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Effect of Temperature on SO_2 Absorption

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Abstract: Wet flue desulfurization methods are commonly used to absorb sulfur oxides produced by burning in large coal-fired power stations. The reaction between aqueous suspensions containing appropriate absorbents and the sulfur oxides in the flue gas forms the basis of these methods. As a result, the effect of temperature on the absorption rates of SO_2 in a solution prepared from Mazıdağı phosphate rock, with appropriate characteristics identified in previous studies, and in pure water were investigated and changes to the rock were observed. In an aquatic environment the effect of temperature on SO_2 absorption rate is negative, though the rate of absorption in the phosphate rock suspension was found to increase up to 30 ºC. According to this result, it was concluded that the Mazıdağı phosphate rock should be investigated for use in a flue gas desulfurization system.

Keywords: Phosphate rock; wet flue gas desulfurization; SO_2 absorption; three-phase reactor; lime/limestone.

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INTRODUCTION

Especially since the 20th century, the concept of energy has become one of the most important elements used to ensure competitive advantage for countries. At the same time, it is an important factor in economic and social development and plays a vital role in raising living standards. However, thermal power stations used to produce energy cause secondary problems like air and water pollution. As a result, attempts have been made to reduce the waste amounts and types caused by thermal power station technologies and incineration processes day to day with a variety of improvements (1, 2).

The most effective method used in flue gas scrubbing units in power stations is the soil alkaline metal processes using lime/limestone. In the lime/limestone process, flue gas is initially cooled and later washed in an absorption tower with a suspension of limestone or aqueous lime. The SO_2 within the gas mixture forms calcium sulfide and/or sulfate and reacts with the suspension. The scrubbed gas is released into the atmosphere (3-6).

The mechanism of SO_2 absorption within limestone sludge may be obtained from the following steps (7);

$$SO_{2(g)} \rightarrow SO_{2(aqueous)} \quad (1)$$

$$SO_{2(aqueous)} + H_2O \rightarrow H_2SO_3 \quad (2)$$

$$H_2SO_3 \rightarrow H^+ + HSO_3^- \quad (3)$$

$$HSO_3^- \rightarrow H^+ + SO_3^{-2} \quad (4)$$

$$CaCO_{3\,(k)} \rightarrow CaCO_{3\,(aqueous)} \quad (5)$$

$$CaCO_{3\,(aqueous)} \rightarrow Ca^{+2} + CO_3^{-2} \quad (6)$$

$$H^+ + CO_3^{-2} \rightarrow HCO_3^- \quad (7)$$

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O \quad (8)$$

$$SO_2 + HCO_3^- \rightarrow HSO_3^- + CO_2 \quad (9)$$

$$SO_2 + SO_3^{-2} + H_2O \rightarrow 2HSO_3^- \quad (10)$$

$$CO_3^{-2} + HSO_3^- \rightarrow HCO_3^- + SO_3^{-2} \quad (11)$$

The majority of currently used flue gas desulfurization systems aim to absorb SO_2 with assessment of products formed a secondary concern. However, assessing these products has great importance for the economics of the process. It is generally expensive to regenerate the absorbent materials used in SO_2 absorbent systems as they contain SO_2. As a result, systems discard the material adsorbing SO_2 at the end of the process and appear to be cheaper in terms of investment. However, as the areas of use of the sludge or dry waste materials formed by these systems are limited, storage difficulties arise. If the solid absorbent in flue gas desulfurization can be used in industry after the reaction, it will both solve the solid waste problem and make the process more economical (8).

The Mazıdağı phosphate rock, outcropping over a large area in the Mazıdağı region of Mardin in Turkey, contains a very small amount of silica in addition to large amounts of calcite. The phosphate rock cannot be used in production of orthophosphoric acid and super phosphate due to a variety of problems such as consuming a high amount of sulfuric acid and creating foaming and blockage. However, this rock was determined to have high porosity and appropriate pore distribution during research into gas-solid reactions. Linked to these properties the Mazıdağı phosphate rock had high SO_2 adsorption efficiency rarely seen in the literature (9-12). Thus, the solid obtained after use of active-structured Mazıdağı phosphate rock in wet flue desulfurization systems contains both phosphate and sulfate and it will be possible to use it in the phosphoric acid and fertilizer industry.

Firstly, it was necessary to investigate the effect of temperature on the SO_2 absorption rate in an aquatic phosphate rock suspension and investigate changes in its structure.

MATERIAL AND METHOD

The phosphate rock used in our research was obtained from the Şemikan deposit in the Mardin-Mazıdağı region. The ore was fragmented with a laboratory-type jaw crusher and ground in a ball mill. After homogenization, chemical analysis was performed. The results are shown in Table 1.

Table 1. Chemical Analysis of Phosphate Rock

Component	%wt
SiO_2	1.60
P_2O_5	25.84
Al_2O_3	1.39
F_2	1.69
CaO	47.11
MgO	1.61
Fe_2O_3	0.71
Loss of ignition	13.79
(CO_2)	(13.02)

According to these results, the sample with moderate degree phosphate ore contains a very high amount of carbonate.

Mineralogical analysis of the sample used the X-ray powder diffraction method and the spectrum is given in Figure 1. In this diagram, the peaks for two mineral types containing phosphate, fluorapatite, and carbonate fluorapatite are clearly observed. In addition to these, $CaCO_3$ is clearly identified. Different from these three minerals, SiO_2 peaks are observed; apart from these, other minerals could not be determined due to low amounts.

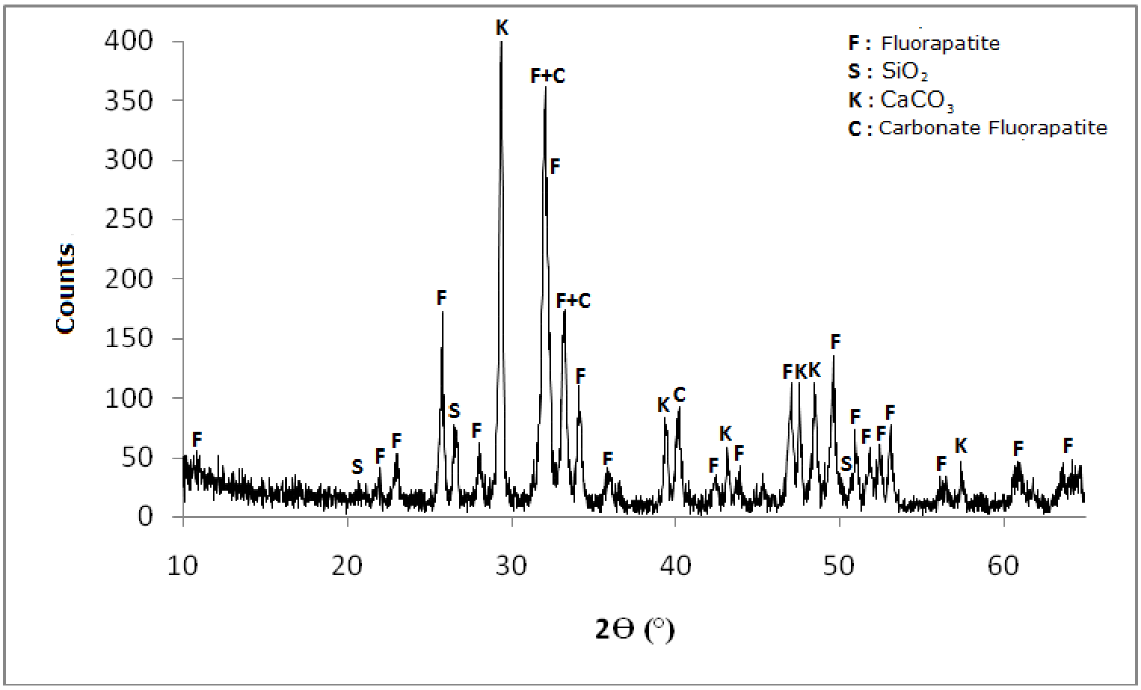

Figure 1. X-ray diffraction spectrum of raw phosphate rock.

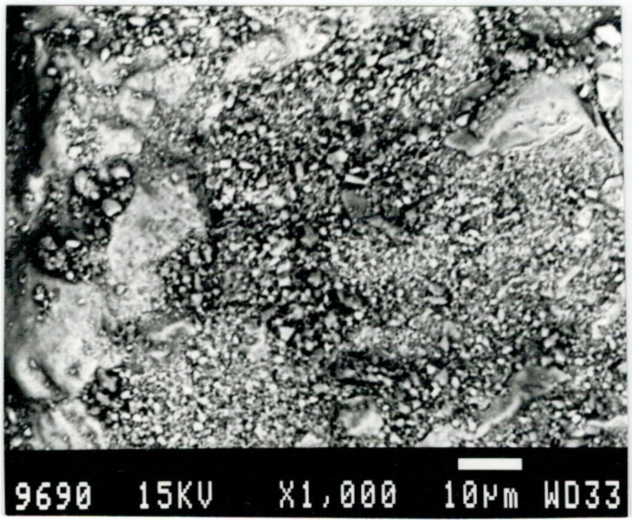

Figure 2. SEM images of raw phosphate rock.

SEM images of raw phosphate rock are given in Figure 2. Here, the large shiny particles and small particles between them are observed. The nearly 2 μm calcite particles between the large phosphate particles are agglomerated. The shiny surface of the phosphate particles indicates a non-porous compact structure. The pore volume in this phosphate rock is 0.0867 cm^3/g with specific surface area identified as 15.68 m^2/g (13).

The TG-DTG-DTA diagram of the raw rock is given in Figure 3. The total weight loss in this diagram appears to agree with the results obtained from chemical analysis. Up to 600 ºC in addition to the weight loss due to water loss and other volatile compounds, there is a slight exothermic peak observed on the DTA curve and the weight loss around 500 ºC is equivalent to combustion of the remaining organic material before evaporation. The weight loss in the region from 600 ºC to 760 ºC is the result of disintegration of $CaCO_3$. At 760 ºC, the shoulder on the DTA curve and following weight loss supports the presence of carbonate fluorapatite identified on the X-ray powder diffraction spectrum and again shows good compatibility with the results of the chemical analysis.

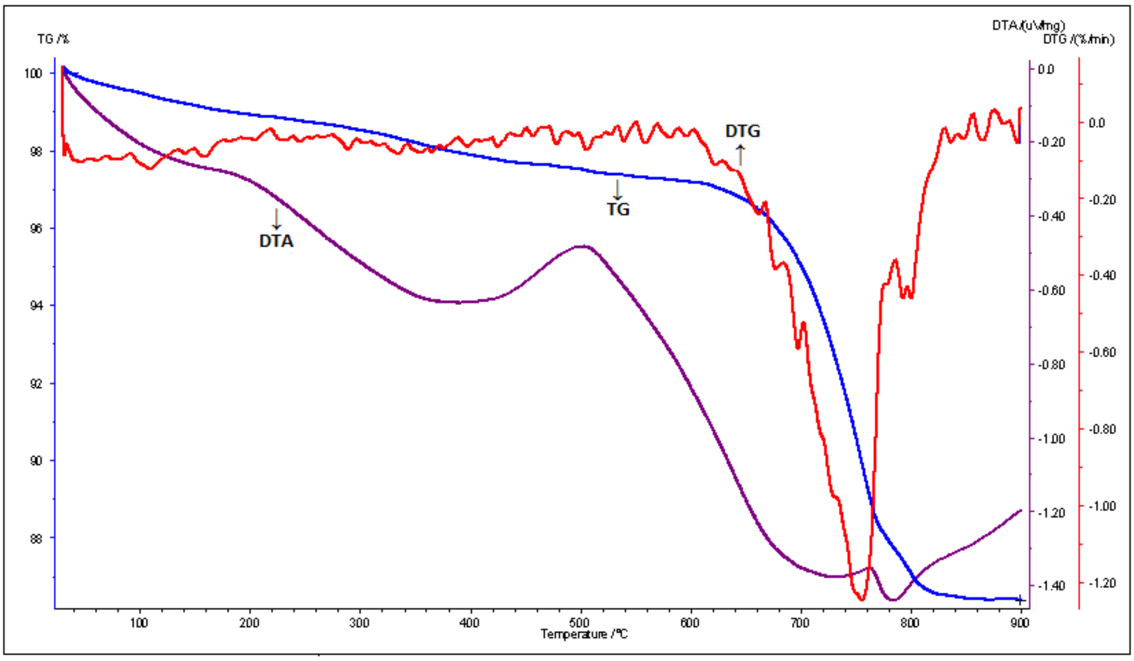

Figure 3. Results of thermal analysis of raw phosphate rock.

To investigate the effect of temperature on SO_2 absorption using the Mardin Mazıdağı phosphate ore and observe changes in the ore, a three-phase reactor as described in the literature was used and the experimental setup is given schematically in Figure 4. The reactor was made of plexi-glass material designed with a fixed surface area to allow contact between fluid and gas phases and to fix the temperature heating or cooling were ensured with the aid of a jacket inside the wall. Additionally it allowed mixing of fluid and gas phases separately at different rates. Air sent into the reactor was heated to the required temperature and humidified before mixing with the determined SO_2 amount. A portion of the "air + SO_2"

mixture was sent to a direct IR spectrometer and the entry concentration of SO_2 was identified. On the far side some of the output gas from the reactor was disposed of, while a portion was sent back to the same analyzer for SO_2 analysis. The values read by the analyzer were recorded with the aid of a computer. Thus the entry and exit values of the "air + SO_2" mixture were identified and the amount of absorbed SO_2 was calculated in terms of molar flux with the aid of the following equation;

$$N_{SO_2} = \frac{P\dot{V}(y_{SO_2,\mathrm{input}} - y_{SO_2,\mathrm{output}})}{RTA} \tag{12}$$

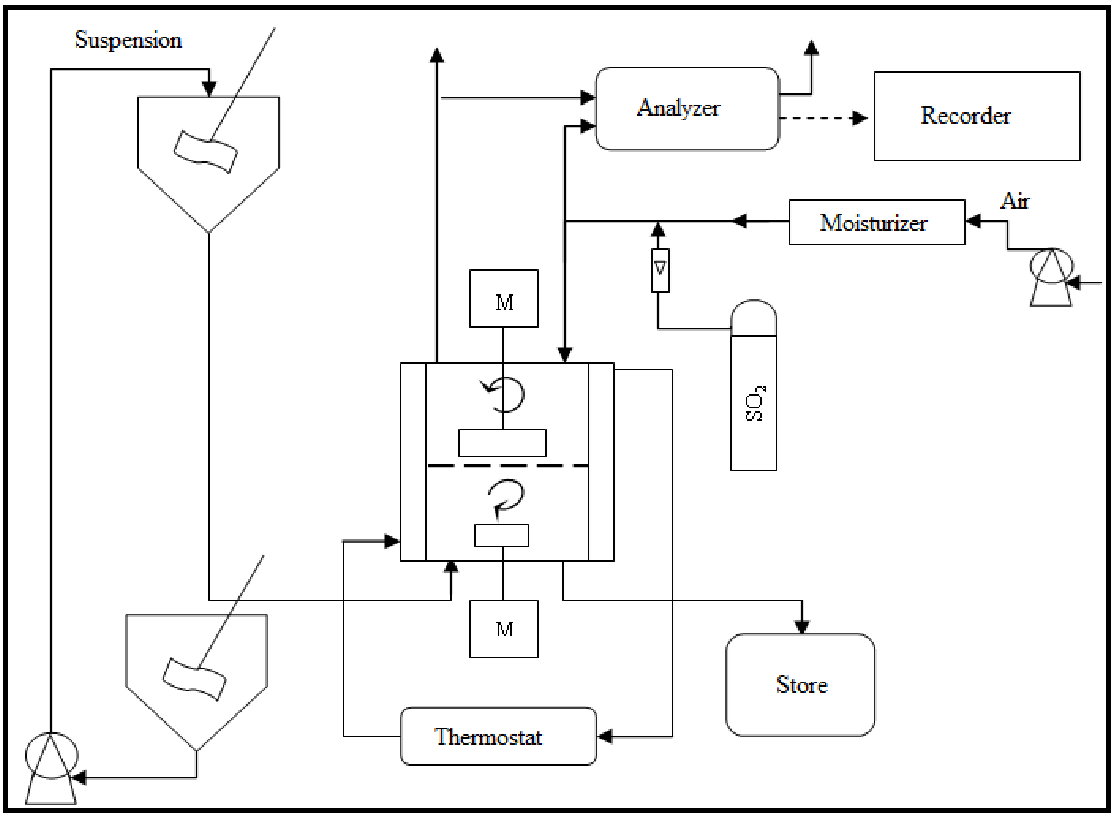

Figure 4. Experimental setup of wet flue gas desulfurization.

Experiments for wet flue gas desulfurization were completed in Erzurum with atmospheric pressure of 610 mmHg.

RESULTS AND DISCUSSION

During experiments to investigate the effect of temperature on absorption, temperature was varied while gas concentration, gas flow, sludge flow, mixing rates and sludge concentration were fixed. Experiments were completed with 3000 ppm SO_2, 4000 mL/min gas flow, 500 mL/min sludge flow, 900 rpm gas mixing rate, 300 rpm fluid mixing rate and 6% sludge concentration. Additionally, measurements were completed under the same conditions with water containing no phosphate rock. The $N_{SO2,s}$ statement is for the suspension (sludge), while the $N_{SO2,w}$ refers to the molar flux obtained for water. The results calculated from experimental data are shown in Figure 5.

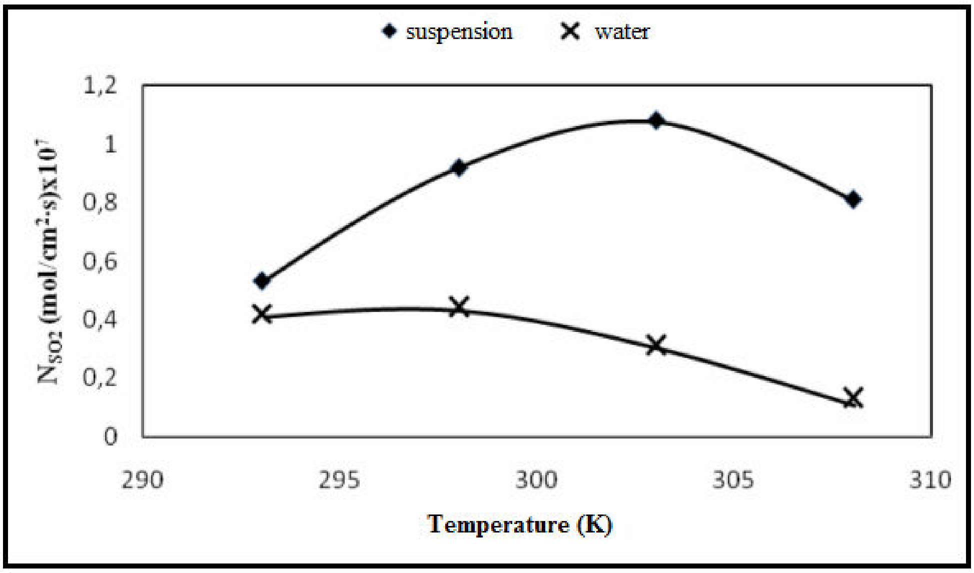

Figure 5. Variation of SO_2 molar flux with temperature.

As the transformation of the solid in this measurement system was very low, the analysis could not be completed so the following procedural examples were prepared. The suspension prepared using phosphate ore obtained from the Şemikan deposit in the Mardin-Mazıdağı region was left in the humidified "Air + SO_2" mix within the semi-batch operated reactor for 16 hours. The experiment used the above experimental conditions; however it was completed on the fluid side with non-flux semi-batch procedure. The sludge was later filtered, dried and investigated with x-ray powder diffraction, SEM and thermal analysis methods.

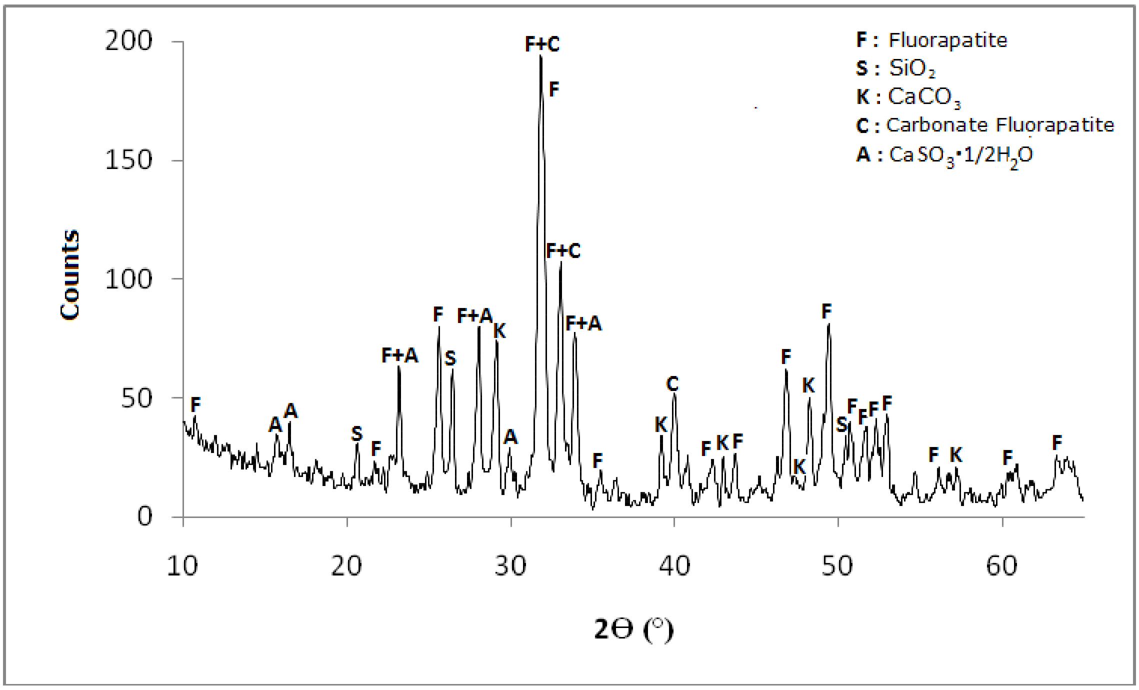

Figure 6. X-ray powder diffraction spectrum of rock processed for 16 hours.

The X-ray powder diffraction diagram for this sample (Figure 6) did not show any significant changes in fluorapatite, carbonate fluorapatite and silicon dioxide peaks. However, the calcium carbonate peak weakened significantly and new peaks shown by A were formed. These peaks were determined to belong to $CaSO_3 \cdot ½H_2O$ compound.

On the thermal analysis diagram shown in Figure 7, the weight loss up to 300 ºC has thermal analysis results similar to raw ore. However, after the rapid weight loss at 400 ºC, there was a weight increase after 550 ºC. This did not occur with the raw ore and is considered to be a result of the reactions occurring between SO_2 and the rock. Later the weight loss beginning around 700 ºC is similar to the behavior of the raw rock. The shoulder belonging to carbonate fluorapatite is repeated with no change observed in the value.

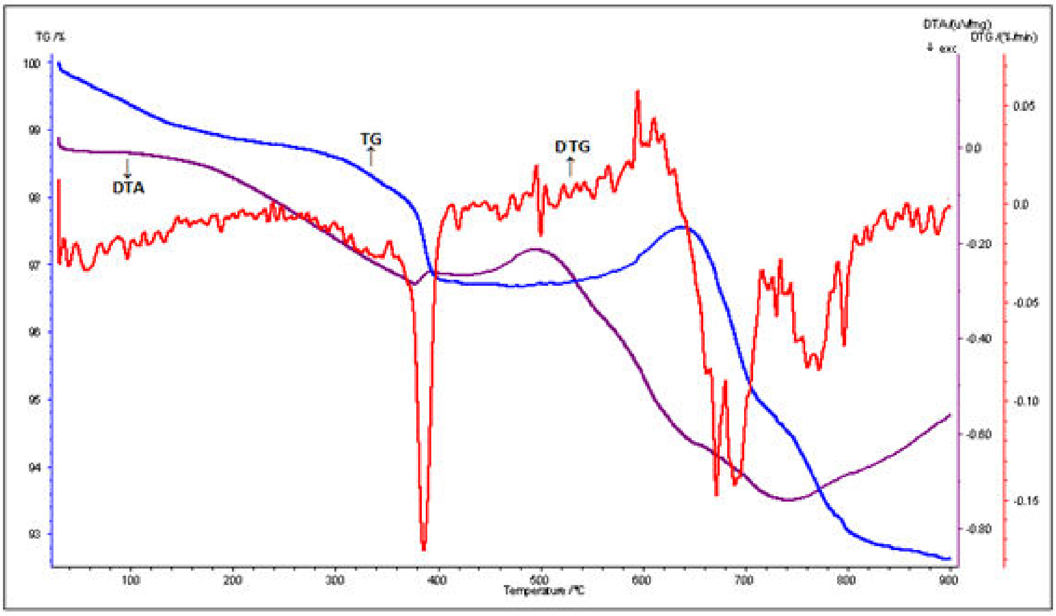

Figure 7. Results of thermal analysis of phosphate rock processed for 16 hours.

Figure 8, in addition to showing the SEM images of the samples, shows the phosphorus and sulfur distribution. From the diagram, it is noteworthy that the large particles rich in phosphorus have less involvement with sulfur. In this way, the small particles are rich in sulfur, which appears to accumulate on all surfaces. Additionally, the measured SEM image shown in Figure 9 confirms that all surfaces of the small $CaSO_3 \cdot ½H_2O$ crystalline agglomerates are covered.

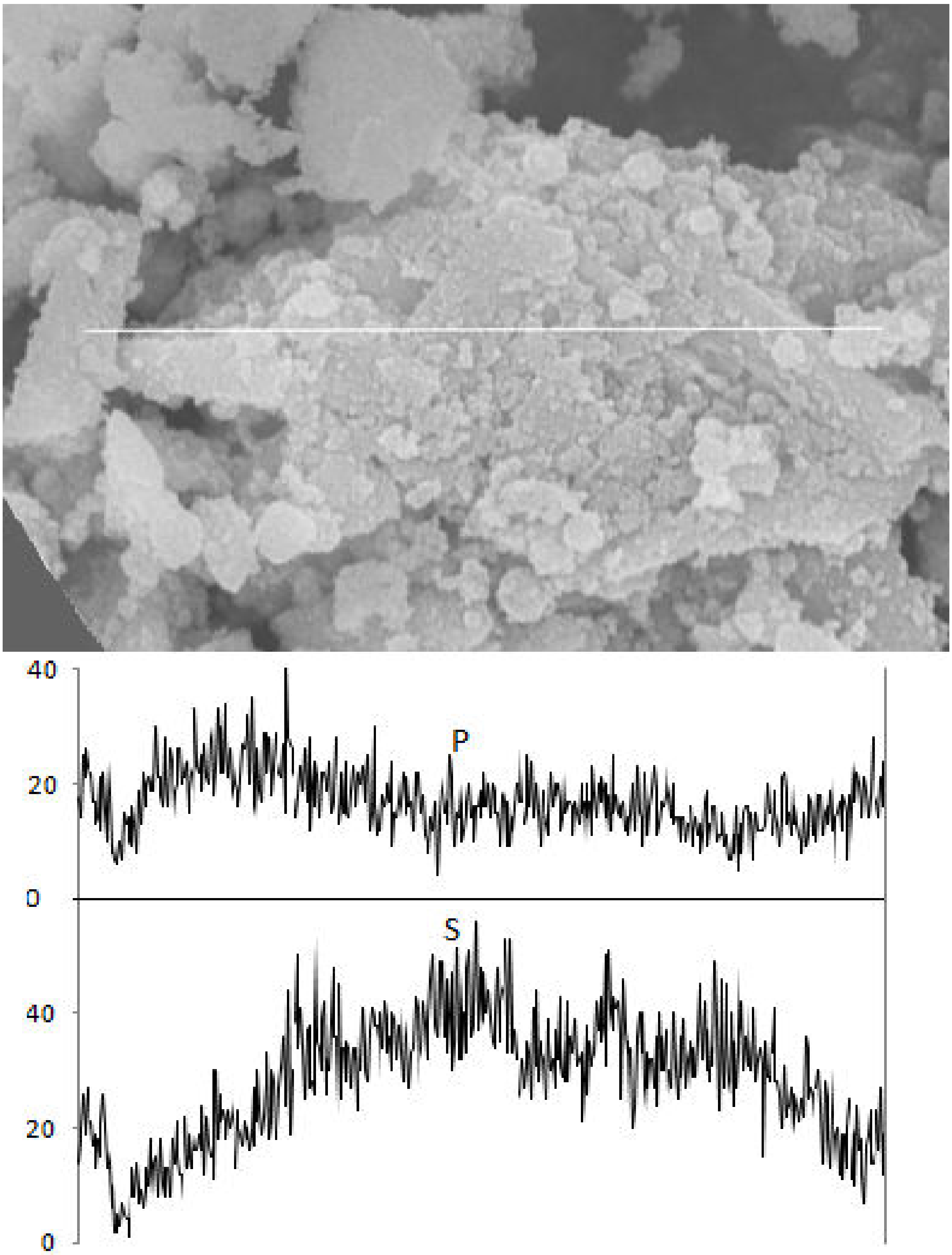

Figure 8. SEM image and elements distribution of the rock processed for 16 hours.

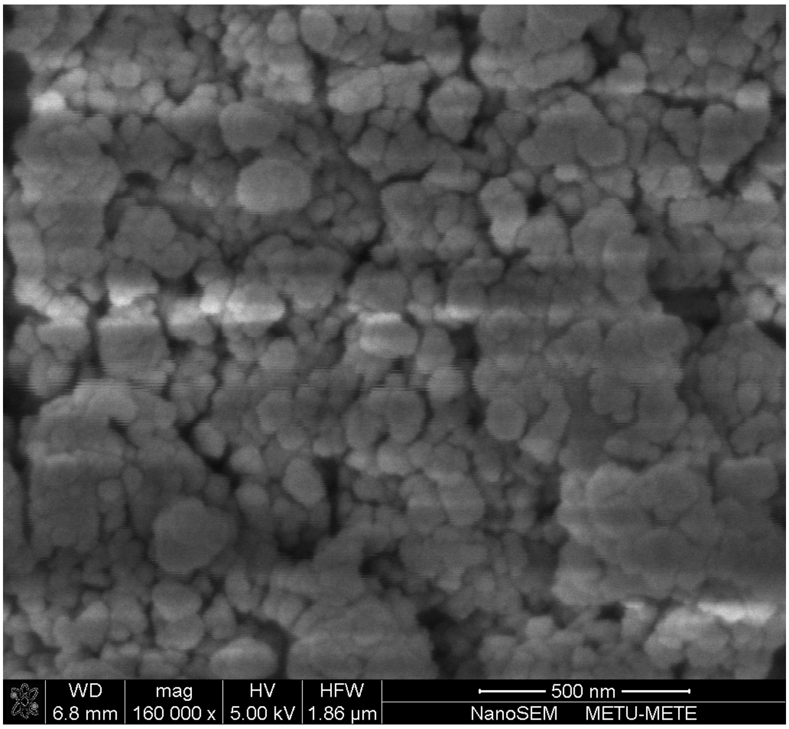

Figure 9. SEM image and elements distribution of the rock processed for 16 hours.

CONCLUSION

In this study, phosphate ore obtained from the Şemikan deposit in the Mardin-Mazıdağı region had chemical and structural characteristics determined with a variety of chemical and instrumental methods. Later, in a multi-phase reactor the suspension containing finely ground ore was placed in contact with "Air + SO_2" gas mix with unchanging surface to investigate the effect of temperature on gas absorption. Analyses were performed to identify changes occurring in the ore. Below these investigations are discussed separately.

As seen in Figure 5, the SO_2 molar flux of the suspension containing phosphate rock initially increased with the increase in temperature and then later reduced. The molar flux in water initially rose slightly but then a significant reduction was observed as temperature increased. Experiments by Long *et al.* (2005) and Mao *et al.* (2008) on chemical reaction absorption concluded that temperature initially increased molar flux by a certain amount and then later reduced it. As observed in Figure 5, the experiments completed in water initially had an insignificant increase in molar flux followed by a significant degree of reduction. Kiil *et al.* (1998) and Mao *et al.* (2008) stated that this situation was based on the reduction in solubility of SO_2 in water at high temperatures. These observed results are in accordance with the reduction in solubility of SO_2 in water identified by Bjerle *et al.* (1972). This variation difference occurring in water and in suspension may be explained by SO_2 transferred into water being directed by the solubility balance, while the SO_2 transferred into the suspension medium has difficulty reaching balance due to chemical linkages (14-17).

As the transformation of products obtained from the continuous system was very small, to identify these products a semi-batch system that could run for longer was used in a 16-hour experiment.

Analysis of samples obtained did not show a reduction in the ratios of fluorapatite and carbonate fluorapatite in the ore structure, though there was a significant reduction in calcite ratio. The X-ray diffractometry diagram showed that it contained the compound $CaSO_3 \cdot ½H_2O$. On SEM images, the agglomeration of small particles described in the literature (18) was clearly observed. Apart from this, in the diagram under the SEM image, the greater intensity of the sulfur peaks compared to phosphorus is clearly observed. The larger scale image of this formation (Figure 9) is in accordance with the agglomerations described by Chu *et al.* (1997).

In conclusion, domestic phosphate rock may be said to easily react with SO_2 with high efficiency under conditions appropriate to wet flue gas desulfurization. With more detailed investigation of conditions and transformation of the product into more stable sulfate form, it will be possible to apply this method in the industry. Local raw phosphate rock cannot be used in H_3PO_4 production as it causes excessive acid consumption due to high carbonate content and because of technological problems like causing foaming and blockage in the system. However, the creation of unused waste by sorbents after use in flue gas desulfurization and the environmental problems caused by these led to consideration of the applicability of a basic sorbent of phosphate rock. As seen in this study, the ore may be a good flue gas sorbent and produces a good raw material for use in H_3PO_4 production. With large reserves and no use due to high carbonate content, Turkey's phosphate deposits may be used for this aim contributing to the country's economy and as an alternative sorbent for use in flue gas desulfurization; as such we believe this study is a pioneer for future studies.

NOMENCLATURE

N_{so2}	SO_2 molar flux, mol cm^{-2} s
P	partial pressure, Pa
v	gas flow, mL min^{-1}
$Y_{SO2,input}$	SO_2 input mole fraction
$Y_{so2,output}$	SO_2 output mole fraction
R	gas constant, J mol^{-1} K^{-1}
T	temperature, K
A	surface area, cm^2

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Türkçe Öz ve Anahtar Kelimeler

SO_2 Soğurulması Üzerine Sıcaklığın Etkisi

Hayrunnisa MAZLUMOĞLU ve Mustafa Şahin GÜLABOĞLU

Öz: Kömür kullanan büyük enerji santrallerinde yanma ürünü olan kükürtoksitlerin tutulması amacıyla yaş baca gazı desülfürizasyon yöntemleri sıklıkla kullanılmaktadır. Uygun absorban içeren sulu süspansiyonların baca gazındaki kükürtoksitler ile olan reaksiyonu, bu yöntemlerin temelini oluşturmaktadır. Bu yüzden daha önceki çalışmalarda uygun özellikleri tespit edilmiş Mazıdağı fosfat kayasından hazırlanmış süspansiyonda ve saf suda SO_2 çözünme hızı üzerine sıcaklığın etkisi incelenmiş ve kullanılan cevherde meydana gelen değişimler gözlenmiştir. Sulu ortamda SO_2'nin çözünme hızı üzerine sıcaklığın etkisinin negatif olmasına karşın fosfat kayası süspansiyonundaki hızın 30 °C'ye kadar artış gösterdiği tespit edilmiştir. Bu sonuca göre yaş baca gazı desülfürizasyon sistemi için Mazıdağı fosfat kayasının incelenmesi sonucuna varılmıştır.

Anahtar kelimeler: Fosfat kayası; yaş baca gazı desülfürizasyonu; SO_2 absorsiyonu; üç fazlı reaktör; kireç/kireçtaşı.

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