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The Enrichment of Low-Grade Mazidagi Phosphates by Calcination and Extraction Methods

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NOTE

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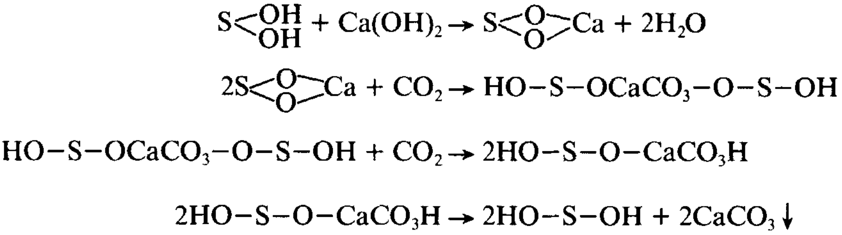
INTRODUCTION

Only Mazidaği phosphate are worthy of processing among the phosphate reserves in Turkey. The benefication problem of low-grade Mazidaği phosphates has not been solved, although they constitute 260 million tons out of a total of 400 million tons of phosphate rocks in the region (*1, 2*). The method used for the benefication of calcerous phosphates is generally calcination at about 800–950°C followed by slating and removal of small particles. Application of this common process gives a highly concentrated end product. When this method is used on the phosphate rocks of Mazidaği, it is not possible to obtain good quality products for industrial purposes. However, in some countries, to remove the excess amount of $Ca(OH)_2$, solutions of NH_4Cl and NaCl are used (*3, 4*). These compounds increase the solubility of $Ca(OH)_2$ about three times. If a solution of sugar is used instead of those solutions mentioned above, it is possible to increase the solubility of $Ca(OH)_2$ about a hundred times (*5*). By making use of this phenomenon, an excess amount of $Ca(OH)_2$ in low-grade Mazidaği phosphates can be extracted into the liquid phase according to the following chemical reactions (where $S(OH)_2$ indicates sugar molecules):



$$\mathrm{S}{<}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}} + \mathrm{Ca(OH)_2} \rightarrow \mathrm{S}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}{>}\mathrm{Ca} + \mathrm{2H_2O}$$

$$\mathrm{2S}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}{>}\mathrm{Ca} + \mathrm{CO_2} \rightarrow \mathrm{HO{-}S{-}OCaCO_3{-}O{-}S{-}OH}$$

$$\mathrm{HO{-}S{-}OCaCO_3{-}O{-}S{-}OH} + \mathrm{CO_2} \rightarrow \mathrm{2HO{-}S{-}O{-}CaCO_3H}$$

$$\mathrm{2HO{-}S{-}O{-}CaCO_3H} \rightarrow \mathrm{2HO{-}S{-}OH} + \mathrm{2CaCO_3}\downarrow$$

Calcium ions which complex with sugar molecules are removed by precipitation in the form of calcium carbonate.

EXPERIMENTAL

Samples (50.0 g) of different sizes were calcined at temperatures between 850 and 950°C for different time periods. A Heraeuse model KR 170 furnace was used for all experiments. After each calcination all the samples were slaked by using the same amount of water, and then the excess amounts of $Ca(OH)_2$ were extracted from the solid phase into the liquid phase by using sugar solutions. For the purpose of separation of small particles, we used a screen of 400 mesh. Concentrated minerals which had been washed and then dried were analyzed by using a Bausch & Lomb Spectronic 20 type spectrophotometer. It is necessary to use an excess of sugar solution when a calcined mineral is reacted directly with sugar solutions. In addition, an unsoluble by-product, tricalcium saccharide, was formed, and at the same time the amount of soluble $Ca(OH)_2$ was decreased (*5, 6*). Therefore, products obtained after calcination were slaked by water and then washed. So, before application of sugar solutions to calcined materials, the concentration of P_2O_5 was increased to about 20%. Finally, by the application of sugar solutions, we obtained concentrated samples which contained over 30% P_2O_5. In these studies, we used an Atago polarimeter to determination the amount of sugar.

RESULTS AND DISCUSSION

As can be seen in Tables 1 and 2, depending on particle size before calcination, time of calcination, temperature, and the methods of differentiation process after calcination, product concentrations were changed from 20 to 27 and 30 to 35% P_2O_5, respectively.

When the sugar solutions used in the experiments settled down, then CO_2 gas was passed through the homogeneous solutions. Calcium ions connected to the sugar molecules are precipitated in the form of calcium carbonate. Through these processes we were able to obtain powder $CaCO_3$ as a by-product and the sugar solution was ready to use again for a new process. For the determination of sugar lost during the processes, we analyzed the amount of sugar at each step of the experiments. The results show there is an average loss of 0.5 g of sugar per 50 g of rocks (Table 3).

When minerals were calcined at about 870°C for 1 h, the calcined products were slaked with water and the parts separated at 400 mesh. We

TABLE 1
The Results of Benefication with Water

Particle size (mm)	Calcination temperature (°C)	Calcination time (h)	P_2O_5 (%)	Yield as P_2O_5 (%)
5	860–870	1	20.0	93.0
1	860–870	1	20.0	82.0
1	860–870	2	27.0	66.0
1	860–870	3.5	23.5	66.0
5	900–920	1	23.4	90.0
1	900–920	1	22.8	77.0

TABLE 2
The Results of Benefication with Sugar Solution

Particle size (mm)	Calcination temperature (°C)	Calcination time (h)	P_2O_5 (%)	Yield as P_2O_5 (%)
5	860–870	1	35.0	—
5	870–880	1.5	34.5	78.0
1	870–880	1.5	35.3	64.0
1	860–870	2	34.7	55.0
5	860–870	2	34.0	67.5
0.149	860–870	1	32.3	—

TABLE 3
Loss of Sugar per 50 g of Phosphate Rocks

Before using, % sugar	After using, % sugar	Loss of sugar (g)
20.28	20.30	−0.02
25.84	25.22	0.62
25.84	25.79	0.05
29.12	28.30	0.82
30.06	29.23	0.83
30.06	29.48	0.58
30.06	29.65	0.41
30.06	29.40	0.66

were able to obtain products which were concentrated to about 20–22% P_2O_5 with a yield of 90–93%.

By increasing the calcination time from 1 to 1.5 h at 870°C and using a sugar solution, and after again removing the small particles, we were able to obtain products which were concentrated to about 34.5% P_2O_5 with a yield of 78%. We regenerated the solution obtained at the end of these processes by passing CO_2 gas through them and obtained powder $CaCO_3$ with a purity of 99.6%.

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