

# **STUDY OF THE EFFECTS OF THERMAL TREATMENT ON CHEMICAL AND PHYSICAL CHARACTERISTICS OF PHOSPHATES**

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## **Abstract**

Via the thermal treatment of natural phosphates and their analysis, it was proved that the decrease in their solubility in the interval 400–550°C is an indication of the degree of incorporation of OH groups into the apatite structure of phosphates, whereas the solubility at 950°C is an indication of the degree of incorporation of the non-volatile components. The higher  $R_{950}$ , the more extensive this substitution, and the more reactive the natural phosphate.

**Keywords:** phosphates

## **Introduction**

In spite of their similar chemical and mineralogical contents, commercial phosphates represent a large group of minerals which are structurally related. However, they differ considerably in their physical, chemical and crystalline properties. For instance, apatites of volcanic origin have a content similar to that of fluorapatites, whereas sedimentary phosphates have a different structure, due to the different extents of substitution of the fundamental ions of Ca, P and F.

Lehr [1] concluded that sedimentary phosphates are fluorapatites in which some of the  $\text{Ca}^{2+}$  and  $\text{PO}_4^{3-}$  are substituted by  $\text{Mg}^{2+}$  or  $\text{Na}^+$  and  $\text{CO}_3^{2-} + \text{F}^-$ , i.e. a knowledge of the  $\text{CO}_2$  content in the apatite structure of a phosphate is enough to allow prediction of the phosphate properties.

When phosphates are thermally treated, the volatile components separate from them:  $\text{H}_2\text{O}$ , organic compounds,  $\text{CO}_2$  from carbonate decomposition, etc. The temperature intervals for the separation of these components depend on their content, on the chemical compounds in which they are present and on the physical properties of the phosphate ore.

Study of the properties of phosphates, when they are treated at different temperatures, reveals the changes occurring in their chemical contents and their physicochemical characteristics, which permits an assessment of the effects of

admixtures in the phosphates and the effects of substitution of the fundamental elements with others on the properties of the phosphates.

## Experimental

Five phosphates, four of sedimentary and one of volcanic origin, were thermally treated from 400 to 950°C at intervals of 50 deg for a period of 1 h. The dimensions of the microcrystallites ( $L$ ) and the elementary cell on axis  $a$  ( $a$ ) were then estimated by X-ray analysis; the  $\text{CO}_2$  content was determined by chemical analysis; the specific surface ( $S$ ) was found by the BET's method; and the solubility in 2% citric acid ( $R$ ) was measured.

The thermoanalytical curves of the studied phosphates (Fig. 1) can be divided into four areas: up to 400°C; 400–550°C; 550–850°C; and over 850°C. Many complicated processes take place in these areas, which can be explained by detailed study of the thermally obtained phosphates.

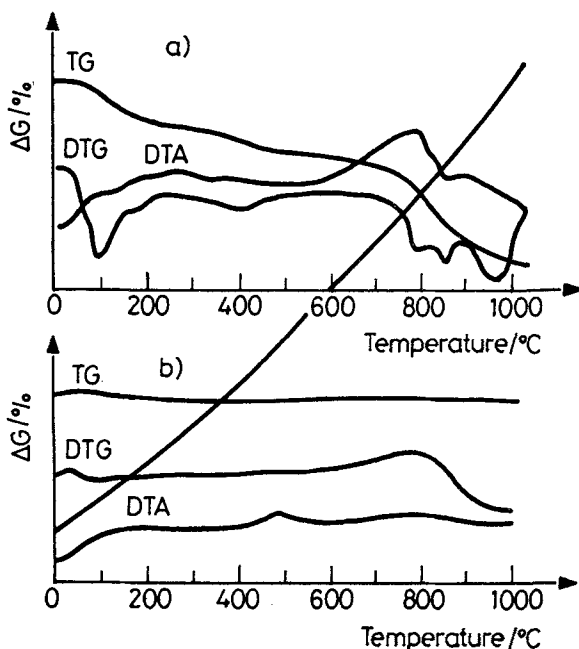


Fig. 1. Thermal curves of initial phosphates, a) - volcanic; b) sedimentary

In the first area, up to 400°C, there is first a mass loss (Fig. 1) connected with the removal of physical moisture from phosphorite. The next mass losses are associated with the appearance of an exo-effect, and are due to the combustion of organic mixtures. Even at 400°C,  $R$  and  $S$  were observed to decrease

(Figs 2 and 3), which we consider to be due to the blocking of some of the micropores of the phosphate particles with the mineral component released during the combustion of organic mixtures.

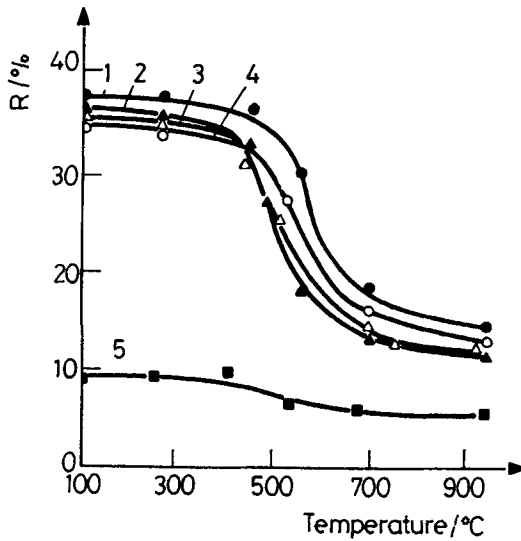


Fig. 2 Changes of phosphates solubility in 2.5% citric acid. 1, 2, 3, 4-sedimentary and 5-volcanic phosphates

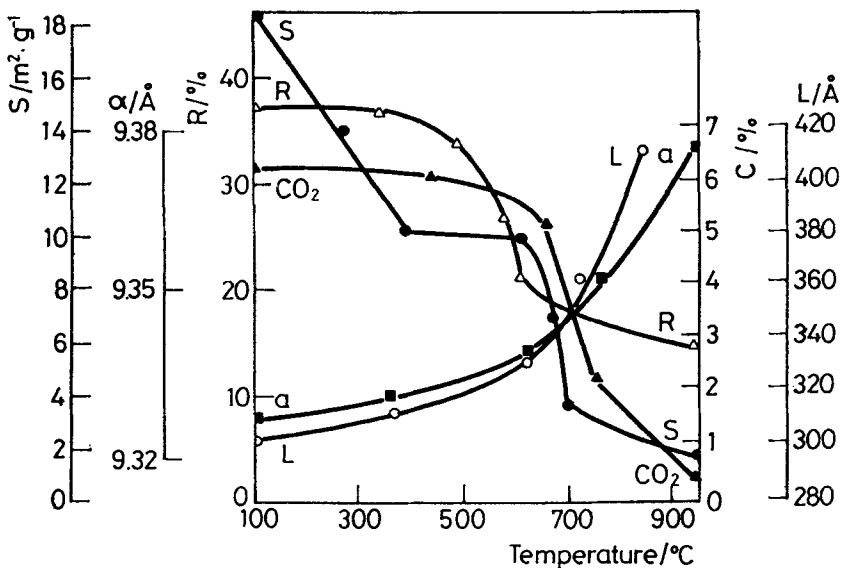
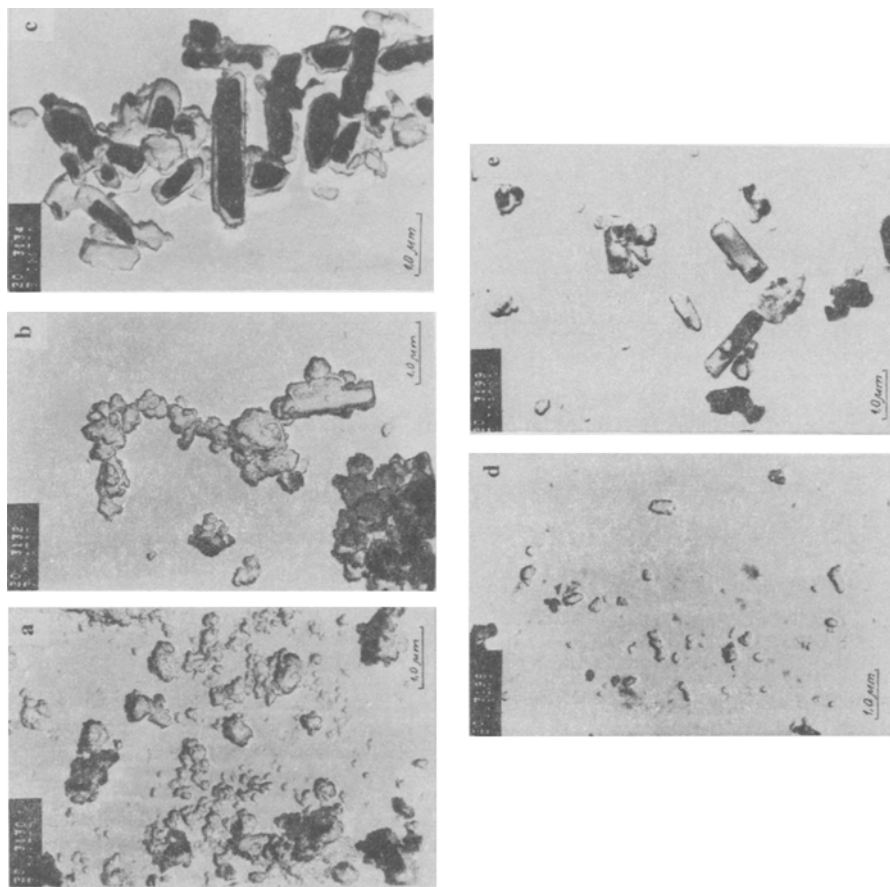


Fig. 3 Change of  $R$ ,  $S$ ,  $L$ ,  $a$  and  $C_{CO_2}$  of phosphorite-1 due to temperature



**Fig. 4** Electronic-microscopic photographs of phosphorite-1, thermally treated at respectively a-initial, b-850°C, c- 950°C, d-800°C, e-900°C, a, b, c increase of 17000, d, e increase of 9000

The further decreases in  $R$  and  $S$  up to  $550^{\circ}\text{C}$  (Figs 2 and 3) are possibly due to the relaxation of the crystalline structure and the liberation of the constituent water from the phosphate. The thermoanalytical curves of phosphates in this interval (Fig. 1) reveal the occurrence of mass losses without changes in the DTA curves.

According to Shumakov [2], this is specific for the release of constituent water from the phosphates, which takes place in precisely this temperature interval.

The mass losses during the next increase of temperature (Figs 2 and 3) are directly related to  $\text{CO}_2$  liberation from the phosphates, which causes very important changes in the textural and structural characteristics of the phosphates.  $\text{CO}_2$  release is accompanied by the formation of  $\text{CaO}$  and  $\text{CaF}_2$ , which block the micropores of the phosphates, i.e.  $S$  decreases (Fig. 3). In the meantime, the apatite structure releases the additional energy acquired as a result of the built-in  $\text{CO}_2$  groups. These two factors further decrease the phosphate solubility (Figs 2 and 3). In this interval, rapid increases in  $L$  and  $a$  are observed, with a decrease in  $S$ . It has been demonstrated by many researchers that  $\text{CO}_2$  release is accompanied by recrystallization of the apatite structure.

Microscopic analysis (Fig. 4) showed that aggregation of the phosphate particles started when the temperature was over  $800^{\circ}\text{C}$ . At this temperature, the solubility of phosphate reaches its lowest degree (Fig. 2) i.e. not the aggregation of the phosphate particles, but the changes in the crystallochemical structure of the phosphates are the cause of their solubility decrease.

Almost total loss of  $\text{CO}_2$  takes place at about  $950^{\circ}\text{C}$  (Fig. 3). Lehr [1] reports that the products thus obtained have structures similar to that of fluorapatite. However, our studies (Figs 2 and 3) prove that phosphates of sedimentary origin have a high solubility and low  $L$  and  $a$  as compared with those of volcanic phosphates, i.e. their structures differ from the ideal one due to the substitution of Ca and P by other elements, which cannot be separated by thermal treatment. Such a substitution is that of P by S. The presence of the  $\text{SO}_4$  group in the apatite structure has been proved [3]. Since the length of the P-O chain in the tetrahedra is very near to that of S-O, the built-in  $\text{SO}_4$  ions have no effect on the dimensions of the elementary cell of phosphate. However, they greatly affect the phosphate solubility, because of the decrease in thermodynamic balance of the crystalline cell. Substitution of Ca also causes a decrease in this thermodynamic balance and an increase in the solubility of the phosphates.

On the above grounds, we conclude that the difference in solubility of volcanic phosphate and sedimentary phosphate calculated at  $950^{\circ}\text{C}$  ( $R_{950}$ ) is an indication of the degree of substitution of Ca and P by non-volatile components, and it can be used for estimation of this substitution, i.e. for estimation of the reactivity of this phosphate.

With increase of the substitution of the basic components of a phosphate, its thermal stability decreases. Figures 2 and 3 show that the phosphorites with the highest solubility, i.e. and those with the highest degree of substitution, begin to undergo destruction at a lower temperature. They reach the lowest solubility at the lowest temperature, but they always have a higher value of  $R$ .

## References

- 1 Y. R. Lehr, Proc. 17th Am. Meeting Fert. Industry Round Table (1967).
- 2 N. C. Shumakov and others, Thermal Treatment (in Bulgarian).
- 3 CR. Acad. Ser. Perir, 281 p. 701 du 5/10/1970.

**Zusammenfassung** — Über die thermische Behandlung natürlicher Phosphate und ihre Analyse wurde nachgewiesen, daß die Abnahme der Löslichkeit im Intervall von 400 bis 550°C ein Zeichen für den Grad des Einbaues von OH-Gruppen in die Apatitstruktur der Phosphate ist, während die Löslichkeit bei 950°C ein Zeichen für den Grad des Einbaues von nichtflüchtigen Komponenten ist. Je größer  $R_{950}$ , um so extensiver ist die Substitution und um so reaktionsfreudiger ist natürliches Phosphat.