

S.S. IBRAHIM*

EFFECT OF INTENSIVE GRINDING ON THE PHYSICOCHEMICAL PROPERTIES AND REACTIVITY OF RED SEA PHOSPHATES

Intensive grinding of raw Red Sea phosphate and its concentrate using a tube rotary chamber vibrating mill was studied. The process was followed by tracing progressive changes in the crystallographic and physical characters of apatite and the accompanied gangue minerals during milling. X-ray diffraction patterns and infrared spectra of milled products showed drastic reduction of the major peaks of apatite, calcite, gypsum and quartz. A decrease in the apatite lattice parameters, particularly the a parameter was noticed. A remarkable increase in the solubility of milled products in 2% citric acid and neutral ammonium citrate was shown. The results proved that the concentrated sample showed less effect towards intensive grinding than the raw sample. This may open the way for utilizing indigenous phosphate ores in many developing countries.

INTRODUCTION

Highly intensive size reduction equipment like vibrating, centrifugal, jet and other types of mills are employed in the treatment of phosphate rocks (Heinicke 1977; Kolosova 1979). It has been determined that the best performance is achieved in the impact and attrition milling (Kozlov and Kozyrev 1982). Owing to high relative velocities between the grinding tube mill and the grinding material, the vibrating tube mill, in comparison with other grinding machines, is characterized by high reserve of stored-up energy as well as high energy intensity collision processes in the grinding tube (Gock et al. 1986).

On the basis of findings obtained from the energy consumption of the common vibrating mills, combined with high speed photometric studies, many disadvantages in the comminution process were recorded (Kurrer et al. 1986). Some of these disadvantages is the tendency of phosphate minerals to cake resulting in operating choking problem of the mill, as well as the limitation of the construction sizes (Gock et al. 1986).

German scientists succeeded in improving the geometry of the grinding chamber of the classic vibrating mill. They introduced a free moving chamber wheel in the milling tube instead of the rigid wheel (Gock et al. 1986). A huge amount of free energy gained during fine grinding of solid materials in the rotary chamber vibrating mill could be

* Central Metallurgical R&D Institute, P.O. Box 87 Helwan, Cairo–Egypt.

dissipated through various modes of energy transitions. Such energy might be high enough to cause imperfection in the internal lattice structure of the ground material. Accordingly significant increase in the solubility behaviour of intensive ground phosphates was shown (Gock, Jacob 1984).

In this study details will be provided on the effects of grinding treatment on pure apatite with variable P_2O_5 content and various contents of the accompanying gangue minerals.

EXPERIMENTAL

Two typical phosphate samples were kindly supplied by the Red Sea Phosphate Co. One of the samples was a crushed run-of-mine material and the other was its final phosphate concentrate. Chemical content, size distribution, and mineralogical evaluations of both samples were carried out. Qualitative and quantitative elemental analy-

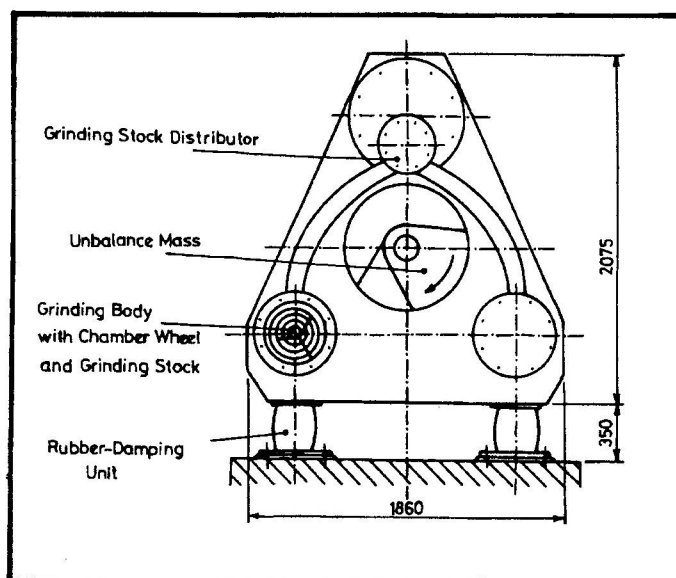


Fig. 1. The rotary-chamber vibrating mill

ses were performed with an X-ray fluorescence apparatus using a Philips PW 1410/10 system at $1 \cdot 10^3$ W, 50 KV/20 mA equipped with a PET crystal. Structural phase analysis of the powdered samples was done with a Philips PW 1050/25 X-ray diffractometer under constant operating conditions of Cu $K\alpha$ tube at 40 KV, 20 mA, 4×10^2 cps, and 1° /cm/10 s scanning speed. Sometimes extraction of the samples with the Silverman reagent was carried out before X-ray investigation to determine unit cell parameters a and

c. For such purpose an X-ray diffractometer (Philips-PM 8203 single pan recorder) was connected to an IBM computer. The computer was also employed to measure the area under specific phosphate peaks in the diffractograms.

Infrared spectra of the samples extracted with Silverman's reagent were also taken using a Philips Pye Unicam spectrometer. The discs containing samples in KBr wafers were used (Esep et al. 1986). In the meantime, DTA and TGA measurements of the ground samples were carried out using a Linseis Unit and a Netzsch thermobalance at a heating rate of 2 °C/min, sometimes at 10 °C/min. The samples were heated up to 1000 °C. Particle size analyses of the ground phosphate products were carried out using PABSICH type 715 laser granulometer. Automatic surface area calculations were also made by the same device during grain size measurements.

Various ground phosphate samples, collected after varying milling times, were subjected to solubility tests using 2% citric acid and neutral ammonium citrate. 2.5 g of ground phosphate is placed in 500 c.c. round flask. 250 ml of 2% citric acid and 1 ml of ethyl alcohol are added. The flask is shaken for 30 min and then centrifuged to separate the filtrate. P_2O_5 is analysed in the filtrate to determine 2% citric acid soluble P_2O_5 (Stetter 1972). Another 2.5 g of ground phosphate is placed in 600 c.c. conical flask and covered with 250 c.c. hot neutral ammonium citrate. The contents is kept hot at 65 °C on a water path. The flask is shaken vigorously every 5 min for 60 min. The solution is filtered and citrate soluble P_2O_5 is determined spectroscopically (Stetter 1972). Both citric and citrate soluble P_2O_5 can be expressed using the absolute solubility index (ASI), where

$$ASI = \frac{\text{Solvent-soluble } P_2O_5, \%}{\text{Theoretical } P_2O_5 \text{ concentration of apatite, } \%^*}$$

*Calculated from the empirical formula computed by XRD (Lehr et al. 1973).

RESULTS AND DISCUSSION

Samples Characterization

Complete chemical analysis of the Red Sea phosphate samples shows that they are of low (run-of-mine sample) to medium (concentrate product) grade with a variation in their gangue minerals contents (Table 1). Fig. 2 illustrates the size distribution of the samples with no significant differences between them. The XRD patterns of the samples show a typical francolitic structure. Lines of hydroxyapatite and carbonate apatite can also be identified. Various gangue minerals like quartz, pyrite, calcite, and gypsum are also present in the XRD patterns of the original samples (Fig. 3).

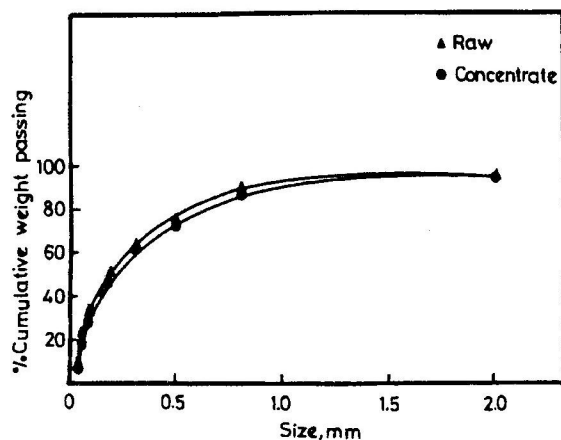


Fig. 2. Size distribution of crushed phosphate samples (mill feed)

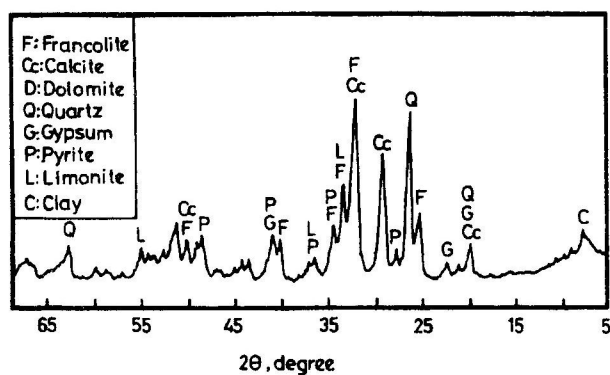


Fig. 3. XRD-pattern of the original Red Sea phosphate

Table 1. Chemical analysis of Red Sea phosphate samples

Constituent	Raw sample*	Concentrate*
P ₂ O ₅	23.48	28.40
CaO	38.05	43.45
Fe ₂ O ₃	1.61	1.12
Al ₂ O ₂	2.38	1.05
MgO	2.64	1.72
SiO ₂	10.14	5.61
CO ₂	6.35	5.58
Moisture	3.83	3.88

*The values are given as weight percents.

Physical and structural changes of the samples after intensive grinding

Figure 4 illustrates the variation in the D_{90} (the size corresponding to 90% by weight) of the ground phosphate samples with time. It is clear that despite marked fineness of the products, agglomeration occurred after a certain time due to surface-surface adhesion (Rebane et al. 1980). The maximum D_{90} was reached in 60 min and 75 min for the raw sample and concentrate, respectively. As a result of prolong milling a dramatic decrease in the surface area of the original sample from 15.76 m²/g to 7.22 m²/g after 90 min milling was observed. However, these optima in surface area production do not necessarily mean that the same optima exist for the milling effect as it will be shown later. This means that both effects are not interdependent. Figure 5 compares the effect of progressive milling on the XRD impulses for the main apatite peaks at 2 θ between 30° and 35° for the samples. It appears from Fig. 5 that increasing the milling time leads to distortion in the apatitic crystal lattice which is independent of the position of the D_{90} maximum shown in Fig. 4. This means that dispersion is not the main process affecting rock behaviour during intensive milling (Paudert et al. 1979; Steinike et al. 1982). The area under each diffractogram at various milling times could be taken as a measure of crystallinity. Accordingly, it was found that the crystallinity decreased by 43.95% and 29.0% in the raw and concentrated samples, respectively, after 90 minutes of milling.

The unit cell parameters measurements for raw Red Sea phosphate extracted with Silverman's reagent and its ground product (after 90 min milling) were calculated in Table 2. The results show a pronounced decrease in the size of the unit cell of apatite after milling. The change of the apatite lattice parameters indicates a multiple substitution in the phosphate samples and confirms that deformation or dislocations occur in the crystal due to the mechanical stress during milling. Lattice expansion or contraction with ionic substitution in the apatite lattice can be predicted from the ratio of the radii of the ions evolved, utilizing the Vegard rule (Le Geros et al. 1980). The decrease in the apatite lattice parameters, particularly the a parameter, signifies a corresponding enhancement in lattice substitution especially CO_3^{2-} for PO_4^{3-} (Pothig et al. 1978). The substitution, can be expressed by the CO_2 index suggested by Lehr (1967). This is based on the ratio of intensities of the C–O and P–O bands in the IR spectra. This ratio is directly proportional to the weight ratio of CO_3/PO_4 and independent of the apatite concentration (Lehr et al. 1967). The CO_2 index can be calculated from the following equation:

$$\text{CO}_2 \text{ index} = 0.5 (D_1 + D_2)/D_3$$

where $D_1 + D_2$ is the average intensity of the C–O absorption bands and D_3 is the P–O absorption band shown in Fig. 6. The CO_2 index of the raw phosphorite extracted with Silverman's reagent and ground phosphorite (after 90 min milling) are 0.22 and 0.23, respectively. The carbonate substitution in the apatite lattice is unusual because essentially planar CO_3^{2-} anion replaces tetrahedral PO_4^{3-} anion in an uncertain structural

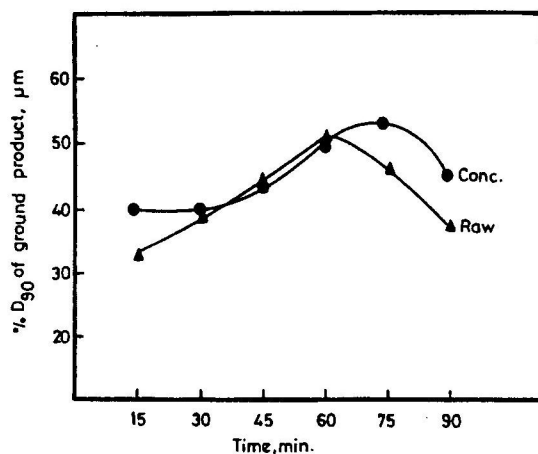


Fig. 4. The effect of milling time on the % D_{90} of the ground products

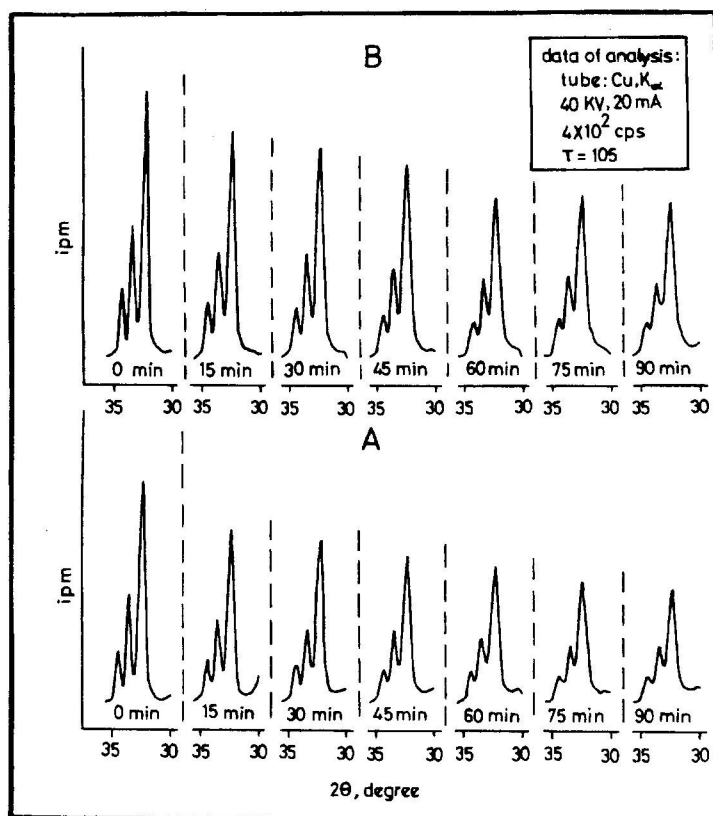


Fig. 5. Diffractograms of Red Sea raw (A) and concentrate (B) of phosphorite samples as a function of milling time by rotary-chamber vibrating mill

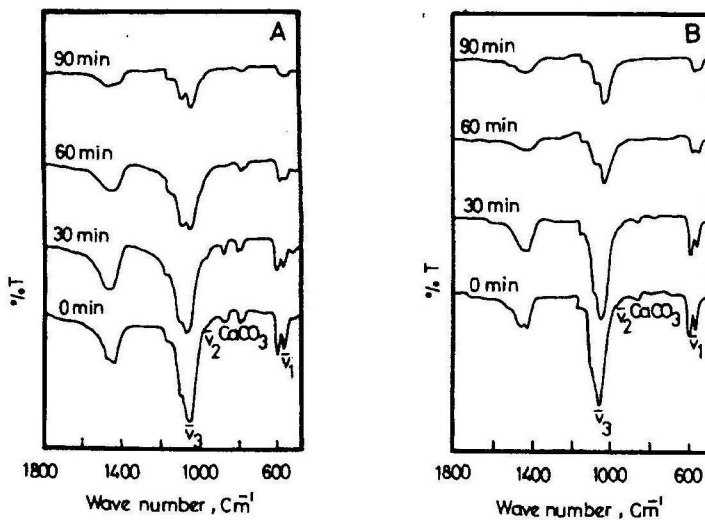


Fig. 6. Infrared spectra of Red Sea raw (A) and concentrate (B) of phosphate samples before and after various milling times by rotary-chamber vibrating mill

position and leads to a questionable charge balance arrangement (McClellan and Lehr 1969). One way of satisfying the requirement for the charge electroneutrality is substitution of F^- in a vacant oxygen site so that a coupled monovalent cation substitution, i.e. Na^+ , Mg^{2+} or K^+ is needed to balance the decrease of negative charges that is caused by CO_3^{2-} substitution (Gulbrandsen et al. 1966).

Table 2. Unit cell dimensions of the raw Red Sea phosphate and its ground product (after 90 minutes of milling)

Phosphate sample	2θ	c , Å	a , Å	c/a
Raw	51.82	6.8926	9.3352	0.7383
	53.15			
Ground	51.94	6.8723	9.3151	0.7378
	53.32			

Effect of intensive grinding on the behaviour of different gangue minerals

Intensive grinding of the Red Sea phosphate using the rotary chamber vibrating mill has unusual effect on the accompanying gangue minerals. A careful examination of the diffractograms of the original samples and their ground products indicates a drastic change in the peaks of quartz, gypsum, iron oxides and calcite (Fig. 7). A complete

disappearance of the XRD peaks of some minerals including calcite and gypsum was observed along with a substantial reduction of the major peaks of quartz and iron oxide. This indicates either deformation of crystal lattice, amorphous appearance, or transformation from one form to another (Boldyrev et al. 1977; Ibrahim 1990).

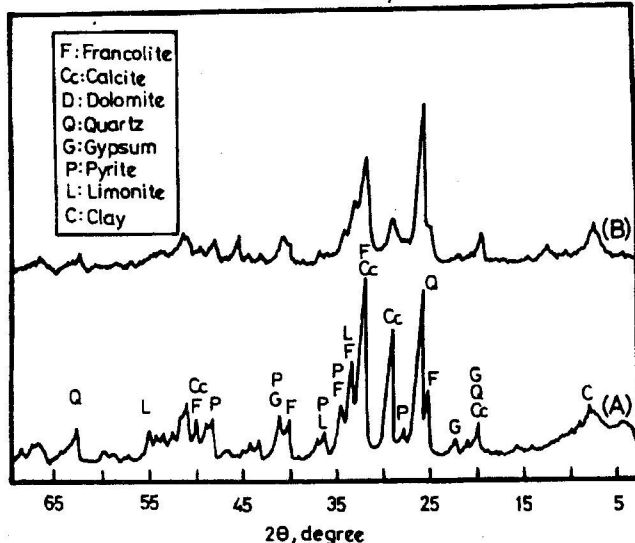


Fig. 7. XRD-patterns of Red Sea raw (A) and ground (B) phosphate samples (after 90 minutes of milling)

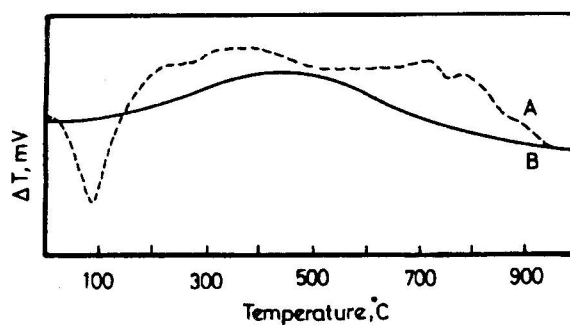


Fig. 8. Differential thermal analysis (DTA) of of Red Sea raw (A) and ground (B) phosphate samples (after 90 minutes of milling)

Thermal analysis of the ground raw sample after 90 min of milling shows a broad exothermic peak in the temperature range from 350 to 550 °C (Fig. 8). This peak may be due to the combustion of organic carbonate which was not affected by the milling. An endo-exothermic peak appears in the DTA of the raw phosphorite above 700 °C

which disappears after grinding (Fig. 8). This can be caused by the decomposition of inorganic carbonate due to the excessive mechanical stress during the milling. Gock and Jacob (1984) assumed that the destruction of the dolomite lattice plane equivalent to $2\theta = 30.94^\circ$ correlates well with the loss of the IR bands between 900 and 1300 cm^{-1} indicating a transformation of carbonate to oxide via a split of CO_2 by the heat evolved during milling (Fig. 6).

Solubility of intensively ground Red Sea phosphates

A remarkable increase in solubility of phosphate samples in 2% citric acid (CA) and neutral ammonium citrate (NAC) with milling time is shown in Figs 9 and 10,

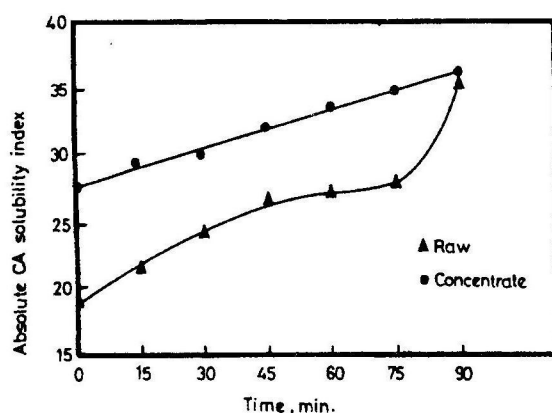


Fig. 9. Solubility of raw and concentrate phosphate samples in 2% citric acid at various milling times

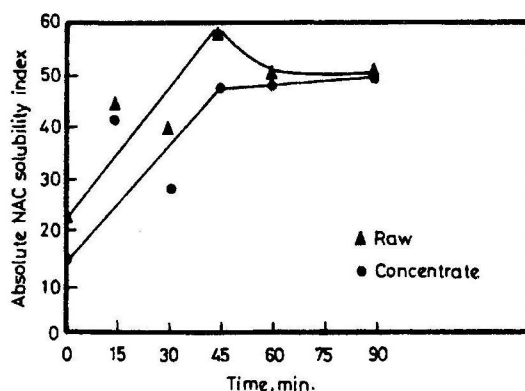


Fig. 10. Solubility of raw and concentrate phosphate samples in neutral ammonium citrate at various milling times

respectively. The plot is nearly linear in the case of CA (Fig. 9) whereas for NAC it forms a curve (Fig. 10) similar in shape to that of the change in D_{90} for the ground products with time (Fig. 4). By comparing (ASI) for the original and ground samples with NAC, it is obvious that the higher phosphate content in the sample does not improve the solubility. The intensive grinding of both samples remarkably increases their ASI values but these values become similar after certain milling time (60 min in case of CA and 90 min in case of NAC). This indicates that the upgrading of the phosphate ore does not affect the grinding process. This may be ascribed in view of silica content which seems to play an important role in the milling process as a grinding aid (Machukov et al. 1983).

CONCLUSIONS

Intensive grinding using a rotary chamber vibrating mill of raw Red Sea phosphorite and its final concentrate product show remarkable changes in the physical and crystal structure characters of both samples. Examination of the diffractograms and IR bands shows a drastic reduction in the apatite peaks as well as complete disappearance of the main peaks of some gangue minerals like calcite and gypsum. The unit cell parameters measurements for the ground samples show a pronounced decrease after 90 minutes of milling. This decrease particularly in the a parameter not only indicates structural deformation but also signifies corresponding enhancement in lattice substitution especially CO_3^{2-} for PO_4^{3-} .

The endothermic peaks appearing in the DTA of the raw phosphorite above 700 °C also disappear after 90 minutes of milling. This may be caused after the decomposition of the inorganic carbonate due to the excessive mechanical stress during milling.

A remarkable increase in the solubility of the ground samples in both 2% citric acid and neutral ammonium citrate was shown, but the Red Sea phosphorite concentrate showed less response towards intensive grinding than the raw samples. This may be due to its silica content which seems to have an important role as a grinding aid.

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Ibrahim S.S. (1996), Wpływ intensywnego mieszania na fizykochemiczne właściwości i reaktywność fosforytów z rejonu Morza Czerwonego, *Fizykochemiczne Problemy Mineralurgii*, 30, 95–106 (w jęz. angielskim).

Próbki surowego fosforytu z rejonu Morza Czerwonego i jego koncentraty poddano intensywnemu mieleniu w komorze rotacyjnej młyna wibracyjnego. Badano również stopniowe zmiany krystalograficzne i zmiany fizycznego charakteru apatytu oraz towarzyszących mine-

rałów płonnych zachodzące podczas mielenia. Badania rentgenowskie i spektroskopowe w podczerwieni mielonych produktów wykazały drastyczną redukcję głównych pików apatytu, kalcytu, gipsu i kwarcu. Zauważono również zmniejszenie się parametrów sieciowych apatytu, szczególnie stałej a komórki sieciowej. Znaczący wzrost rozpuszczalności mielonych produktów w 2% kwasie cytrynowym wskazuje na mniejszy wpływ mielenia na koncentrat fosforytowy niż na surowy fosforyt. Uzyskane wyniki mogą stworzyć nowe sposoby wykorzystania rud fosforytowych w wielu rozwijających się krajach.