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Impact of mechanical activation on physical and chemical properties of phosphorite concentrates

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ABSTRACT

The mineralogical and chemical composition of phosphorite concentrates from Tunisia, Estonia (from the Kabala and Toolse deposits), Uzbekistan (Dzheroi-Sardara) and Kazakhstan (Dzhanatas) as well as their apatite structures were studied before and after mechanical activation in a planetary mill for 5 to 240 min. The specific surface area of these concentrates increased during the first 10–30 min and thereafter decreased. The solubility of phosphorus increased proportionally with the size of the apatite crystallites. The changes in the physical and chemical properties following mechanical activation depend mainly on the mineralogical composition of phosphorite concentrates and on the structural characteristics of the apatite. Mechanical treatment in a planetary mill is more efficient in the case of sedimentary phosphorites, particularly Estonian phosphorites, and is less effective in the case of igneous phosphorites.

1. Introduction

Mechanical activation can be characterised as an ecologically clean method for increasing the reactivity of minerals, as it does not need any chemicals and does not produce wastes. Mechanically activated apatites can be used as fertilisers directly or in a composition of complex fertilisers (Kolosov et al., 1979; Paudert et al., 1979; Boldyrev, 2006). It has been shown that the increase in solubility due to mechanical activation depends on the origin of the apatite mineral (Heinicke et al., 1977; Chaikina, 1986). The impact of mechanical activation on the reactivity of apatites is based not only on the decrease in particle size but can also depend on changes in their crystal structure (Chaikina and Aman, 2005; Yaneva et al., 2005). Less attention has been paid to changes in the chemical composition of phosphorites and to their possible contamination with metals from working bodies during mechanical treatment.

The aim of our study was to compare the impact of mechanical activation on phosphorite concentrates with different mineralogical compositions and apatite structures.

2. Experimental

2.1. Methods

Mechanical activation was carried out in a Pulverisette-55 planetary mill (Fritsch Co, Germany) at a rotating speed of 320 rpm for 5 to 240 min using Cr–Ni milling bodies with a diameter of 20 mm and a sample mass of 20 g.

The chemical composition and phosphorus solubility in a 2% citric acid solution[1] were determined by standard analytical methods. The content of Cr and Ni was assessed by AAS (Varian AA 220FS). Carbonate content was determined using an ELTRA CS-580 carbon analyzer.

The specific surface area (SSA) measurements were performed by the BET-method (adsorptive gas N_2, carrier gas He, heating temperature 150 °C) using an EMS-53 sorptometer and KELVIN 1040/1042 software (Costech International).

Powder diffraction (XRD) data were collected with a Bruker D5005 diffractometer (2θ 15–100°, step 0.02°, count time 15 s/step, Cu $K\alpha$ radiation). The cell dimensions were determined using the FullProf program. The median crystallite size was calculated from XRD patterns by the Scherrer equation (Klugg and Alexander, 1974).

The FTIR spectra were recorded on Interspectrum 2000 equipment in the range of 400–4000 cm^{-1} with a resolution 4 cm^{-1} and 10

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Table 1
Chemical and mineralogical composition, crystallite size and specific surface area (SSA) of the phosphorite concentrates.

Sample	Tunisian	Kabala (EST)	Toolse (EST)	Dhzanatas (KAZ)	Dzheroi-Sardara (UZB)
SSA (m^2/g)	14.43	3.60	2.45	2.10	8.90
Chemical composition (%)					
P_2O_5	29.6	29.1	26.6	25.2	24.1
CaO	50.1	43.1	40.4	42.1	46.5
MgO	0.9	1.2	0.9	4.0	–
F	3.5	2.4	3.0	2.7	2.4
CO_2	3.5	5.9	4.7	7.9	9.6
SiO_2	1.9	10.2	16.2	11.7	7.7
$Fe_2O_3+Al_2O_3$	1.3	3.2	3.8	1.8	1.6
SO_3	3.6	1.9	2.7	0.7	2.4
Mineralogical composition (%)					
Francolite	94.5	73.8	67.2	66.0	73.1
Quartz	0.3	12.2	17.1	10.4	6.0
Calcite	2.9	2.3	5.3	2.9	15.8
Dolomite	1.1	10.0	2.7	17.5	0.9
Anhydrite	1.1	–	–	–	1.0
Feldspar	tr.	tr.	1.2	2.5	2.9
Crystallite size (Å)					
Francolite	461	430	474	649	634
Quartz	1560	1802	1892	1652	1531

scans. The samples were pressed into KBr pellets (1 mg sample per 300 mg KBr). The peaks were fitted using the Thermo Galactic GRAMS/AI program (GRAMS/AI, 2003).

2.2. Materials

The studied samples were phosphorite concentrates from Tunisia, Estonia (from the Kabala and Toolse deposits), Uzbekistan (Dzheroi-Sardara) and Kazakhstan (Dzhanatas). Their mineralogical and chemical compositions are given in Table 1. The main impurity minerals in these concentrates are quartz, calcite, dolomite and feldspar. Additionally, Estonian phosphorites contain pyrite and hematite. The samples differ mainly in their content of silicates and carbonates. The content of P_2O_5 varies from 24.1 to 29.6%, CO_2 from 3.5 to 9.6% and fluorine from 2.4 to 3.5%.

The apatite structure, revealed by XRD and FTIR analyses, corresponds to fluor-carbonate apatite (francolite), but due to the different formation conditions, their structural characteristics vary. Estonian phosphorites were formed as a result of biomineralisation (shelly phosphorites) (Ilyin and Heinsalu, 1990), Tunisian and Uzbekistan phosphorites were formed as a result of precipitation (Cook, 1984) and Dhzanatas apatite was formed in magmatic processes (Pozin, 1975).

The initial specific surface area of the samples (Table 1) varied from 2.10 to 14.43 m^2·g^{-1}. The crystallite size, calculated from the XRD patterns, varied from 430 to 649 for francolite and from 1531 to 1892 for quartz (Table 1).

3. Results and discussion

3.1. Specific surface area

As a result of treatment in the planetary mill, the SSA of phosphorite concentrates increased during the first 10–30 min and subsequently decreased (Fig. 1). The decrease in SSA could be a result of adhesion of the micro-particles (Yaneva et al., 2005; Baláž, 2008). The highest value of SSA depends on the mineralogical composition and initial SSA of the sample. For the Tunisian phosphorite, which contains the lowest amount of impurities, particularly quartz, and has the highest initial SSA, the value of SSA increased in 10 min from 14 to 20 m^2·g^{-1}. For the Estonian and Kazakhstan phosphorites with low initial SSA and a high SiO_2content, the highest values of SSA (10–12 and 7 m^2·g^{-1}, respectively) were obtained in 30 min. As exhibited in Fig. 2, the relative increases in SSA were greater for the samples that contained less P_2O_5 and more impurity minerals, particularly silicates.

3.2. Chemical composition

In the solid state process of mechanical activation, the content of the main elements stays constant and may change only due to the evolvement of CO_2 in the case of a local temperature increase. In the studied samples, the amount of carbonate after mechanical activation did not change.

A serious problem, which is usually cited in mechanochemical research, is contamination with metals (Baláž, 2008) which must be taken into consideration when the material is used as a fertiliser. The analyses of the phosphorites before and after milling show that long-term treatment with Cr-Ni balls led to an increase in the Cr and Ni content in the samples by up to three-fold (up to 0.05–0.08% over 240 min). The increase was proportional to the milling time (Fig. 3). The impact of the mineralogical composition on the Cr and Ni content in milling products was not investigated.

3.3. Phosphorus solubility

Phosphorus solubility in 2% citric acid increased for all samples by about 30–45 rel. % as a result of milling for 240 min. (Fig. 4). The level

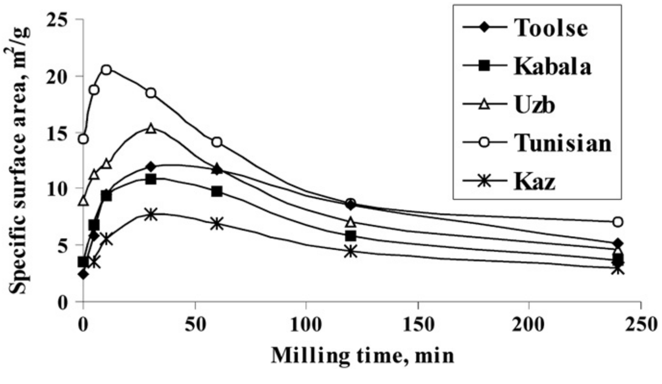

Fig. 1. The specific surface area as a function of milling time.

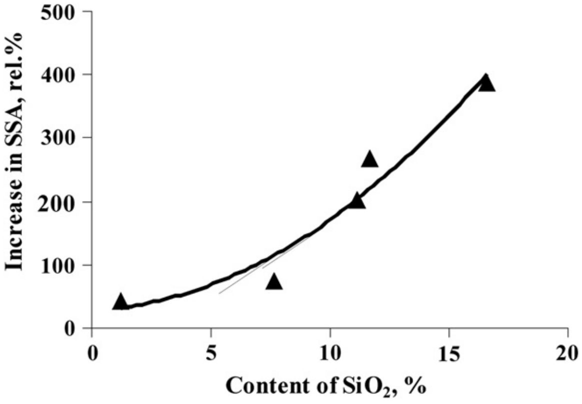

Fig. 2. The relative increase in SSA as a function of the content of SiO_2 in phosphorite concentrate with a milling time of 30 min.