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Investigation of the changes of P_2O_5 content of phosphate rock during simultaneous calcination/sulfation

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ABSTRACT

In this study, the changes of P_2O_5 content of phosphate rock during simultaneous calcination/sulfation in a fluidized-bed were investigated. P_2O_5 determination was carried out on samples with and without quenching of sulfated rock. The effects of the temperature and particle size on P_2O_5 content of either sample were determined. It was found that the decrease in process temperature favorably increased the P_2O_5 content of the sulfated samples. Since the calcination was the dominant reaction during the early stages of the process, there was an initial increase in P_2O_5 content of the sulfated samples. However, at later stages, there was a decrease in P_2O_5 extent of sulfated samples with an increase in the extent of $CaSO_4$ formed during the reaction. The P_2O_5 extent, on the other hand, increased with decreasing particle size. The results showed that P_2O_5 content of 23.27% in raw ore may be increased up to 36% following the quenching of sulfated samples.

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1. Introduction

Practically almost all phosphoric acid needed for the fertilizer industry is produced by wet processes. In many of these processes, the raw phosphate ore is converted into phosphoric acid and calcium sulfate dihydrate (gypsum) by adding sulfuric acid to the reactor [1].

Many chemical reactions take place in the reactor depending upon the ore complexity, but two main reactions are considered here. The first one is the fluorapatite ore attacked by sulfuric acid according to the following reaction;

$$12\ Ca_5(PO_4)_3F + 60\ H_2SO_4 + 120\ H_2O + SiO_2 \rightarrow 36\ H_3PO_4 + 60\ CaSO_4 \cdot 2H_2O + H_2SiF_6 + 6HF + 2H_2O. \quad (1)$$

The second reaction is between calcite and sulfuric acid, which is given as follows;

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2. \quad (2)$$

The carbonates in the phosphate rocks consume an additional acidulent (sulphuric acid) during the production of phosphoric acid and super phosphates. During the reaction, carbon dioxide produced causes more foaming and also results in production of smaller size gypsum crystals, that may blind the downstream phosphogypsum filters, and a low quality phosphoric acid may be produced [2].

In addition to above consequence, the emission of SO_2 from different industrial activities such as power production, the metallurgical processes and cement production is undesired due to its harmful effects. By using a suitable sorbent as the bed material, high sulfur containing coal can be burned while maintaining low SO_2 emissions without substantial decrease in combustion efficiency. The most commonly used sorbents in these procedures are calcium-based materials; in particular, limestone and dolomite, which capture released sulfur oxides in the form of calcium sulfate [3].

When the limestone is used as sorbent, the SO_2 removal process takes place through the two reaction steps. These are the calcination of the sorbent to produce high surface area and high porosity CaO and sulfation in the presence of O_2 to form the higher molar volume solid product, $CaSO_4$, which are given, respectively, as below:

$$CaCO_{3(s)} <=> CaO_{(s)} + CO_{2(g)} \quad (3)$$

$$CaO_{(s)} + SO_{2(g)} + 1/2O_{2(g)} <=> CaSO_{4(s)}. \quad (4)$$

The major disadvantage of using a natural limestone or dolomite as a bed material is the environmental impact of large quantities of limestone particles carried over and disposal of large quantities of solid waste. The inefficient use of calcium can introduce an economic disadvantage to a power plant, especially when transportation of sorbent over long distances is involved [4]. Because of the limited utilization of the solid waste obtained from flue gas desulphurization of the basic materials such as limestone and dolomite, difficulties in storage causing environmental problems have been occurred. If this

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Table 1
Analysis of the phosphate rock samples.

Components	710–1000 μm	500–710 μm	355–500 μm	250–355 μm
		wt (%)		
CaO	50.50	50.27	50.18	50.36
P_2O_5	22.34	23.27	24.53	25.09
MgO	1.59	1.60	1.59	1.62
Fe_2O_3	0.01	0.03	0.04	0.06
Al_2O_3	1.14	1.13	1.13	1.14
SiO_2	4.26	4.05	3.34	2.86
F_2	3.28	3.60	3.77	3.85
Loss on ignition (CO_2)	15.41 (12.06)	14.85 (11.23)	13.86 (8.57)	13.09 (6.98)

byproduct is used in the industry, the environmental problem will be reduced, which in turn may favor the process economically [5].

In a previous study, the possibility of using the Mazıdagı (Turkey) raw phosphate ore as an alternative to basic materials such as limestone and dolomite in the flue gas desulphurization was investigated [6]. The results showed that the conversion of sulfate obtained in the case of phosphate ore is higher than that obtained with limestone and dolomite.

In another study, the authors also investigated the kinetics of sulfation between SO_2 and calcareous phosphate rock [7]. It was found that the sulfation reaction is well represented by the shrinking core model and can be divided into two regions with different rate controlling steps. For low conversions, the controlling step was found to be chemical reaction at the interface, while for high conversion it was the diffusion through the product layer. The activation energies for the chemical reaction at the interface and diffusion through the product layer cases were calculated as 100 and 296 kJ/mol, respectively.

In this study, in the light of previous studies, the change of P_2O_5 content during simultaneous calcination/sulfation of phosphate rock in a fluidized bed was investigated by taking into account the parameters including the effect of the process temperature and particle size of the samples which were obtained either by being sulfated in fluidized bed or by removing free CaO as $Ca(OH)_2$ in water after sulfating.

2. Experimental

2.1. Material

Phosphate rock used in this investigation was provided from the phosphate deposits in the Mazıdağı. The sample was crushed, ground, and then sieved to give 250–355, 355–500, 500–710 and 710–1000 μm size fractions using ASTM standard sieves. A detailed mineralogical study on the phosphate rock can be found elsewhere [8]. The results of X-ray powder diffraction analysis showed that the main minerals of the rock are calcite, fluorapatite and carbonate-fluorapatite. It was found that the rock consisted of two different phases: a heterogeneously, calcite-rich phase and a phosphorus-rich phase as observed in the microscopical examination.

The chemical analysis of the phosphate rock according to particle sizes was carried out by standard gravimetric, volumetric and spectrometric methods, and the results of chemical analysis are given in Table 1.

X-ray powder diffractometry (XRD) was used in order to identify the products existing at the end of the reaction using conventional X-ray technique and X-ray tables. The X-ray analysis was carried out by a Rikagu DMAX-3C X-ray diffraction machine.

2.2. Experimental procedure

A schematic diagram of experimental set-up is shown in Fig. 1. Experiments were performed in a fluidized-bed reactor which consisted of quartz (3 cm i.d.) with a gas preheating section below the distributor. The reactor was heated by positioning the tubular electric furnace centrally. A chromel–alumel thermocouple and a temperature controller were used to control the temperature of the bed. The reacting gas was prepared by mixing O_2, N_2, SO_2 and CO_2 in order to obtain a synthetic flue gas composition. Minimum practical quantity of phosphate rock (approximately 1 g) was used in order to minimize variations in the bed temperature resulting from the heat absorbed/released during calcination/sulfation and achieve the differential conditions. The velocity of the fluidizing gas was maintained twice of the minimum fluidization velocity to ensure fluidizing conditions of the phosphate rock particles. Temperature of the bed was raised and kept for 10 min at the desired level, before charging the phosphate rock sample from the top of the bed. Sample in the reactor, discharged by applying vacuum at the end of the reaction and was collected in the sample hold up. Sample of dust and fine particles was recovered using two cyclones connected to this sample hold up. In the first group of experiments, the P_2O_5 content of these samples was directly determined. During the second group of experiments, in order to remove the oxides formed from carbonate decomposition quenching process was applied to the samples which were sulfated in the fluidized bed before determining their P_2O_5 content. The sulfated

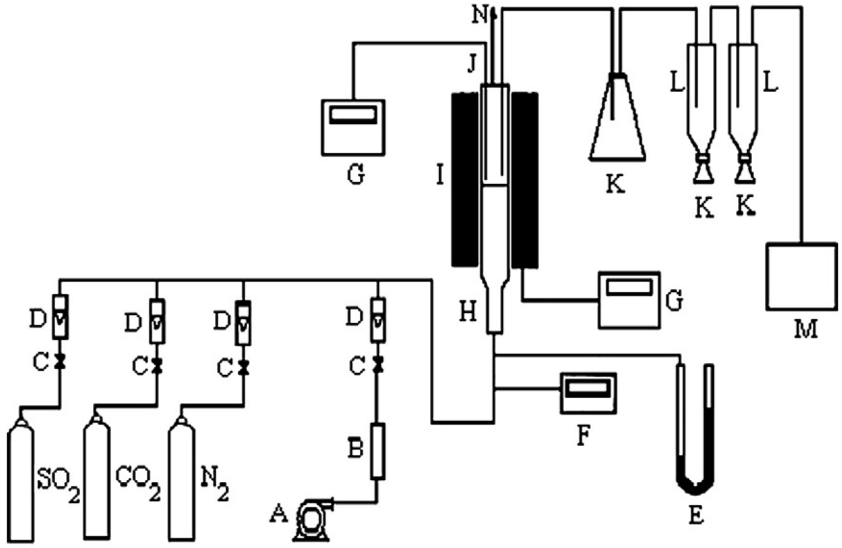

Fig. 1. Schematic diagram of experimental set up. (A) air compressor, (B) dryer, (C) control valve, (D) flowmeter, (E) manometer, (F) SO_2 analyzer, (G) temperature controller, (H) preheating column, (I) reactor, (J) thermocouple, (K) sample hold up, (L) cyclone, (M) vacuum pump, (N) gas out.

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