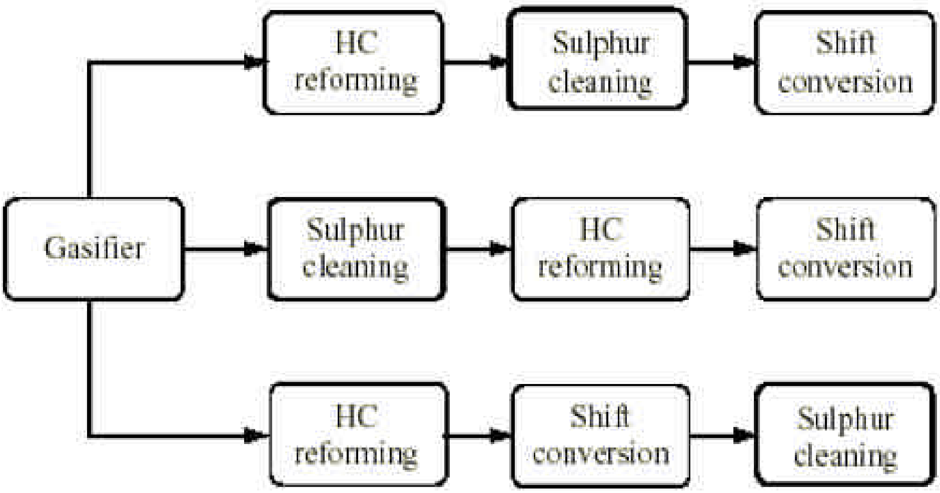

Figure 1. *Possible configurations for integration of sulfur cleaning step in a gasification process.* [1](Zintl & Padban)

As reported by Thambimuthu et el. [2], conventional processes for removing H_2S from fuel gas are wet processes operated within a liquid phase, for example an amine solution. These processes operate at relative low temperature (typically from -20 to 60ºC), which limits the applicability of such systems only to clean side of the process, e.g. the step after shift conversion. The very low operational temperature for the conventional systems requires cooling of the fuel gas and therefore impose a severe thermal penalty and additional capital cost for heat exchangers. Moreover, the costs for treatment of process-generated wastewater are relatively high. In other words, the conventional methods are energy and chemical intensive processes. Therefore, it is desirable to have sorbent materials for dry removal of sulfur species at high temperature.

Sorbent materials for sulfur removal can be classified as either disposable or regenerable. Ca-based materials, such as limestone and dolomite, are cheap and abundantly available and are frequently used in a "once-through" mode to remove sulfur both in combustion and gasification systems. Ca-based sorbents can be used in-bed, by injection into the gas stream, or by direct contact in an external reactor. In gasification systems, however, the sulfur capture efficiency is low, thereby creating more waste products, and the thermodynamics at low temperature are not favourable. Therefore Ca-based sorbents are only used as a primary in-bed desulfurization agent.

R&D in the field of sulfur removal at high temperature has been quite active for the last two decades. The development in hot gas desulfurization technologies has focused on the use of regenerable sorbents, mainly metal oxides. Over the last years, according to the number of papers published, interest has shifted from USA and Europe to Asia [3-21], being South Korea particularly active in the field. Mitchell in his report made a compilation of desulfurization characteristics of a selection of metal oxide sorbent materials which are listed in Table 1[3].

Table 1. *Characteristics of metal oxide sorbent materials*

Sorbent material	Sulfidation temperature, ºC	Regeneration temperature, ºC	Sorbent utilisation, %	H_2S outlet concentration, ppmv
Tin oxide	350-500	400-500	85	<100
Copper oxide	350-550	650	70	<20
Manganese oxide	350-870	900	50	<10
Iron oxide	360-500	500-650	25-45	<100
Zinc oxide	480-540	500-700	50-70	<1
Zinc ferrite	450-600	600	20-80	<20
Zinc titanate	450-750	600-750	40-60	<10
Copper chromite	650-850	750	40-80	<10
Cerium oxide	750-1000	600	90	<100

Good regenerability would decrease not only the cost of the sorbent but also the costs associated with frequent loading and unloading of the reactors and the costs associated with disposal of spent sorbent. Early studies focused on the use of sorbents at temperatures above 600ºC, particularly for IGCC, since operation at high temperatures was thought to improve the efficiency of the overall cycle. However, according to the thermodynamics studies published by Westmoreland and Harrison [22], few metal oxides are capable of significantly reducing the H_2S content of the fuel stream at so high temperatures. Although desulfurization above 600ºC would be compulsory if it is carried out before HC reforming, in recent years the research emphasis has shifted to desulfurization in external beds and at lower temperatures (350-550ºC), where there are many metal oxides that are potentially candidates for hot gas desulfurization.

In the work published by Sanchez et al. it is concluded that the external adsorption bed processes, which are in the most advanced stages, are those based on the zinc titanate or zinc oxide sorbents [9].

The basic chemistry involved in desulfurization using a metal oxide sorbent is the non-catalytic reaction between H_2S and a reactive transition metal oxide to form a metal sulfide and H_2O according to the reaction

$$\mathrm{MyOx\ (s)} + \mathrm{xH_2S\ (g)} \leftrightarrow \mathrm{MySx\ (s)} + \mathrm{xH_2O\ (g)}$$

The regeneration of sulfided sorbent using air can be described as

$$\mathrm{MySx\ (s)} + 3/2\ \mathrm{xO_2\ (g)} \rightarrow \mathrm{MyOx\ (s)} + \mathrm{xSO_2\ (g)}$$

The Claus process is usually the preferred method to treat the effluent gas to produce elemental sulfur through the reaction

$$2\ H_2S + SO_2 \rightarrow 2\ H_2O + 3\ S$$

In order to avoid the Claus step, a lot of effort has been put into developing sorbents that can be regenerated to produce elemental sulfur directly.

Unfortunately, the following potentially detrimental and undesirable reactions can also occur during sulfidation and regeneration

$$MO + H_2(CO) \rightarrow M + H_2O(CO_2) \text{ metal oxide reduction during sulfidation}$$

$$MS + 2\ O_2 \rightarrow MSO_4 \text{ (sulate formation during regeneration)}$$

The above reactions, which can result in poor sorbent utilization and sorbent degradation, need to be minimized by optimizing the process operating conditions. In addition other gas phase reactions, such as the Boudouard, methanation and Fischer-Tropsch reactions can occur in strongly reducing gases and can even be catalysed by some of the above listed desulfurization sorbents, causing undesirable temperature excursions which in turn can damage the sorbent.

So, following the study of Williams et al. the main requirements on a metal oxide sorbent are listed below [4]

– It should selectively react with H_2S in a reducing coal-gas environment at desired conditions. The thermodynamics of the reaction should be favourable enough to achieve the desired level of H_2S (and COS) removal, while the reduction of the metal oxide to metal should be slow or thermodynamically unfavourable to avoid metal vaporisation, and loss of sorbent structure.

– The sulfided sorbent should be easily regenerable- it should easily convert back into the corresponding oxide.

– Kinetics of sulfidation and regeneration reactions at desired temperatures should be sufficiently fast to allow reasonable reactor sizes.

– The sorbent should be thermally and mechanically stable in both oxide and sulfide state.

In general a two-reactor configuration is necessary for any hot gas desulfurization due to its cyclic nature. The four main reactor types – fixed bed, moving bed, bubbling fluidised bed and transport reactors- have been studied. The reactors used for sulfidation and regeneration are normally of the same type, dimensions and materials of construction in spite of the fact that the operating conditions and gaseous environments are different.

3 EXPERIMENTAL

3.1 Test Rig.

CIEMAT has studied the technology of removal of hydrogen sulfide with regenerable sorbents in a high temperature, high-pressure (HTHP) bench scale sorbent test facility whose flow diagram is shown in Figure 2. The plant can treat up to 20 Nm^3/h of a gas mixture simulating the composition of the flue gases from different processes such as combustion or gasification gases. It is designed to operate at a maximum temperature of 700ºC and a pressure of 30 bar.

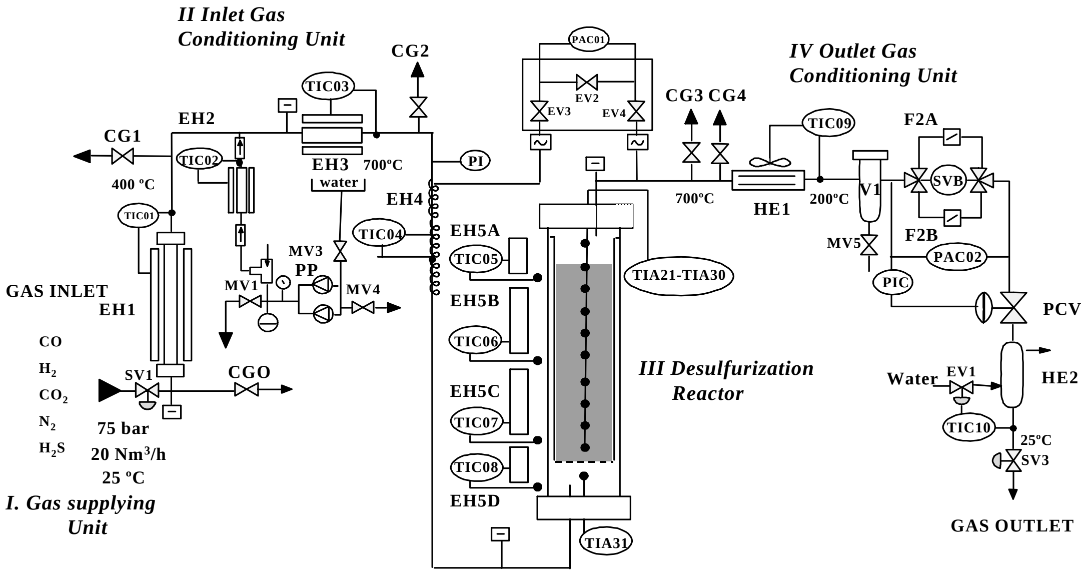

***Figure 2**. Schematic of CIEMAT´s Hot Gas Desulfurization Plant*

A battery of mass flow controllers (MFCs), capable of operation at pressures up to 80 atm, controls the flow rate and composition of simulated gases using bottled gases for CO, H_2, CO_2, N_2, H_2S and air. A positive displacement pump (PP) feeds de-ionized water to a boiler (EH2) and a super heater (EH3) to generate steam. The delivery system can generate simulated coal gases representative of all types of gasifiers. Gases are heated up to 400ºC and 700ºC respectively, in a pre-heater (EH1) and a super-heater (EH3) connected in series. Each temperature is controlled by means of separate temperature controllers (TIC1-TIC4).

The reactor (R) is constructed in Incolloy ® 800 H. It has a height of 1 m and an internal diameter of 80 mm, with a distributor plate of a-alumina at the bottom. Fixed and fluidized bed implementations are possible. For this project, fixed bed desulfurization is studied given the characteristics of the sorbent. The reactor is housed inside a four-zone furnace equipped with separate temperature controllers (TIC5A-TIC5D) for each zone. The reactor can withstand temperatures up to 900ºC. Gas temperature in the reactor is monitored at different heights, bed inlet, free board and bed outlet using 11 type K thermocouples (TIA21-TIA31).

The reactor exit gas is cooled using an air heat exchanger (HE1). Sulfur condensates and water are removed in a water-refrigerated vessel (V1). Two filters (F2A, F2B) downstream of the condenser capture particles from the sulfidation and regeneration lines upstream of the pressure control valve (PCV), which precisely controls pressure. A differential pressure transducer (PAC01) across the reactor detects any plugging. Furthermore, this differential pressure module can be used to ascertain good quality fluidization in the reactor, when fluidized bed is used. Gases downstream of the pressure control valve are cooled down to ambient temperature in a water heat exchanger (HE2). The sulfidation exit gases containing toxic CO and H_2S and regeneration off-gases are properly disposed. Firstly, gases pass through an active carbon bed, and then a high-powered blower is used to dilute the gases before emitting them into the atmosphere.

Slipstreams of the gas (CG0-CG4) are diverted to the gas analysis system, which consists of two gas chromatographs each equipped with two detectors. The first one has a thermal conductivity detector (TCD). The second one has a flame photometric detector (FPD), specific for sulfur compounds and a flame ionisation detector (FID) to determine hydrocarbons. Chromatographic data are collected and analyzed by the GC ChemStation Software from Agilent Technologies.

3.2 Test Programme

Testing programme was undertaken in different stages. The first one dealt with experiments under simplified conditions in order to gain knowledge of the process. This stage was defined as sulfidation tests under simplified atmosphere. The objective of the tests was to understand the performance of the sorbent under a wide range of experimental conditions. The influence of the following parameters has been studied:

i) Effect of gas components using binary and ternary mixtures (H_2S/N_2, $H_2S/H_2/N_2$, $H_2S/CO/N_2$, $H_2S/H_2O/N_2$)

ii) Effect of temperature (250-600ºC),

iii) Effect of gas space velocity, (3.500-10.000 h^{-1})

iv) Effect of sulfidation pressure (2-20 atm)

v) Effect of H_2S concentration (1-5%v/v)

Regeneration of the sorbent was studied, looking for a successful, reproducible regeneration procedure. As discussed in the background section, the objective of the regeneration stage is to convert the formed metal sulfide back to its original metal oxide state. There are a number of possibilities to do so, such as the use of air diluted with nitrogen or steam. Therefore, a set of regeneration tests was devoted to evaluate the regenerability of the sorbent, and to determine the maximum concentration of the oxidant to control the increase of sorbent temperature due to the exothermicity of the regeneration reaction. The following parameters have been studied:

i) Regeneration agent: Steam, Oxygen in Nitrogen

ii) Regeneration agent content (steam or oxygen to nitrogen ratio)

Next stage focused on the study of desulfurization of synthetic gasification gases. After proving that the sorbent was capable of removing hydrogen sulfide from hot gases, new tests were conducted including all main components of gasification gases. H_2S content in the feed syngas ranged from 500 ppmv to 10000 ppmv. Besides, different syngas composition was used to determine sulfur capture ability under various CO, H_2 and CO_2 content, that is, gases with different reducing power. Gas A simulates the composition of a high sulfur feedstock, oxygen-rich gasification process, whereas Gas B reproduces the composition of a low-sulfur feedstock, air-blown gasification cycle.

Finally, since one of the requirements imposed on a desulfurization sorbent to be successfully implemented for hot gas cleanup is its ability to withstand cycles of sulfidation regeneration, short series of cycles have been conducted to gather preliminary data on the performance of the sorbent over subsequent cycles. Nine sulfidation-regeneration cycles have been performed for an A-type gas.

3.3 Experimental Procedure.

In a typical run, the procedure followed is as follows: A given amount of sorbent (usually 2500 grams) is loaded into the sorbent cage. The cage is then placed in the reactor shell and the entire reactor system is assembled. After that, the reactor is pressurized to the operating pressure and heated to the desired temperature under nitrogen, whose flow rate is set according to the calculated gas hourly space velocity, given by the ratio of volumetric gas flow rate (F_{gas}) to the volumetric sorbent batch (V_{sorb})

$$\text{GHSV} = \frac{F_{\text{gas}}\ (\text{standard conditions})}{V_{\text{sorb}}} \qquad (1)$$

When the desired temperature is attained, the nitrogen flow is stopped, and the flow of simulated sulfidation gas is started. The reactor has been operated in a fixed bed, down flow mode. Sulfidation is accomplished by feeding simulated compositions produced by blending of individual metered components upstream of the reactor. The sulfidation reaction considered is

$$\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O} \qquad \{1\}$$

During this step, the H_2S-containing gas stream is brought into contact with the sorbent and sulfur is removed from the fluid stream. The progress of the sorption process has been followed by measuring the hydrogen sulfide and sulfur dioxide content in the reactor outlet gas using the flame photometric detector. Other components of the gas stream are also analyzed by gas chromatography.

During sulfidation, the sorbent becomes spent, as is evidenced by the sharp increase in the amount of H_2S that breaks through the bed of sorbent. Sulfidation of the sorbent is continued until the H_2S concentration in the reactor exit reaches 500 ppmv, defined as the breakthrough point. At this point, the flow of simulated coal gas is stopped and switched to nitrogen to purge the system. The reactor temperature is then raised to about 550ºC (starting regeneration temperature). Dry mild regeneration, in which air for regeneration is diluted with nitrogen, has proved to be an efficient way to regenerate the sulfided sorbent. Oxidative regeneration of zinc sulfide back to the original zinc oxide structure is given by the following overall reaction

$$\text{ZnS} + 3/2\ \text{O}_2 \rightarrow \text{ZnO} + \text{SO}_2\ ?\ \text{Hr}\ (400^{\circ}\text{C}) = -\ 446\ \text{KJ/mol ZnS}\ \{2\}$$

Sorbent regeneration is continued until SO_2 concentration in the regeneration tail gas falls below 200 ppmv. At this point, the regeneration gas is switched to nitrogen purge to cool down the system.

The suitability of the sorbent has been evaluated by the sulfur level achieved in the reactor exit, sulfur loading, and regenerability. Sulfur loading capacity is expressed by

$$\text{sulfur loading}(\%) = \frac{M_{\text{H2S}}\ (\text{g})}{M_{\text{sorb}}\ (\text{g})} \cdot 100 \qquad (2)$$

In this particular case, the theoretical saturation sulfur capacity of the sorbent, on weight basis, is about 19.5% (19.5g sulfur/100g fresh sorbent), based on $ZnO + H_2S \rightarrow ZnS + H_2O$ stoichiometry and on the fresh sorbent composition analysis provided by its supplier. Therefore, the estimation of maximum sulfur uptake (M_0), for a given sorbent inventory M_{sorb}, when the sorbent becomes fully sulfided would be

$$M_0(g) = 0.195 \cdot M_{sorb}(g) \qquad (3)$$

The theoretical time (t_0) to achieve complete sulfidation of the sorbent, for a given set of experimental conditions, is calculated according to equation (4),

$$t_0(min) = \frac{M_0(g)}{\left[MW_{H_sS} \cdot \dfrac{PF_{gas}\,y_{H_sS}}{R_g T} \right]} \qquad (4)$$

As can be seen, the theoretical time depends on initial hydrogen sulfide concentration, sulfidation pressure and temperature, as well as on gas flow rate, and it will vary according to experimental conditions.

The actual sulfur captured by the sorbent (M_{H2S}), until a given sulfidation time t_s, is calculated by the expression

$$M_{H2S} = \left[MW_{H_sS} \cdot \frac{PF_{gas}\,y_{H_sS}}{R_g T} \right] \cdot t_s \qquad (5)$$

where MW_{H2S} is the molecular weight of H_2S, P is the absolute pressure at sulfidation conditions, F_{gas} is the volumetric gas flow rate at process conditions, y_{H2S} represents the inlet H_2S mol fraction, R_g is the universal gas constant and T is the absolute temperature at sulfidation conditions.

The above calculation procedure assumes that all sulfur is picked up by the sorbent and no sulfur escapes with the gas leaving the reactor.

The ratio of actual sulfidation time until breakthrough (typically 500 ppmv) under a given set of experimental conditions to theoretical sulfidation time for the same conditions, what is usually called dimensionless time, provides a measurement of sorbent performance and makes possible the comparison of desulfurization results under different operation conditions.

Similar equations can be written to calculate the theoretical regeneration time (t_{0reg})

$$M_0 O_2(g) = \frac{3}{2} \cdot \frac{MW_{O2}}{MW_{H2S}} \cdot M_{H2S} \quad (6)$$

$$m_{O2}(g/min) = \frac{MW_{O_2} \cdot F_{reg} \cdot y_{O_2} P}{R_g T} \quad (7)$$

$$t_{oreg}(min) = \frac{M_0 O_2(g)}{m_{O2}(g/min)} \quad (8)$$

where M_0O_2 (g) is the oxygen required to regenerate sorbent loaded with a known amount of sulfur M_{H2S}, MW_{O2} and MW_{H2S} are the molecular weight of O_2 and H_2S respectively, m_{O2} is the oxygen mass flow rate, F_{reg} represents the volumetric gas flow rate in the regeneration stage, P is the pressure of the system, T is the temperature of the system, y_{O2} represents the inlet O_2 mol fraction, and R_g is the universal gas constant.

4 RESULTS AND DISCUSSION

4.1 Sulfidation Tests

The objective of bench-scale testing has been to determine the desulfurization performance of the sorbent under high temperature and pressure reducing conditions.

4.1.1 Effect of Sulfidation Atmosphere.

The first set of experiments was carried out under simplified atmospheres compared to the gasification fuel gas environment. Desulfurization runs were conducted on binary and ternary mixtures, as Table 2 shows. The objective of these tests was to analyze the deleterious effect of reducing components, such as hydrogen and carbon monoxide, present in any gasification gas. Reduction of zinc-based sorbents in the presence of reducing agents followed by evaporation of zinc from the surface in the temperature range of 720 – 800 ºC has been reported by Siriwardane et al. [23]. Similarly, Sasaoka et al. [24] studied experimentally the stability of ZnO for reduction under desulfurization conditions. They found out that high concentration of H_2 or CO led to the reduction of the sorbent. Reduction was depressed in the presence of H_2O and CO_2.

Table 2. *Experimental runs on binary and ternary mixtures*

Test	Mixture	GHSV (h^{-1})	Sorbent (g)	P (atm)	T(ºC)	Gas flow-rate (Nl/min)
SS1	H_2S/N_2	3500	600	10	400	34
SS2	$H_2S/H_2/N_2$	3500	600	10	400	34
SS3	$H_2S/H_2O/N_2$	3500	600	10	400	34
SS4	$H_2S/CO/N_2$	3500	2500	10	400	141,67

In Figure 3, the evolution of H_2S concentration at the reactor outlet is plotted against normalized time, t/t_0, where t_0 is the minimum required time for the complete sulfidation of the metal oxide.

Essentially, almost no H_2S is measured in the exit stream prior to breakthrough. The dimensionless time that corresponds to the breakthrough point (sharp increase of the H_2S concentration in the reactor outlet) is a measure of the sorbent utilization, i.e., the average conversion of the solid reactant. Estimation of sorbent utilization yields values that range from 55% for $H_2S/H_2O/N_2$ up to 80% in the case of H_2S/N_2 mixture.

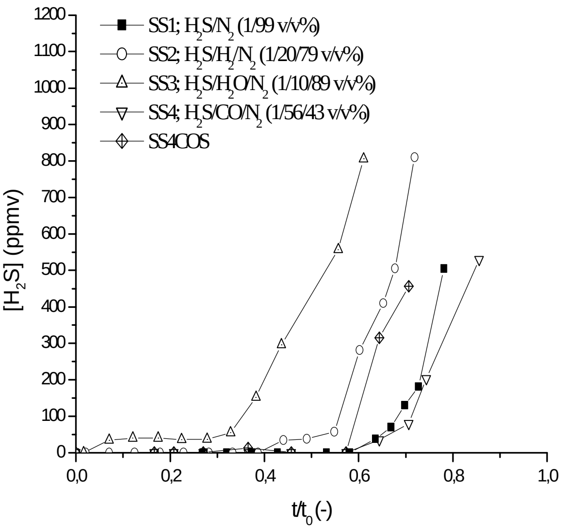

Figure 3. *Sulfidation breakthrough curves. Effect of gas components (P=10 atm, T=400ºC, GHSV=3500 h^{-1}, $[H_2S]$ = 1%v/v).*

When CO together with H_2S was fed into the system, (run SS4) some COS formation took place, and therefore this compound was detected at the reactor outlet. This significant feature was observed by Pineda et al. [25] and it is assumed to be formed through the reaction

$$H_2S + CO \rightarrow COS + H_2$$

Given that before the breakthrough time COS is not detected in the outlet gas, two different explanations could be possible: Either the sorbent is capable of COS retention or this compound does not form until the sorbent becomes spent by the adsorption of H_2S, since reaction between ZnO and H_2S is thermodynamically favored, therefore decreasing the concentration of the latter to very low values.

4.1.2 Effect of Sulfidation Temperature

For many years, much of the sorbent development work was devoted to sorbents suitable for temperatures greater than 650ºC, since a higher temperature application would offer better overall IGCC process efficiency. However, because of process equipment limitations and other process variables such as the alkali content in the fuel gas, in the study published by NOVEM a temperature range from 300 to 500ºC was recommended as the optimum desulfurization temperature [26].

In accordance with this trend, the effect of the temperature on the performance of the sorbent has been studied between 250 and 600ºC. Binary mixtures of 1%v/v of H_2S in nitrogen have been used for this evaluation, as shown in Table 3. Desulfurization has been conducted at high pressure, 10 atm and at moderate gas space velocity, 3500 h^{-1}. Figure 4 shows the hydrogen sulfide breakthrough curves as a function of temperature.

***Table 3.** Experimental tests for determining the effect of sulfidation temperature*

Test	Mixture	GHSV (h^{-1})	Sorbent (g)	P (atm)	T(ºC)	Gas flow-rate (Nl/min)
STS1	H_2S/N_2	3500	600	10	400	34
STS2	H_2S/N_2	3500	600	10	250	34
STS3	H_2S/N_2	3500	600	10	600	34

It is noticeable to see that even at 250ºC, there was no H_2S detected in the reactor outlet gas stream prior to breakthrough. It is clear that, when the concentration of H_2S is 10000 ppmv, sulfur uptake at 650ºC is higher than at 400 and 250ºC. This may be an indication of higher diffusion resistance at lower temperature when the H_2S concentration is high. Similar findings have been reported by other authors, for example Siriwardane et al. [27].

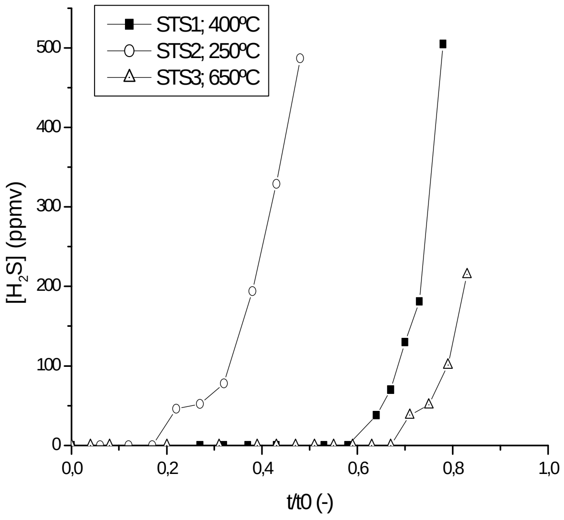

***Figure 4.** Sulfidation breakthrough curves. Effect of temperature (GHSV=3500 h^{-1}, P=10 atm, $[H_2S]$=1%v/v).*

4.1.3 Effect of Gas Hourly Space Velocity

Sorbent-gas reactions kinetics tend to be diffusion-limited, and thus the amount of sulfur absorbed before breakthrough is affected by the velocity of the gas stream. The effect of gas residence time across the sorbent bed was evaluated using binary mixtures of 1%v/v of H_2S

in nitrogen. As Table 4 shows, sulfidation of the sorbent has been conducted under high pressure, 10 atm, and high temperature, 400ºC conditions at 3500 h^{-1} (2,78 cm/s) and 10000 h^{-1} (7,98 cm/s) of gas space velocity.

Table 4. *Experimental runs to determine the effect of space velocity on desulfurization performance*

Test	Mixture	GHSV (h^{-1})	Sorbent (g)	P (atm)	T(ºC)	Gas flow-rate (Nl/min)
SVS1	H_2S/N_2	3500	600	10	400	34
SVS2	H_2S/N_2	10000	600	10	400	97

Linear velocity data in Figure 5 show that, at the higher velocity, sulfur uptake by the sorbent is lower. In addition to diffusion resistance, one possible explanation for the decrease of sulfur loading when gas space velocity increases would be that at the higher velocity, the bed length might be shorter than the absorption front.

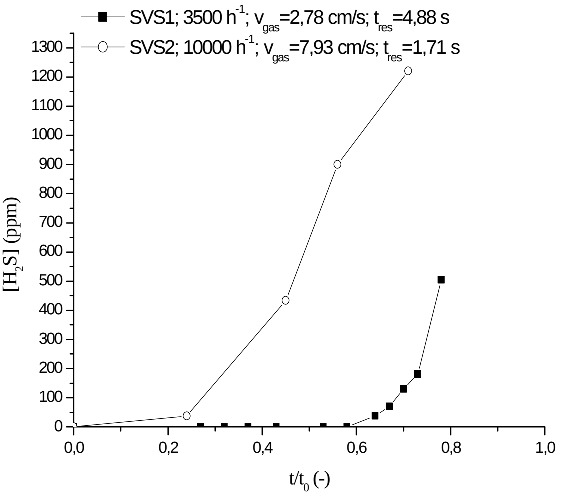

Figure 5. *Sulfidation breakthrough curves. Effect of gas hourly space velocity (P=10 atm, T=400ºC, $[H_2S]$=1%v/v).*

4.1.4 Effect of Sulfidation Pressure

In order to assess the effect of pressure on sulfur uptake, three different levels were studied (2, 10 and 20 atm) using binary mixtures of 1%v/v of H_2S in nitrogen – see Table 5-.

Gas hourly space velocity was kept at 3500 h^{-1}, while desulfurization temperature was set at

400ºC to compare results.

Table 5. *Study of the effect of pressure on desulfurization*

Test	Mixture	GHSV (h^{-1})	Sorbent (g)	P (atm)	T(ºC)	Gas flow-rate (Nl/min)
SPS1	H_2S/N_2	3500	600	10	400	34
SPS2	H_2S/N_2	3500	600	2	400	34
SPS3	H_2S/N_2	3500	2500	5	400	141,67

The dimensionless breakthrough curves at different pressures are shown in Figure 6. It is evident that the pressure has a significant effect on the performance of this sorbent. At higher pressures, the sulfur loading values are considerably higher, reaching estimated values as high as 97% of the maximum loading capacity at 20 atm, than those at 2 atm in which sorbent utilization is only 52% of the maximum capacity. This may be an indication that the diffusion of H_2S to the interior of the pellet is enhanced at higher pressure.

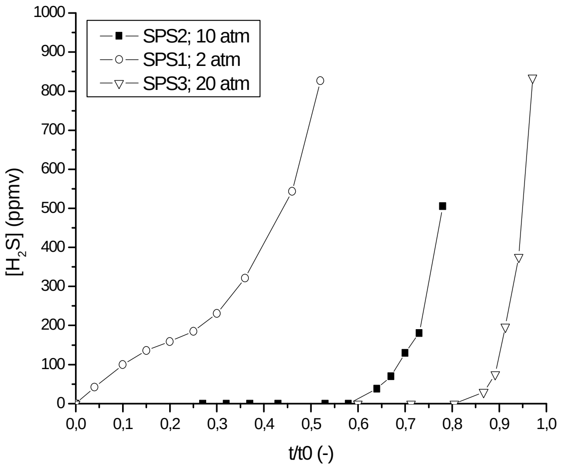

Figure 6. *Sulfidation breakthrough curves. Effect of pressure (GHSV=3500 h^{-1}, T=400ºC, [H_2S]=1%v/v).*

4.1.5 Effect of Hydrogen Sulfide Concentration

To determine if the sorbent would function satisfactorily under a wide range of hydrogen sulfide concentrations, sulfidation runs were carried out varying the H_2S content in the binary mixture (1-5 %v/v), as shown in Table 6.

Table 6. *Study of the influence of H_2S inlet content on desulfurization*

Test	Mixture	$[H_2S]$ (%v/v)	GHSV (h^{-1})	Sorbent (g)	P (atm)	T(ºC)	Gas flow-rate (Nl/min)
SCS1	H_2S/N_2	1	3500	600	10	400	34
SCS2	H_2S/N_2	2	3500	600	10	400	34
SCS3	H_2S/N_2	5	3500	600	10	400	34
SCS4	H_2S/N_2	5	3500	600	2	400	34

In Figure 7, the evolution of H_2S concentration at the reactor outlet with the normalized time, t/t0, has been plotted.

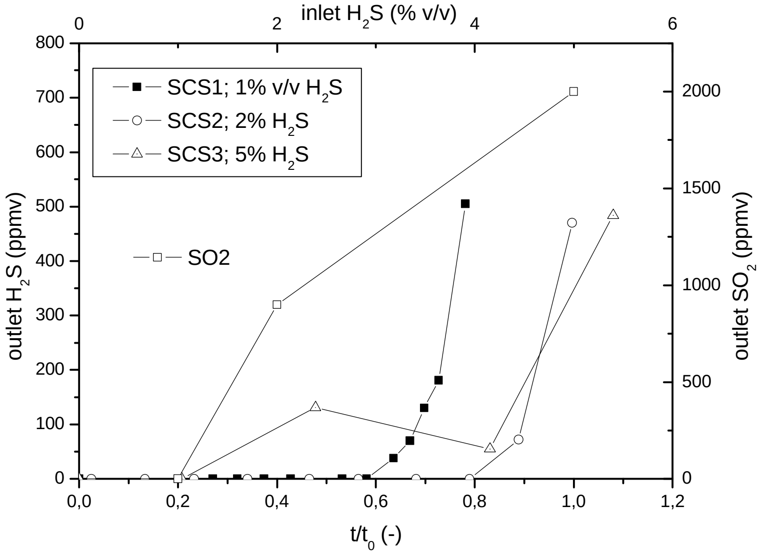

***Figure** 7. Sulfidation breakthrough curves. Effect of H_2S Concentration on Sulfidation (GHSV=3500 h^{-1}, T=400ºC, P=10 atm).*

Although the sorbent is able to absorb effectively all of the hydrogen sulfide from the fluid stream, even with concentration as high as 5% v/v, it has also been found that concentration of H_2S in the gas stream has an important effect on the sulfur retention capacity. The sorbent oxidizes a certain amount of hydrogen sulfide to sulfur dioxide. The resulting sulfur dioxide is not captured by the sorbent, and, thus passes unabsorbed through the bed. Nevertheless, sulfur dioxide concentration in the outlet gas stream is very low, less than 2000 ppmv, compared to the hydrogen sulfide content of the inlet stream, 5%.

4.2 Regeneration Tests

During the sulfidation stage, the sorbent becomes saturated with sulfur due to the reaction between zinc oxide and hydrogen sulfide. The primary objective of the regeneration stage is to reactivate the zinc oxide through oxidation of the formed metal sulfide back to its original state. The easiest way to do so is by using oxygen. Regeneration reaction would take place with sulfur dioxide release , and would be written as follows,

$$MySx\ (s) + 3/2\ xO_2\ (g) \rightarrow MyOx\ (s) + xSO_2\ (g)$$

Apparently regeneration looks like a simple task. There are, however, a number of points which need to be taken into account. Regeneration is quite exothermic, with a local increase of temperature that can lead to sorbent degradation –physically and chemically- as well as to sintering. Moreover, during regeneration other reactions such as sulfate formation can happen.

$$MS + 2\ O_2 \rightarrow MSO_4$$

Sulfate molecules are fairly big which may cause the sorbent to break and which are difficult to convert into the corresponding oxide. Sulfate formation can be controlled by adjusting regeneration temperature.

Regeneration rate, nature and distribution of regeneration products and temperature of the sorbent bed are influenced by several operating parameters, in addition to oxygen content. As reported in literature e.g. Woods, Gangwal, Woods, Bagjajewicz, Yrjas [28-32], the most relevant ones are: starting regeneration temperature, gas space velocity and pressure.

Therefore a systematic study was conducted to analyse in first place if the sorbent is regenerable, and subsequently to establish successful operation conditions for regeneration. The nature of the regeneration agent was evaluated and then the maximum oxygen content in the regeneration gas was determined in order to prevent sorbent deterioration.

4.2.1 Effect of the Regeneration Agent

According to literature, there are a number of possibilities to regenerate a spent sorbent, such as the use of air, steam, sulfur dioxide, air diluted with nitrogen or steam. In the case of zinc sulphide, Williams et al published in their work that regeneration with sulfur dioxide was not feasible, [4], and consequently regeneration with sulphur dioxide was not considered any longer under the scope of this work.

A first set of regeneration tests was devoted, therefore, to select the regeneration agent, evaluate the regenerability of the sorbent, and to study the effect of the diluent. Test conditions are summarised in Table 7

Table 7. *Tests to determine regeneration agent*

Test	Gas	$[O_2]/[H_2O]$	GHSV (h^{-1})	Sorbent (g)	P (atm)	Gas flow-rate F (Nl/min)
AR1	H_2O/N_2	0 %/40 %	3500	600	2	34
AR2	$O_2/H_2O/N_2$	2 %/40 %	3500	600	2	34
AR3	$O_2/H_2O/N_2$	2 %/40 %	2000	600	2	19,43
AR4	O_2/N_2	2 %	3500	600	2	34
AR5	O_2/N_2	2 %	2000	600	2	19,43

In principle, regeneration of the spent sorbent could be achievable by using oxygen or steam as oxidation agents. Although it is reported in literature that regeneration of zinc sulfide with steam could be feasible, – see for instance the work by Sasaoka et al. [33]- , for this sorbent reaction between ZnS and steam was not detected during test AR1. During test AR1, a mixture of H_2S (max concentration around 600 ppmv) and SO_2, (max concentration about 9000 ppmv) formed. Moreover, as regeneration proceeded a bed temperature decrease was recorded instead of an increase as was expected. It was concluded that steam regeneration was not feasible since regeneration time would be so long that its industrial implementation would be non viable. Therefore, the remaining experimental regeneration work focused on oxygen as the oxidant to regenerate the spent sorbent.

Table 8 shows the highest sulfur dioxide concentration reached for every regeneration test.

Table 8. *Comparison of theoretical and experimental values obtained during regeneration runs devoted to determine regeneration agent*

Run	$[H_2O]$ (%v/v)	$[O_2]$ (%v/v)	$[SO_2]$ (%v/v) theoretical	$[SO_2]$ (%v/v) actual	Theoretical regeneration time (min)	Actual regeneration time (min)
AR2	40	2,8	1,88	1,53	278	225
AR3	40	3,5	2,36	1,71	193	95
AR4	0	2,5	1,68	1,41	93	200
AR5	0	3,6	2,43	1,65	136	206

In none of them the maximum theoretical concentration, estimated on account of the input oxygen, was reached. Besides, for the oxygen-steam runs, actual regeneration time was shorter than the theoretical one, which was estimated by the amount of sulfur picked-up by the sorbent during the corresponding sulfidation run. This indicates that the sorbent might not be fully regenerated what was confirmed by the dark-greyish colour of some of the sorbent pellets, when it was discharged from the reactor.

The fact that dilution of the regeneration gas stream with steam – tests AR2 and AR3- might have resulted in incomplete regeneration of the sorbent can be deduced from Figure 8. In this Figure, the dimensionless concentration of SO_2 at the reactor outlet ($[SO_2]/[SO_2]_{theor.}$), estimated as the ratio of SO_2 measured by GC to the maximum concentration given by the oxygen concentration in the regeneration feeding gas is plotted against dimensionless time (t/t_0). The normalized time, t/t_0, is the ratio of actual regeneration time to the minimum theoretical time required for complete regeneration of the metal sulfide, t_0. For runs AR2 and AR3, normalized time values lower than 1 were obtained, though SO_2 concentration at the reactor outlet did not reach the theoretical value. Consequently, sorbent regeneration under those conditions must be necessarily incomplete.

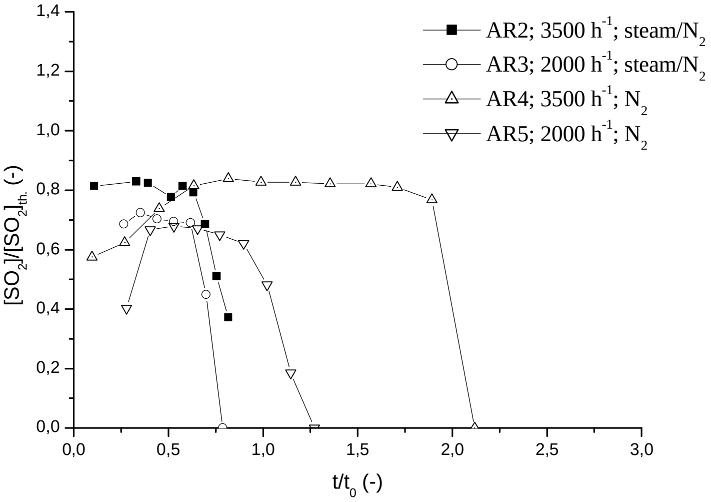

Figure 8. *Normalized Regeneration Curves for N_2- and H_2O-N_2-diluted Regeneration Runs (P=2 atm, T=550ºC, $[O_2]$=2%v/v).*

On the other hand, dry regeneration using oxygen diluted in nitrogen –tests AR4 and AR5- is complete, although the required time until completion is longer than t_0. As regeneration proceeds, oxygen is fully spent as gas analysis of the outlet gas stream showed. Sulfur dioxide content, however, is lower than the theoretical value and hence the time required to achieve complete regeneration exceeds the theroretical value. This means, that regeneration mechanism might not be the straight oxidation of zinc sulfide but intermediate compounds e.g. sulfite, sulfate, oxysulfide, etc. may form which would then decompose to the corresponding oxide as several authors- e.g. Woods and Yrjas- have suggested [30], [32] (Yrjas, Woods) .

In our studies the primary reaction found to be taking place during regeneration of the sulfided product has been direct oxidation of the metal sulfide, with sulfur dioxide release. One of the typical regeneration curves obtained is shown in Figure 9, where SO_2 and O_2 profiles measured by GC at the reactor outlet have been plotted against regeneration time.

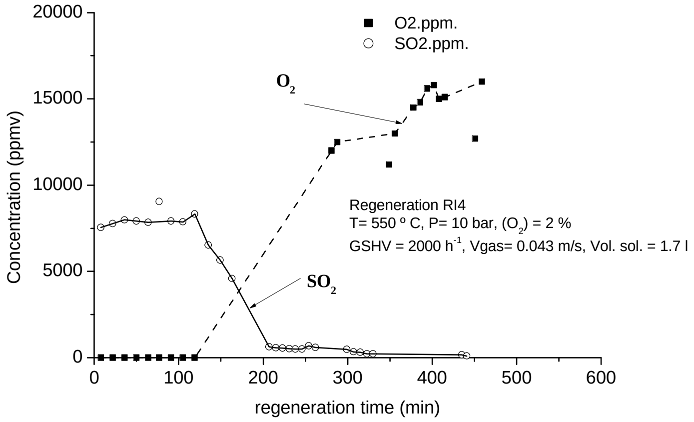

Figure 9. *Experimental Regeneration Curve (P=10 atm, T=550ºC, $[O_2]$=2%v/v/N_2).*

Figure 9 shows that essentially there is no free oxygen in the regeneration gas which leaves the reactor. When the sorbent is completely regenerated, O_2 concentration increases until reaching the inlet value. The exothermic nature of the regeneration reaction brings about temperature changes with time and position in the bed as shown in Figure 10.

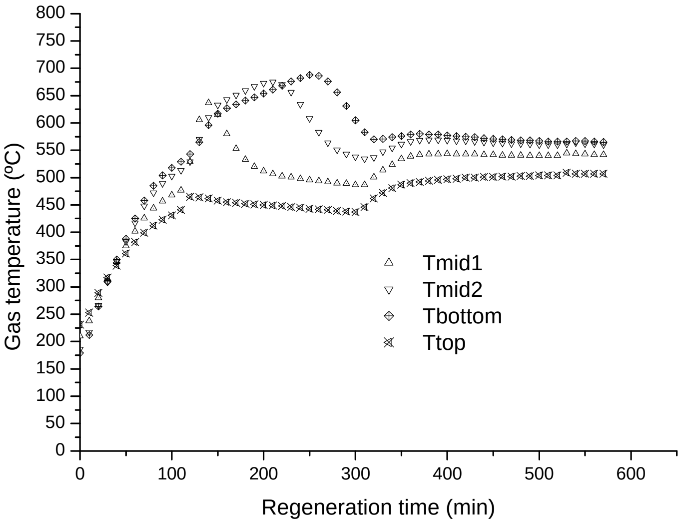

Figure 10. *Temperature Profile during a Regeneration Run (P=10 atm, T=550ºC, [O_2]=2%v/v/N_2).*

Figure 10 shows the temperature profile along the sorbent bed. The progress of the reaction in the fixed bed is easily seen from this Figure. As time increases, temperature also increases within the reaction zone, which moves downwards.

4.2.2 Effect of the Oxygen Content in Regeneration Gas

From the first set of tests it was concluded that oxygen is an effective regeneration agent. Nevertheless, as discussed before, fixed bed and thermogravimetric studies conducted by Woods and co-workers [29] showed that regeneration reaction rate increases with oxygen content. They found that for the temperature range in which regeneration takes place, its rate in fixed bed is limited by mass transfer and gas diffusion inside the pellets. Reaction rate increased with higher oxygen content. The reason is that the concentration gradient across the external gas film, which is directly related to the mass transfer rate, increases when oxygen content is higher. One must bear in mind, however, that regeneration with O^2 is an exothermic reaction and hence controlling the temperature of the solid bed in the regenerator reactor is not easy, particularly in a fixed bed. Increase of temperature is directly related to the oxygen content in regeneration gas. This increase of temperature arising from the regeneration reaction must be controlled otherwise it will lead to physical and chemical damage of the sorbent. Furthermore, regeneration in large excess of oxygen can lead to sulfate formation as the thermodynamics studies published by Ingraham, Gray, Kubaschewski have shown [34], [35], [36]. Sulfate formation can take place through direct oxidation of the sulfide,

$$ZnS + 2O_2 \rightarrow ZnSO_4 ; \Delta H_{298} = -779{,}7 kJ / mol$$

Its formation may also happen through the following reactions

$$SO_2 + \frac{1}{2} O_2 \rightarrow SO_3 ; SO_3 + ZnO \rightarrow ZnSO_4 ; \Delta H_{298} = -336{,}4 kJ / mol$$

$ZnO.2ZnSO_4$ may form as well, which is much more stable than the simple sulphate.

As discussed before due to the highly exothermic nature of the regeneration reaction (301,4 kJ/mol $_{O2)}$ the sorbent can sinter decreasing surface area and losing zinc as a result of vaporisation. For that reason the maximum content of oxygen in the regeneration gas should be determined experimentally or by mathematical modelling. A second set of runs was therefore devoted to determine the maximum concentration of oxygen in the regeneration gas to control the increase of sorbent temperature due to the exothermicity of the regeneration reaction and to avoid sulfate formation. Based on the results above, it was only consider to dilute air with nitrogen. Table 9 presents the different tests carried out.

Table 9. *Tests conducted to determine maximum O_2 content in regeneration gas.*

Test	[O_2] (% v/v))	GHSV (h-1)	Sorbent (g)	P (atm)	Gas flow rate F (Nl/min)
CO1	21	3500	600	10	34
CO2	7	3500	600	10	34
CO3	5	3500	600	10	34
CO4	2	3500	600	10	34

To select appropriate regeneration conditions, analysis of the results has been based on the maximum temperature recorded in the sorbent bed, with the target of limiting that temperature to 750ºC to avoid zinc vaporisation. Gas space velocity and pressure were kept constant for all runs. The facility was heated in nitrogen-flow up to 500ºC, and then the regeneration mixture was flowed in.

In test CO1, as soon as air was fed to the system, there was an instantaneous surge of temperature, reaching a value beyond 900ºC. Reaction was chilled out letting nitrogen flow in. For the other oxygen content tested, regeneration gas composition and temperature profiles were similar to the ones presented in Figures 9 and 10.

Figure 11 shows regeneration temperature profile for the mid-section of the sorbent bed, for tests CO2, CO3 and CO4 -oxygen content 7, 5 and 2% v/v respectively). This section showed the highest increase of temperature during regeneration.

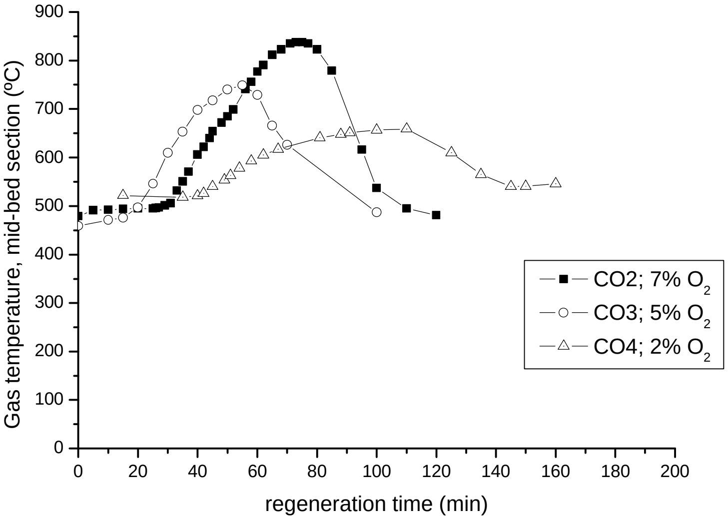

Figure 11. *Gas temperature profile in the mid-bed section during regeneration runs CO2, CO3 and CO4. (O_2/N_2, 10 atm, 3500 h^{-1}, 550ºC)*

On Figure 12, maximum regeneration temperature for the three sorbent bed sections and for the three oxygen contents is presented. It can be seen that although the trend is similar, saturation degree from the corresponding sulfidation run- bed history- also has an influence.

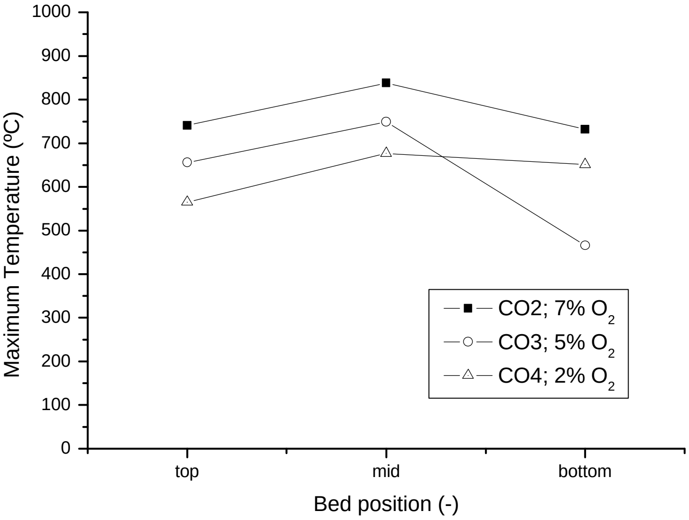

Figure 12. *Maximum temperature for each sorbent bed section during regeneration runs CO2 to CO4. (O_2/N_2, 10 atm, 3500 h^{-1}, 550ºC)*

From the previous Figures it can be concluded that mild regeneration schemes are deemed necessary to prevent excessive temperature excursions as shown on Figure 13.

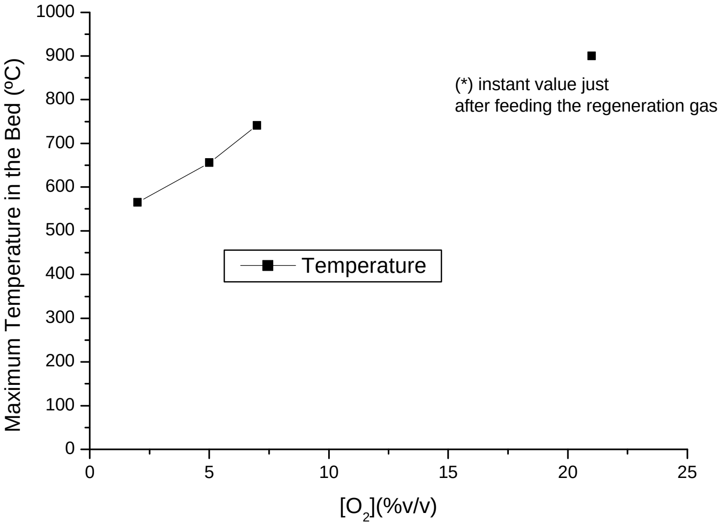

Figure 13. *Influence of oxygen concentration on the increase of sorbent temperature during regeneration runs (P=10 atm, T=550ºC, GHSV= 3500 h^{-1}, O_2/N_2).*

Regeneration with neat air leads to temperature far beyond 900ºC. Decreasing oxygen content in the regeneration gas makes possible to control temperature's spike. Thus, when oxygen concentration values are 7, 5 and 2 % by volume, the maximum temperature in the reactor is 838ºC, 749ºC and 677ºC respectively. In all cases, starting temperature for regeneration was set at 550ºC. Therefore, in order to maintain a high chemical reactivity and physical integrity of the sorbent over cycles, regeneration must be carried out keeping oxygen content below 2%v/v.

These results are in agreement with the estimation of the increase of bed temperature for an adiabatic reactor as a result of regeneration reaction, summarised in Table 10

Table 10*. Increase of temperature for an adiabatic discontinuous regeneration reactor as a function of oxygen molar fraction (Y_{O2}).*

Y_{O2}	ΔTmax (ºC)
0,01	95
0,02	189
0,03	284
0,04	378
0,05	472

According to the estimation above, regeneration using O_2/N_2 mixtures cannot be conducted using more than 2.5% v/v oxygen, on the account that regeneration thermodynamics predicts that regeneration starts at 500ºC and that temperature spike should be kept below 750ºC to avoid zinc loses due to vaporisation. Theoretical estimation has been confirmed by our results.

4.2.3 Effect of Space Velocity and Pressure on Regeneration

Surface velocity of the gas through the sorbent bed is directly related to mass transfer across the external film surrounding sorbent particles. Besides, heat transfer rate depends on the relationship between gas flow-rate and sorbent mass. So, in principle, regeneration would be different depending on the gas hourly space velocity established.

Total system pressure may also have an influence on regeneration rate, due to the fact that for a given oxygen content on the regeneration gas, oxygen partial pressure will change with total pressure.

To determine the effect of space velocity and pressure on regeneration pattern, some of the tests conducted have been chosen, as summarised in Table 11

Table 11. *Runs selected to determine the influence of gas space velocity and pressure on the regeneration of the sorbent*

Test	t/t_0 sulfidation	$[O_2]$ (%v/v)	GHSV (h^{-1})	Sorbent (g)	P (atm)	T(K)	Gas flow-rate (Nl/min)
RMC1	0,57	1	2300	2500	10	823	100
RMC2	0,85	1	1092	2500	10	823	47,5
RMC3	0,90	1	3275	2500	10	823	142,5
RRV3	0,96	2	2000	2500	10	823	87
RRV4	0,95	2	2000	2500	10	823	87
AR4	0,52	2	3500	600	2	823	34
AR5	0,3	2	2000	600	2	823	19,43
CO4	0,48	2	3500	600	10	823	34
9R	0,86	2	1000	2500	10	823	40,5

On runs RMC1, RMC2 y RMC3, gas hourly space velocity was changed, while system pressure and oxygen were kept constant at 10 atm and 1% v/v Runs RRV3, RRV4, CO4 y 9R were conducted at 10 atm, and 2% v/v O_2 and changing gas space velocity. Finally, the effect of pressure can be determined by comparison of runs AR4 y CO4 since the first one was done at 2 atm and the second one at 10 atm, maintaining the other parameters constant. Runs AR4 and AR5, carried out during the selection of regeneration agent stage were conducted at the same pressure, 2 atm, but using different space velocity -3500 y 2000 h^{-1}, respectively

Table 12 shows a comparison of the results of the tests conducted at several gas space velocities. Pressure was kept at 10 bar. Maximum SO_2 content in the gas for the reactor outlet stream and the actual regeneration time are compared to the theoretical values (SO_{2max}/SO_{2theor} and t/t_0), estimated on account of the oxygen fed and amount of sulfur picked up by the sorbent during the sulfidation stage. Maximum gas temperature reached during regeneration of temperature is presented.

***Table 12**. Comparison of regeneration runs conducted at different space velocity*

Run	t/t_0 sulfidation	$[O_2]$ (%v/v)	GHVS (h^{-1})	$[SO_2]_{max.}/[SO_2]_{theor.}$	t/t_0 (-)	Ttop (ºC)	Tmid (ºC)	Tbot (ºC)
RMC2	0,85	1	1092	0,71	1,08	607	670	719
RMC3	0,90	1	3275	0,72	1,02	601	689	724
9R	0,86	2	1000	0,73	1,11	681	717	784
RRV3	0,96	2	2000	0,99	1,32	540	741	760
RRV4	0,95	2	2000	*	1,82	577	725	737
AR5	0,3	2	2000	0,68	1,51	623	637	682

(*) SO_2 content was not measured due to GC problems

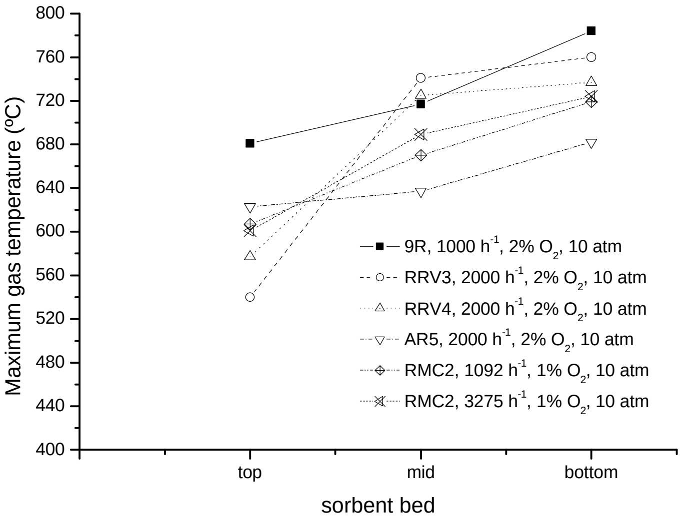

***Figure 14.** Maximum gas temperature for the different sorbent bed sections (P=10 atm, starting regeneration T=550ºC)*

Figure 14 shows maximum gas temperature reached on the different sorbent bed sections, top, mid and bottom, as a function of gas space velocity. There is no clear trend. For low-oxygen-content regeneration gas (1% O_2v/v) gas profile is quite flat and space velocity apparently does not affect gas regeneration temperature. For the runs conducted at 2% O_2 inlet content, the temperature evolution is somewhat erratic.

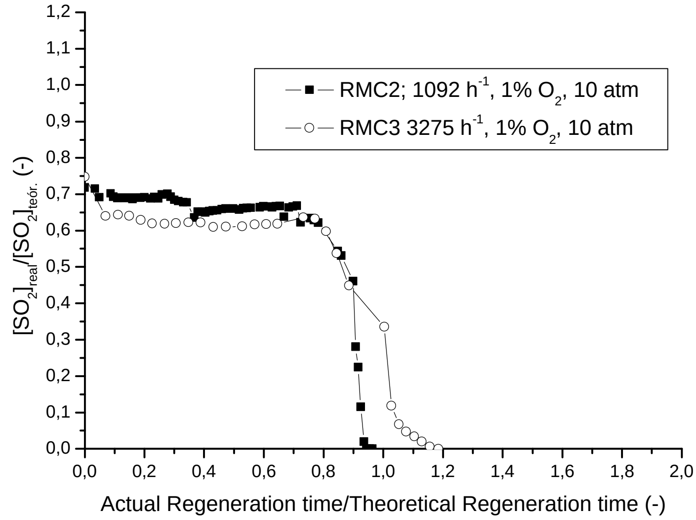

Figure 15. *Effect of space velocity on SO_2 concentration profile during regeneration (1% v/v O_2 P=10 atm, starting regeneration T=550ºC).*

Similarly, as shown in Figure 15, SO_2 profile is basically independent of gas space velocity. It should be highlighted that SO_2 profile reaches a stationary value, which remains constant until regeneration finishes, i.e., until the sorbent bed is fully regenerated.

Table 13 compares results of the runs performed at different pressure. Relationship between maximum SO_2 content measured at the reactor outlet and the theoretical one based on the oxygen fed in is shown. Actual and theoretical regeneration time length-on account of sulfur uptake during previous sulfidation stage- is also presented as are gas temperatures across the sorbent bed.

Table 13. *Comparison of regeneration runs at different pressure*

Run	t/t_0 sulfidation	$[O_2]$ (%v/v)	P (atm)	$[SO_2]_{máx.}$/ $[SO_2]_{theor.}$	t/t0 (-)	Ttop (ºC)	Tmid (ºC)	Tbot (ºC)
AR4	0,52	2	2	0,84	2,15	638	650	625
CO4	0,48	2	10	0,68	0,96	677	659	565

GHSV=3500 h^{-1}, T=550ºC (starting regeneration temperature)

Sulfur uptake from the sulfidation stage previous to regeneration was similar, what in principle would make possible the comparison of both regeneration runs. It seems, however, that no clear effect of pressure on regeneration can be found.

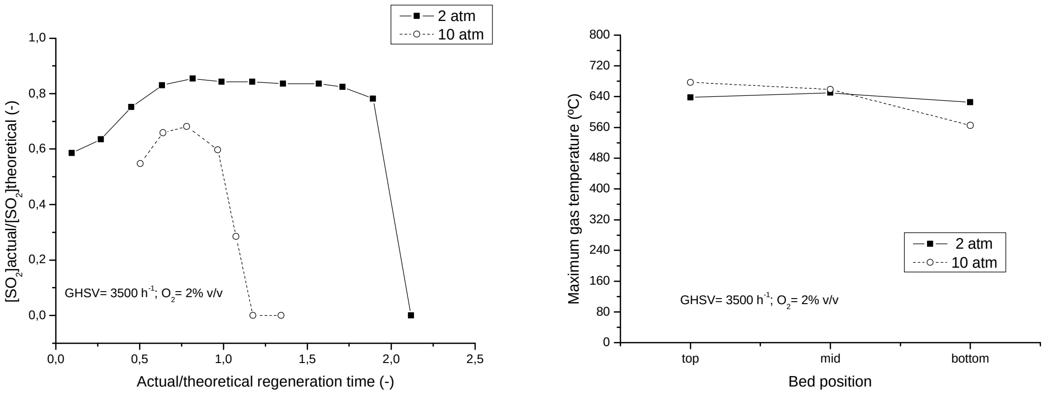

Figure 16. *Effect of pressure on (a) SO_2 concentration profile and (b) temperature during regeneration (2% v/v O_2 GHSV=3500 h^{-1}, starting regeneration T=550ºC).*

As Figure 16 (a) shows, at low pressure, SO_2 concentration reaches a value close to the theoretical one but regeneration time is considerably longer than the theoretical one. On the contrary, at high pressure, regeneration time is similar to the theoretical one, although in this particular case, concentration is significantly lower than the estimated theoretical SO_2 concentration, what would mean that regeneration would be incomplete. This was attributed to the fact that apparently the bottom section of the bed remained un-regenerated, since -as Figure 16 (b) shows- temperature kept fairly constant, without showing the expected increase.

However as far as gas temperature is concerned, for the high-pressure case, temperature profile showed the expected trend, as can be seen on Figure 17, whereas it was not so clear at low pressure.

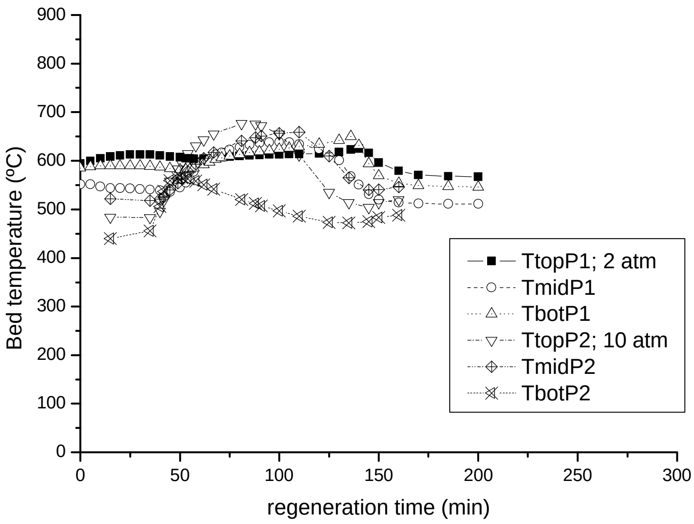

Figure 17. *Gas temperature profile across sorbent bed during regeneration runs at 2 and 10 atm (2% v/v O_2/N_2, GHSV=3500 h^{-1}, starting regeneration T=550ºC)*

4.3 Desulfurization of Synthetic Gasification Gases

Having proved that the sorbent is capable of removing hydrogen sulfide from hot gases, new tests were conducted including all major components of gasification gases. Gas composition used in those runs is summarized in Table 14.

H_2S content in the feed syngas ranged from 500 ppmv to 10000 ppmv. Besides, different syngas composition was used to determine sulfur capture ability under various CO, H_2 and CO_2 content, that is, gases with different reducing power.

Gas A simulates the composition of a high sulfur feedstock, oxygen-rich gasification process, whereas Gas B reproduces the composition of a low-sulfur feedstock, air-blown gasification cycle.

Table 14. *Gas composition of the simulated ELCOGAS and ABGC Gases*

% v/v	A	B
CO	56	16
H_2	20	15
CO_2	4	8.5
N_2	9	45.2
H_2S	1	0.05
H_2O	10	15

Table 15 presents the experimental conditions under which desulfurization tests were conducted.

Table 15. *Nominal conditions for simulated coal gas desulfurization tests*

Gas	$[H_2S]$ (ppmv)	GHSV (h^{-1})	sorbent (g)	P (atm)	T(ºC)	F_{gas} (Nl/min)
A	10000	5000	2500	10	500	217,5
B	500	6000	750	10	540	81

According to Figure 18, breakthrough behaviour of the sorbent is not affected neither by the hydrogen sulfide content of the gas, nor by its composition. Almost complete removal of H_2S from the fuel gas is achieved both in high-H_2S content gases as in the A-gas case and in low-H_2S-containing gases such as for the B-type gas. The sorbent did an excellent job at desulfurization, with H_2S levels leaving the reactor prior to breakthrough of less than 20 ppmv. These levels correspond to more than 99% desulfurization (based on 1% H_2S in the inlet gas). The total sulfur captured by the sorbent shows it is very reactive on a mass basis.

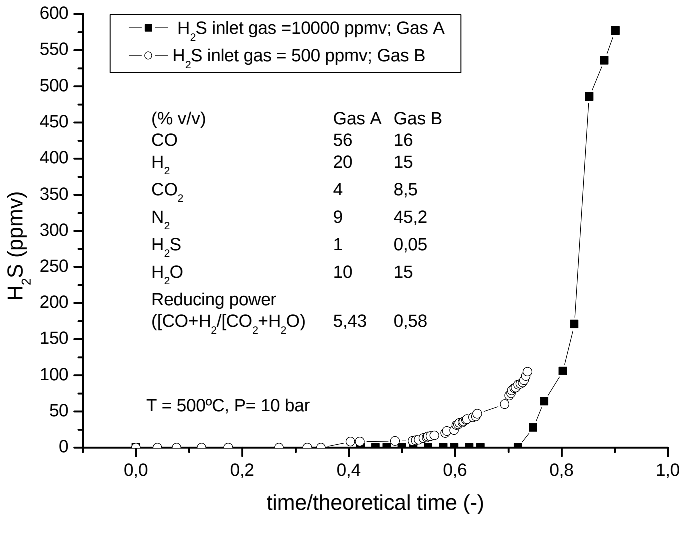

Figure 18. *Desulfurization performance of the ZnO sorbent for different syngas compositions*

According to **Figure 18**, the sorbent has high desulfurization capacity either for bulk sulfur removal in highly reducing gases (A-type Gas) or for a polishing stage in low sulfur content gases (B-type Gas).

After the tests the bed was sectioned, and sulfur and carbon content of the sorbent was been determined. Position *"Top"* corresponds to the gas inlet location of the reactor bed, while position *"Bottom"* corresponds to the gas outlet location. The estimated sulfur loading is calculated by the use of equations (2) and (3). Results of the sulfur content compared to the estimated sulfur uptake have been summarized in Table 16.

Table 16. *Estimated and measured sulfur content of the sorbent from desulfurization of synthetic gasification gas*

Test	Estimated Sulfur Loading (% w)	Sulfur Top (% w)	Sulfur Mid (% w)	Sulfur Bottom (% w)
A	17,2	16,4	13,2	14,9
B	14,9	13,3	11,5	9

Sulfur distribution pattern along the sorbent bed, is typical of down-flow mode fixed beds where the reaction zone moves downwards with time. Higher sulfidation loading and fairly uniform distribution in the reactor bed is achieved for the A-type gas, which has higher content of H_2S. This may be an indication of absence of diffusion resistance through within the sorbent pellets.

Carbon content of the used material was also determined. The results of the analyses are shown in Table 17. Only trace amounts of carbon were observed. This, together with the fact that the chromatographic analyses performed during the sulfidation runs did not show any significant change of the gas composition, proves that desulfurization under the experimental conditions tested essentially proceeds without the occurrence of secondary reactions to a significant extent.

Table 17. *Measured carbon content of the sorbent from desulfurization of synthetic gasification gas*

Gas	Carbon Top (% w)	Carbon Mid (% w)	Carbon Bottom (% w)
A	0,08	0,10	0,09
B	0,15	0,17	0,21

4.4 Multi-cycle Desulfurization of Synthetic Coal Gases

Finally, since one of the requirements imposed on a desulfurization sorbent to be successfully implemented for hot gas cleanup is its ability to withstand cycles of sulfidation followed by regeneration, several cycles have been conducted to gather preliminary data on the performance of the sorbent over subsequent cycles. Nine sulfidation-regeneration cycles were performed for an A-type gas under the following experimental conditions:

i) Sulfidation stage: 400ºC, 20 bar and at a gas space velocity of 3500 h^{-1}, gas flow-rate 150 Nl/min, v_{gas}= 6 cm/s. Last two cycles were conducted at 10 bar due to operational problems

ii) Regeneration stage: 550ºC, 10 bar, 2000 h^{-1}, O_2 content 1,5-2% v/v, N_2 balance, gas flow-rate 75 Nl/min, v_{gas}= 7 cm/s

Experimental conditions were set according to results obtained during sulfidation and regeneration studies reported in previous sections.

The amount of sorbent loaded in the reactor was 2500 g.

Figure 19(a) shows H_2S profile at the reactor outlet during sulfidation runs at 20 bar. Pre-breakthrough H_2S concentrations were below the FPD detection limit (< 1ppmv), which suggest very good desulfurization kinetics and thermodynamics. Although the sorbent showed poorer desulfurization performance in cycle 2, it recovered sulfur loading capacity in the third cycle, remaining fairly steady afterwards. Based on zinc oxide content and operating conditions, the estimated theoretical sulfidation time is 240 min. Actual sulfidation time ranged between 158 min (second cycle) and 236 min (first cycle). For the last cycle sulfidation time was 195 min Estimated sorbent loading capacity in every cycle is depicted in Figure 19(b). Apart from cycle 2, sulfur capacity is quite close to the maximum theoretical sorbent´s capacity. Cycle nine shows a lower sulfur uptake because it was conducted at 10 bar

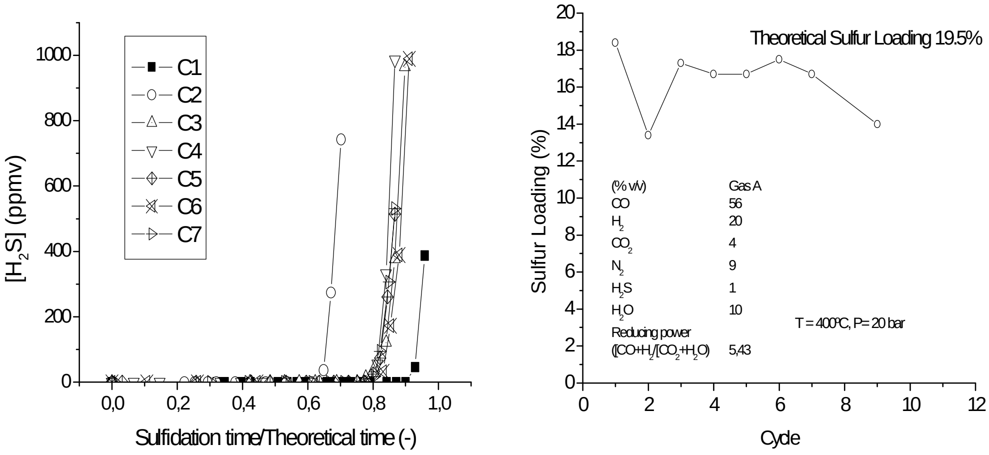

***Figure 19**. Long term performance tests (GHSV=3500 h^{-1}, T=400ºC, P=20 bar, sorbent volume=2.85 l, $(H_2S)i$=10000 ppm): (a) H_2S breakthrough curves; (b) Sulfur loading capacity over cycles*

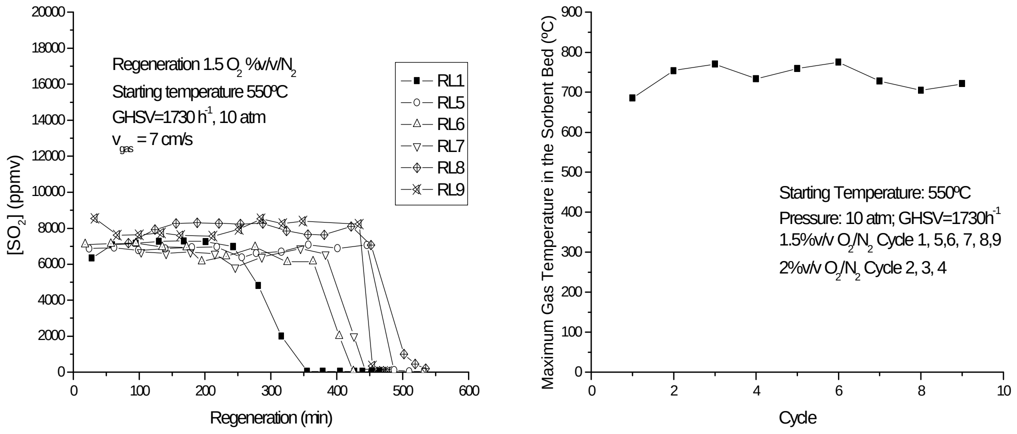

Figure 20. *Regeneration curves: (a) SO_2 breakthrough curves for different cycles (1.5% vol., O_2, 1730 h^{-1}, 10 atm) (b) Maximum gas temperature in the sorbent bed*

Figure 20(a) shows SO_2 breakthrough curves for selected regeneration cycles. Flowrates of air and nitrogen were adjusted to obtain an oxygen concentration in the regeneration gas either of 1.5% or 2% vol. All the oxygen was used up in the reactor as was confirmed by the GC analysis of the regeneration tail gas. Regeneration with 1.5% vol O_2, occurred in a more stable manner, with less SO_2 concentration fluctuation.

Based on the results shown in Figure 20(b), where maximum gas temperature in the sorbent bed has been drawn for the 9-cycle test, it is demonstrated that for mixtures of 1.5-2% vol. O_2 it is possible to fully regenerate the sorbent, without large excursions of temperature. Maximum gas temperature in the sorbent bed remained below 775ºC for all cycles.

Table 18.*Sorbent analysis at different stages*

Sample	Zn (% w/w)	Ni (% w/w)	S (% w/w)	C (% w/w)
Fresh	34,5	5,4	0	0
After 1-cycle regeneration	35	1,6	1,3	0,05
After 3-cycle regeneration	31	4,6	2,1	0,03
After 9-cycle regeneration TOP	34	4,5	3	0,07
After 9-cycle regeneration MID	33	4,7	1,7	0,06
After 9-cycle regeneration BOTTOM	31	6,3	1,2	0,07

Samples of sorbent from different bed locations were removed after the first, third and last regeneration cycle. Sulfur and carbon content was determined, remaining in all cases below 3% w/w as can be seen looking at Table 18.

Although Zhao et al. reported that regeneration can be complicated by the tendency to form

$ZnSO_4$ at sufficiently low temperature and/or high O_2 and SO_2 concentrations, particularly at high pressure, [17], in our case sulfate content measured after the last cycle resulted to be below 2% w/w as Table 19 shows.

Table 19. Sulfate content of samples from the Multi-cycle Desulfurizatin Tests

Sorbent location	S (% w/w)	$SO_4^{=}$ (% w/w)
Bed-Top	3	1,69
Bed-Mid	1,7	2,29
Bed-Bottom	1,2	1,48

5 CONCLUSIONS

The zinc oxide sorbent studied under the scope of the FLEXGAS project has proved to be suitable for ex-bed hot gas desulfurization. The sorbent is effective in H_2S removal in a wide range of gas compositions. The presence of H_2, CO, H_2O does not have deleterious effect on its performance. The sorbent is operational in a wide range of temperature (250-650ºC), pressure (2-20 atm) and gas velocity (3500-10000 h^{-1}) with very low H_2S leakage and sharp breakthrough characteristics. It has demonstrated high desulfurization capacity either in bulk sulfur removal in highly reducing gases such –inlet hydrogen sulfide content close to 10000 ppmv, which would be typical for co-gasification of coal and waste such as pet coke- or for low sulfur-containing gases- 500 ppmv which would be closer to the expected H_2S content in co-gasification of coal and biomass. Dry diluted-oxygen regeneration schemes are deemed as appropriate to restore the metal sulfide to its original sate, metal oxide. The multi-cycle fixed bed tests carried out, though limited in number, show promise for long time performance durability and stability for hot gas desulfurization of gases with high sulfur content and with high reducing power.

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