REGENERATION BY AIR OXIDATION OF $ZnO-TiO_2-Al_2O_3$ TYPE SORBENTS FOR HTGD PROCESSES

Annette Madelene DĂNCILĂ[1], Oanamari Daniela ORBULEŢ[1], Delia GÂRLEANU[2*], Gabriel GÂRLEANU[2]

The article follows the best regeneration conditions for the restoration of the structure of the $ZnO-TiO_2-Al_2O_3$ type sorbent and the possible formation of $ZnSO_4$. The study looked at the structural, morphological and textural changes of zinc titanate with the addition of alumina with a molar ratio of 2: 1: 0.5, saturated with H_2S, which occur during sorbent regeneration at different temperatures (500, 600 and 700°C) and at intervals of different time. This mixing ratio ensures a high content of ZnO and Zn_2TiO4 (the desulfurizing agent itself), respectively; a high sulfur retention capacity (19.01% S), a high degree of ZnO utilization (96.69%); an adequate morphology of the sorbent granules and a developed texture that favors the diffusion access of H_2S in the internal structure during the desulfurization process.

Keywords: desulfurization; zinc titanate sorbents; Al_2O_3 adding; regeneration; characterization; $ZnSO_4$

1. Introduction

High-Temperature Gas Desulfurization (HTGD) represents an essential stage in the development of modern coal and biomass gasification technologies, as it enables the removal of sulphur compounds from syngas under severe operating conditions, thus protecting downstream catalysts and reducing environmental impact [1,2]. Among the various regenerable sorbents investigated, zinc titanate has emerged due to its high sulphur retention capacity, good thermal stability, and potential for multiple sulfurization–regeneration cycles [3-5]. However, one of the main limitations of regeneration by air oxidation is the formation of zinc sulfate, a compound that is thermodynamically favored at lower temperatures and adversely affects sorbent performance in subsequent cycles [5-7].

Previous research has mainly focused on optimizing regeneration parameters - such as temperature, oxygen concentration, and oxidizing agent flow rate - as well as on modifying sorbent composition by adding secondary oxides such as TiO_2, SiO_2, or Al_2O_3, which play a stabilizing role and help prevent sintering

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phenomena [8-12]. Nevertheless, despite the progress achieved, issues such as incomplete regeneration, structural collapse at high temperatures, or zinc loss through sulphate formation continue to limit large-scale applicability [9,13-17].

TiO_2 has multiple applications, most recently in orthopedic or dental implantology, in hydrogen generation when used as a catalyst in alkaline water splitting [18, 19].

The present work brings new contributions by preparing ZnO-TiO_2-Al_2O_3 sorbents with a controlled molar ratio (2:1:0.5), which ensures both a high availability of ZnO and stabilization of the zinc titanate crystalline phase. The study investigates the influence of regeneration temperature (500–700 °C) and time (4–30 minutes) on the restoration of sorbent activity, correlating the degree of regeneration with XRD, SEM, and EDAX analyses. The results demonstrated that, under the investigated conditions, $ZnSO_4$ does not form even in the case of incomplete regeneration or at lower temperatures, which confirms the inhibiting role of Al_2O_3 and represents an important advantage for the cyclic reuse of these sorbents. Furthermore, it was shown that complete regeneration obtained at 700 °C for 30 minutes leads to a structural restoration comparable to that of the fresh material, allowing the sorbent to be reintegrated into the desulfurization process without performance losses [20].

Therefore, this study highlights the stabilizing and protective role of alumina and provides new data regarding the optimal regeneration conditions, demonstrating the feasibility of direct oxidation with air while avoiding both zinc sulfate formation and thermal degradation of the sorbents. These results complement the existing literature and contribute to the development of high-performance ZnO-TiO_2-Al_2O_3 sorbents suitable for industrial-scale high-temperature desulfurization processes, with potential integration into cleaner and more sustainable energy technologies. Thus, although the ZnO-TiO_2-Al_2O_3 sorbent with the 2:1:0.5 molar ratio was previously synthesized in our earlier studies, the novelty of the present work lies in the detailed investigation of its regeneration by direct air oxidation, where the optimal conditions were identified and the absence of $ZnSO_4$ formation was confirmed.

2. Materials and Methods

2.1. Sorbents preparation

The sorbent type ZnO-TiO_2-Al_2O_3 with molar raport 2:1:0.5 was prepared through semi-wet mechanical blending of oxides [1,2,3]. The 2:1:0.5 molar ratio was deliberately chosen since previous studies indicated that this composition maximizes sulfur retention capacity and ZnO utilization, while alumina addition improves the thermal stability of zinc titanate and inhibits $ZnSO_4$ formation.

Therefore, the present work focused exclusively on this composition in order to investigate in detail its regeneration behavior.

The product resulting after calcination at 700°C for 4 hours was granulated to the size of 0.5-0.63 mm and saturated with H_2S (under nitrogen atmosphere) for 4 hours at 500-550°C. The saturated sorbent with code ZTA_S was characterized morphologically and structurally and determined the total sulphur content before moving on to the actual study of regeneration.

2.2. Regeneration of sulfur-saturated sorbents

The regeneration was performed in a plant described in figure 1 in which the saturated sorbent was oxidized with oxygen from the air.

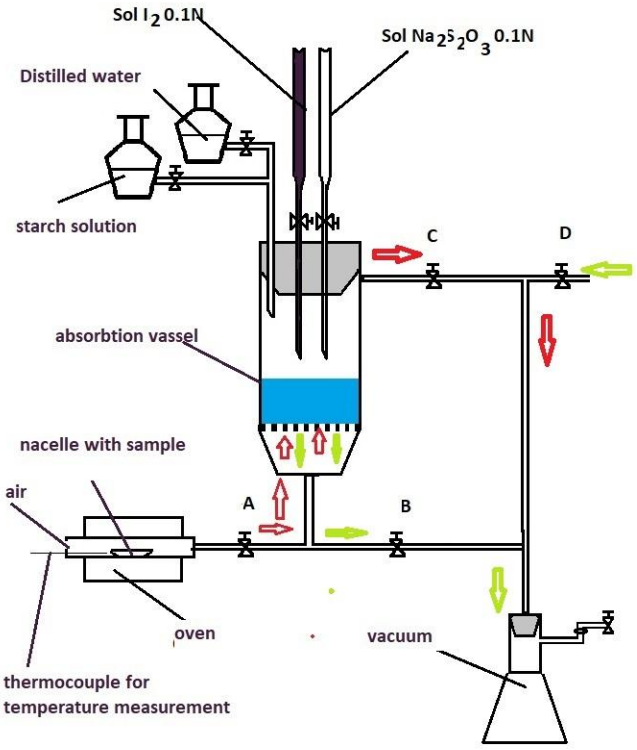

Fig. 1. Laboratory installation for regeneration of sulfur-saturated sorbents

In oven was introduced a nacelle with a weighed sample with mass between 0.1- 0.2 g. Taps A and C are opened, while taps B and D are closed. To calculate the degree of regeneration, the sample was heated from room temperature to 950 °C. The regeneration is done with oxygen from the air that enters the oven through a hole. The reaction that takes place during regeneration is:

$$ZnS + 3/2O_2 \rightarrow ZnO + SO_2\uparrow$$

$$ZnO + TiO_2 \rightarrow Zn_2TiO_4$$

SO_2 leaves the oven and enters the absorption vessel in which is the I_2 solution 0.1 N. In figure 1, the SO_2 way is marked with red arrows. The reaction that takes place in the absorption vessel is:

$$SO_2 + I_2 + 2H_2O \rightarrow 2HI + H_2SO_4$$

When the oven has reached 950 ^oC it is maintained for another 15 minutes then the excess I_2 is titrated with $Na_2S_2O_3$ solution. The reaction that takes place in the absorption vessel is

$$I_2 + Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

The regeneration efficiency was evaluated by iodometric titration. During the experiment, iodine solution was periodically added until the solution in the absorption vessel retained a persistent coloration, after which the residual iodine was titrated with standardized $Na_2S_2O_3$ solution. The test was conducted at constant temperature for 30 minutes.

2.3. Sorbents analysis and characterization

The phase composition analysis of the sorbents was performed by X-ray diffraction method (XRD analyses) using a Shimadzu-6000 diffractometer (2θ Bragg-Brentano geometry, using the CuKα characteristic radiations). The elimination of the CuKβ component was achieved by a Ni filter. The experimental data were digitally collected by the "step by step" scanning method in the 2θ angle interval of 10÷80 degrees.

Scanning Electron Microscopy (SEM analysis), Secondary Electron Images (SEI) and Energy Dispersive Spectroscopy (EDAX analysis) were performed by the means of a scanning electron microscope Hitachi S2600N. The qualitative and quantitative X-ray microanalyses were carried out using an energy-dispersive spectrometer of the Röntec type. The average crystallite size, $\overline{d}$ [Å], was estimated according to the Scherrer equation (relation 1) [21,22]:

$$\overline{d} = \frac{0{,}89 \cdot \lambda}{\beta \cdot \cos(2\theta)} \quad (1)$$

where: λ is the wave length of the radiation (1,54065 Å); β is the semi-width of the maximum of the difraction [rad] and 2θ is the angle corresponding to the maximum of the difraction in Bragg-Bretano geometry.

The average crystallite size was estimated using the Scherrer equation (relation 1). For the main ZnS and Zn_2TiO_4 reflections, the crystallite sizes fall in

the nanometric range (25–40 nm), confirming the nanocrystalline nature of the sorbent.

2.4. Chemical Reagents

Zinc oxide (ZnO), titanium dioxide (TiO_2) and aluminum oxide (Al_2O_3) were purchased from Sigma Aldrich (Merck KGaA, Darmstadt, Germany). Hydrogen sulphide (H_2S, 99.5% purity) and nitrogen (N_2, 99.999% purity) were supplied by Linde Gas and were used as received, without further purification. In addition, iodine solution (0.1 N), sodium thiosulfate ($Na_2S_2O_3$) solution, starch solution (as indicator), and distilled water were employed for the quantitative determination of SO_2 released during the regeneration process. All materials and reagents were of analytical grade.

3. Results and discussion

3.1. The influence of temperature on the regeneration degree of sorbent

The results and discussions of the study were also established according to the saturated sorbent ZTA_S for which morphological and structural characterizations were made. From figure 2, the temperatures of 500, 600, 700ºC were chosen and the saturated sorbents were regenerated for 30 minutes. These temperatures signify the beginning of the oxidation reaction as well as the optimal temperature range due to the high regeneration rate.

Figure 2 shows the dependence of the degree of regeneration depending on the temperature.

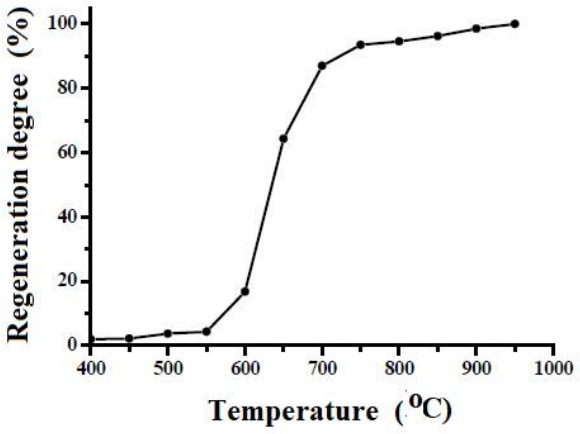

Fig. 2. The dependence of the regeneration degree on temperature

It is observed that at temperatures lower than 500 ºC the regeneration degree is below 5%, and the increase of the temperature favors the increase of the regeneration degree, so that at 600ºC it is approximately 20%.

It is noted that between 600 and 700ºC the regeneration degree increases suddenly, the reaction takes place at a very high rate, after which the regeneration rate of the sorbent decreases as the temperature increases up to 950ºC. As a result, the saturated sorbent was regenerated at different temperatures (500-700ºC) for different periods of time. Table 1 shows the samples, the code used in this article, the regeneration conditions and the degree of regeneration.

Table 1

The regeneration conditions and the degree of regeneration for sorbents

Nr. crt.	Code sample	Conditions for regeneration	Regeneration degree X[%]
1	ZTA_S 1	T = 500ºC, τ = 30 min	3.29
2	ZTA_S 2	T = 600ºC, τ = 30 min	81.75
3	ZTA_S 3	T = 600ºC, τ = 10 min	28.32
4	ZTA_S 4	T = 700ºC, τ = 30 min	100
5	ZTA_S 5	T = 700ºC, τ = 4 min	35.72

Table 1 shows that the variation of the regeneration degree at different temperatures when the regeneration was done over a constant period of time increases with increasing temperature. The regeneration degree after 30 minutes at 500ºC is 3.29%, at 600 ºC it increases to 81.75% reaching 700ºC to be 100%. So the increase in temperature favors the regeneration speed.

In order to facilitate a clearer comparison of the XRD results, the crystalline phases identified in the regenerated ZTA_S samples are summarized in Table 2. The data show that at lower regeneration temperatures (500–600 °C), ZnS remains the dominant phase, accompanied by residual ZnO, TiO_2, and Al_2O_3. With increasing temperature, especially at 700 °C, the characteristic reflections of Zn_2TiO_4 and $ZnAl_2O_4$ become predominant, confirming the almost complete regeneration of the sorbent. Thus, Table 2 provides a concise overview of the relationship between regeneration conditions, regeneration degree, and the crystalline phases detected.

Table 2

Crystalline phases identified inregenerated ZTAS samples

Sample code	Regeneration conditions	Degree of regeneration (%)	Crystalline phases identified (XRD)
ZTA_S 1	500 °C, 30 min	3.29	ZnS (major), ZnO (minor), TiO_2, Al_2O_3

ZTA_S 2	600 °C, 30 min	81.75	Zn_2TiO_4, $Zn_2Ti_3O_8$, $ZnAl_2O_4$, ZnS (minor)
ZTA_S 3	600 °C, 10 min	28.32	ZnS (major), Zn_2TiO_4 (incipient), TiO_2, Al_2O_3
ZTA_S 4	700 °C, 30 min	100	Zn_2TiO_4, $ZnAl_2O_4$
ZTA_S 5	700 °C, 4 min	35.72	ZnS, Zn_2TiO_4, $ZnAl_2O_4$, TiO_2

The determination of the sulfur retention capacity and the degree of utilization of ZnO was achieved by analyzing the total sulfur content of the saturated ZTAS sample, correlated with the theoretical chemical composition of the material.

Calculation note: sulfur retention capacity and ZnO utilization (for ZTA_S):

Basis (as prepared): molar ratio ZnO:TiO_2:Al_2O_3 = 2:1:0.5.

• Molar masses:

ZnO = 81.408 g/mol; TiO_2 = 79.866 g/mol; Al_2O_3= 101.961 g/mol; ZnS = 97.474 g/mol; S = 32.065 g/mol.

• Initial sorbent mass (per formula batch):

$m_0 = 2 \times 81.408 + 1 \times 79.866 + 0.5 \times 101.961 = 293.6625$ g

• Sulfidation reaction (per ZnO):

$ZnO + H_2S \rightarrow ZnS + H_2O$

$\Rightarrow$ net mass gain in the solid per mol ZnO: 97.474 – 81.408 = 16.066 g

• If all Zn (from 2 ZnO) sulfides:

Sulfur fixed in solid: $n_S = 2$ mol $\Rightarrow m_S = 2 \times 32.065 = 64.130$ g

Final saturated mass: $m_f = m_0 + 2 \times 16.066 = 325.7945$ g

• Theoretical sulfur capacity (100% ZnO utilization):

$(m_S / m_f) \times 100 = (64.130 / 325.7945) \times 100 = 19.68$ wt.% S

• Measured sulfur in ZTA_S (this work): 19.01 wt.% S (iodometric quantification of SO_2 evolved during regeneration / total S in saturated ZTA_S).

• ZnO utilization degree:

U_{ZnO} = (measured (%S) / theoretical (%S)) × 100 = (19.01 / 19.68) × 100 = 96.6% (≈ 96.69%)

Chemical analysis of the H_2S-saturated ZTA_S sample confirmed a sulfur retention capacity of 19.01% S, which corresponds to a ZnO utilization of 96.69%. These values reflect the performance of the sorbent prepared in a molar ratio of 2:1:0.5.

3.1.2. Compositional-structural changes

The regenerated samples at temperatures of 500, 600, 700°C over a period of 30 minutes were analyzed and the corresponding XRD spectra ZTA_S 1, ZTA_S 2, ZTA_S 4 are shown in figure 3 compared to the non-regenerated saturated sample whose DRX spectrum is shown in figure 4.

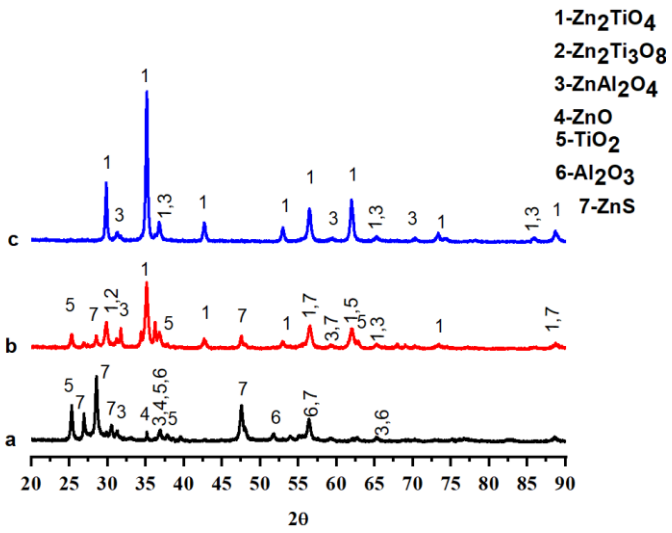

Fig 3. XRD spectra of saturated samples, regenerated at different temperatures for 30 minutes: (a) ZTA_S 1; (b) ZTA_S 2; (c) ZTA_S 4.

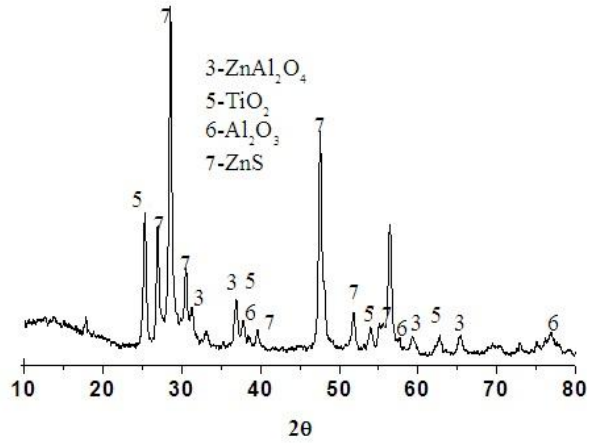

Fig. 4. XRD pattern of the non-regenerated saturated ZTA_S sample

In the case of regeneration at a temperature of 500°C for 30 minutes the XRD spectrum (Figure 3.a) indicates the massive presence of ZnS in the sample, which denotes a very low degree of regeneration (evaluated from the sulfur content as < 5%) in these conditions. The spectrum of the ZTA_S 1 sample can be compared with the spectrum of the non-regenerated saturated sample (Figure 4).

On the other hand, the identification of the ZnO crystalline phase certifies the partial regeneration of the sorbent but also the absence of the interaction between ZnO and TiO_2 with the formation of zinc titanate at this temperature.

Noteworthy is the absence of crystalline phase $ZnSO_4$ suggesting that zinc sulfate is either not formed on regeneration or, whether formed, but in an amount insufficient to detection by XRD analysis.

Experimental results for the regeneration of the ZTA_S 2 sample by air oxidation at 600°C for 30 minutes indicate the presence of ZnS, but in a much lower proportion compared to regeneration at 500°C. This corresponds to a high regeneration degree, estimated from the sulfur content to be about 80%The absence of ZnO as a distinct crystalline phase and the presence of Zn_2TiO_4 and $Zn_2Ti_3O_8$ certify the interaction between ZnO formed at regeneration and TiO_2 with the formation of zinc titanates. In this case, too, the absence of the $ZnSO_4$ crystalline phase is noted, suggesting that zinc sulphate does not form during regeneration.

Regeneration of the sample by air oxidation at 700°C for 30 minutes (Figure 3c) shows the complete absence of ZnS, confirming full sorbent regeneration. The XRD spectrum reveals only two distinct crystalline phases: zinc titanate (Zn_2TiO_4) and zinc aluminate ($ZnAl_2O_4$).

The absence of zinc titanate $Zn_2Ti_3O_8$ (identified in the XRD spectrum of the sample regenerated at 600 °C) is explained by its thermal instability and its transformation at higher temperatures into Zn_2TiO_4, the more thermodynamically stable crystalline form. It is also noteworthy that the $ZnSO_4$ crystalline phase is completely absent, confirming that it does not form even during high-temperature regeneration."

3.1.3. The morphological changes

The influence of the regeneration temperature on the morphological aspect of the saturated sorbent was highlighted by SEM analyzes; the experimental results being presented in figures 5.a ÷ c.

The sulfiding process induces important changes in the structure of the particle surface, respectively an increase in the particle size with the simultaneous reorganization of the crystalline structure. These changes can be explained by the disappearance of zinc titanate and the formation of a new crystalline phase, ZnS.

The radius of the S^{2-} ion is much larger than that of the O^{2-} which results in a significant increase in crystal size.

The very low degree of regeneration in the case of ZTA_S 1 is also put in evidence by the SEM image of the sample (Figure 5a.), those morphology being practically similar to that saturated sample with sulfur (Figure 6) [3, 23-26]. The appearance of crystallites is uniform, with dimensions close due to the presence of ZnS as the majority phase.

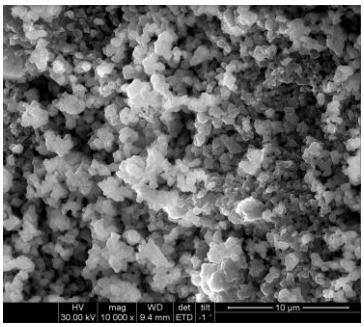

Fig. 5.a SEM image of the ZTA_S 1 sample regenerated at 500 °C for 30 minutes

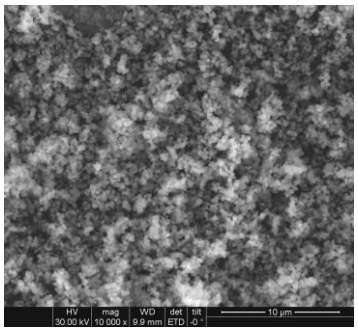

Fig. 5.b SEM image of the ZTA_S 2 sample regenerated at 600 °C for 30 minutes

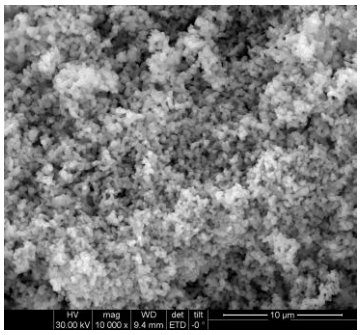

Fig. 5.c SEM image of the ZTA_S 4 sample regenerated at 700 °C for 30 minutes

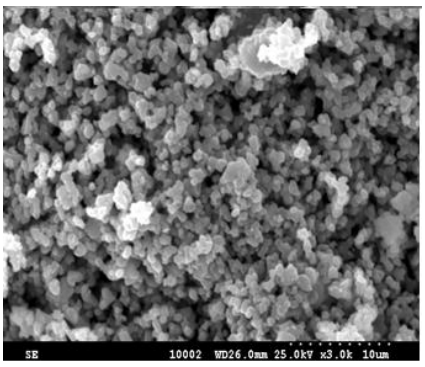

Fig. 6. SEM image of the ZTA_S sample

The high degree of regeneration of the ZTA_S 2 sample is also highlighted by the SEM image of the sample (Figure 5.b), its morphology being relatively similar to that of the fresh sample [3,27,28]. The complete regeneration of the sulfur-saturated sorbent ZTA_S 4 is also highlighted by the SEM image of the

sample (Figure 5.c), its morphology being similar to that of the fresh sample [3, 29,30].

The EDAX analysis of the ZTA_S 1 sample shows a high sulfur content (Figure 7.a) and a relatively uniform distribution of it in the sample (Figure 7.b.), similar with the sulphur distribution in the sulfur-saturated sample (ZTA_S sample).

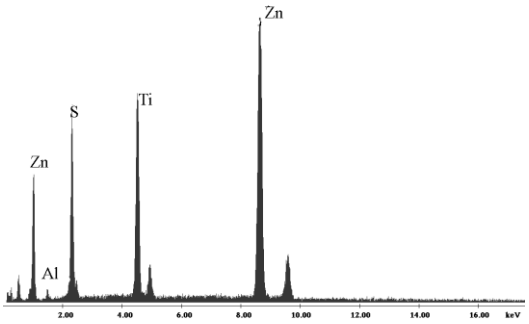

Fig. 7.a EDAX analysis of ZTA_S 1 sample

Fig. 7.b S distribution in ZTA_S 1 sample

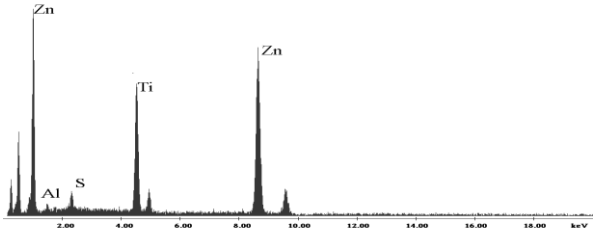

Fig. 8.a EDAX analysis of ZTA_S 2 sample

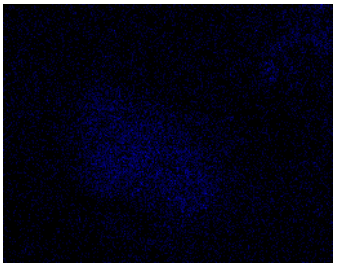

Fig. 8.b S distribution in ZTAS 2 sample

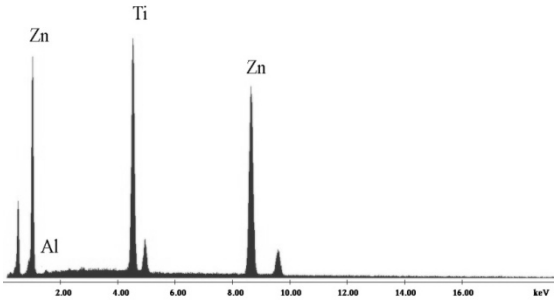

Fig. 9.a EDAX analysis of ZTA_S 4 sample

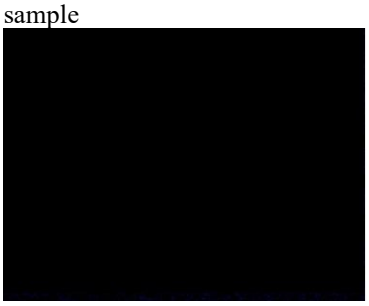

Fig. 9.b S elemental map of ZTA_S 4 after regeneration showing no detectable sulfur (signal at background level).

The EDAX analysis of the ZTA_S 2 sample shows a low residual sulfur content (Figure 8.a) and a rather uneven distribution of it in the sample (Figure 8.b), the S concentration in the central area being much higher than in the peripheral area, suggesting a granular reaction mechanism with unreacted core.

On the other hand, in the case of the ZTA_S 4 sample, the EDAX analysis claims that at this temperature the regeneration was complete due to the lack of sulfur and from the distribution of sulfur in the sample there is no evidence of presence of sulfur (Figures 9.a). As shown in Figure 9b, the S elemental map of the ZTAS 4 sample does not display any signal above the background. Within the acquisition parameters used for SEM image of the sample, sulfur is below the detection limit, which is consistent with the EDAX spectrum in Fig. 9.a and confirms the complete regeneration of the sorbent at 700°C for 30 min.

3.2. Influence of regeneration time on sorbent's regeneration

Since the degree of regeneration at 500°C was very low, the effect of regeneration time was further investigated at two higher temperatures (600 and 700°C). As shown in Table 1, an additional regeneration was carried out at 600°C for 10 minutes (ZTA_S 3), and at 700 °C for 4 minutes ZTA_S 4

For regenerations performed at temperatures of 600ºC and 700ºC respectively, at shorter intervals, it was found that in the ZTAS 3 test the degree of regeneration is lower than the regeneration degree of the ZTA_S 2 sample and even lower than in the ZTA_S 5 test for 4 minutes at 700ºC. The samples were analyzed by X-ray diffraction and SEM microscopy.

3.2.1. Compositional-structural changes

In case of regeneration at 600ºC the spectra of ZTA_S 2 and ZTA_S 3 samples are presented in (Figure 10. a, b).

In the ZTA_S 3 spectrum (Figure 10b), significant amounts of ZnS are observed. Zn_2TiO_4 formation becomes noticeable, although only in small amounts after 10 minutes of regeneration at 600°C However, the proportion of titanate is initially low but increases with longer regeneration times, with a duration of 10 minutes being sufficient to achieve adsorbent reformation.

In the case of regeneration at 700°C the spectra of samples ZTA_S 4 and ZTA_S 5 are illustrated in figures 11a, 11b. Several compounds are identified in the ZTA_S 5 spectrum. At 4 minutes, $ZnAl_2O_4$ also appears, in addition to Zn_2TiO_4, which is in a small proportion, but also ZnS, which confirms that the regeneration is not over. After 30 minutes the entire amount of ZnS is converted to Zn_2TiO_4 and $ZnAl_2O_4$.

The degree of regeneration for a 4 minute regeneration is about 35%. What is important to present is the fact that $ZnSO_4$ formation was not identified during regeneration process at any time period has been studied:

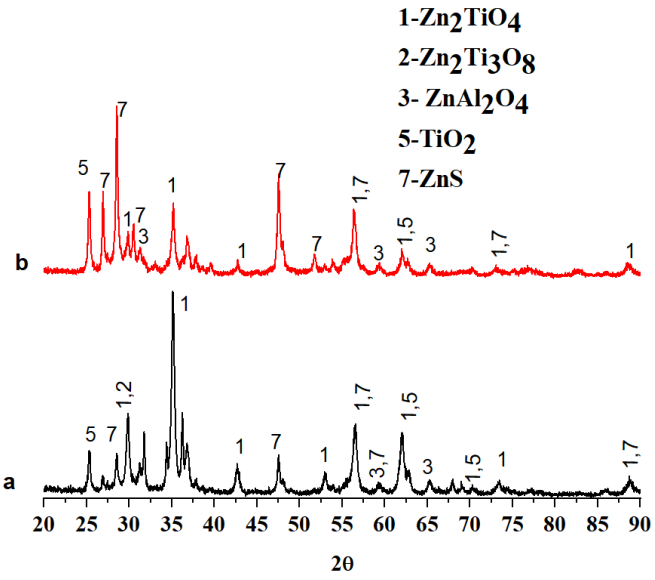

Fig. 10. XRD spectra of ZTA_S 2, ZTA_S 3 samples regenerated at 600°C and different time periods: (a) 30 minutes, (b) 10 minutes

This aspect makes important the mode of regeneration by oxidation with air (with excess oxygen), because there is no possibility of losing the amount of zinc in the sorbent through the formation of $ZnSO_4$. The regenerated sorbent can be reintroduced in the desulfurization process without reducing the initial amount of sorbent.

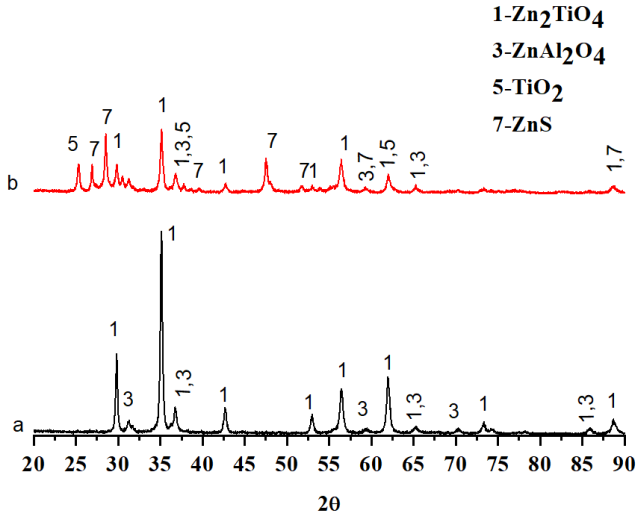

Fig. 11. XRD spectra of ZTA$_S$ 4, ZTA$_S$ 5 samples regenerated at 700°C and different time periods: (a) 30 minutes, (b) 4 minutes

3.2.2. The morphological changes

The incomplete regeneration of the sulfur-saturated sorbent ZTA$_S$ 5 is also evidenced by the SEM image of the sample (Figure 12 and Figure 13), its morphology being different from that of the fresh sample.

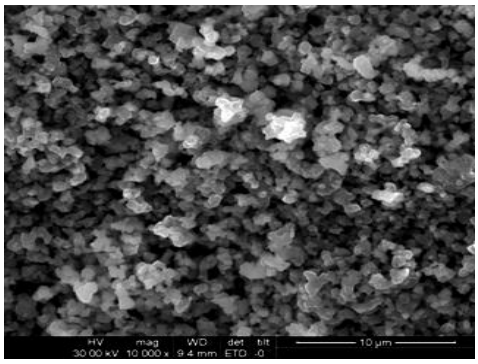

Fig. 12. SEM image of ZTA$_S$ 3 sample regenerated at 600°C, 10 min

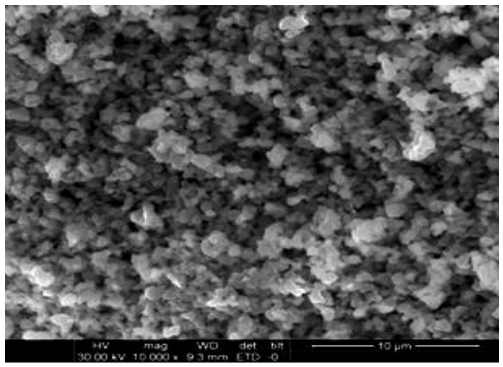

Fig. 13. SEM image of ZTA$_S$ 5 sample regenerated at 700°C, 4 min

The SEM analysis further confirms the influence of regeneration conditions on the morphology of the samples. In the case of ZTA$_S$ 3, regenerated at 600°C for 10 minutes, the images indicate only a partial restoration of the sorbent surface, the presence of ZnS being still evident. At higher temperature, namely 700°C but for a

shorter duration of 4 minutes (ZTA_S 5), the sorbent also exhibits an incomplete regeneration, with morphological features clearly different from those of the fresh material. These observations are consistent with the regeneration degree of about 35% obtained experimentally. The persistence of sulfur, confirmed by EDAX analysis, demonstrates that the oxidation of ZnS to ZnO and its subsequent transformation into zinc titanate phases was not completed. Therefore, both the SEM and EDAX results emphasize that regeneration efficiency depends not only on temperature but also on sufficient reaction time, which ensures the full restoration of the sorbent's morphology and structure.

The SEM analyses clearly illustrate the morphological evolution of the sorbents under different regeneration conditions (Figures 5). For the ZTA_S 1 sample, regenerated at 500°C for 30 minutes, the surface morphology is practically identical to that of the sulphur-saturated material, with uniform crystallites dominated by ZnS, which confirms the very low degree of regeneration observed by XRD and chemical analysis. In contrast, the ZTA_S 2 sample, regenerated at 600°C for 30 minutes, shows a morphology closer to that of the fresh sorbent, highlighting the progress of the regeneration process. The surface becomes less uniform, suggesting the transformation of ZnS and the formation of zinc titanate phases, which is consistent with the higher regeneration degree (~82%).

Complete regeneration is achieved in the case of ZTA_S 4, treated at 700°C for 30 minutes, where the SEM image reveals a morphology almost identical to that of the fresh material. The absence of residual sulphur is further confirmed by EDAX, indicating the complete reformation of zinc titanate (Zn_2TiO_4) and zinc aluminate ($ZnAl_2O_4$) phases [31-33].

By comparison, the ZTA_S 5 sample, regenerated at 700°C for only 4 minutes, exhibits a morphology distinct from that of the fresh sorbent, confirming that the short reaction time is insufficient to achieve full regeneration. The presence of sulphur identified by EDAX supports this observation, demonstrating that ZnS was only partially oxidized. Thus, the combined SEM and EDAX analyses highlight that while high temperature accelerates regeneration, sufficient reaction time is equally essential to ensure the complete restoration of the sorbent structure and morphology.

4. Conclusions

The XRD, SEM and EDAX analyses of the ZnO–TiO_2–Al_2O_3 sorbent with a molar ratio of 2:1:0.5, saturated with H_2S and regenerated under different conditions, demonstrated that $ZnSO_4$ does not form, even at low or incomplete regeneration temperatures. This confirms the stabilizing and protective role of alumina, which inhibits the secondary reaction between ZnO and SO_2.

The results showed that zinc titanate (Zn_2TiO_4) begins to form at 600°C, with $Zn_2Ti_3O_8$ being detected only at this temperature, while at 700°C $Zn_2Ti_3O_8$ disappears due to its lower stability, leaving Zn_2TiO_4 as the thermodynamically stable phase. Complete regeneration was achieved at 700°C for 30 minutes, with full structural restoration of Zn_2TiO_4 and $ZnAl_2O_4$, allowing the sorbent to be reused in successive desulfurization cycles.

Chemical analysis confirmed a sulphur retention capacity of 19.01 wt.% S and a ZnO utilization degree of 96.69%, values which demonstrate the high performance of the prepared sorbent. These results, not previously reported, represent an important novelty of the present study, as they provide quantitative confirmation of sorbent efficiency under regeneration conditions.

Overall, the study highlights that regeneration at high temperature is a complex process, combining both gas–solid oxidation of ZnS to ZnO and solid–solid interactions with TiO_2 and Al_2O_3, leading to the complete structural and textural restoration of the sorbent. This ensures the feasibility of using ZnO–TiO_2–Al_2O_3 sorbents in repeated desulfurization–regeneration cycles and supports their potential application in industrial-scale HTGD processes.

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