

Experimental tests on a high-temperature H₂S removal bench-scale system

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Abstract

The behaviour of different commercial sorbents based on zinc oxides has been investigated as high temperature desulphurizing agents from a syngas from high sulphur content coal. A non-reducing gaseous streams containing 1.5 % H₂S diluted in N₂ has been used as simulated syngas.

Comparative tests have been performed isothermally in a bench-scale fixed-bed reactor. In order to check the modifications induced by desulphurization process and to correlate the physicochemical properties of different samples with their performance as H₂S sorbents, fresh and sulphurized samples were characterized by X-Ray Diffraction (XRD), N₂ physisorption at -196 °C, CHS Elemental Analysis (EA), Scanning Electron Microscopy (SEM), Temperature-Programmed Desorption/Reduction/Oxidation (TPD/R/O). Sorbents showed a good performance as desulphurizing agents and maintained the H₂S concentration in the outlet gas below 10 ppm.

This paper shows the main results of the experimental tests on the bench-scale reactor. Moreover a simulation model has been developed and validated. Under the operating conditions considered, the rate of ZnO pellet sulphidation was limited by mass-transfer resistance, and kinetic parameters of overall reaction were obtained assuming a shrinking core model. A good agreement was obtained between theoretical and experimental results.

Keywords: *Hydrogen production, Zero emissions, Clean Coal Technologies*

1. INTRODUCTION

Nowadays, the need to release energy production from the use of oil and natural gas as primary energy sources and, in general, to diversify such sources in order to assure the supplying, is making coal more and more interesting. The use of fossil fuels for power generation is expected to increase in the coming years due to industrialization and population growth. Most of the current methods for the conversion of chemical to electrical energy using conventional technologies are relatively inefficient and from both the energetic and environmental point of view. The two main objectives of emerging technologies for power generation plants are the reduction of energy costs and pollutant emissions [1].

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Moreover, the advanced in development of clean coal technologies, allows an environmental-friendly use of coal, in particularly with reference to low rank coal. Among clean coal technologies, gasification is very interesting since it allows both power generation and clean fuels production, with particular reference to hydrogen.

Syngas coming from coal needs a proper treatment line before its final use. When coal is gasified and converted to fuel gas, chemical compounds are released as gaseous contaminants and mineral matter is released as particulates. All these contaminants must be removed to protect the equipments from corrosion and erosion and simultaneously to keep the emissions level below the standards and to prevent environmental pollution.

Particularly, a highly efficient sulphur removal from several thousand parts per million down to about 1 ppm for hydrogen production or about 100 ppm for gas turbine is needed. Amount of H₂S in syngas depends on the coal rank: in general sulphur content in coal is between 0.50 %wt and 3.5 %wt, but in high sulphur coal (i.e. Sulcis coal from South West Sardinia) can reach 6 %wt.

Commercial desulphurization processes are usually based on liquid scrubbing at or below ambient temperatures, resulting in a reduction thermal efficiency as well as the need for expensive wastewater treatment. In order to achieve maximum thermal efficiency, fuel gas should be desulphurized at temperatures approaching that at which it leaves the gasifier. Developments in hot-gas desulphurization have focused on regenerable solid metal oxides as promising candidates sorbents: pure oxides, solid mixtures of metal oxides, or mixtures of an inert oxide with a solid reactant [2-7] have been tested as sorbents to remove reduced sulphur species (mainly H₂S, COS). Among the different oxides, zinc oxide has the highest equilibrium constant for sulphidation, yielding H₂S removal down to even fraction of 1 ppm. Its principal limitation is that in the highly reducing atmosphere of synthesis gas it is partially reduced to elemental zinc, volatile above 600 °C, with irreversible damage by thermal sintering. In contrast, if the operating temperature is low (480-540 °C), pure zinc oxide has been singled out as the sorbent of choice for desulphurization of coal gas.

This paper reports the results of a screening of the high-temperature desulphurization process in a fixed bed reactor of three commercial single-metal Zn based oxides. The characterization of the fresh and sulphurized sorbents using different techniques has allowed a better knowledge of the involved process. Furthermore a model of the H₂S adsorber based on a ZnO pellets bed was developed as well, with the main purpose of enlightening the mechanism governing the system performance and outlining pathways for further improvements.

2. EXPERIMENTAL SECTION

2.1. Sorbent Characterization

The sorbents in form of powders were characterized by X-Ray Diffraction (XRD), using a Seifert diffractometer with a θ - θ Bragg Brentano geometry and Cu-K α wavelength. The mean dimension of crystallites ($\langle D_{XRD} \rangle$) was obtained by the Scherrer equation,

$$\langle D_{XRD} \rangle = K\lambda / \beta \cos\Theta \quad (1)$$

by elaborating the most intense X-ray peaks with Origin Software using the PseudoVoigt function to fit the peaks and to extrapolate β and Θ . In equation (1), K is a constant related to the crystallite shape (0.9), β is the pure breath of the powder reflection free of the broadening

due to instrumental contributions. This calibration was performed by means of the XRD pattern of a standard Si sample and using the Warren correction $\beta_{\text{sample}} = (\beta_{\text{exp}}^2 - \beta_{\text{std}}^2)^{1/2}$.

Textural analyses were carried out on a Sorptomatic 1990 System (Fisons Instruments), by determining the nitrogen adsorption/desorption isotherms at -196 °C. Before analysis, the samples were heated overnight under vacuum up to 400 °C (heating rate = 1 °C/min).

CHNS Elemental Analysis (EA) was carried out with an EA 1108 CHNS-O analyzer (Fisons Instruments) by total combustion of the samples in an oxygen/helium mixture.

Semiquantitative elemental analyses were performed by using an environmental scanning electron microscope (ESEM QUANTA 200, FEI, Hillsboro, Oregon, USA) equipped with microanalysis system EDS for EDX analysis.

Temperature Programmed Desorption (TPD), Reduction (TPR) and Oxidation (TPO) profiles were obtained with a TPD/R/O 1100 apparatus (ThermoQuest), by heating the sample from 40 to 800 °C (rate 10 °C/min) under flowing (20 cm³/min) nitrogen, hydrogen and air, respectively. Besides a thermal conductivity detector (TCD), a Mass Spectrometry (MS) detector (ProLab, Thermo Electron Corporation) was also used.

2.2. Bench-Scale Reactor System and Test Procedures

Tests about adsorption of H₂S were carried out at Sotacarbo Research Centre in Carbonia, Italy, in a bench scale continuous flow fixed bed reactor.

The flow sheet of the whole experimental system is shown in Figure 1. The system consists of a feed gas apparatus, a fixed bed reactor, a washing bottle for cleaning up the off gas, a gas sampling and analysis equipment. Gas stream was supplied from gas cylinders using suitable distribution system. The flow rate was monitored through flow meter. A bicomponent mixture H₂S/N₂, on dilution of 1.5 % H₂S has been used in order to reproduce the H₂S concentration typical in syngas from Sulcis coal gasification in an air-blown fixed bed gasifier.

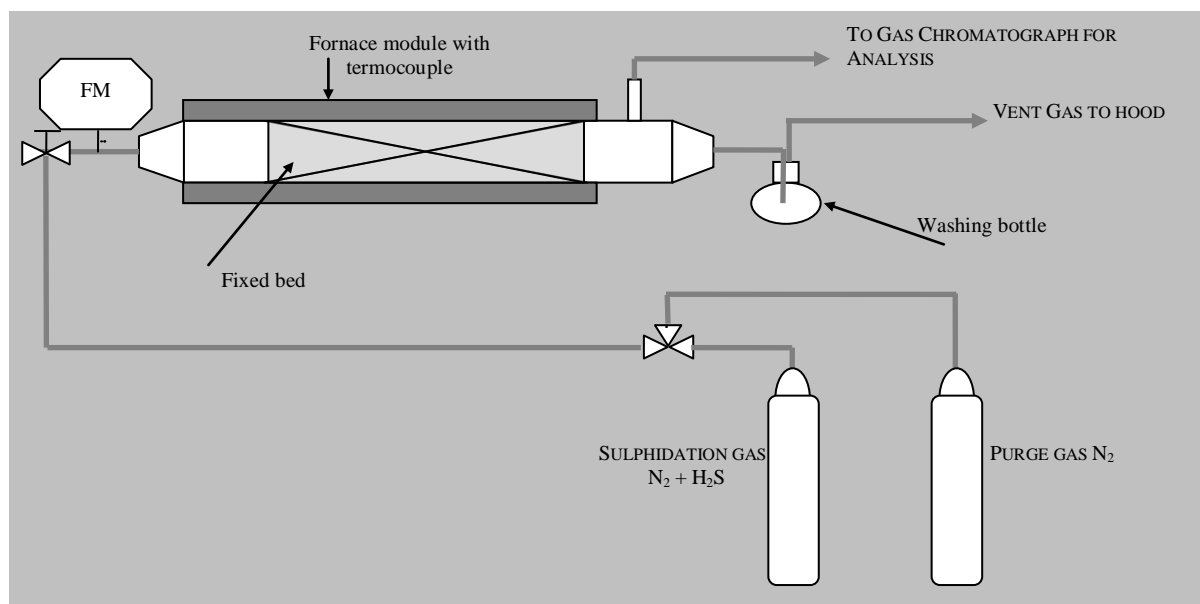


Figure 1 Bench-scale experiment test setup.

The desulphurization performance of all of the sorbents was investigated in this bench scale system designed for operations up to 550 °C. A fixed bed of 40 cm in length containing a volume of 785 cm³ of sorbent particles was enclosed in a borosilicate glass tube (i.d. of 5 cm).

The reactor bed is sandwiched between two perforated borosilicate glass disks. In order to assure a uniform distribution of flow a quiet zone has been designed upstream the fixed bed. It also allows pre-heating of the gas. Quiet zone downstream fixed bed has been required in order to refresh the outlet gas before sampling.



Figure 2. The experimental reactor designed by Sotacarbo and borosilicate glass manufactured for operations up to 550 °C to high temperature desulphuration H_2S removal from gaseous stream.

The reactor (Figure 2) was placed horizontally in a tubular furnace which is equipped with graphite elements. A constant temperature of 300 °C was maintained by PID furnace controller. Temperature of the flow gas in a packed bed was assumed the same of temperature recorded by the S-thermocouple located in the heating elements into furnace. Experimental system has operated in open-circuit at 1.4 bar a. of gas feed pressure.

Before experimental runs, blank adsorption test was executed under the same condition in order to verify

that no reaction was taking place between H_2S and lines/reactor.

A typical bench run consisted of the following steps: the sorbent, in the 2-4.5 mm particle size range, was charged in the reactor; then the reactor was heated to the desired gas desulphurization temperature with a continuous stream of pure nitrogen gas (purity 99.99 %). Nitrogen was fed into the reactor for 90 min at 300 °C also in order to remove from particles sorbent water and impure materials, which coated on the particles surface. During the reaction step, a constant mixed gas flow rate of 80 Ndm³/h was fed to the reactor. A space velocity of 100 h⁻¹ was adopted for the sulphidation runs.

The outlet gas stream was sampled every 3 minutes and analyzed on H_2S concentration through a micro gas-chromatograph (MGC Agilent 3000). Aliquots of gas sampled volume were injected in a capillary column (Poraplot Q; 10m x 0.32mm) eluted with a helium flow. Therefore, H_2S concentration plots versus time were obtained.

Each test has been performed for 6 hours on desulphurization reaction period.

2.3. Model equation

The behaviour of the reaction system has been analyzed by a one dimensional model.

The involved chemistry between the gas phase and the metal oxide particles has been represented according to reaction $ZnO(s) + H_2S(g) \rightarrow ZnS(s) + H_2O$ and the rate of the heterogeneous reaction has been evaluated according to an unreacted shrinking-core model.

Moreover, the followings assumptions have been done:

- plug-flow pattern fluid dynamics;
- negligible axial-back mixing;
- no radial-mixing [8];
- constant pressure along the reactor;
- thermal equilibrium between solid-phase and gas-phase.

Based on previous assumptions the model here presented consists of a set of the mass-balance equations for gas-phase reactants and the energy-balance equation. A further mass-balance

equation is considered for remaining gas-phase compounds, collected as inert-phase. Therefore a set of four ordinary differential equations is obtained. The H₂S mass-balance and energy-balance equation are:

$$\frac{dN_{H_2S}}{dz} = -S\rho_s(1-\theta)R_{H_2S} \quad (2)$$

$$\frac{dH}{dz} = R_{H_2S}S\rho_s(1-\theta)\Delta H_r - \pi D_r U(T - T_e) - S\rho_s(1-\theta)C_{p_{sol}} \frac{dT}{dt} \quad (3)$$

Equations for mass-balance and energy-balance are coupled through the kinetic term R_{H_2S} . Because of demand to apply a simple and reliable correlation for the overall kinetics on sorbent pellet, the unreacted shrinking core model is applied to this purpose in this study. The R_{H_2S} that appears in previous equations is the specific adsorption rate of H₂S, that can be expressed as [9]

$$\rho_s R_{H_2S} = -K_a \frac{C_{H_2S}}{r_e} \quad (4)$$

The overall kinetic constant K_a of equation (4) is obtained by integration of transport equation. The following expression is accomplished:

$$\frac{1}{K_a} = \frac{4}{3} \pi r_e^3 \left(\frac{1}{4\pi r_e^2 K_{ext}} + \frac{r_e - r_i}{D_{eff} 4\pi r_i r_e} \right) \quad (5)$$

The external mass transport coefficient K_{ext} of H₂S in a fixed-bed system is evaluated by the equations:

$$\begin{cases} J_d = 0.91 Re^{-0.51} \psi & 0.01 \leq Re \leq 50 \\ J_d = 0.61 Re^{-0.41} \psi & 50 \leq Re \leq 1000 \end{cases} \quad (6)$$

where [10]:

$$Re = \frac{Gdp}{6\mu(1-\theta)} \quad (7); \quad J_d = \frac{Sh}{Re Sc^{0.33}} \quad (8); \quad Sh = \frac{K_{ext} dp}{D_r} \quad (9); \quad Sc = \frac{\mu}{\rho D} \quad (10)$$

To calculate the diffusion coefficient D_{eff} it is accounted both molecular diffusivity and Knudsen mechanism, by:

$$\frac{1}{D_{eff}} = \frac{1}{D_{H_2S}} + \frac{1}{D_k} \quad (11)$$

The molecular diffusivity D_{H_2S} value is calculated by the Chapman-Enskog equation [11]. The Knudsen diffusivity is calculated with the following expression [12]:

$$D_k = 9700 r_e \sqrt{\frac{T}{PM_{H_2S}}} \quad (11)$$

3. RESULTS AND DISCUSSION

3.1. Screening test for the sorbents

In order to find the optimal sorbent, three commercial ZnO based sorbents (named Z-1, Z-2, Z-3) have been assessed.

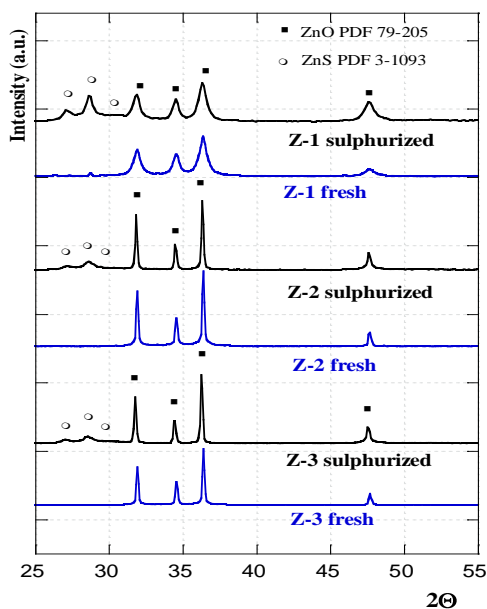


Figure 3. XRD patterns of the fresh and sulphurized sorbents (θ : diffraction angle)

XRD data of the three fresh sorbents (Figure 3) show the presence of an ordered zinc oxide (ZnO) phase whose reflections match the literature values of PDF (Powder Diffraction Files) Card 79-205. Z-2 and Z-3 sorbents show similar features, while broader ZnO reflections are clearly visible for the Z-1 sorbent, suggesting a smaller crystallite size. Moreover, besides the main phase, low intensity reflections associated to small amounts of other phases – that cannot be easily assigned – are observable in Z-1 pattern. The mean crystallite sizes calculated by applying the Scherrer equation to the most intense reflections are reported in Table 1.

For the three sorbents the nitrogen adsorption isotherm appeared to be of type IV with a hysteresis loop (type H3), typical of mesoporous systems. The textural properties of the samples are summarized in Table 1, where the specific surface area calculated with the BET equation (S_{BET}) is reported together with the total pore volume (V_p). The pore size

distribution (obtained by applying the BJH method to the desorption branch) was quite “homogeneous” through the mesopore region (2-50 nm).

Table 1. Structural and textural properties of the fresh sorbents

Sorbent	$\langle D_{\text{XRD}} \rangle$ [nm]	S_{BET} [m ² /g]	V_p [cm ³ /g]
Z-1	13	47	0.18
Z-2	55	23	0.11
Z-3	58	9	0.08

Results of gas chromatograph analysis, based on the stream gas containing 1.5 %vol H₂S treated in the desulphurization process at 300 °C and 1.4 bar(a), are shown in Figure 4 in terms of time-H₂S concentration curves. As it is noticeable, experimental data indicate that H₂S average concentration in outlet gas was maintained below 1 ppmv. The observations are in direct agreement with the thermodynamic predictions previously mentioned. As it is noticeable, Z-1 sorbent has shown higher reaction rate, yielding H₂S removal down to 0.35 ppm in the outlet stream gas. By comparison of this result with the BET data of fresh sorbents (shown in Table 1) the important role of pellet structural properties in sulphur trapping

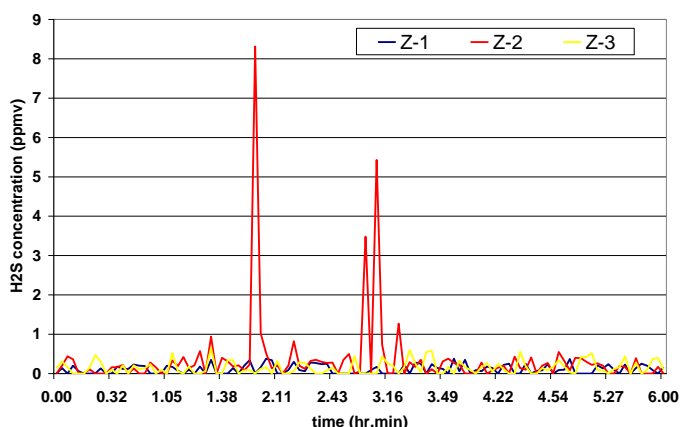


Figure 4. Time- H_2S concentration curves at 300°C for the desulphurization of the stream gas containing 1.5 %vol H_2S and N_2 balance.

can be unequivocally indexed as the ZnS phase (PDF_Card 3-1093). No peaks of any other phase are detected.

The sulphur content determined by Elemental Analysis was around 12 %wt for the three sulphurized sorbents. EA also revealed small amounts of carbon and hydrogen, most probably due to the presence of some adsorbed molecules (hydrocarbons and/or carbon oxides and/or water).

For the sample Z-3 the sulphur distribution within the pellet was determined by SEM-EDX analysis. As shown in Figure 5, the sulphur content decreases from the surface to the inner part of the pellet from 22 ± 2 %wt to 11 ± 1 %wt.

The sulphurized Z-3 sample was also characterized by TPD/R/O. The only species desorbed by the sample upon TPD treatment was H_2O (mostly between 150 and 450°C). By treating

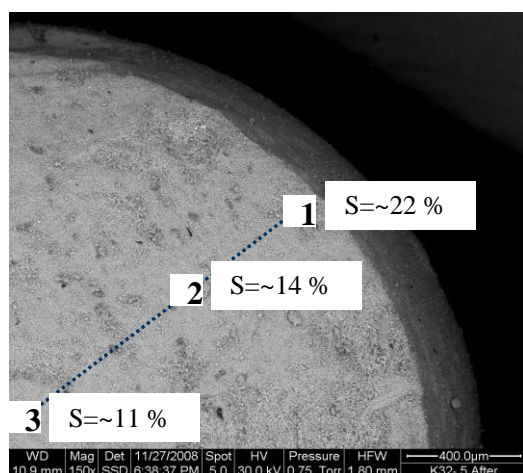


Figure 5. SEM image of a section of the sulphurized Z-3 sorbent.

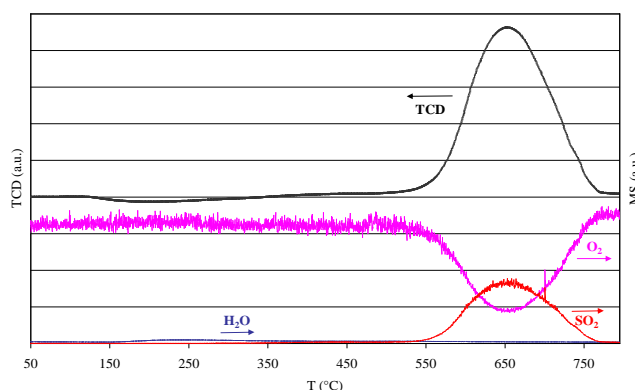


Figure 6. TCD and MS signals for TPO of sulphurized Z-3 sorbent.

the sulphurized sorbent under H_2 -atmosphere, H_2S and SO_2 were also released (370 – 450 and 500 – 700°C , respectively). XRD analysis revealed that the TPR treatment resulted only in a partial removal of sulphur (at the end of the run the sample was still dark). As shown in Figure 6, the treatment under TP conditions in flowing air (TPO) results in a consumption of O_2 and a corresponding release of SO_2 between 550 and 760°C (besides a small amount of H_2O desorbed at lower temperature). After such treatment, the sample appeared white and its

XRD pattern was practically the same as that of the fresh sorbent (cf. Figure 3), thus indicating the regeneration of ZnO upon TPO treatment.

3.2. Modeling and related issues

Differential equations (2) and (3) that, together with chemical kinetics and mass transfer equations, form the mathematical model of the process, have been integrated by a numerical method. For sake of simplicity, an explicit finite difference method has been adopted. Main results obtained by integration are the longitudinal profiles of H_2S -concentration in gas phase and conversion degree of ZnO in the sorption bed.

Some of the results obtained by model integration are reported in Figure 7. H_2S concentration is plotted in first figure and conversion degree in the second one at three different times of exposure.

As expected, the shapes of the two series are hardly distinguishable, leaving a part the scale factor. It is also apparent that H_2S trapping takes place in a very thin front line. This result seems to be in agreement with the qualitative results obtained

experimentally. In fact, pictures of the fixed bed (cf Figure 8), taken during the experimental runs show a plug-flow well-rendered separation between sulphurized sorbent and fresh sorbent. Such a behaviour of calculated data is due to the high overall reaction rate used in the



Figure 8. Fixed bed after a experimental run of 6 hours it shows a plug-flow well-rendered separation between sulphurized sorbent and fresh sorbent.

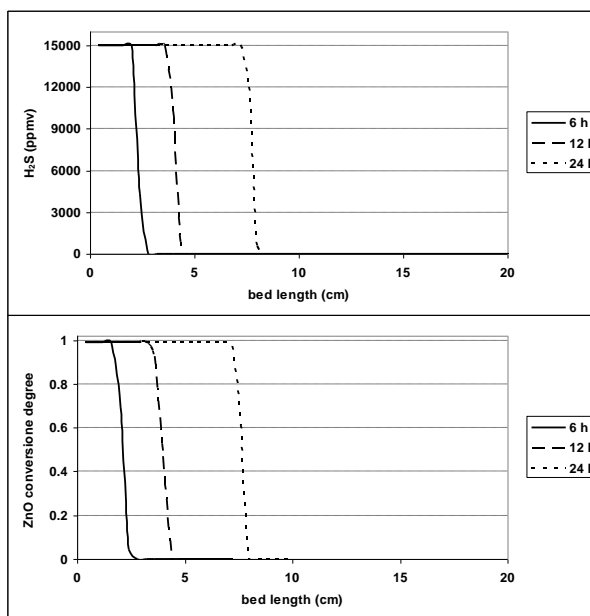


Figure 7. Longitudinal profiles of H_2S -concentration in gas phase (above) and conversion degree of ZnO in the sorption bed (below). As it is noticeable H_2S trapping takes place in a very thin front line

mathematical model.

Overall reaction rate depends above all on two components: surface reaction rate and diffusion rate of the reagent inside the particle. A decrease of one or both parameters can produce a substantial change of the curves shape, making slighter the variation of the two cited concentration parameters along the bed. This behaviour is well shown by the results plotted as two different curves in Figure 9. The solid curve represents values of H_2S -concentration obtained for 10 hours of exposure time using the same data used also for all previous calculations. The dashed curve has

been obtained using a value of solid diffusion that is ten times lower than the value previously used.

It has been verified with a further test if calculation results somehow depend on the integration step used. Integration of the two differential equations has been then carried out by using two different steps of 3 and 30 s. The result is reported in Figure 10. Curves are obtained for 6 hours of exposure times and show some, but not substantial, difference.

One of the calculation results is the temperature change in the longitudinal direction in the bed. This result is not reported in this paper since it cannot be compared with the laboratory results. In fact, the experimental tests have been carried out in a reactor put inside a tubular furnace kept at a constant temperature.

It is now possible to discuss some hypothesis assumed as the base of the theoretical model.

First hypothesis is the complete lack of back-mixing, that is to say the assumption of a plug flow fluidynamic model for the reactor. This assumption shows a good agreement with the experimental results, as previously described.

On the contrary, it is not so much easy to verify the presence in the reaction bed of a radial dispersion. An evidence of its occurrence could be shown by a different sulphidation amount registered by the particles having a different radial position in the same section of the reactor. Unfortunately, it is too difficult to make such observation during each experimental test.

Finally, the results of chemical analysis carried on the particles convinced us that the assumption of a Shrinking Core kinetic model (SCM) is an excessive simplification. In fact, the results obtained with a SEM-EDX show that sulphur concentration decreases along the particle radius and is always greater than zero. If the assumptions of SCM be correct, sulphur concentration should be zero in a core inside the particle. The analytic results obtained make us convinced that a model of the diffusion kind (homogeneous or grain or other kind) is more appropriate. Then, next step in modelling should be the introduction of this new model.

4. CONCLUSIONS

Hot gas desulphurization performances of three selected ZnO based commercial sorbents was studied in a bench scale reaction system, borosilicate glass manufactured, designed for operations up to 550 °C by Sotacarbo. Chemical and physical characterization of sorbent samples are performed by different test analysis. Hydrogen sulphide concentration remaining after reaction has been determined in the outlet gas.

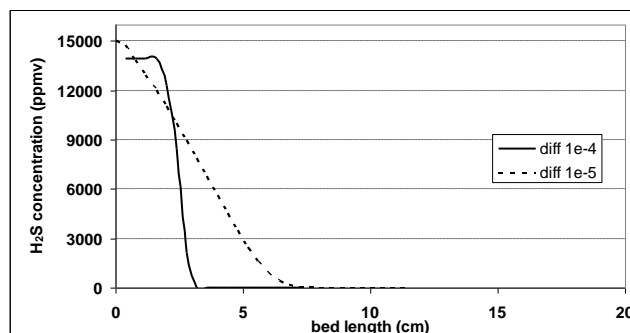


Figure 9. H_2S -concentration curves obtained for 10 hours using different value of solid diffusion.

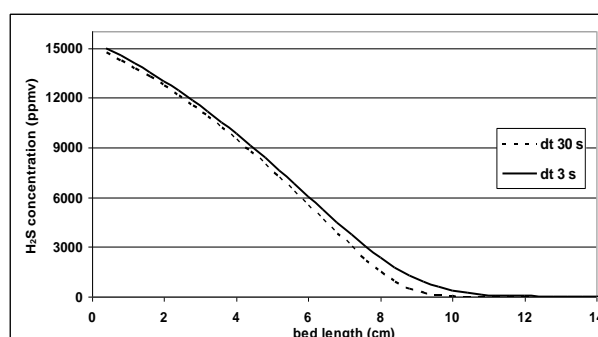


Figure 10. H_2S -concentration curves obtained for 6 hours. Integration of model differential equations has been carried out by using two different time steps

All sorbents have shown a good behaviour in H₂S retention being able to achieve very low emission level in treated gas. Experimental data indicate that H₂S average concentration in outlet gas was maintained below 1 ppmv. The observations are in direct agreement with the thermodynamic predictions. Z-1 sorbent has shown a higher reaction rate, yielding H₂S removal down to 0.35 ppm in the outlet stream gas.

A numerical model of the reaction system was developed and validated, with a good agreement, by comparison with experimental observations.

Acknowledgements

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Notation

C_{H_2S}	<i>molar concentration of H₂S in the gas phase, in [kmol/m³];</i>
C_p	<i>specific heat at constant pressure, in [kJ/kg];</i>
d_p	<i>diameter of sorbent particle, in [m];</i>
d_r	<i>diameter of reactor, in [m];</i>
D_{eff}	<i>effective diffusivity, in [m²/s];</i>
D_{H_2S}	<i>molecular diffusivity, in [m²/s];</i>
D_K	<i>Knudsen diffusivity, in [m²/s];</i>
$\langle D_{XRD} \rangle$	<i>mean dimension of crystallites, in [nm];</i>
G	<i>specific flow rate, in [kg/m²s];</i>
H	<i>heat flow rate, in [kJ/s];</i>
ΔH	<i>reaction heat, in [kJ/kmol];</i>
J_d	<i>mass-transfer factor;</i>
K	<i>constant related to the crystallite shape (0.9)</i>
K_{ext}	<i>kinetic constant of gas-phase transport, in [m/s];</i>
$(K_a)_{ov}$	<i>overall kinetic constant multiplied by a mean exchange area, in [s⁻¹];</i>
N	<i>molar flow rate, in [kmol/s];</i>
PM	<i>molecular weight, [kg/kmol];</i>
r_e	<i>mean pore radius, in [m];</i>
r_i	<i>initial radius of the sorbent particle, in [m];</i>
r_i	<i>radius of internal unreacted core of sorbent particle, in [m];</i>
Re	<i>Reynolds number;</i>
R_{H_2S}	<i>specific adsorption rate, in [kmol_{H2S}/kg_ss];</i>
S	<i>reactor cross section, in [m²];</i>
Sc	<i>Schmidt number;</i>
Sh	<i>Sherwood number;</i>
t	<i>time, in [s];</i>
T	<i>temperature, in [K];</i>
U	<i>heat-transfer overall factor, in [W/m²K];</i>
Z	<i>reactor axial coordinate, in [m];</i>
β	<i>the pure breath of the powder reflection free of the broadening due to instrumental contributions [rad]</i>
β_{exp}	<i>experimental breath of the powder reflection [rad]</i>

β_{std}	<i>breath of the powder reflection of a standard Si sample [rad]</i>
λ	<i>wavelength [nm]</i>
θ	<i>void fraction</i>
Θ	<i>diffraction angle [°]</i>
λ	<i>wavelength [nm]</i>
μ	<i>gas viscosity, in [kg/m s];</i>
ρ	<i>mass density, in [kg/m³];</i>
ρ_s	<i>sorbent mass density, in [kg/m³];</i>
ψ	<i>shape factor</i>

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