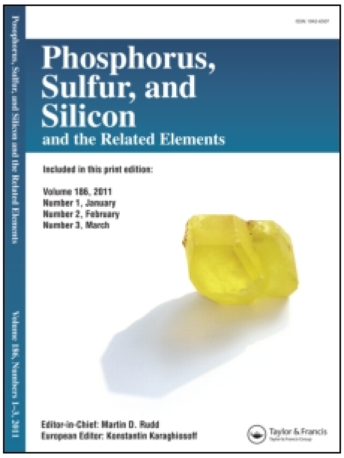

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CALCINATION OF NEGEV PHOSPHORITES AND POSSIBLE CAUSES FOR TECHNOLOGICAL PROBLEMS

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Abstract Carbonate removal in the apatite structure was observed at temperatures from 600 to 900°C. The carbonate ions are also partially relocated from the orthophosphate site, into others such as interstitial positions and OH site. Hydroxyl groups form hydrogen bonds along the hexagonal axis; partial condensation of the orthophosphate groups takes place. Oxidation of organic-rich phosphorites, with a high S content in the organic matter, during calcination, causes the introduction of SO_4 in the apatite structure in orthophosphate sites. Similarly SiO_4 may also be introduced in these sites. In all cases the residence time during calcination is of great importance. Flash calcination is not only significantly cheaper than conventional calcination but is preferable because of the very short residence time of the phosphorites at high temperatures.

Key words: Phosphorite, Flash Calcination, Apatite, Substitutions in Apatite

INTRODUCTION

Calcination is an efficient beneficiation method for phosphorites with a high carbonate and/or high organic matter content. The advantages of calcination are: the decomposition coefficient of the phosphate increases, flotation properties of some phosphorites are improved, consumption of sulfuric acid decreases, the filtration rate of the precipitated phospho-gypsum increases, abundant foaming in the reactor is eliminated, the humidity of the phospho-gypsum is decreased [1]. Thermal beneficiation enables the inclusion of some types of poor quality phosphate rock, which would have been almost impossible to process by acidic treatment, in the production of mineral fertilizers. The drawbacks of calcination are its high price and in some cases calcination causes a worsening of the indices of acidic treatment or of flotation properties. This shows the possibility of different changes of the properties of phosphorites by thermal treatment sometimes even for phosphorites characterized by almost the same chemical composition. The reason may be connected with the differences of the real (detailed) structure of apatites [2]. Therefore the mineralogy of phosphorites and the crystallochemistry of apatites are of great importance for prediction of the properties of calcined product.

METHODS

Phosphorites from various deposits of Israel - Nahal Zin, Saraf, Arad, Oron, Yorkeam - were supplied by the Rotem-Amfert-Negev Company and the Geological Survey of Israel. The samples included a suite of phosphorites from Nahal Zin deposit, before and after flash calcination (900°C during a few seconds). Some samples were subjected to thermal treatment in the laboratory at temperatures from 600°C to 950°C for periods from a few seconds up to several hours. Admixtures of phosphorites with gypsum or with quartz, 10:1 w/w, were prepared and analyzed after thermal treatment. Chemical analysis, Fourier Transform Infrared spectroscopy (FTIR) and X-Ray (powder) Diffraction (XRD) were used to characterize the samples.

RESULTS AND DISCUSSION

In Nahal Zin phosphorites, after flash calcination, about half of the original calcite (9%) was decarbonated, calcium oxide (hydroxide) formed and transformation of gypsum to anhydrite took place. The amount of organic matter decreased significantly and its composition changed. Trace element concentrations also changed. The contents of Cd, Cr, Mo, Ni, V and Zn decreased while the contents of Ba, Eu, La, Sr and Y increased (Table 1).

Structural Changes In Apatite

Structural changes in apatite were registered after flash calcination: the amount of structural carbonate was drastically reduced (more than 50%) together with a corresponding reduction of F, the F/P_2O_5 ratio was reduced from 0.095 to 0.088. As a result the P_2O_5 content in the calcined rock increased by a little more than 10% from 29.5% to 33% (Table 1). The actual beneficiation is better, since CaO and MgO are separated by wet slaking of the calcined rock. The ousting of most of the structural

Table I

A - Crystallite size (XRD), structural CO_2 (XRD) and major element composition(ICP-AES)

Sample No.	size of cryst. along the a direction in A	c direction in A	CaO %	P_2O_5 %	CO_2[1] %	CO_2[2] %	F %	F/P_2O_5
25	280	550	51.4	30.5	8.3	4.1	2.99	0.098
26	750	1530	55.1	33.6	3.7	1.5	3.02	0.090
27	270	660	52.4	30.1	7.5	4.2	2.71	0.090
28	790	1480	55.5	33.4	3.0	1.5	2.86	0.086
29	290	540	51.4	29.1	7.9	3.7	2.97	0.102
30	830	1090	55.0	32.6	3.1	1.8	3.08	0.094
31	370	640	50.9	27.8	7.5	3.5	2.71	0.097
32	840	1250	54.7	32.6	3.1	1.4	2.83	0.087
33	310	550	52.5	29.8	8.6	3.8	2.70	0.091
34	820	1240	54.6	31.7	3.1	1.6	2.71	0.085

1 - Total CO_2. 2 - Structural CO_2.

B - Trace element composition(ICP- AES)

Sample No	Ba ppm	Cd ppm	Cr ppm	Eu ppm	La ppm	Mo ppm	Ni ppm	Sr ppm	V ppm	Y ppm	Zn ppm
25	749	29	117	0.3	16	23	46	2800	164	54	474
26	1056	17	74	0.5	18	16	35	3076	136	60	408
27	430	31	119	0.2	17	38	47	2660	161	55	453
28	736	18	70	0.4	18	25	32	2997	131	60	404
29	800	30	108	0.4	17	35	47	2748	159	57	471
30	691	18	69	0.5	19	27	42	2952	127	63	411
31	568	31	122	0.3	16	26	57	2592	168	53	487
32	726	20	73	0.5	18	29	42	2970	138	60	422
33	581	32	105	0.3	16	35	54	2562	154	54	473
34	764	19	74	0.1	18	27	42	2898	122	58	430

Samples 25, 27, 29, 31 and 33 are field samples (FEED) and samples 26, 28, 30, 32 and 34 are samples after flash calcination.

carbonate increased the crystallinity of the apatites, and the sizes of their crystallites (Table I). Only one type out of the observed crystallochemical type of the apatites (FTIR) in Negev phosphorites was found in the flash calcined Nahal Zin phosphorites.

After flash calcination, carbonate ions were not only ousted from the structure, but also partially relocated from one site (orthophosphate group) of the structure to others, interstitial and along the hexagonal axis.

Orthophosphate groups were partially condensed to pyrophosphate: vibration bands of the P-O-P bridge bonds appeared in the IR spectra. Hydroxyl groups formed hydrogen bonds with fluorine on the hexagonal axis of the structure. The structural changes of the apatites during flash calcination caused changes in the properties of calcined phosphorite; the solubility of the concentrates decreased by 50%. After prolonged calcination, sulfate (SO_4) and silicate (SiO_4) enter the apatite structure, in the vacant phosphate positions produced by the ousting of the carbonate, at 800°C and sometimes already at 700°C. Appearance of the bands at 530, 930, 1150 cm-1 in the IR spectra of calcined apatite when no other phases is present (according to X-ray diffractions) is indicative of isomorphous substitution of phosphorus by sulfur and/or silicon. The organic matter in the Negev phosphorite is rich in sulfur (10% by weight of organic matter). During calcination a partial decomposition of organic matter occurs, S is liberated, some of it enters the apatite structure as SO_4. We found a correlation between the concentration of organic matter in the original samples and the amount of SO_4 in the structure of the calcined product. The residence time during calcination is of great importance. Entering of SO_4 and SiO_4 in the apatite structure takes place only at 950°C with flash calcination. This shows that use of flash calcination at 950°C is not desirable in spite of the more complete liberation from carbonate at this temperature.

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