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Fundamentals of the Wet-Process Phosphoric Acid Production. 2. Kinetics and Mechanism of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ Surface Crystallization and Coating Formation

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This paper is devoted to fundamentals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ surface crystallization on a being dissolved surface of natural fluorapatite (FAP) crystals under conditions simulating the industrial process of wet-process phosphoric acid production. Methods of optical and scanning electron microscopy were used for the investigations. Single crystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ on the FAP crystal surface were found to grow by an aggregation mechanism with rates decreasing until zero. The mechanism included two stages: ultramicrocrystals formation, followed by their aggregation to microcrystals. The presence of dissolved FAP crystals was found not to change the crystallization mechanism of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, but it changed the kinetics of their growth. Later the crystallization process resulted in the continuous formation of a multiple-layer coating of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ on the FAP crystal surface. Some average characteristics of the above coating (thickness and fragility) were analyzed for different hydrodynamics. An aggregation process for FAP crystals under poor agitation intensity and a possibility for the above coating to be partly removed with mutual collisions of FAP crystals under strong agitation conditions were established for the first time. Based on the experimental results, some technological conclusions about hydrodynamics inside industrial reactors of wet-process phosphoric production were made.

1. Introduction

Wet-process phosphoric acid (WPPA) is the main intermediate for phosphorus-containing fertilizers production. Together with the WPPA, a great number of phosphogypsum (i.e., calcium sulfate with admixtures of calcium phosphates, calcium fluorides, silicates, water, and phosphoric acid) is obtained as a byproduct. The amount and chemical composition of the phosphogypsum obtained depend on the quality of phosphate rock and the industrial process being chosen. Usually there are about 3–7 tons of phosphogypsum per each 1 ton of WPPA solution (Becker, 1989; Slack, 1967; Noyes, 1967).

An excellent description of all modern routes of WPPA production (including major equipment) is given in the literature (Becker, 1989). Here one should briefly mention that to produce WPPA one should dissolve natural phosphate rock (usually apatite) in a mixture of phosphoric and sulfuric acid, followed by filtration of the calcium sulfate byproduct obtained. The process of phosphate rock dissolution usually occurs in large chemical reactors with agitators at temperatures of 70–100 °C.

Industrial processes can be separated into two big groups: single-staged and multiple-staged. The groups differ by the presence of an intermediate recrystallization of calcium sulfate. If it is present, it is a multiple (double, triple) process; if not, it is a single process. Single processes are divided by the chemical composition of calcium sulfate being obtained. Calcium sulfate ($\text{CaSO}_4 \cdot x\text{H}_2\text{O}$) is able to form different hydrates. If $x = 2$ (i.e., $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is obtained), the process is called “dihydrate”, if $x = 0.5$ (i.e., $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ is obtained), the process is called “hemihydrate”, and if $x = 0$ (i.e., CaSO_4 is obtained), the process is called “anhydrite”.

Further details about industrial processes of WPPA production are described in the literature (Becker, 1989; Slack, 1967; Noyes, 1967).

The industrial processes of WPPA production are based on the results of earlier physicochemical investigations. Some of them are mentioned in the reference list of this paper. The others are in the references therein. In spite of this, the processes of phosphate rock dissolution and calcium sulfate crystallization occurring inside industrial reactors are not quite clear yet (Becker, 1989 and references therein). Thus, investigations in this field of science and technology are being made now in different countries (Najjar *et al.*, 1992; Beskov *et al.*, 1991; Kafarov *et al.*, 1990, 1991; Elnashaie *et al.*, 1990; Calmanovici and Guiletti, 1990; Grinevich *et al.*, 1983, 1987, 1988; Blose *et al.*, 1984; Giola *et al.*, 1977).

Recently, a great number of investigations have been made in our laboratory. Some results concerning the fundamentals of natural fluorapatite (FAP) crystals dissolution in phosphoric acid medium have been described in part 1 of this series (Dorozhkin, 1996). All the experiments described there were made for simplicity in pure phosphoric acid solutions, but such dissolution conditions are well-known not to be used in the industry of WPPA production. As briefly mentioned above, the dissolution process of natural phosphate rock always takes place in a mixture of phosphoric and sulfuric acids. As a result, the process of natural phosphate rock dissolution occurs simultaneously with the process of calcium sulfate crystallization (Becker, 1989; Slack, 1967; Noyes, 1967).

Thus, the present investigation is devoted to fundamentals of the process of natural FAP crystals dissolution under conditions of simultaneous calcium sulfate crystallization. The purpose of this paper is to give an answer for the question, How are crystals of calcium sulfate being formed and grown under conditions of the WPPA production?. There are three possible hydrate forms of calcium sulfate: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, and CaSO_4 . All of them are typical for the WPPA

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production industry, and special investigations should be made for each of them, but the hemihydrate process of WPPA production happens to have become very popular in USSR/Russia in the 1980s (Beskov *et al.*, 1991; Kafarov *et al.*, 1990; Grinevich *et al.*, 1983, 1987). So in Russia special attention was paid to fundamentals of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ crystallization mechanism (Melikhov *et al.*, 1985, 1988, 1989). As a result this paper is also limited with investigations of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ surface crystallization only.

2. Experimental Section

2.1. Optical Microscopy. The FAP crystals, experimental setup, and the analytical techniques employed have been described previously (Dorozhkin, 1996). Briefly, experiments were performed under thermostatic conditions with 50–2000 μm single natural FAP crystals from the Khibin (Kola) deposit. One or several FAP crystals were placed on a thermostatic holder. Then the holder was placed inside the flow installation, and a stream of phosphoric and sulfuric acids was created there. Any changes of the crystal shape and size during their dissolution were constantly observed and filmed by the optical microscope MIN-8 provided with the photographic adapter MFNE-1U4.2 (both made in LOMO, Russia). The technique was able to follow the crystals dissolution permanently until the very end, but it was limited by the microscope magnification (up to 100 times) and stream rates of the acid (Re hydrodynamics < 100).

2.2. Scanning Electron Microscopy. To increase the magnification range, a special group of experiments was made with the scanning electron microscope (SEM) JEOL 35-CF. A large (1–2 mm) crystal of FAP glued directly onto a microscope stub was dipped into a glass with the thermostatic mixture of phosphoric and sulfuric acids for 3–5 s. Then the stub with the crystal was quickly (< 0.5 s) transferred into acetone for 15–20 s to stop the dissolution process and to remove traces of acids, followed by drying the specimen in air at room temperature. Then the crystal was studied and filmed in the SEM in the secondary electron mode. After being filmed, the crystal was taken out of the SEM and additional treatment in the acid followed. Thus, the technique was able to follow the crystal dissolution periodically, but under great magnifications and hydrodynamical conditions.

However, the above technique is not good for investigations of the crystallization process at the very beginning (i.e., initial 1–5 s of chemical interaction). So, the following manipulations were used in this case. Crystals of FAP were placed on a thermostatic glass filter connected to a vacuum line. Then the crystals were quickly treated by the previously heated mixture of acids during 1–5 s followed by washing them in acetone. An interaction time between acid and crystals was regulated by means of the amount of the acid and the vacuum value. Then the crystals were dried in air, covered with the golden film (vacuum deposition), and studied with the SEM.

The experimental conditions were as follows: acid solution contained 52% (7.2 M) H_3PO_4 and 2.5% (0.26 M) H_2SO_4 , temperature 80.0 ± 0.1 °C, Reynolds hydrodynamics (Re) 0–5000, dissolution time 1 s to 3 h. All chemical reagents were of “pure-grade” quality ($< 0.01\%$ of total impurities), with correlation between masses of acid solution and FAP crystals $> 1000:1$.

3. Results and Discussion

3.1. Macrokinetics and the Macromechanism of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ Surface Crystallization. Macrokinetics and the macromechanism of surface crystallization have been studied by flow installation (optical microscopy) under Re hydrodynamics < 100 . The experiments have resulted in successive photographs which show a process of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ surface crystallization on the FAP crystal surface (Figure 1). The first crystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ appear to be visible at 15–20 s from the beginning of the experiment (Figure 1a). One minute later crystals of FAP were already completely covered with a $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating (Figure 1b). From this moment one could not follow the FAP crystal surface during dissolution, but one could follow the total size of FAP crystal + coating of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ only (Figures 1b–f). Certainly, this is an additional drawback of the technique. Nevertheless, following the total size of FAP crystal + $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating gives interesting information also (Figure 2). For example, curve 1 is the relative size of a FAP crystal + coating ($R_{eq}/R_{eq,0}$) versus the relative dissolution time t/t_0 . Here, $R_{eq,0}$ is the initial equivalent radius for a FAP crystal, and t_0 is the total dissolution time for this FAP crystal + coating.

From the results in Figures 1 and 2 (curve 1) one can see the coating is not able to prevent dissolution of the FAP crystal. The kinetics of dissolution here are about 10 times slower than those obtained in pure phosphoric acid (Dorozhkin, 1996). When the coating is formed, a dissolution process of FAP crystals is possible to separate three successive periods. The initial period is the shortest one. It lasts during $0 < t/t_0 < 0.05$ s and corresponds to parts a and b of Figure 1. During the initial period, the coating is being quickly formed and the total size of FAP crystal + coating increases very rapidly. The second period is the longest. It lasts during $0.05 < t/t_0 < 0.7$ s and corresponds to parts c and d of Figure 1. During the second period, FAP crystals are slowly dissolved under the coating. The period comes to an end when FAP crystals are dissolved completely and porous granules of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ are formed instead (Figure 1e). Unfortunately, one can say nothing about a real thickness during the second period. The third dissolution period lasts during $0.7 < t/t_0 < 1$ s and corresponds to parts e and f of Figure 1. During the third period, the obtained porous granules are dissolved in a mixture of phosphoric and sulfuric acids. Small additives of calcium sulfate in the solution were found to prolong the third dissolution period. When $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ saturated solutions were used, the third period lasted endlessly.

As follows from Figure 1, the technique used cannot separate dimensions of FAP crystals and thicknesses of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating from each other. Nevertheless, some approximate information can be obtained from the mutual comparison of some results. As the first approach, one can consider that the FAP crystals are always dissolved according to the model of dislocation acceleration (Melikhov *et al.*, 1990). The results of this model are plotted in Figure 2 (curve 2). A subtraction of curve 2 (size of a FAP crystal according to model) from curve 1 (total size of a FAP crystal + coating) results in curve 3 (Figure 2). This curve may be approximately considered as a relative thickness of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating for the chosen experimental conditions ($Re < 100$).

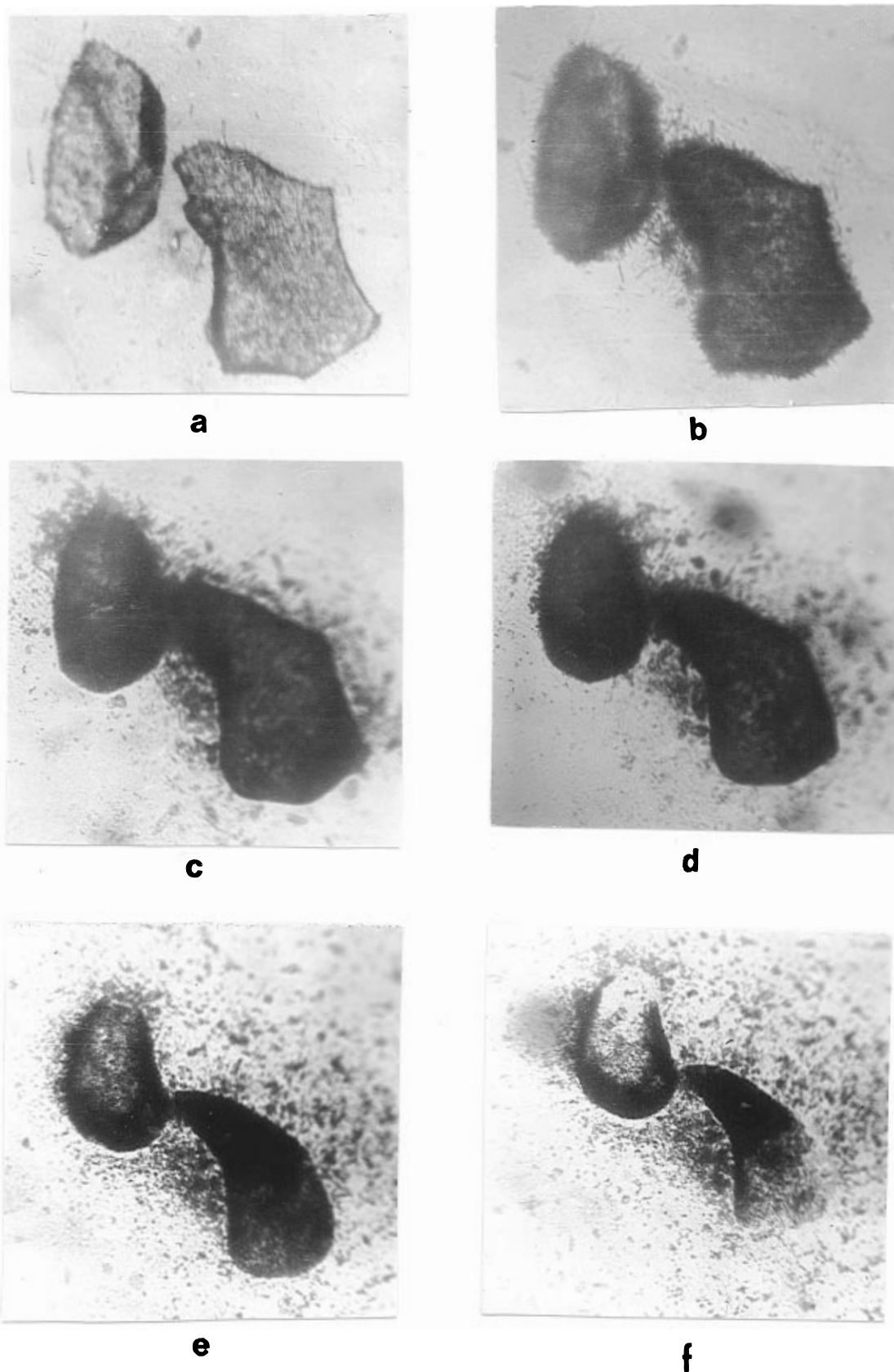


Figure 1. Example of FAP crystals dissolution under conditions of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating formation obtained with the flow installation (optical microscopy). Experimental conditions: 52% (7.2 M) H_3PO_4 and 2.5% (0.26 M) H_2SO_4 in solution, $t = 80^\circ\text{C}$, $Re < 100$ hydrodynamics, initial size of FAP crystals is 150–250 μm . Dissolution times are (a) 15 s, (b) 1 min, (c) 45 min, (d) 90 min, (e) 125 min, (f) 135 min. Magnification 100 \times . Horizontal field width is 700 μm .

Thus, the macrokinetics and macromechanism of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ surface crystallization can be described by a process of coating formation for whole crystals of natural phosphate rock. The process starts, most probably, at the very beginning of chemical interaction, but

at the macrolevel (i.e., for a whole crystal) it can be observed and studied not earlier than after 15 s from the beginning. Some average parameters of the coating (thickness, porosity, hardness) were found to depend mainly on the hydrodynamics and chemical composition

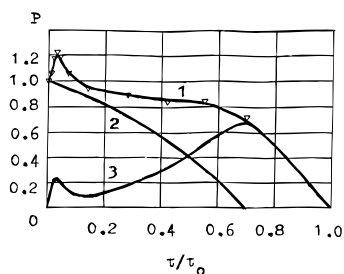


Figure 2. Process of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating formation on a FAP crystal surface: (1) relative size of a FAP crystal + coating, (2) relative size of a FAP crystal according to the model of dislocation acceleration (Melikhov *et al.*, 1990), (3) thickness of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating. Experimental conditions: 52% (7.2 M) H_3PO_4 and 2.5% (0.26 M) H_2SO_4 in solution, $t = 80^\circ\text{C}$, $Re < 100$ hydrodynamics. Here, P is a relative size ($R_{eq}/R_{eq,0}$) for curves 1 and 2, and a relative thickness of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating for curve 3.

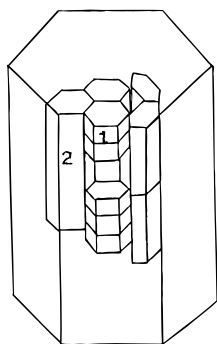


Figure 3. Hierarchical structure for a $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ crystal: (1) ultramicrocrystals, (2) microcrystals (Melikhov *et al.*, 1985, 1988, 1989).

of the solution (Dorozhkin and Nikolaev, 1991; Melikhov *et al.*, 1992).

3.2. Microkinetics and the Micromechanism of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ Surface Crystallization. **3.2.1. Crystal Structure of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$.** A complete investigation of the structure and crystallization mechanism of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ in phosphoric acid medium was done in the USSR in the middle 1980s (Melikhov *et al.*, 1985, 1988, 1989). Crystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ were found to have a complicated hierarchical structure (Figure 3). The smallest particles (they have been called "ultramicrocrystals") have the shape of hexagonal nuts (but without the central hole) and sizes of about $0.1\ \mu\text{m}$ (1). They appear at the very beginning of crystallization. Later the ultramicrocrystals were found to be united with each other by their pinacoid faces. As a result, microcrystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ are formed (2). The microcrystals usually have a shape of long hexagonal prisms (like pencils) and a length of about $5\text{--}15\ \mu\text{m}$. The microcrystals were established to be united with each other later to form macrocrystals. The macrocrystals are also able to form aggregates (not shown in Figure 3). Details about the crystal structure of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ were published earlier (Melikhov *et al.*, 1985, 1988, 1989).

The above investigations of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ structure and crystallization mechanism were made in pure phosphoric acid solutions only. In our case the process of crystallization is complicated with simultaneous dissolution of FAP crystals. Moreover, according to the results obtained in the flow installation (section 3.1), the crystallization process of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ occurs mainly on the surface of FAP crystals (Figure 1). The influence of the FAP dissolution process on the crystallization mechanism of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ should be studied.

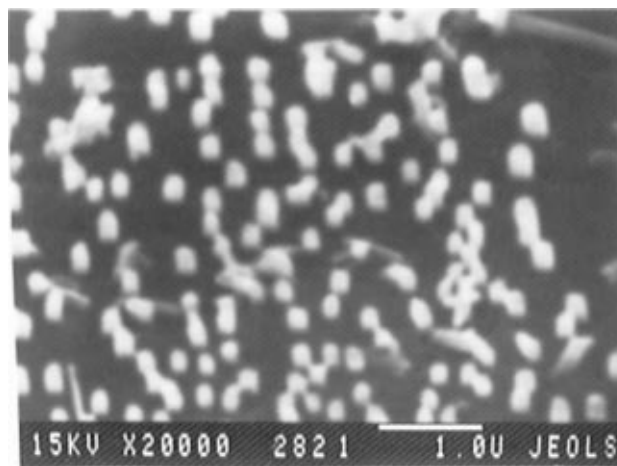


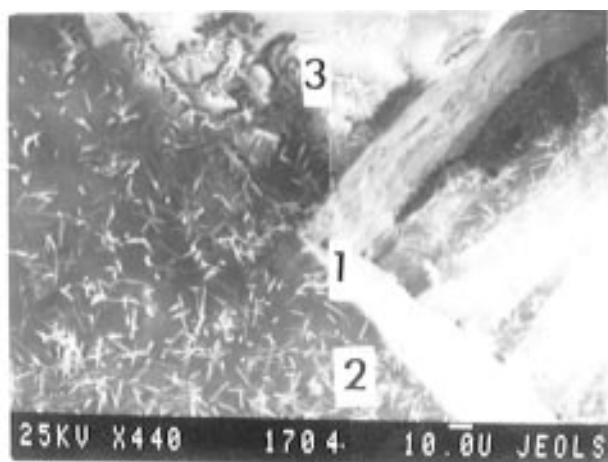
Figure 4. Ultramicrocrystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ on a FAP crystal surface (white spots). Experimental conditions: 52% (7.2 M) H_3PO_4 and 2.5% (0.26 M) H_2SO_4 in solution, $t = 80^\circ\text{C}$, $Re \approx 1000$ hydrodynamics, initial size of FAP crystals is $150\text{--}250\ \mu\text{m}$. Dissolution time is 1 s. Bar is $1\ \mu\text{m}$.

3.2.2. Surface Crystallization of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$.

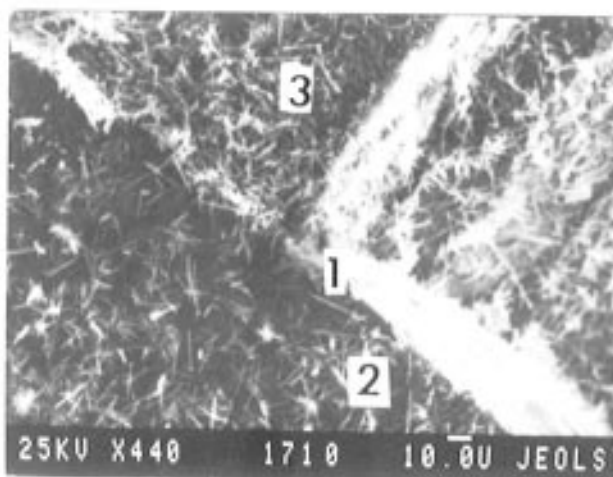
The main stages of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating formation were discovered with the SEM investigations (Dorozhkin and Nikolaev, 1991). The process of coating formation was found to begin immediately (1 s) with the ultramicrocrystals formation (Figure 4). There were approximately 10^9 ultramicrocrystals (average size $0.10 \pm 0.03\ \mu\text{m}$) per each $1\ \text{cm}^2$ of FAP crystal surface. Only 2–3 s later the pencil-like microcrystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, in an amount of $10^7\ \text{cm}^{-2}$, were found to appear (Figure 5a). One can see the ultramicrocrystals were already absent. So the microcrystals, most probably, were formed from the ultramicrocrystals by the aggregation mechanism, as described above (Melikhov *et al.*, 1985, 1988, 1989). In which case, each microcrystal consisted of at least 100 ultramicrocrystals. From the moment of microcrystals formation, we succeeded in following them with the SEM (Figure 5a–c). Single microcrystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ were found to grow with rates decreasing until zero. Length versus dissolution time is plotted in Figure 6 for some microcrystals. The reason for decreasing rates was explained earlier by means of adsorption of random impurities on the ends of the microcrystals (Melikhov *et al.*, 1985, 1988, 1989).

The process of crystal growth for single microcrystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ was found to occur together with simultaneous nucleation of new microcrystals. As a result, a multiple-layer coating was formed on the FAP crystals (Figure 5). Under experimental conditions (52% H_3PO_4 , 2.5% H_2SO_4 , $t = 80^\circ\text{C}$) a process of multiple-layer coating formation began after approximately 10–15 s of chemical interaction. The thickness of the coating rapidly increased, which made it possible to observe it in an optical microscopy from this moment (Figure 1a).

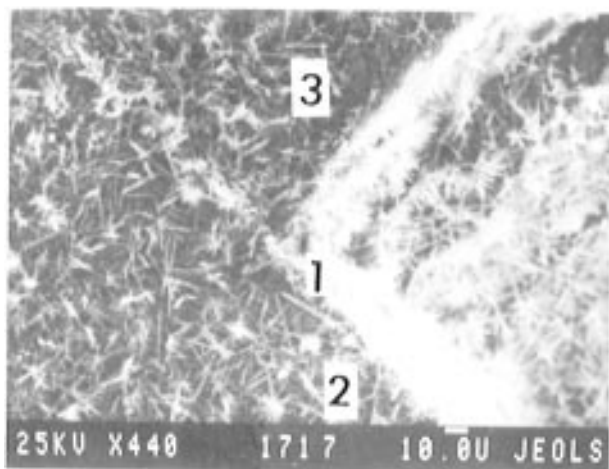
By means of the SEM one can also establish some specific places on the FAP crystal surface which are good for formation of single $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ microcrystals. Results obtained for the ultramicrocrystals indicated there were usually not any specific places on the FAP crystal surface for the ultramicrocrystals formation (Figure 4). They seemed to be formed randomly on all faces. This is not true for the microcrystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. They were found to appear mainly in holes, cracks, and other inhomogeneities of the FAP crystal surface. From the moment of etch pits formation, many of the microcrystals were also formed there (Figure 7). However, one cannot claim that the microcrystals were



a



b



c

Figure 5. Example of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating formation on the FAP crystal surface, studied with the SEM. Experimental conditions: 52% (7.2 M) H_3PO_4 and 2.5% (0.26 M) H_2SO_4 in solution, $t = 80^\circ\text{C}$, $Re < 10$ hydrodynamics, initial size of FAP crystal is $2000\ \mu\text{m}$. Dissolution times are (a) 3, (b) 7, and (c) 11 s. Bar is equal to $10\ \mu\text{m}$. Some single microcrystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ that are good for direct measurements are marked with numbers 1, 2, and 3.

formed in etch pits only, because, on the one hand, there were pits without any microcrystals and, on the other hand, other pits contained a lot of the microcrystals. The reason for this difference is not clear yet.

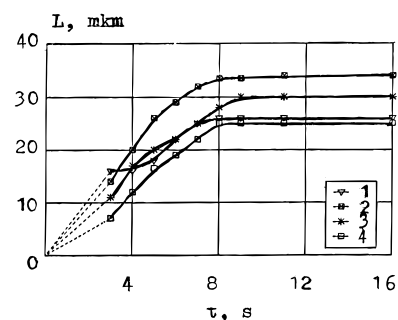


Figure 6. Length for some single microcrystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (L) versus a dissolution time t . 1–4 are numbers of the single microcrystals. Experimental conditions: 52% (7.2 M) H_3PO_4 and 2.5% (0.26 M) H_2SO_4 in solution, $t = 80^\circ\text{C}$, $Re < 10$ hydrodynamics, initial size of FAP crystal is $2000\ \mu\text{m}$.

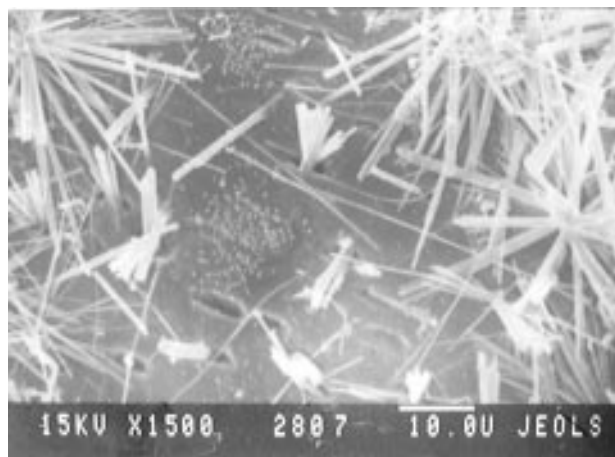


Figure 7. Various places of microcrystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ formation on a FAP crystal surface. One can see the microcrystals in etch pits and the pits without microcrystals. Experimental conditions: 52% (7.2 M) H_3PO_4 and 2.5% (0.26 M) H_2SO_4 in solution, $t = 80^\circ\text{C}$, $Re \approx 1000$ hydrodynamics, initial size of FAP crystals is $150\text{--}250\ \mu\text{m}$. Bar is $10\ \mu\text{m}$.

3.2.3. Influence of Hydrodynamics on Some Properties of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ Coating. The thickness of the coating was found to be very sensitive to the hydrodynamics of dissolution. For hydrodynamic values $Re < 100$, some indirect information about the coating thickness was obtained with the flow installation (Figure 2). Unfortunately, the high fragility of the coating obtained under $Re < 100$ prevented any direct measurements, but an increase of agitation intensity above $Re > 1000$ was found to provide a possibility for direct measurements with the SEM. For this purpose, some big FAP crystals covered with the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating were split in half and studied with the SEM. The coating thickness was found to be approximately $3\text{--}7\ \mu\text{m}$ independently of the dissolution time (Figure 8).

At higher agitation intensity ($Re > 3000$), the energy of colliding particles appears to be sufficient for knocking fragments of the coating out of FAP crystals. As a result, different "breaches" in the coating were formed. One can easily see an etched FAP crystal surface there (Figure 9). Edges of such places appear to be also good for the direct measurements of the coating thickness. This happens to be also about $4\text{--}6\ \mu\text{m}$. So, an increase of agitation intensity from $Re \approx 1500$ up to $Re \approx 3500$ does not influence the coating thickness, but the "breaches" in $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating being obtained at $Re > 3000$ are very interesting from other points of view. First, etch pits on the FAP crystal surface (Figure 9) clearly indicate that dislocations also play an important

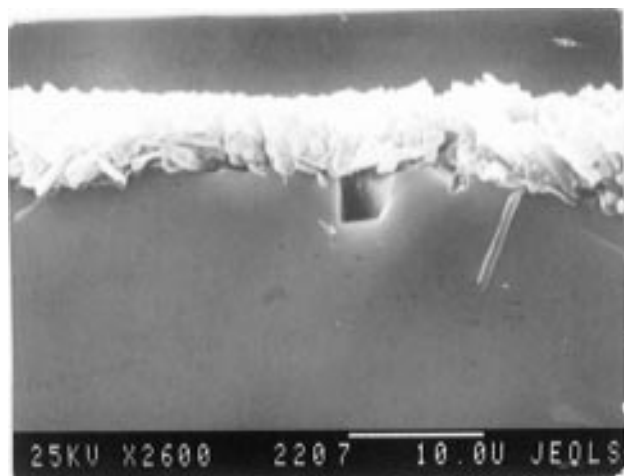


Figure 8. Thickness of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating on a FAP crystal surface (white color). Experimental conditions: 52% (7.2 M) H_3PO_4 and 2.5% (0.26 M) H_2SO_4 in solution, $t = 80^\circ\text{C}$, $Re \approx 1500$ hydrodynamics, initial size of FAP crystals is $2000\ \mu\text{m}$. Bar is $10\ \mu\text{m}$.

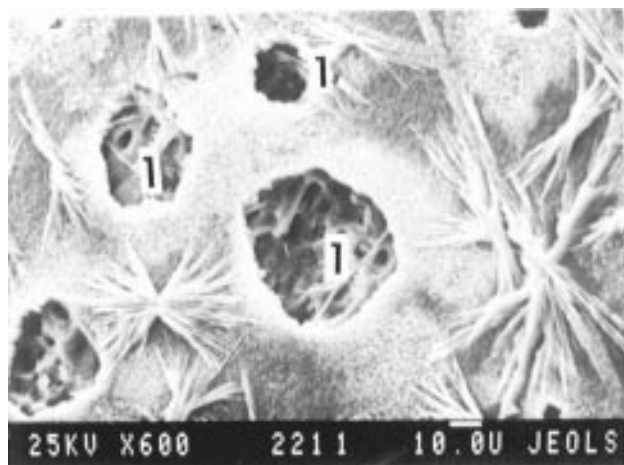


Figure 9. Example of FAP crystal covered with $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coating (white color) together with some breaches in it (black spots). One can see etch pits inside the breaches. Experimental conditions: 52% (7.2 M) H_3PO_4 and 2.5% (0.26 M) H_2SO_4 in solution, $t = 80^\circ\text{C}$, $Re \approx 3500$ hydrodynamics, initial size of FAP crystals is $150\text{--}250\ \mu\text{m}$. Bar is $10\ \mu\text{m}$.

role for the dissolution process. Therefore, simulations by the model of dislocation acceleration (Melikhov *et al.*, 1990) can also be applied here. The model is plotted in Figure 2 (curve 2). Second, the dissolution rate of FAP crystals at the breaches obviously has a higher value until a new coating is formed here. Processes of breaches formation and their termination were found to occur randomly and simultaneously under $Re > 3000$. So, in principle, it is possible to calculate an average area of FAP crystal that is free from the coating. Under the above-described experimental conditions, the breaches were found to remove about 7–10% of the coating. This hypothesis is able to explain some industrial results; e.g., an increase of agitation intensity in reactors often resulted in increase of dissolution rates (Becker, 1989; Slack, 1967; Noyes, 1967). Nevertheless, the process of the breach formation should be studied better. For example, the influence of agitation intensity and the concentration of sulfuric acid in solution to the number of breaches have not been studied yet.

As discussed above, a small agitation intensity ($Re < 200$) resulted in a fragile coating (Figure 1e). Its thickness increased while the FAP crystal dissolved inside (Figure 2, curve 3). Finally, any FAP crystal was

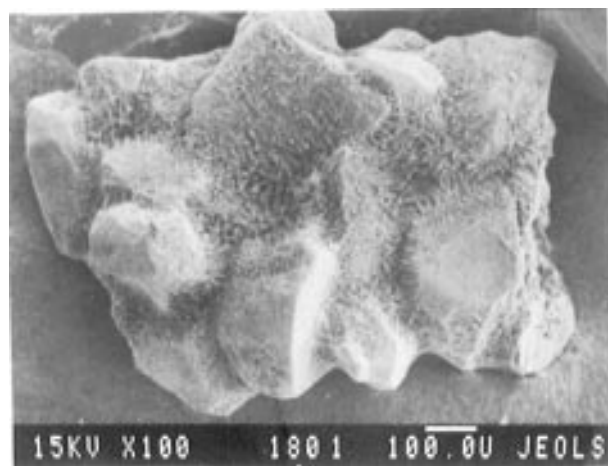


Figure 10. Aggregate of some FAP crystals. The FAP crystals are mutually pasted with their $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ coatings. Experimental conditions: 52% (7.2 M) H_3PO_4 and 2.5% (0.26 M) H_2SO_4 in solution, $t = 80^\circ\text{C}$, $Re < 300$ hydrodynamics, initial size of FAP crystals is $150\text{--}250\ \mu\text{m}$. Bar is $100\ \mu\text{m}$.

transformed into a porous granule with dimensions close to those for the initial FAP crystal (Figure 1a,e). This transformation was found to occur by a topochemical mechanism (Melikhov *et al.*, 1992).

Moreover, under conditions of small agitation intensity, different FAP crystals were found to be pasted with each other. As a result, aggregates of FAP crystals were obtained (Figure 10). One can see that the aggregates consist of at least 10 single FAP crystals and that the crystals are fastened with their coatings. The aggregates were found to be formed at the very beginning (5–15 s) of the chemical interaction between FAP and the acid mixture. A cohesion force among the single FAP crystals in each aggregate appeared to be strong enough to prevent the aggregates from destruction even if one increased agitation intensity up to $Re \approx 5000$. After being formed, the aggregates were found to be always dissolved like equivalent big single FAP crystals. The dissolution time for aggregates appeared to be proportional to their total size and might be 10 times as big as that for a single FAP crystal.

Thus, microkinetics and the micromechanism of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ surface crystallization can be described as a process of single crystals formation and growth. The single crystals were found to grow by the aggregation mechanism, described in the literature (Melikhov *et al.*, 1985, 1988, 1989). The presence of dissolving FAP crystals appears not to be able to change the crystallization mechanism, but it is able to change the kinetics (in our case growing rates for single crystals of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ were 2–3 times as big as those in pure solutions). The obtained difference in the kinetics most probably depends on a supersaturation value. Unlike the results obtained by Melikhov *et al.*, who were able to make exact measurements of the supersaturation in solution, our case required very precise measurements of supersaturation at the interface of FAP crystals–acid solution. We failed to determine it.

4. Some Technological Conclusions

For most industrial WPPA production plants, a circulating WPPA solution, sulfuric acid, and phosphate rock are fed into one (or several next-door) section(s) of the dissolving reactor (Becker, 1989; Slack, 1967; Noyes, 1967). As a result, the processes of phosphate rock dissolution and calcium sulfate crystallization occur simultaneously. The above results make possible for

the first time the description of processes occurring inside industrial reactors.

After being filtered, an output WPPA solution is always divided into two nonequal parts. The smaller part is the product (it is forwarded to a consumer), and the greater part is a circulating solution. The latter is forwarded to the dissolving reactor (Becker, 1989; Slack, 1967; Noyes, 1967). The obtained WPPA solution is always saturated with calcium sulfate and usually contains a small amount of free sulfuric acid and small crystals of calcium sulfate having passed through pores of a filter. Then the circulating solution is usually mixed with sulfuric acid and forwarded into the chemical reactor. As a result, a WPPA solution containing 1.5–4% of free H_2SO_4 is obtained there (Becker, 1989; Slack, 1967; Noyes, 1967). So, according to the above, FAP crystals are always dissolved under conditions of $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ ($x = 0, 0.5, 2$) coating formation.

Industrial reactors of the WPPA production are usually different in design. So some technological parameters, like agitation intensity, are also different. If the agitation intensity is great enough, FAP crystals are more likely to be dissolved with the breaches formation (Figure 9). In this case, a model of dislocation acceleration (Melikhov *et al.*, 1990) can be used for simulations. If the agitation intensity is small (e.g., under conditions outside of the technological regime), FAP crystals are more likely to be partly aggregated (Figure 10). The formed aggregates probably collect in places of the poorest agitation intensity (because they are the heaviest), and together with crystals of calcium sulfate, the aggregates can form deposits on walls and bottoms of industrial reactors. Cases of phosphate inclusions into such deposits were described in the literature (Becker, 1989; Slack, 1967; Noyes, 1967).

Hence, some technological conclusions about agitation intensity can be made. Hydrodynamical conditions inside industrial reactors should be great enough to secure the following: (i) the duration of mutual contacts among FAP crystals should be short enough to prevent their aggregation and (ii) the collision energy among FAP crystals should be sufficient for knocking fragments of coating out of the FAP crystal surface. So our results point to a necessity of additional hydrodynamical intensification (e.g., ultrasonic) to be used in industrial reactors of WPPA production. Some preliminary laboratory experiments have shown the ultrasonic did increase dissolution rates and to a greater extent when the greater amount of sulfuric acid was present in the solution.

To conclude the paper, one should recall that the paper is devoted to the fundamentals of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ crystallization process occurring on surfaces of the natural Khibin (Kola) FAP only. We have not been able to extend experimental investigations to other kinds of natural phosphate rock nor to study the fundamentals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 surface crystallization. Such experiments should be made in the future. Up to that time all the above-mentioned results and conclusions can be used for both cases as a first approach.

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