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THE ROLE OF CALCIUM SULPHATE IN THE REACTION
BETWEEN SULPHURIC ACID AND KOLA APATITE

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1. INTRODUCTION

The curing of superphosphate is a relatively slow reaction which takes weeks to approach completion. When phosphoric acid is being produced, the raw phosphate dissolves in sulphuric acid fairly rapidly; but in practice the process is complicated and subject to various disturbances. In particular, Kola apatite is a non-porous, magmatic mineral whose conversion is beset with difficulty. The aim of the work described below was to clarify those factors which are responsible for the irregularities in the conversion process. The information available on the system consisting of calcium sulphate, sulphuric acid and phosphoric acid will be reviewed first and the reports dealing with the effect of calcium sulphate on the reaction between raw phosphate and sulphuric acid will be summarised. The data described in the experimental part are the results of investigations in which optical and electron microscopy, x-ray diffractometry and kinetic methods were employed to clarify the course of the reaction of Kola apatite with sulphuric acid.

II. REVIEW OF EARLIER WORK

1. The Crystallization of Calcium Sulphate from Sulphuric acid - Phosphoric acid Mixtures.

In superphosphate manufacture, the system $\text{CaSO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ is formed in the early stages when sulphuric acid acts upon the raw phosphate. As the reaction proceeds, the sulphuric acid is gradually replaced by phosphoric acid and the system then comprises calcium sulphate, sulphuric acid, phosphoric acid, and water. At a certain stage the sulphuric acid

disappears and the system consists of calcium sulphate, phosphoric acid, monocalcium phosphate and water. In the manufacture of phosphoric acid, the system is one composed of calcium sulphate, phosphoric acid, and water because the relative amount of sulphuric acid is kept low.

As the conditions during and immediately after mixing the components greatly influence the rate of curing of superphosphate, particular attention was directed to the properties of the system composed of calcium sulphate, sulphuric acid, and water. Very little information is available on the properties of this ternary mixture. The readily soluble addition compounds $\text{CaSO}_4 \cdot \text{H}_2\text{SO}_4$ and $\text{CaSO}_4 \cdot 3\text{H}_2\text{SO}_4$ have, however, been prepared and isolated (1). Yamada et al. (2) have investigated by differential thermal analysis the effects of temperature, time and sulphuric acid concentration on the crystalline modification of the calcium sulphate formed by the action of sulphuric acid on raw phosphate. The following are some of the results they obtained:

Calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) separates mainly from 50 per cent sulphuric acid at temperatures below 70° and a mixture of calcium sulphate dihydrate and calcium sulphate hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) at 90° .

A mixture comprising mainly calcium sulphate hemihydrate and anhydrous calcium sulphate separates from 60 per cent sulphuric acid at temperatures below 70° .

A mixture of calcium sulphate hemihydrate and anhydrous calcium sulphate separates from 70 % sulphuric acid at temperatures below 70° .

Anhydrous calcium sulphate separates from 80% sulphuric acid regardless of the temperature.

The system comprising calcium sulphate, phosphoric acid, and water was studied by van't Hoff (3), Nordengren (4), Taperova and Schulgina (5) (6) and others. They studied the transition points of different crystalline forms of calcium sulphate as a function of phosphoric acid concentration and temperature and proposed a theory of their crystallization from supersaturated solutions. The modification first formed when

sulphuric acid is added to the monocalcium phosphate phosphoric acid system was found to be the hemihydrate under all conditions. The hemihydrate changes into the stable either directly or by way of a metastable form. Since Dahlgren (7) has discussed this matter we shall not go into details in this connection.(x)

Ikeno (8) has concluded that the addition of sulphuric acid to the system $\text{CaSO}_4 - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$ shifts the equilibrium $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + 3/2\text{H}_2\text{O}$ to the right. Kurteva and Brutskus (9) studied the changes taking place in the system $\text{CaSO}_4 - \text{H}_3\text{PO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ with a microscope and determined the water content of the solid phase by drying the latter at 180°C . The transitions that occurred at 70° are shown in Table 1.

Table I Phase transitions of calcium sulphate
in mixtures of sulphuric and phosphoric acids

% P_2O_5	% H_2SO_4	Transition
15	0 - 9	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} \longrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
20	0 - 8	" " "
20	8 - 10	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} \longrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \longrightarrow \text{CaSO}_4$
25	0 - 8	" " "
30	0 - 8	" " "
35	0 - 8	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} \longrightarrow \text{CaSO}_4$

The modification that crystallizes first under the conditions is hence the metastable hemihydrate. This changes into a stable form which is either gypsum or anhydrite depending on the conditions. Under certain conditions the transformation to anhydrite may take place by way of gypsum. Also the following observations relate to the phase transitions:

- The higher the phosphorus pentoxide concentration, the lower the rate of change from the hemihydrate to gypsum and the lower the sulphuric acid concentration.
- The rate of transformation of the hemihydrate and gypsum to anhydrite increases with the concentrations of both acids.
- A higher temperature accelerates the phase transitions.

(x) ISMA congress, 1959 Stockholm.

- As reported earlier by Ikeno et al (8), the transition of the hemihydrate to gypsum occurs at lower phosphoric acid concentrations with increasing sulphuric acid concentration.

The solubility of calcium sulphate in mixtures of phosphoric and sulphuric acids increases with temperature. At constant phosphoric acid concentration, the solubility decreases with increasing sulphuric acid concentration.

Pozin, Kopylev, Varshavski, and Pinter (10) observed that the crystals of calcium sulphate decrease in size when the concentrations of sulphuric and phosphoric acids increase on adding sulphuric acid to the system $H_3PO_4 - Ca(H_2PO_4)_2 - H_2O$. Also the tendency of the crystals to agglomerate increases with increasing phosphoric acid concentration. This has been concluded to be the reason for the abrupt decrease in the solubility of apatite when the sulphuric acid concentration exceeds 70 per cent.

X-ray studies have revealed that the greater part of the calcium sulphate in cured superphosphate is present as anhydrate (11), (12), (13). Also the hemihydrate has been found in freshly manufactured superphosphate and small amounts of the dihydrate have been found in superphosphate stored for longer periods.

2. The Lowering of the Rate of Solution of Raw Phosphate Caused by the Crystallization of Calcium Sulphate.

As the reaction between raw phosphate and sulphuric acid is heterogeneous, the rate of the overall process is determined by the rates of the following three stages:

- The rate of diffusion of the acid reagent from the liquid phase to the surface of the raw phosphate.
- The rate of reaction of the sulphuric acid with the phosphate at the interface.
- The rates of diffusion of the reaction products from the interface

Since the calcium sulphate formed is not very soluble, its crystallization at the interface slows down the diffusion of reactant and products and hence lowers the rate of the overall reaction.

The first to observe the effect of calcium sulphate on the rate of conversion of raw phosphate was Schucht (14) who reported that a gypsum crust is formed around the raw phosphate particles. Although the presence of gypsum under the conditions of superphosphate manufacture has later been proved highly improbable, the basic idea is, however, close to the truth.

Meppen (25) has stated that the slowing down of the conversion of raw phosphate is due to a mass-action effect of the calcium sulphate dissolved in the liquid phase. Subsequently the presence of a calcium sulphate crust has been frequently postulated, especially by Russian investigators in connection with Kola apatite. Tsepelevetski et al. (15) mention that calcium sulphate forms a dense layer around the apatite particles at high temperatures in the presence of a high acid concentration, whereas dilute sulphuric acid and the presence of phosphoric acid promote the formation of a porous crust.

Brutskus and Tsepelevetski (16) stated that the thickness of the acid-impermeable calcium sulphate crust is of the order of 8-12 μ . Apatite particles less than 20-25 μ in diameter they claimed to dissolve before the crust is formed. Grinshpan and Korbin (17) observed that apatite particles less than 100 μ in diameter dissolve relatively rapidly even in unfavourable conditions. On the basis of electron microscopic observations, they claimed that the apatite particles are scale-like with a thickness small in comparison with the length and breadth (18).

Pozin, Kopylev, and Varshavski (20) detected isolated calcium sulphate crystals on the surface of apatite treated with sulphuric acid and attributed the slow reaction to a greater resistance to diffusion in the vicinity of the reacting surface. The calcium sulphate

crystals were found to be oriented in parallel. When high magnification is employed, the depth is difficult to estimate accurately because the calcium sulphate crystals are very small in comparison with the apatite particles. The different rates of reaction in dilute and concentrated acid were ascribed to the formation of larger crystals separated by large pores in the former case.

Also Janysheva et al. (19) reported that a permeable layer of gypsum is formed on the calcite surface in dilute sulphuric acid and an impermeable layer in concentrated sulphuric acid. By electron microscopy the latter layer was found to consist of parallel, densely packed crystals and the former layer of irregularly oriented gypsum crystals separated by large pores. The investigators prepared a polystyrene cast of the gypsum layer, dissolved the calcite from the cast with hydrochloric acid, and prepared a positive quartz powder reproduction of the gypsum layer.

In agreement with the earlier report that the primary precipitate formed when sulphuric acid is added to the system $\text{Ca}(\text{H}_2\text{PO}_4)_2 - \text{H}_3\text{PO}_4 - \text{H}_2\text{O}$ is always the hemihydrate, Pozin et al. (20) stated that the hemihydrate crystallizes first in the conditions of superphosphate manufacture and changes later into the stable anhydrite. They concluded that phosphoric acid retards the phase transition of calcium sulphate and the anhydrite forms relatively large crystals. The solution of the hemihydrate and crystallization of the anhydrite take place in succession at low temperatures, whereas these stages overlap at high temperatures in the presence of concentrated sulphuric acid.

Dee et al. (21) report that the pores in phosphorite tend to become occluded with calcium sulphate in the sulphuric acid treatment. When however, the raw phosphate is treated with phosphoric acid present the diffusion may take place at a high rate.

the reaction of apatite with sulphuric acid. The rate of the reaction depends primarily on the activity of the acid and secondly on the resistance to diffusion at the surface of the apatite. Immediately after the reactants are mixed, the rate is high and the liquid phase becomes rapidly supersaturated with calcium sulphate. The calcium sulphate then precipitates as a more or less dense crystalline layer depending on the degree of supersaturation at the apatite surface. When the acid is dilute, the initial reaction proceeds relatively slowly and the degree of supersaturation remains low, and hence, despite the weaker activity of the dilute acid, the reaction proceeds further than when concentrated acid is employed. In order to promote the reaction, it is advantageous to lower the resistance to diffusion which slows down the initially fast reaction. This can be effected by diluting the acid with material that has already reacted, i.e. by adding acid and raw phosphate gradually to the mixture. The writers claim that it is thus possible to use a more concentrated acid than in the customary mixing process.

Pozin, Grigorjeff et al. (22)

presented the following review of the course of the reaction of apatite with sulphuric acid. The rate of the reaction depends primarily on the activity of the acid and secondly on the resistance to diffusion at the surface of the apatite. Immediately after the reactants are mixed, the rate is high and the liquid phase becomes rapidly supersaturated with calcium sulphate. The calcium sulphate then precipitates as a more or less dense crystalline layer depending on the degree of supersaturation at the apatite surface. When the acid is dilute, the initial reaction proceeds relatively slowly and the degree of supersaturation remains low, and hence, despite the weaker activity of the dilute acid, the reaction proceeds further than when concentrated acid is employed. In order to promote the reaction, it is advantageous to lower the resistance to diffusion which slows down the initially fast reaction. This can be effected by diluting the acid with material that has already reacted, i.e. by adding acid and raw phosphate gradually to the mixture. The writers claim that it is thus possible to use a more concentrated acid than in the customary mixing process.

The following method of super-phosphate manufacture where the interference of the calcium sulphate precipitation is reduced has been described in patent literature (23). About 30 per cent of the raw phosphate is added per unit of sulphuric acid in the first stage. After reaction the mixture contains unchanged sulphuric acid in addition to phosphoric acid and calcium sulphate. The rest of the raw phosphate is added in the second stage and the calcium sulphate which then forms crystallizes on the crystals of calcium sulphate that already exist. One of the advantages mentioned is the possibility of using more concentrated acid than normally.

Advantage is taken of this when a high recycle ratio is used in phosphoric acid manufacture. The recycling leads to

- a) a dilution of the added sulphuric acid
- b) a lowering of the temperature at the point of contact of reactants.
- c) an equalisation of the variations in reactant input
- d) the introduction of calcium sulphate crystal nuclei.

It is important in phosphoric acid manufacture that the rate of solution of raw phosphate does not exceed the rate at which calcium ions diffuse from the reaction zone to a gypsum surface located some distance away (24). Dahlgren (7) presents the following view. As the raw phosphate dissolves, calcium ions diffuse from the phosphate surface. At a certain distance from this surface the liquid phase has a constant composition owing to the mechanical agitation, and depending on the sulphate ion concentration, the degree of supersaturation of the calcium sulphate may exceed the critical value already in the immediate vicinity of the raw phosphate surface. The rate of reaction decreases owing to the deposited calcium sulphate crystals and the sulphate ion concentration of the liquid phase increases as more reagent is added; this again leads to a greater inactivation of the surfaces.

The optimal sulphate ion concentration in phosphoric acid manufacture is generally held to be about 1 per cent. When this level is exceeded, difficulties arise according to the patent literature. It is hence advisable to adjust the conditions so that the degree of supersaturation of calcium sulphate is as low as possible. This will also reduce the precipitation of calcium sulphate in pipelines and filters(9).

3. Additives Employed in the Treatment of Raw Phosphate with Sulphuric Acid.

A matter quite different from the foregoing blocking effect is in the manufacture of phosphoric acid the filterability of the so-called phosphogypsum. In order to obtain uniform crystals of large size, it is possible

not only to vary the factors directly affecting the process such as the sulphuric acid concentration, the particle size distribution of the raw phosphate, the recycle ratio, temperature, etc., but also to introduce various additives. The influence of alkylbenzenesulphonic acid (26) and sodium tartrate (27) on the crystallization of phosphogypsum has been studied, as also the effect of cations such as aluminium, iron, and magnesium (28). The marked differences noted in the filtering properties of phosphogypsum produced from various raw phosphates, Dahlgren (7) has attributed to the presence in some of these phosphates of impurities that influence the crystallization of calcium sulphate favourably. A favourable phosphate in this respect is for example Florida pebble phosphate. The effect of various additives on the crystallization of calcium sulphate is discussed in the literature on the setting of gypsum.

The additives are usually anionic surface active agents whose activity increases with pH. Very little information is available on additives that influence the crystallization of calcium sulphate in acid media.

The additives have mainly been studied to determine their influence on the filtering properties of phosphogypsum, but they might also be used to modify the nature of the crystals that deposit on raw phosphate surfaces in superphosphate manufacture.

TVA has examined the effects of the following additives in superphosphate manufacture: potassium chloride, ammonium nitrate, ammonium sulphate, phosphoric acid, and a surface-active agent such as aliphatic polyoxyethylene adducts (29). Potassium chloride and ammonium nitrate promoted, and ammonium sulphate retarded the curing re-action. The surface-active agent had no effect. However, Fox et al. (30) found that surface-active agents promote the conversion of Florida phosphate in the early stages, but their effect is not observed 1-24 hours later. These authors employed both

anionic alkylarylsulphonates and non-ionic surface-active agents in their studies.

III. Experimental

1. The Solubility of Apatite in the Early Stage of Treatment with Sulphuric Acid.

The effects of various factors on the solubility of Kola apatite were examined by carrying out phosphorus pentoxide determinations. The per cent ratio of the dissolved phosphorus pentoxide to the total phosphorus pentoxide in the system, the degree of decomposition, has been employed as a measure of the solubility.

Owing to the lack of homogeneity of the apatite-sulphuric acid mixtures in the early stages of mixing, it is impossible to determine exactly the variation of the degree of decomposition by analysing samples taken from the mixtures. For this reason, batches were made that were so small that the whole batch could be dissolved for analysis. In each experiment five grams of Kola apatite was added gradually to sulphuric acid at a constant temperature during the course of ten seconds. The amount of acid was 3.25 grams of 100 per cent sulphuric acid. The resulting ratio of sulphuric acid to phosphorus pentoxide is nearly the mean ratio in superphosphate as normally employed at Rikkihappo Oy.

The Kola apatite was used as received from the supplier or it was sieved to obtain material of definite particle size. A typical sieve analysis of Kola apatite is the following:

	+ 60 mesh	1.6 %
- 60	+ 100 mesh	14.3 %
- 100	+ 200 mesh	33.6 %
- 200	+ 250 mesh	4.4 %
- 250	+ 325 mesh	11.1 %
- 325 mesh		35.0 %

In the normal determination method of water-soluble phosphorus pentoxide, the weighed sample is agitated with distilled water for 30 minutes. Because

the mixtures examined in this study contained large quantities of unchanged sulphuric acid, the possible solution of apatite during the analysis had to be taken into account. For this reason acetone, which is known to dissolve phosphoric acid, was added to the samples to decrease the activity of sulphuric acid. The phosphorus pentoxide contents of the filtered solutions were determined colorimetrically by the vanadomolybdate method employing a Beckman B spectrophotometer (31).

Table 2 Solubility determinations for acetone and aqueous extracts of apatite - H_2SO_4 mixtures after agitation for different periods of time (5 g of apatite and 5 g of 65% H_2SO_4 agitated at 80°C)

Time of agitation of apatite- H_2SO_4 mixture in minutes	Degree of decomposition %		
	Water extract 30 min.	Water extract 15 secs.	Acetone extract 15 secs.
0	29.9	11.8	0.5
3	41.6	33.4	32.2
20	48.1	42.2	40.7
90	47.9	40.9	41.3
300	50.8	48.8	42.5

Solubility determinations computed from analytical data for the acetone and water extracts of apatite-sulphuric acid mixtures after different periods of reaction are shown in Table 2. The sample at zero time is a blank prepared by adding the solvent first to the 5 grams of apatite and then the 5 grams of 65% sulphuric acid. The results of this test for the two extraction solvents show that the untreated apatite dissolves to a considerable extent when extracted with water for 15 seconds and 30 minutes, but is practically insoluble when a rapid extraction with acetone is performed.

On the basis of the data in Table 2, a 15-second extraction with acetone was chosen for later experiments. It may be mentioned that a similar procedure has been developed in the laboratory of Fisons Ltd.

(32) in which the mixture of equal parts of dioxan and acetone is employed as the extracting solvent. Dioxan forms weak addition compounds with sulphuric and phosphoric acids which react very slowly with raw phosphate. The function of acetone is to increase the miscibility with water. The undissolved monocalcium phosphate is extracted with boiling saturated sodium oxalate solution after the acetone extraction.

From the data in Table 2, the use of acetone only may be considered appropriate, because no appreciable solution of apatite in acetone containing sulphuric acid took place. Because the analysed samples contained free sulphuric acid it was not necessary to determine the monocalcium phosphate in the insoluble residue.

The variation with time of the degree of decomposition of Kola apatite employing different sulphuric acid concentrations at 20°C and 80°C is shown by the data in Appendix 1, Fig. 1. The curve for the reaction with 80 per cent sulphuric acid at 20°C gives a clear picture of the various stages of the conversion of raw phosphate. About 20 per cent of the total phosphorus pentoxide dissolved during the course of half a minute and the reaction came practically to a standstill after three minutes. At 80°C the dissolution in 80 per cent sulphuric acid proceeded more slowly and did not cease abruptly after an initial stage, but continued at a slowly decreasing rate. The influence of temperature is very slight during 60 minutes when the acid concentration is 80 per cent, but much more marked when the acid concentration is 50 per cent. At 20°C the reaction seems to stop after 20-40 minutes, but at 80°C no essential decrease occurs in the rate up to 60 minutes. In general a rapid initial reaction is followed by a slow rate of solution, whereas the reaction proceeds at a fairly even rate when the initial reaction is slow.

In Appendix 1, Fig. 2 shows the variation in the degree of decomposition of the Kola apatite as a function of sulphuric acid concentration after a reaction period of 20 minutes at 20°C and 80°C. At 20°C the sulphuric acid concentration has no marked influence on the variation. There is a shallow minimum in the rate at 60-70%. A sharp peak is noted in the curve for 80°C

when the acid concentration is about 60 per cent. Similar curves showing that there is a maximum in the rate of decomposition of apatite at a sulphuric acid concentration of 58-62 per cent have been published by Pozin, Grigorjeff et al. (22).

As the rate of conversion of the coarser apatite particles is the greatest problem in view of the long curing time of superphosphate, the solubility of apatite sieve fraction of -60 + 100 mesh was studied in separate experiments. The variation of the degree of decomposition of coarse -60 + 100 mesh apatite under conditions identical with those when the data in Appendix 1 were collected are shown in Appendix 2. The solubility values are lower for the coarse than for the unsieved material owing to the smaller reaction surfaces. As expected, an increase in temperature promotes the solution when the acid is dilute, but the solubility in concentrated acid decreases with increasing temperature. This anomalous behaviour is illustrated by the data in App. 3, Fig. 1 as a function of temperature when the reaction period was 20 minutes. Similarly as the data in Appendix 1, the curves plotting these data show that the solubility in dilute acid increases, but the solubility in concentrated acid decreases with rising temperature. Also the solubility of unsieved apatite in dilute acid increases considerably, whereas the solubility in 80 per cent acid increases only slightly with rising temperature. The abnormal behaviour observed when the acid is concentrated is more clearly evident when the reacting surface is small in area.

The different rates of solution in dilute and concentrated acids are also shown by the data in App. 3. Fig. 2 on the variation of the solubility of -60 + 100 mesh apatite with acid concentration at 20°C and 80°C. An abrupt increase in the solubility at a sulphuric acid concentration of 70-80 per cent is noted at 20°C. At 80°C the solubility decreases rapidly in the acid concentration range from 55 to 65 per cent and is a minimum when the concentration is 70-75 per cent.

2. Optical Microphotography

The microphotographs were taken with a Reichert microscope equipped with a camera and polarizing filters.

used for polarizing filters. The samples examined were prepared by stirring 10-gram portions of apatite with 6.5 g 100 per cent sulphuric acid added as different dilutions in a thermostat. After the reaction had proceeded 20 minutes, it was quenched by diluting the mixture rapidly with 500 ml of acetone. The undissolved apatite was allowed to settle and the acetone layer containing the acids and suspended particles was decanted into another vessel. The residue and the container were washed with several portions of acetone to remove all traces of sulphuric and phosphoric acids. Each residue was immersed on a microscopic slide in a liquid with an index of refraction of 1.46 and photographed, employing exposure periods varying from 4 to 10 seconds. When the polarizing filters were used, the best photographs were obtained employing an immersion liquid with an index of refraction of 1.57, but the light intensity was then so weak that the period of exposure was 8 minutes. The adjustment of depth was difficult because of the small size of the calcium sulphate crystals as compared with the apatite particles. Attempts were made to find an apatite particle with its upper surface horizontal and the microscope was then focussed on this surface.

Appendix 4 shows micro-photographs of untreated apatite and undissolved apatite obtained from process samples from superphosphate manufacture. Pure apatite is composed of transparent, highly refractive particles in which cleavage lines are not distinguished (photos 1 and 2). A photograph of an apatite particle taken between polarizing filters is shown in Photo 3. The background light was eliminated by placing the analyser and polarizer at right angles. By turning the stage, it is possible to prevent light from passing through the apatite particle which does not then appear in the photographs; the polarization planes at right angles in the apatite particle then coincide with the polarization planes of the polarizer and analyser (extinction angle). In order that the apatite particle would form an image in the microphotograph,

the microscope stage must be rotated 20 degrees from the extinction angle (Photo 3). The Photos 4-6 were taken with a particle of undissolved apatite in the extinction angle. The doubly-refracting calcium sulphate crystals on the surface of the apatite have rotated the plane of polarization of the light that passed through the apatite and are visible as white specks on a dark background. Photos 7 and 8 show microphotographs of undissolved Moroccan phosphate isolated from superphosphate. The Moroccan phosphate consists of small primary particles of the order of 0.01 microns in diameter and therefore does not transmit light after treatment with sulphuric acid. For this reason only calcium sulphate crystals close to the periphery are visible.

The undissolved residue of apatite treated with 50-80 per cent sulphuric acid at 80°C photographed with and without polarizing filters are shown in Appendix 5. Different types of calcium sulphate crust are formed on the apatite surface during treatment with sulphuric acid solutions of different concentrations. Fairly large crystals and crystal aggregates which are white on the apatite surface with the polarizing filters in place, but dark when the polarizing plates are absent, are produced when the apatite reacts with 50 per cent acid for 20 minutes. Large crystals covering only a part of the apatite surface are formed when the apatite is treated with 60 per cent acid. The uncovered areas may have resulted by the fragility of the crust which had been broken down by mechanical action, but nevertheless the result was found characteristic for the material treated with 60 per cent acid. As shown in App. 1 Fig. 2, the solubility of apatite is maximum at this sulphuric acid concentration. The surfaces of the apatite particles exposed to 65 and 80 per cent sulphuric acid seems to be covered by progressively denser layers of calcium sulphate crystals of decreasing size in accordance with the decreasing solubility shown by the data in App. 1 Fig. 2.

3. Electron Microscope Studies

The studies with the electron microscope were carried out with a Hitachi electron microscope HU - II owned by Vuorikemia Oy. Each sample was attached with nitrocellulose lacquer to a copper gauze and an area on an apatite surface typical for the sample was selected for photography.

As in optical microscopy, difficulties in depth adjustment were encountered owing to the small sizes of the calcium sulphate crystals in relation to the apatite particles. The undissolved apatite particles were isolated from the mixtures of apatite and sulphuric acid in the same manner as the samples of undecomposed apatite for optical microscopy.

Photographs of surfaces of undissolved raw phosphate isolated from superphosphate process samples and apatite not treated with sulphuric acid are shown in Appendix 6. The raw phosphate surface in the Moriz-Standaert Mixer is covered by needle-shaped crystals, but the surfaces of undissolved raw phosphates isolated from superphosphate and Kotka phosphate are covered by platelike crystals. The surface of the untreated apatite is either quite smooth or irregular in places only (Photos 6-8)

Profile photographs of undissolved apatites isolated from mixtures of apatite and sulphuric acid are shown in Appendix 7. The mixtures were those examined by optical microscopy (App. 5) Needle-like crystals were formed on apatite treated with 50 per cent acid; these crystals increased in size with the time of mixing. Treatment with 60 per cent acid led to the formation of needle-shaped crystals after half a minute and to large plate-like crystals after 20 minutes (Photos 3-4). Small numbers of needle-like crystals were observed after the 20 minute period, but these disappeared on exposure to the electron beam for a few seconds. As in optical micro-

scopy, the needle-like crystals were observed on the surface of the apatite particles. The plate-like crystals were observed on the surface of the apatite particles. The needle-like crystals were observed on the surface of the apatite particles. The plate-like crystals were observed on the surface of the apatite particles.

scopy, areas devoid of crystals were observed on the profiles of apatite particles treated with 60 per cent acid (see Photos 3 and 4 in Appendix 5). An electron microphotograph of such a point is shown in Photo 5. The calcium sulphate crystals produced by 65 per cent acid were plate-like already after a reaction period of half a minute. The shapes of the crystals formed on apatite surfaces treated with 80 per cent acid could not be determined.

Electron micrographs of coarsest apatite sieve fraction treated with sulphuric acid are shown in Photos 1-4 in Appendix B. The samples were prepared as in the solubility determinations (App.3) Large rod-like crystals that appeared to be corroded occurred on the coarse apatite crystals that had been treated at 80 C with 50% acid in which the apatite solubility was high. Photographs of calcium sulphate crystals detached by grinding the undecomposed apatite from the apatite surfaces are shown in Photos 5-7. Three different crystal forms can be distinguished. The rod-like crystals shown in Photo 5 were produced by dilute acid or by 60-65 per cent acid after a short period of mixing (Fig. 1-2 in App. 6 and Fig. 1-3 in App.7). Crystals typical in photo (App.8) can be seen on the surface of apatite treated with 60-65 per cent H_2SO_4 in short mixing periods (Photo 6 in App. 7 and Photo 3 in App. 8) Square crystals which are known to be anhydrite are produced by 60 per cent and more concentrated sulphuric acid, especially after a longer reaction period (storage superphosphate).

Photo 8 in Appendix B shows apatite particles that were treated with 80 per cent sulphuric acid on a microscope slide. Plate-like crystals arranged like scales that are difficult to distinguish in the profile photographs taken with the electron microscope are present on the apatite surfaces.

4. Crystal Forms of Calcium Sulphate Attached to Apatite Surfaces as Deduced by X-ray Diffractometry

Samples of apatite not decomposed by sulphuric acid were prepared for this study as described in connection with the microscope study. A Philips x-ray diffractometer PW 1050/1051 and a stabilized x-ray generator PW 1010/30 were employed to measure the diffraction.

X-ray diffractograms of different forms of calcium sulphate and untreated apatite are shown in Appendix 9. These were recorded under the following conditions:

- x-ray tube emitting $\text{CuK}\alpha$ radiation
- tube load 34 KV, 14 mA
- divergence slit 1°
- scanning speed $2\theta = 1^\circ/\text{min}$.
- paper speed $1/2$ inch/min.
- ratemeter factor 16
- time constant 8

On the basis of diffractograms of the pure compounds, an scanning range of $29.5^\circ - 32.0^\circ$ was chosen to permit rapid working and to attain sufficient resolution. A diffraction maximum at 29.9° relates to the hemihydrate and a diffraction maximum at 31.5° to anhydrite. Also apatite has a diffraction maximum at $31.9^\circ - 32.0^\circ$ near the end of the range, but this can be clearly distinguished from the anhydrite maximum. The diffraction maxima of the various forms of calcium sulphate do not coincide with any other maxima in the selected range. Diffractograms of apatite not dissolved in sulphuric acid were recorded as above with exception:

- scanning speed (2θ) was $1/4^\circ/\text{min}$
- ratemeter factor 2
- time constant 16

The x-ray diffractograms of undissolved apatite particles isolated from apatite-sulphuric acid mixtures are shown in Appendix 10. The mixtures were prepared as described in connection with the

the solubility and microscope studies. The diffractograms of the acid-treated apatite particles differ from the diffractogram of pure apatite in showing maxima due to the hemihydrate and anhydrite.

The diffractograms (curves) in Photo 1 relate to unsieved apatite. According to previous reports, the form of calcium sulphate produced first is the hemihydrate (H) which is transformed later into anhydrite (A) (5) (6). The transformation is more rapid by a higher sulphuric acid concentration and a higher temperature (2). This transformation does not occur during a 20 minute mixing of apatite with 50 per cent sulphuric acid; only the hemihydrate is present. With 60 per cent acid, an appreciable amount of anhydrite is formed during 10 minutes. During the greater part of the reaction period, the hemihydrate on the apatite surface is dissolving and anhydrite is crystallizing (see microphotographs). On treatment with 65 per cent acid, the hemihydrate is transformed nearly completely into anhydrite within three minutes, the transformation is rapid and the crystalline crust consists of only one form of calcium sulphate during the greater part of the reaction period. The maximum solubility in 60 per cent acid can hence be attributed to the continuous exposure of the apatite surface as the hemihydrate dissolves.

The diffractograms 7-17 in Appendix 10 were recorded for coarse (-60 + 100 mesh) apatite and should be compared with the solubility curves for this material in Appendix 3. According to curve 7, only hemihydrate was present on apatite exposed 20 minutes at 50°C to 50 per cent acid, in which it is

not very soluble in this temperature. An abrupt increase in solubility occurred when the temperature rose above 50°C . During 10 minutes appears at 80°C also anhydrite together with hemihydrate in the crust on the surface of undecomposed apatite and the conversion of hemihydrate to anhydrite was not complete even after 20 minutes.

The curves 8-16 reveal the reason for the abrupt decrease in the solubility of coarse apatite with increasing acid concentration. The conversion of hemihydrate to anhydrite takes place slowly in 50 and 55 per cent acid, in which the solubility of coarse apatite is high, but rapidly, within three minutes in the 60 per cent acid in which the solubility is low. In the latter case only anhydrite is present during the greater part of the reaction period.

In all three cases a high rate of solution is associated with a slow transformation of hemihydrate and a low rate of solution with either rapid transformation or no transformation at all.

IV. Summary

Previously reported information, especially published by Russian investigators, on the lowering of the rate of reaction of apatite with sulphuric acid due to the crystallization of calcium sulphate is reviewed.

Acetone was used as diluent in studies of the rate of solution of apatite in sulphuric acid in order to obtain reliable data on the degree of solubility also in the early stages of the reaction when a large amount of sulphuric acid is present. When values of the degree of decomposition were plotted against the time of reaction, curves were obtained which increased rapidly at first and then as calcium sulphate crystallized on the apatite surface increased less rapidly. The rate of reaction decreased more rapidly at high acid concentrations and at lower temperatures. The rate of solution of unsieved

apatite at 80°C was a maximum when the sulphuric acid concentration was 60 per cent. When the acid was more concentrated, the solubility decreased abruptly. This decrease in solubility of coarse apatite particles (-60 + 100 mesh) appears at lower acid concentrations.

Optical and electron microphotographs of process samples from superphosphate manufacture and samples of undissolved apatite isolated from apatite-sulphuric acid mixtures prepared in the laboratory show that the apatite surfaces become covered by a layer of calcium sulphate crystals. A method was developed for the visualization of the crystals of calcium sulphate, in which light passing through the underlying apatite particles is eliminated by means of crossed polarizing filters. When the acid is dilute, fairly large, rodlike calcium sulphate crystals are deposited. With increasing acid concentration, the crystals become plate-like and decrease in size. Areas free of calcium sulphate were observed by both optical and electron microscopy on the undissolved apatite particles remaining when unsieved apatite was treated with 60 percent sulphuric acid in which the rate of solution is a maximum.

X-ray diffractograms revealed that the transformation of hemihydrate to anhydrite takes place during the greater part of the reaction of apatite with sulphuric acid when the rate of solution is high, but either very rapidly or not at all when the rate of solution is low. In the latter case, only one form of calcium sulphate prevails during the greater part of the reaction period.

The x-ray diffraction studies were carried out in the Spectrographic Laboratory of the Finland Institute of Technology. We wish to thank Prof. Olavi Erametsä for the interest he has shown in this work and for the valuable advice he has given.

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APPENDICESAppendix 1

- Fig. 1. Variation of the degree of decomposition of apatite in sulphuric acid with time.
- Fig. 2. Variation of the degree of decomposition of apatite with sulphuric acid concentration. Reaction time 20 min.

Appendix 2

Variation of the degree of decomposition of -60 + 100 mesh apatite in sulphuric acid with the time.

Appendix 3

- Fig. 1 Variation of the degree of decomposition of -60 + 100 mesh apatite with temperature. Reaction time 20 mins.
- Fig. 2 Variation of the degree of decomposition of -60 + 100 mesh apatite with sulphuric acid concentration. Reaction time 20 mins.

Appendix 4

Microphotographs of untreated apatite and from undecomposed apatite separated from process samples of Moritz-Standaert system. Photos 4-8 between crossed polarizing filters and apatite grain rotated in extinction angle. The grains are immersed in the refractive index liquid 1.57.

- Fig. 1. Kola apatite photographed in refractive index liquid 1.57. 320 x.
- Fig. 2. Kola apatite photographed in air. 320 x.
- Fig. 3. Kola apatite between crossed polarizing filters rotated 20° from extinction angle. 360 x.
- Fig. 4. Undecomposed apatite from the mixer of the Moritz-Standaert. 360 x.
- Fig. 5. Undecomposed apatite from fresh superphosphate 360 x.
- Fig. 6. Undecomposed apatite from storage superphosphate. 360 x.
- Fig. 7. Undecomposed Moroccan phosphate from fresh superphosphate 360 x.
- Fig. 8. Undecomposed Moroccan phosphate from storage phosphate 360 x.

Appendix 5. Microphotographs from the undecomposed apatite separated from the apatite-sulphuric acid mixtures with various acid concentrations (at 80°C, 20 min.). In the vertical line on the left the samples are photographed between crossed polarizing filters and apatite grain rotated in extinction angle (refractive index liquid 1.57) On the right the same samples photographed without polarizing filters (refractive index liquid 1.46).

- | | | | |
|---------|----------------|---------|----------------|
| Fig. 1. | 50 % H_2SO_4 | Fig. 2. | 50 % H_2SO_4 |
| Fig. 3. | 60 % H_2SO_4 | Fig. 4. | 60 % H_2SO_4 |
| Fig. 5. | 65 % H_2SO_4 | Fig. 6. | 65 % H_2SO_4 |
| Fig. 7. | 80 % H_2SO_4 | Fig. 8. | 80 % H_2SO_4 |

Appendix 6. Electron micrographs of undecomposed raw phosphate (Moroccan phosphate + Kola apatite 30:70) isolated from Moritz-Standaert process samples and of untreated apatite. 4000 x.

- | | |
|---------|---------------------------|
| Fig. 1. | Mixer of Moritz-Standaert |
| Fig. 2. | Mixer of Moritz-Standaert |
| Fig. 3. | Fresh superphosphate. |
| Fig. 4. | Storage superphosphate. |
| Fig. 5. | Kotka phosphate. |
| Fig. 6. | Untreated apatite. |
| Fig. 7. | Untreated apatite. |
| Fig. 8. | Untreated apatite. |

Appendix 7. Electron micrographs of undecomposed apatite isolated from apatite-sulphuric acid mixtures. Reaction temperature 80°C. 4000 x.

- | | | | |
|---------|---|---------|---|
| Fig. 1. | 50 % H_2SO_4 ½ min. | Fig. 2. | 50 % H_2SO_4 20min. |
| Fig. 3. | 60 % H_2SO_4 ½ min. | Fig. 4. | 60 % H_2SO_4 20min.,
covered area. |
| Fig. 5. | 60 % H_2SO_4 20 min.
Uncovered area. | Fig. 6. | 65 % H_2SO_4 ½ min. |
| Fig. 7. | 65 % H_2SO_4 20 min. | Fig. 8. | 80 % H_2SO_4 20 min. |

Appendix 8. Photos 1-4. Coarse (-60 + 100 mesh) apatite treated with sulphuric acid at 80°C (cf. decomposition curves in App. 3. Fig. 2) 4000 x. Photos 5-7. Various types of calcium sulphate crystals detached from apatite surfaces. 4000 x. Photo 8. Optical microphotograph of mixture of apatite and 80 % sulphuric acid.

- Fig. 1. Coarse apatite, 50 % H_2SO_4 , 10 min.
 Fig. 2. Coarse apatite, 50 % H_2SO_4 , 20 min.
 Fig. 3. Coarse apatite, 60 % H_2SO_4 , $\frac{1}{2}$ min.
 Fig. 4. Coarse apatite, 60 % H_2SO_4 , 20 min.
 Fig. 5. Electron micrograph of calcium sulphate crystals detached from apatite surface (unsieved apatite, 50 % H_2SO_4 , 20 min.).
 Fig. 6. Electron micrograph of calcium sulphate crystals detached from apatite surface (coarse apatite, 60 % H_2SO_4 , $\frac{1}{2}$ min.).
 Fig. 7. Electron micrograph of calcium sulphate crystals detached from the surface of undecomposed raw phosphate in storage superphosphate.
 Fig. 8. Optical microphotograph of apatite exposed on a slide to 80 % H_2SO_4 for 60 minutes.

Appendix 9. X-ray diffractograms of different forms of calcium sulphate and Kola apatite.

Appendix 10. X-ray diffractograms of undecomposed Kola apatite isolated from apatite-sulphuric acid mixtures and of pure Kola apatite.

- Fig. 1. Unsieved Kola apatite, 80°C.
 Fig. 2. Coarse Kola apatite (-60 + 100 mesh). Curve 7: 50°C; curves 8-10: 80°C.
 Fig. 3. Coarse Kola apatite (-60 + 100 mesh), 80°C.

Fig.1

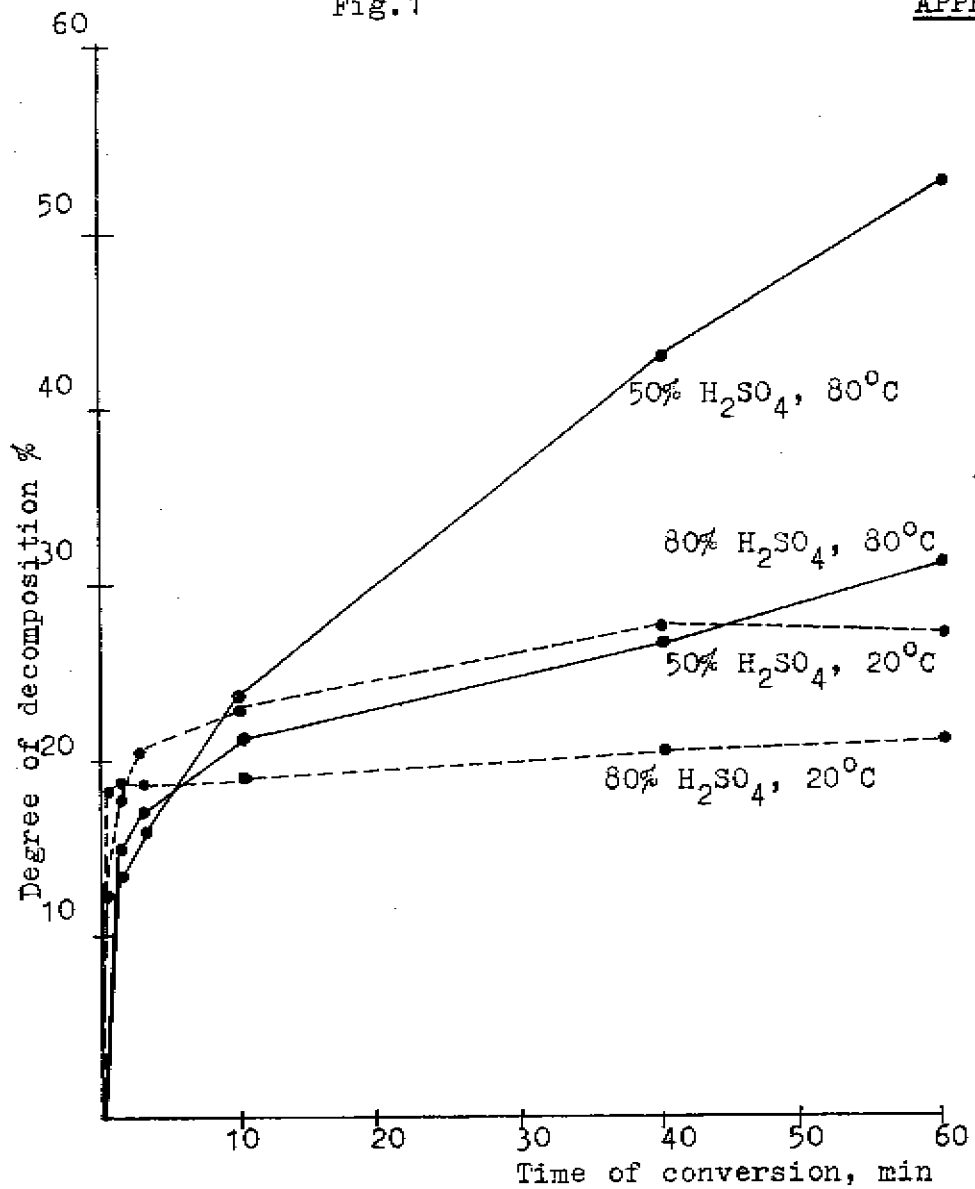
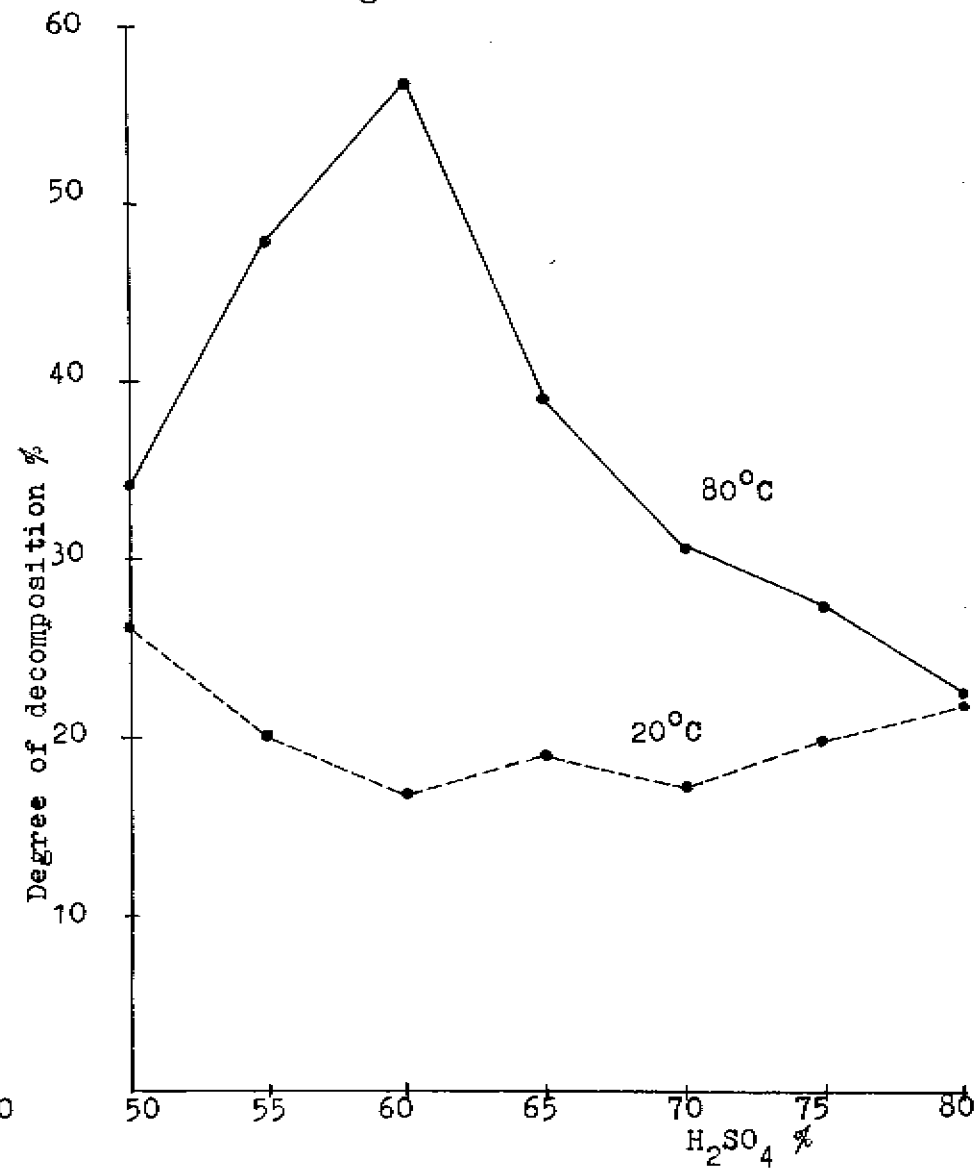


Fig.2

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APPENDIX 2

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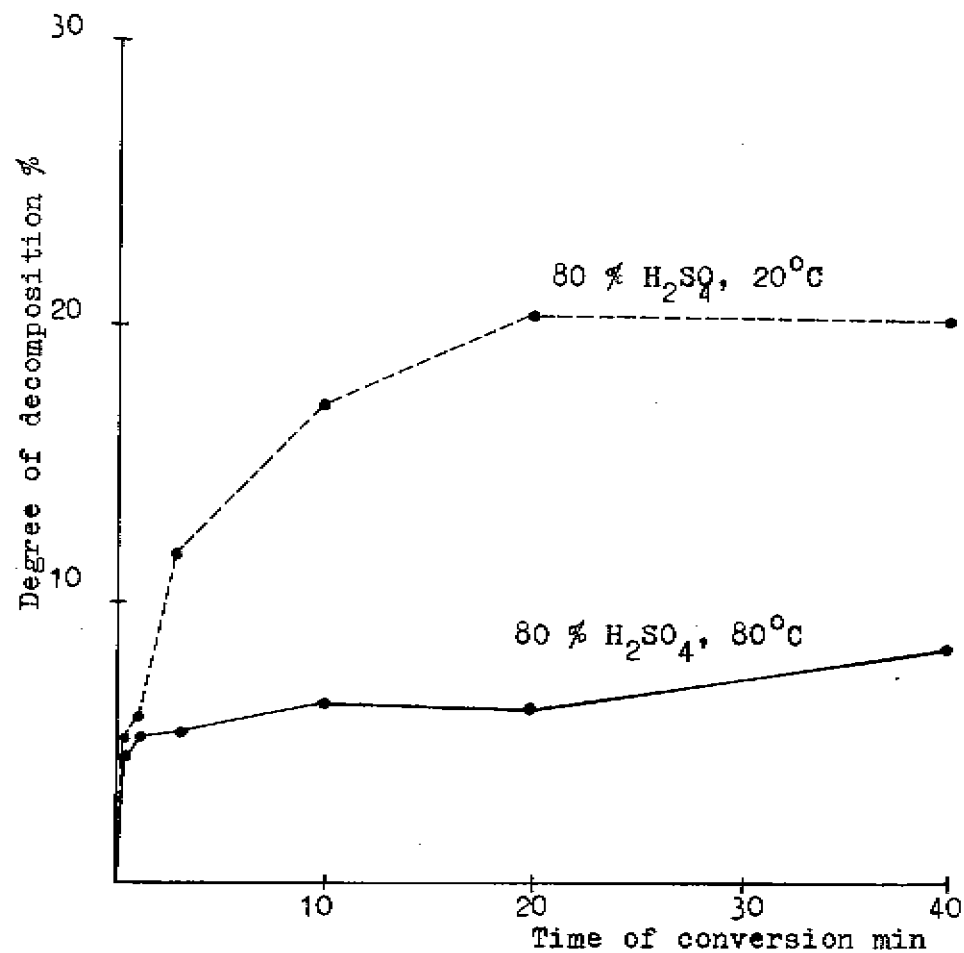
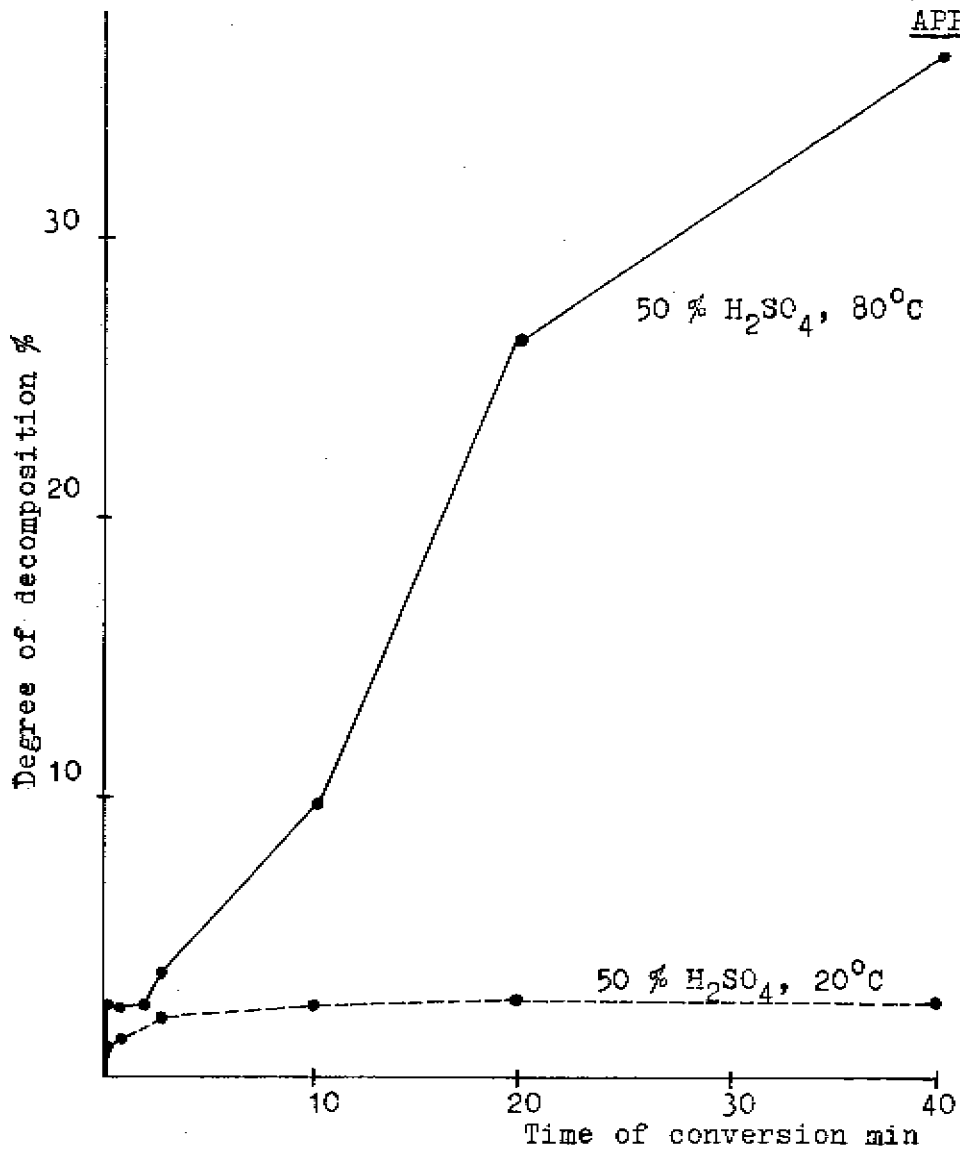
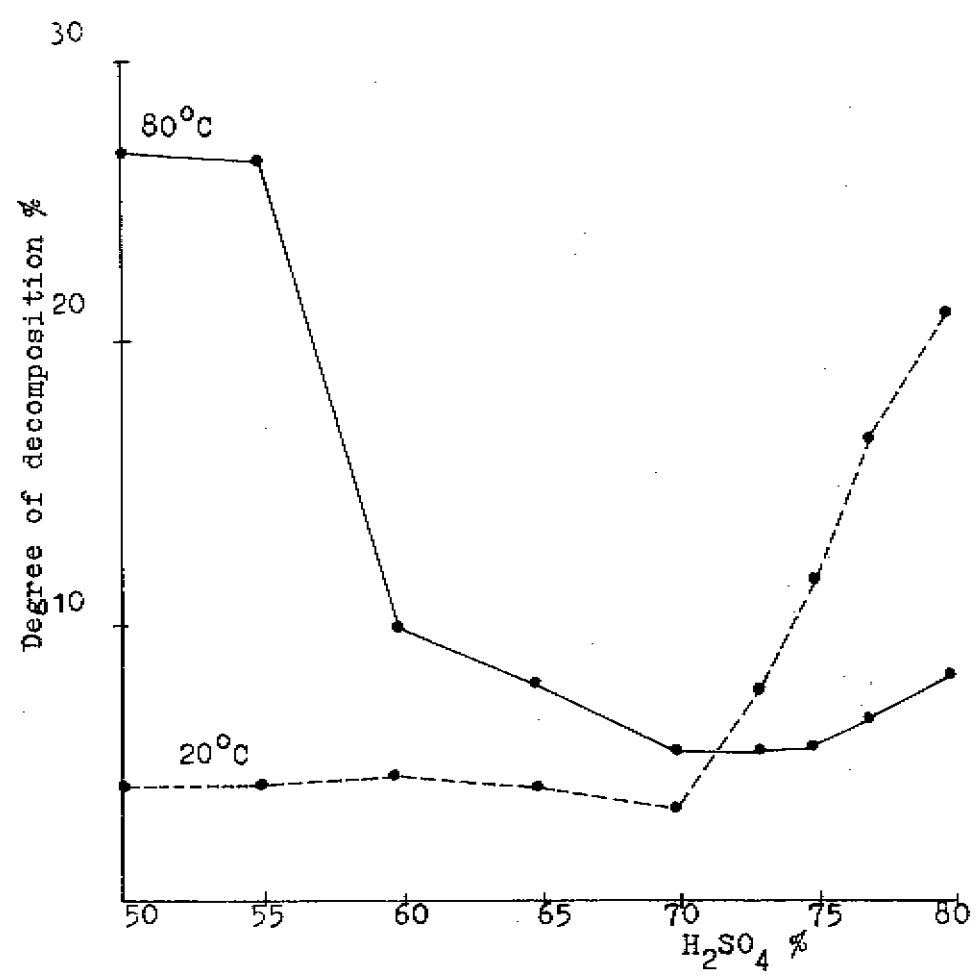
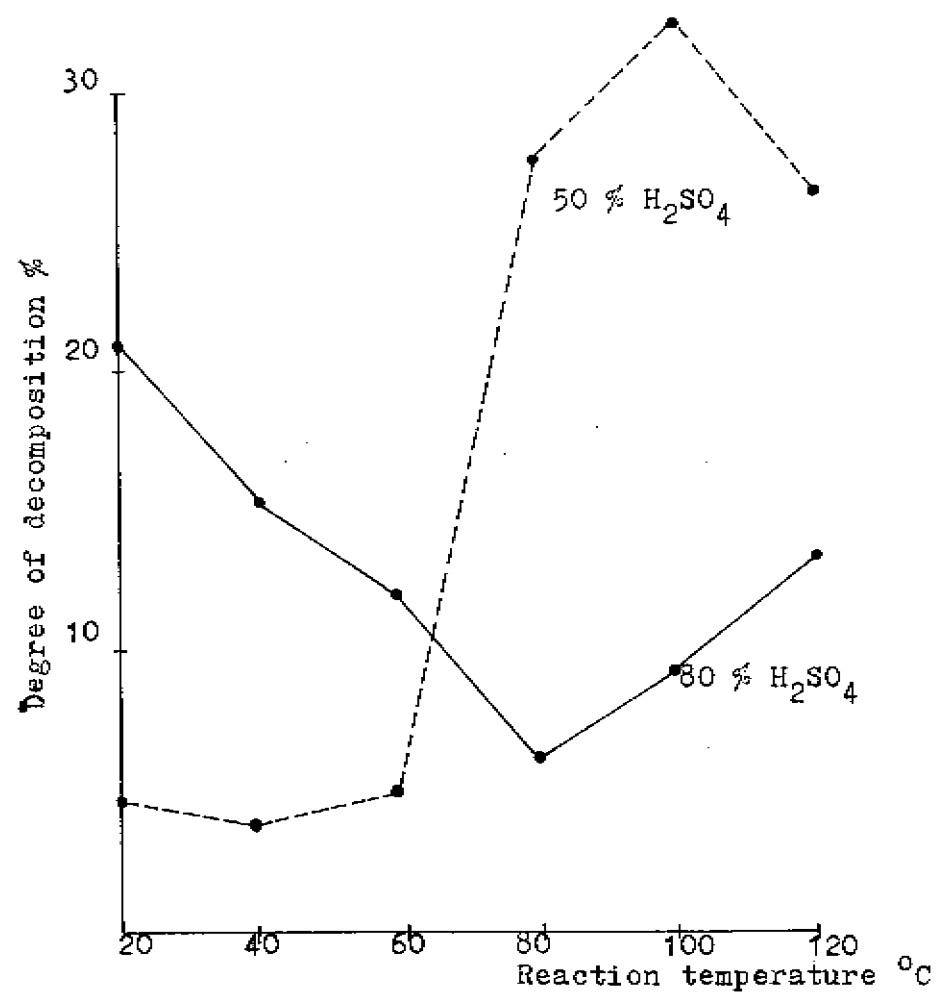


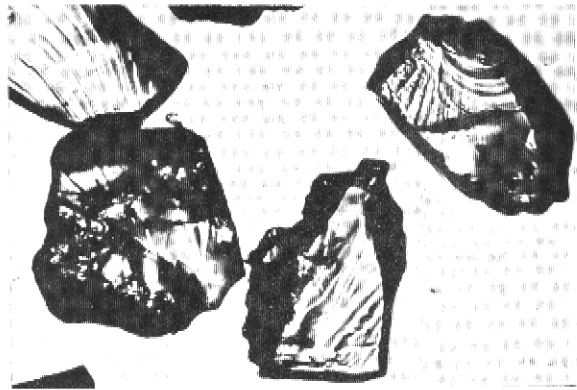
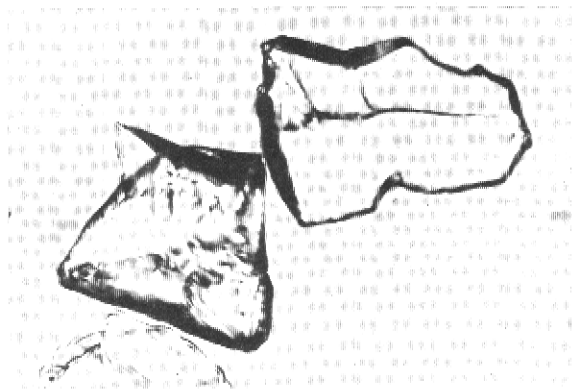
Fig.1

APPENDIX 3

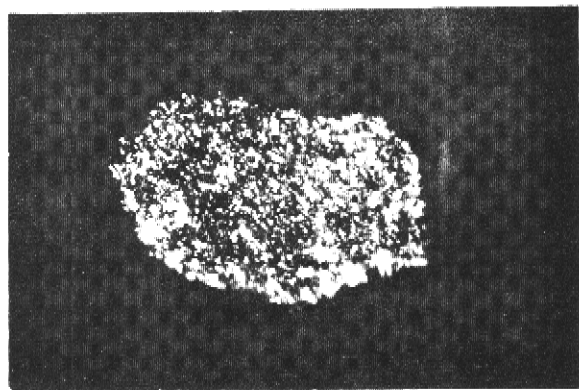
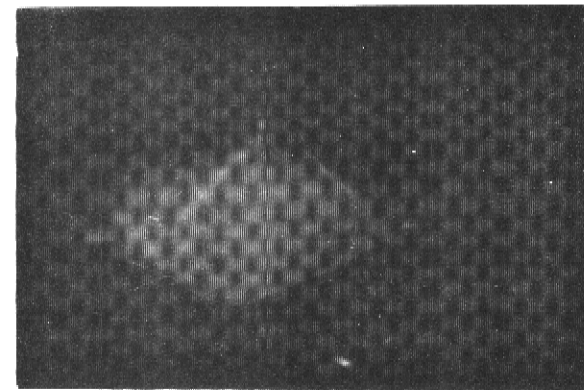
Fig.2

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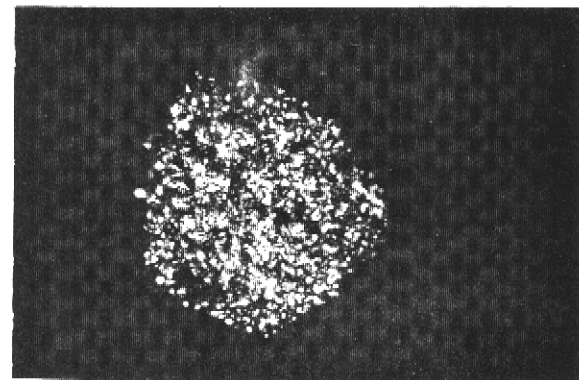
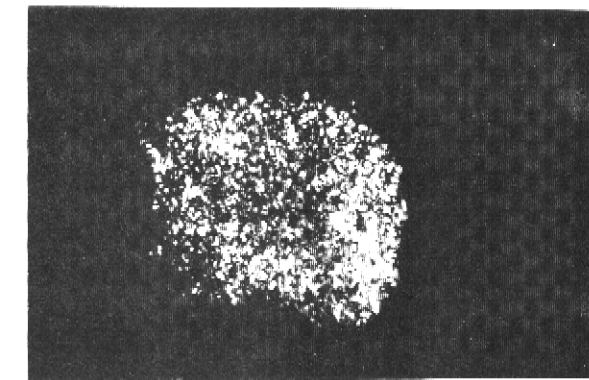




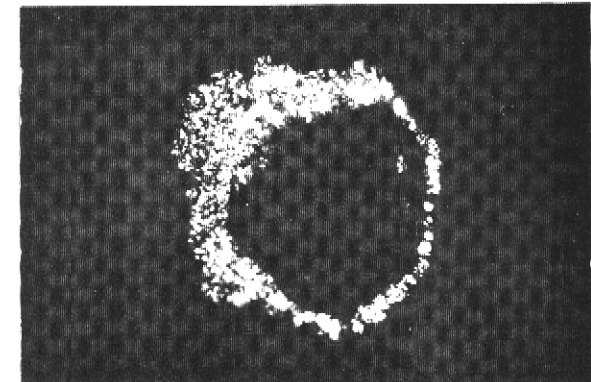
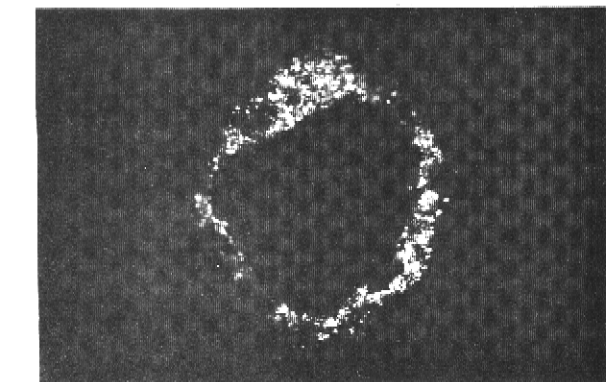
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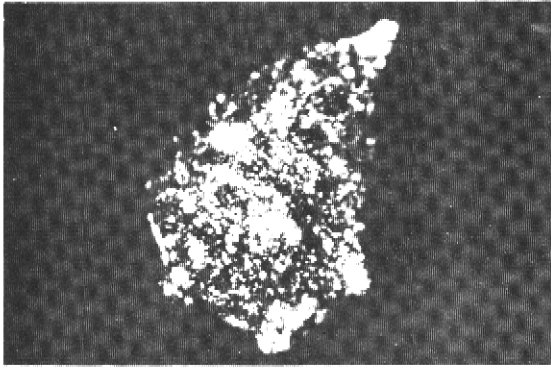


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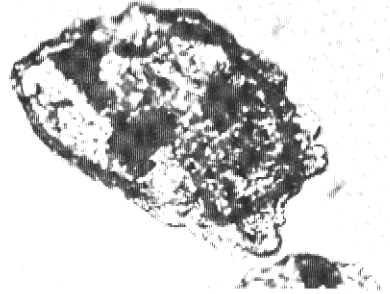


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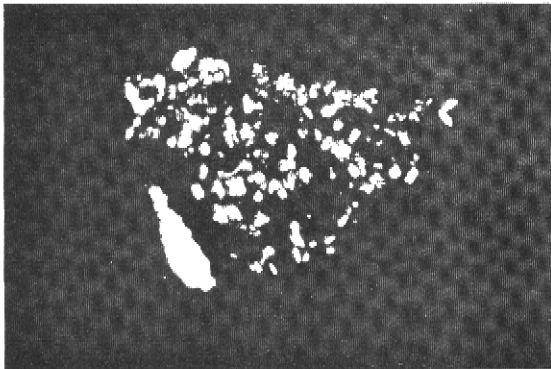
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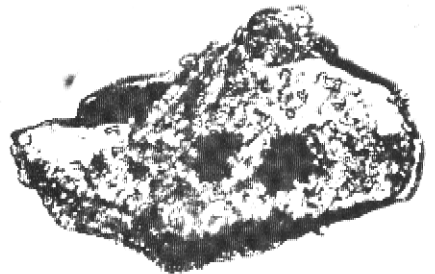
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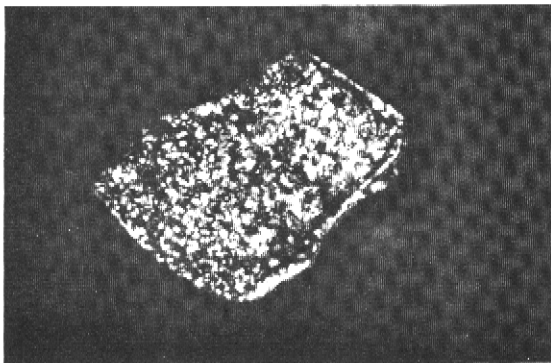
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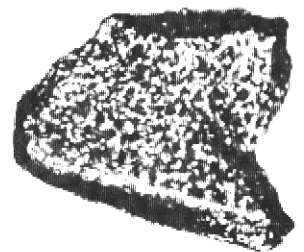
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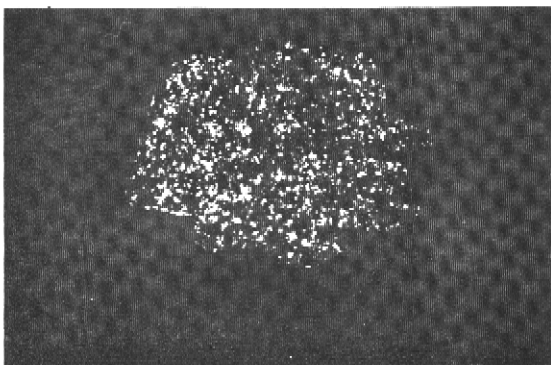
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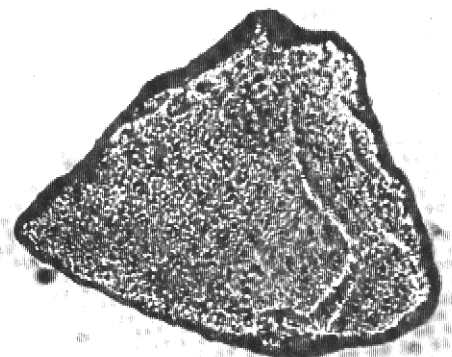
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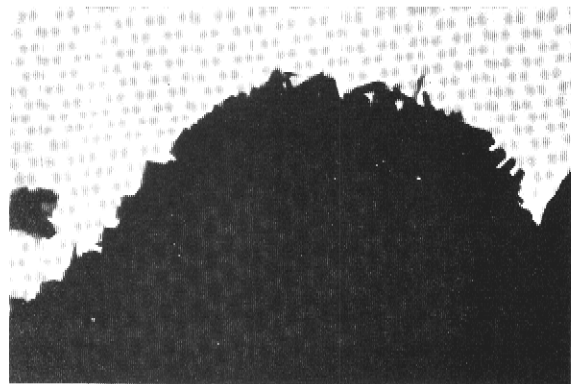
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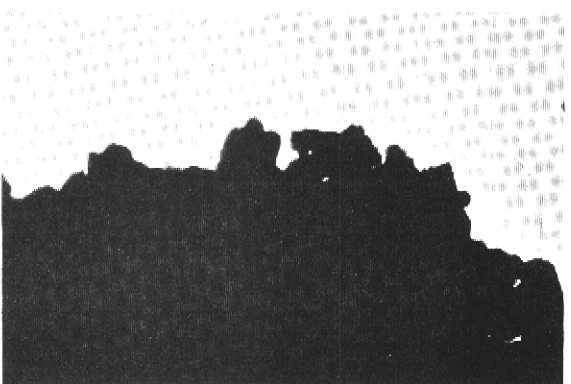
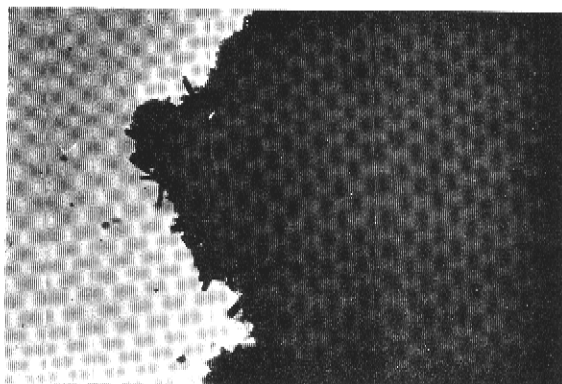
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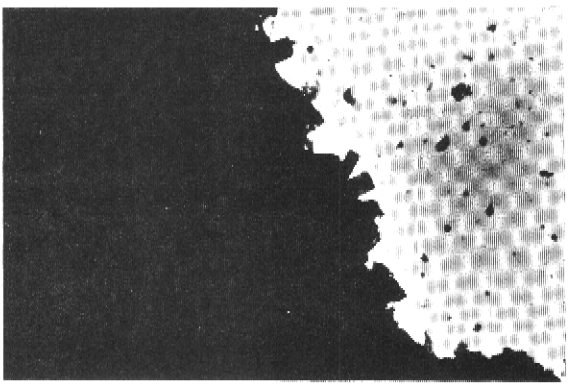
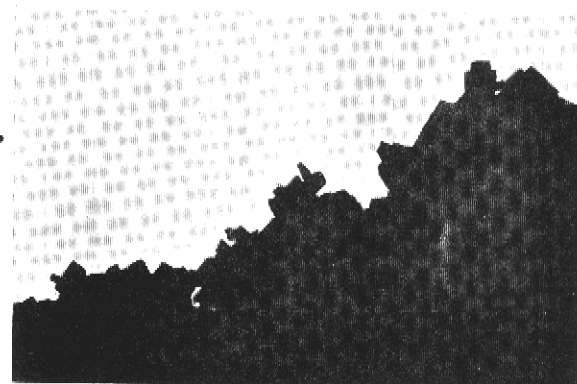
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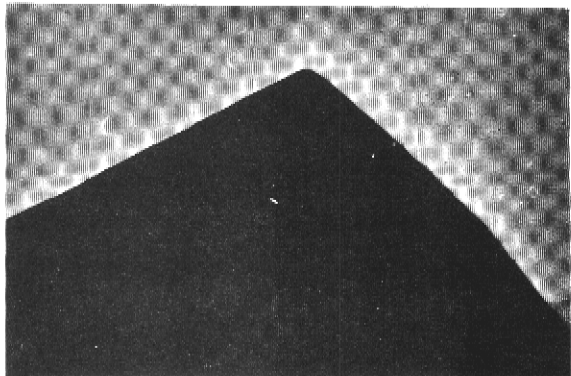
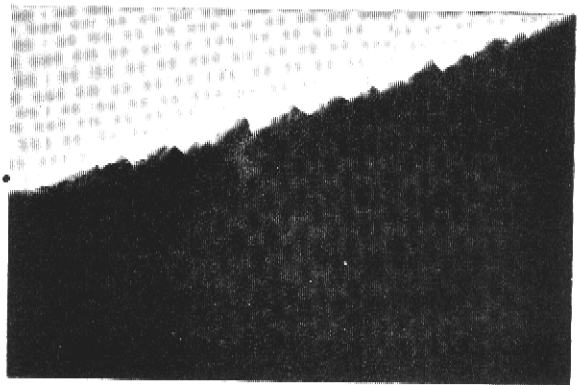
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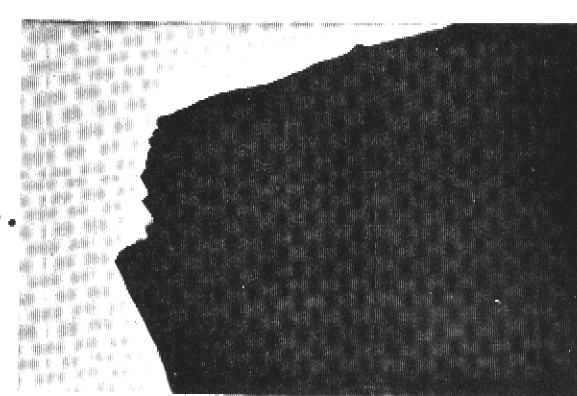
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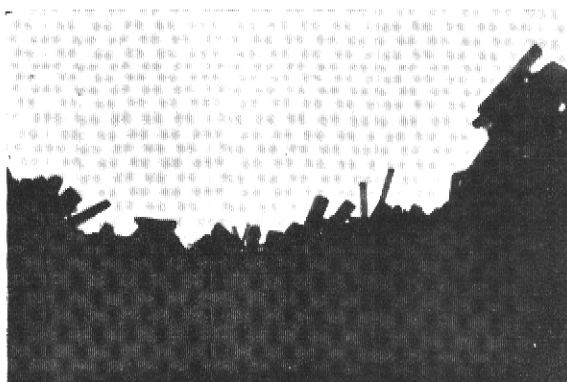


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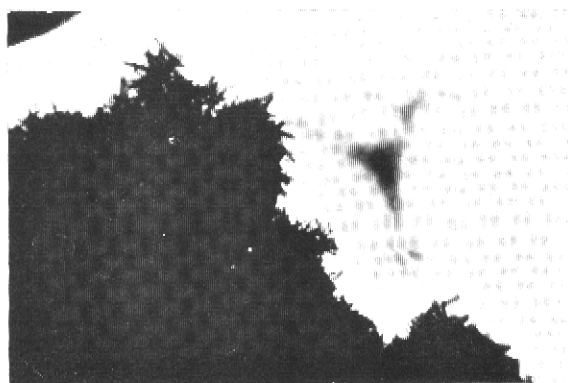
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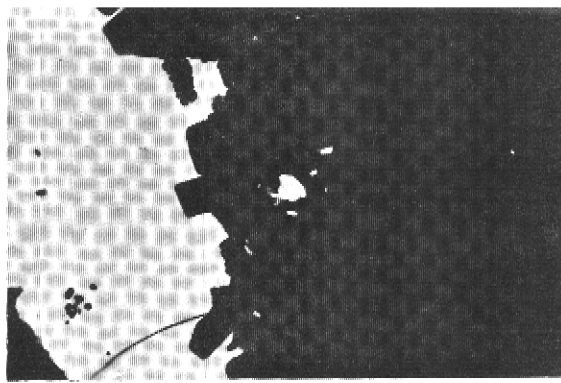
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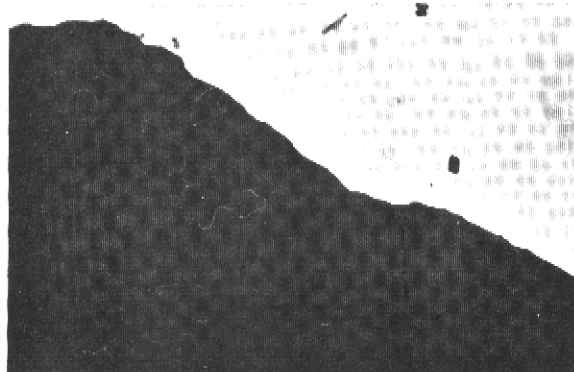
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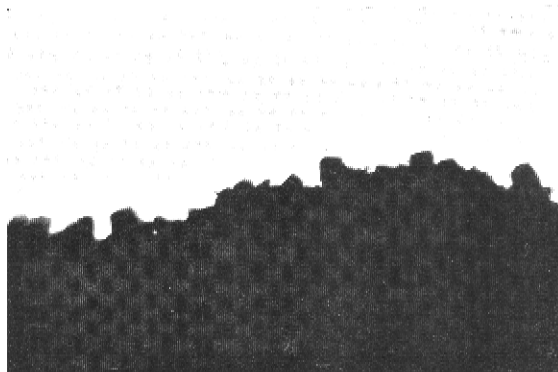
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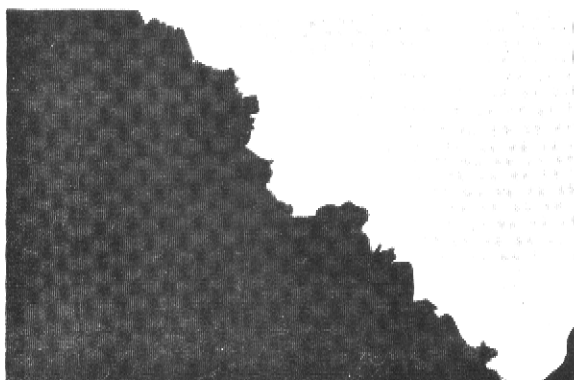
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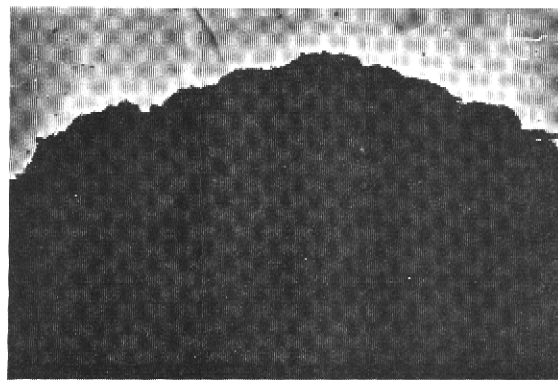
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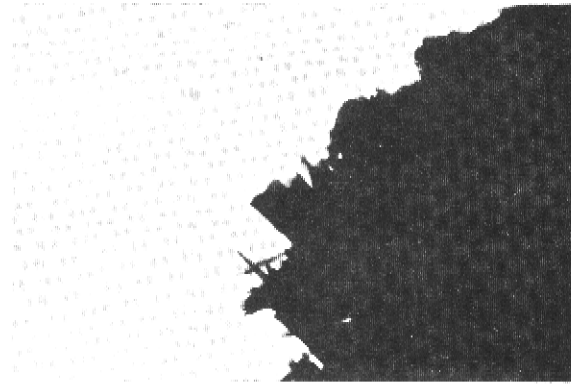
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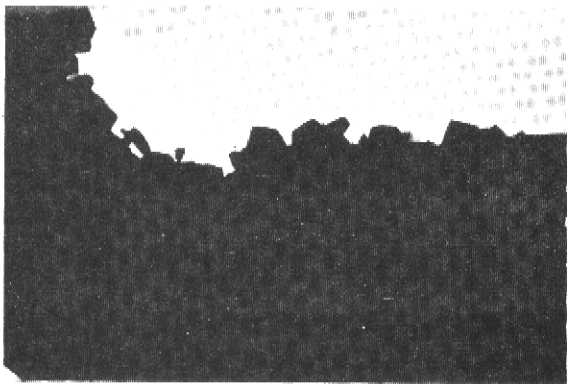
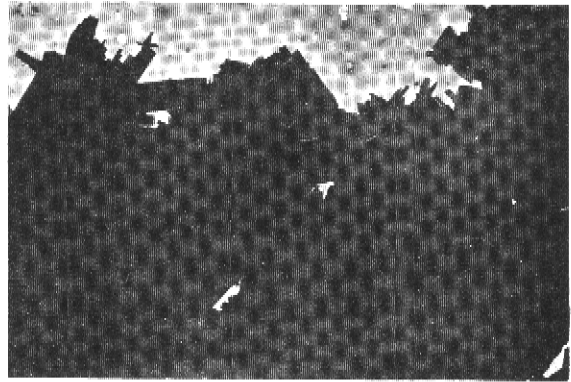
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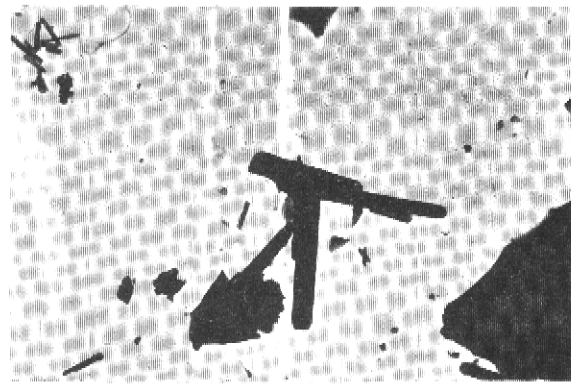
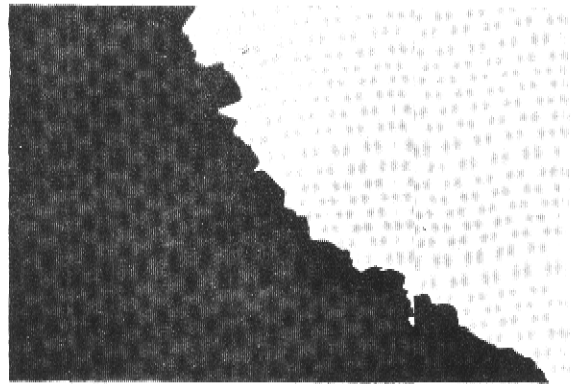
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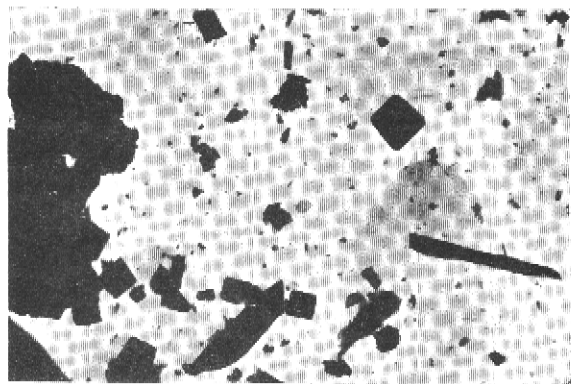
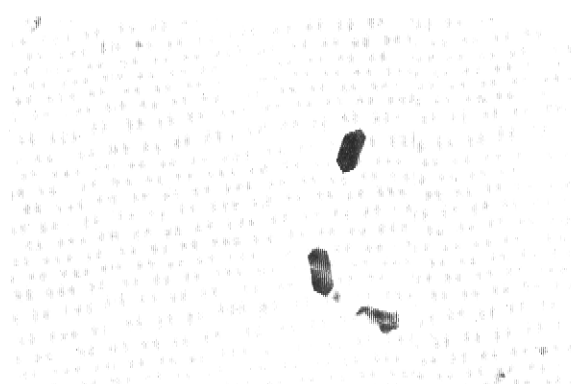
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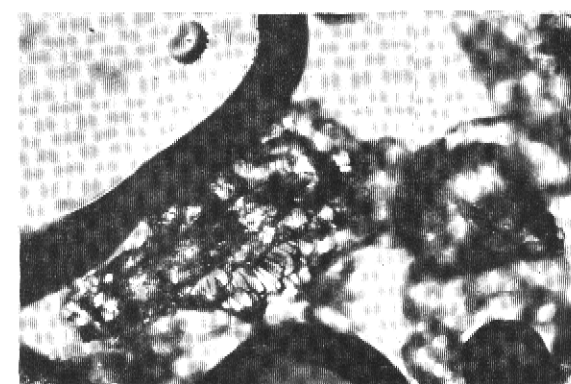
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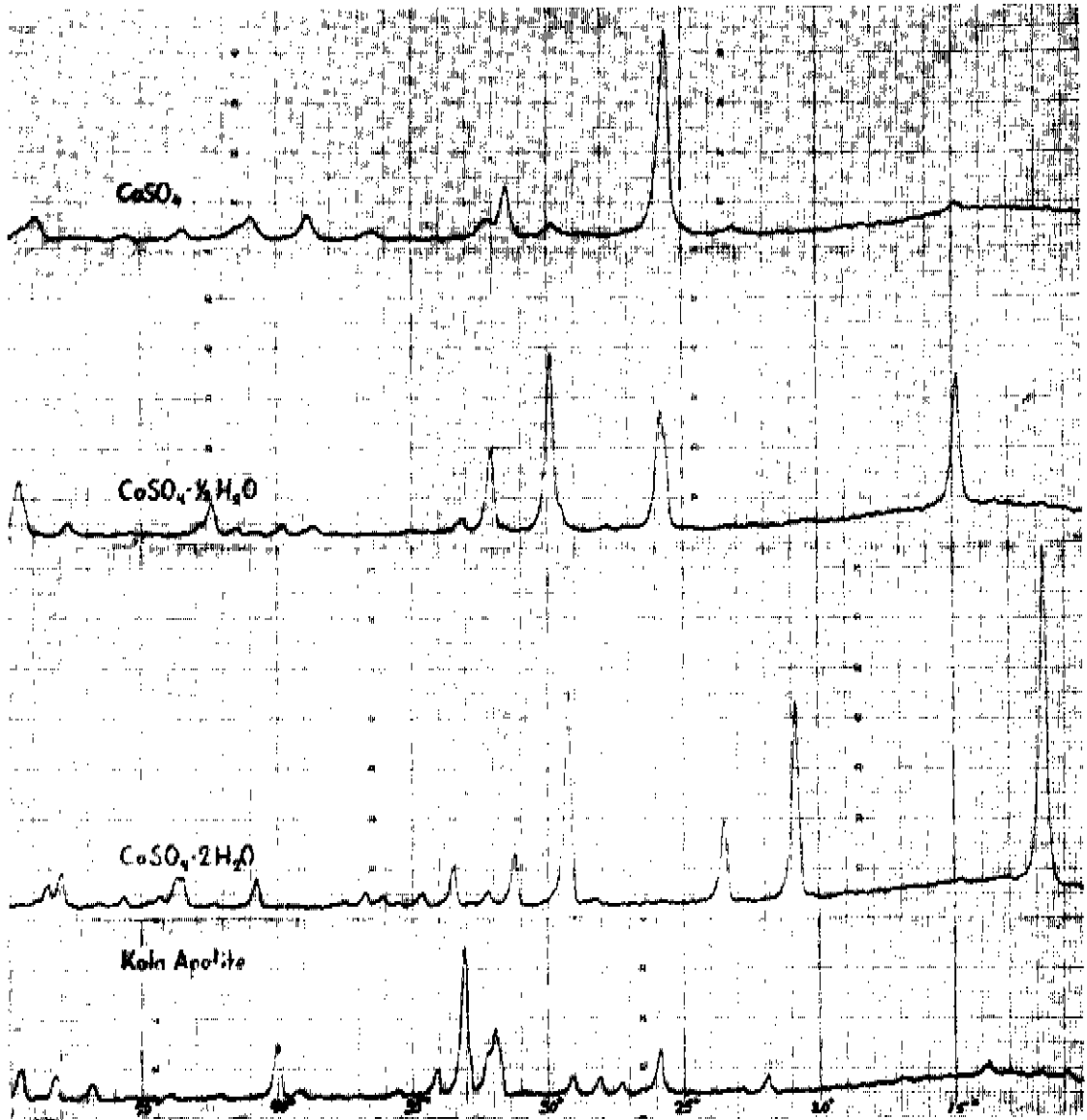
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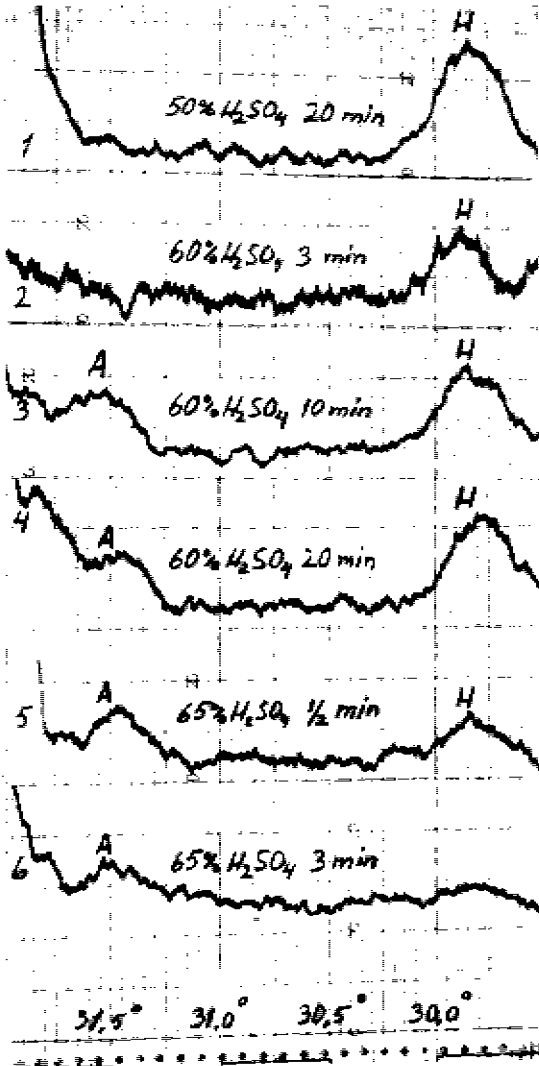


APPENDIX 9

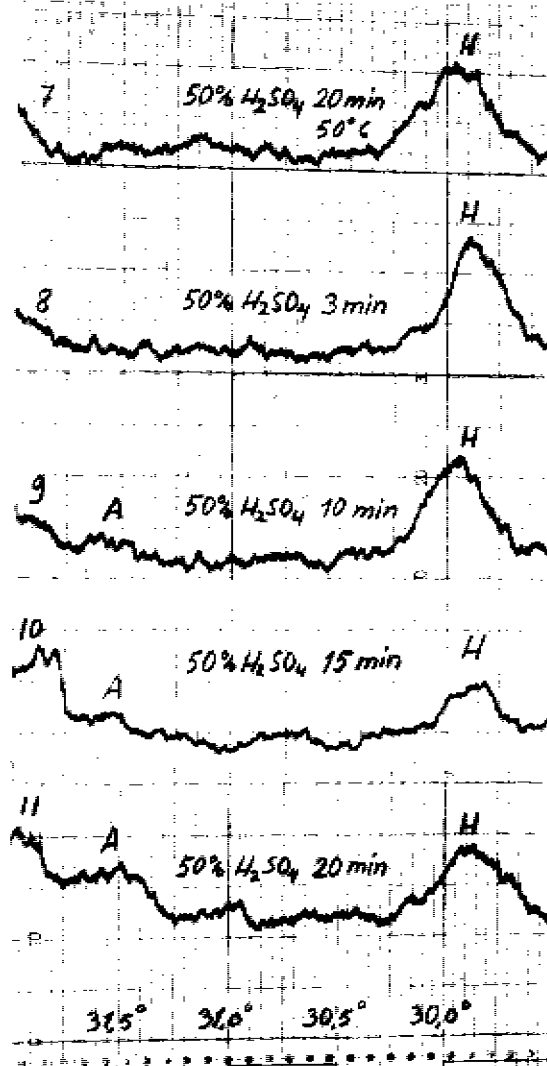


APPENDIX 10

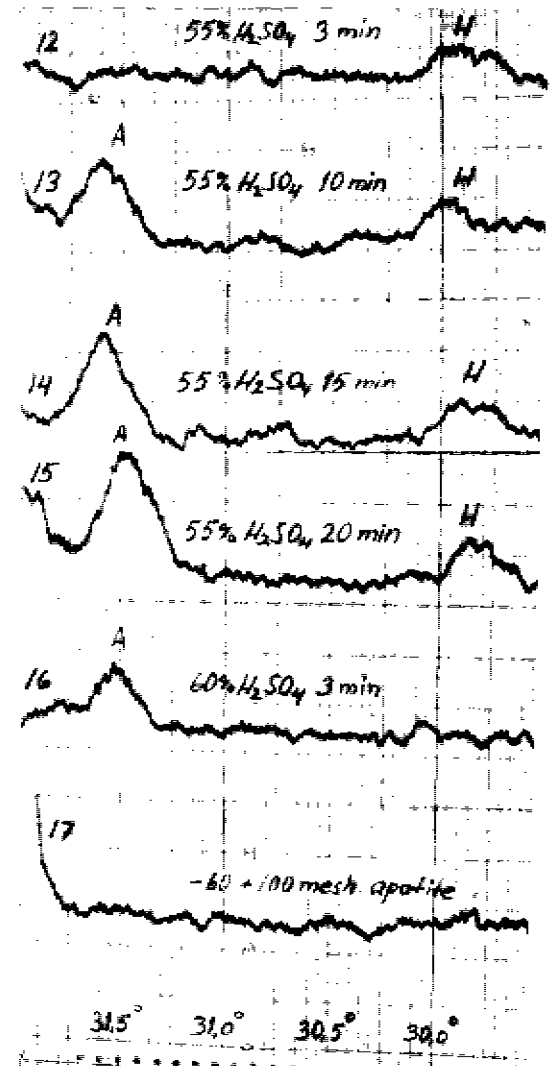
1.



2.



3.



DISCUSSION

Mr. E. AALTO (Finland) : The curing of superphosphate is a very slow process, taking weeks to approach completion. This is particularly true of superphosphate made from Kola apatite, which, in contrast to phosphorite, is a non-porous, magmatic mineral. In addition to greater than normal storage costs, the so-called apatite superphosphate has physical properties, such as high moisture content and plasticity, which cause handling difficulties. This is due to the necessity for using dilute acid to shorten the curing period. However, since Kola apatite is the main raw material of the superphosphate industry in Finland, our paper seeks to clarify the factors responsible for the low rate of conversion of apatite. As the ammoniation of the so-called rapidly cured superphosphate was considered, for the manufacture of compound fertilisers, and then a concentration of acid differing from the customary might be necessary, the solubility of Kola apatite in very dilute and very concentrated acids was studied. The problem has been extensively discussed by Russian investigators. The retardation of the conversion has been found to be due to the formation of crystalline calcium sulphate on the surface of the apatite, resulting in a smaller reactive surface. By varying the conditions during superphosphate manufacture, it is possible to alter the structure of the calcium sulphate layer and thus influence the rate of conversion. The work before you is an attempt to clarify the picture derived from the Russian reports. Solubility curves for apatite as a function of conversion time, acid concentration and reaction temperature have also been constructed.

In the solubility determinations, acetone instead of water was employed as the diluent in order to obtain a more reliable estimate of the solubility at the beginning of the reaction when unconsumed sulphuric acid is still present. The abrupt increase in the solubility as a function of time in the early stages of the reaction and the levelling of the solubility curve towards the end of the reaction clearly shows the influence of the deposition of calcium sulphate crystals on the rate of conversion. The conversion slows down most rapidly when the acid is concentrated, and the solubility is highest when the acid is dilute and hot. The curve plotting solubility

against acid concentration is at its highest with an acid concentration of 60%, after which the solubility decreases rapidly. As the coarsest particles of apatite are obviously the main reason for the long curing time of apatite superphosphate, the solubility of a sieve fraction of -60 to + 100 mesh was examined. In order to clarify the variation in solubility the undissolved apatite particles were isolated with acetone and studied by means of optical and electro-microscopy and X-ray diffractometry. Employing a polarisation microscope, it was possible to visualise the calcium sulphate layer quite clearly after the apatite crystals were made invisible by means of crossed polarising filters. The microphotographs revealed that large calcium sulphate crystals are formed under the action of dilute acid. With increasing acid concentration, the crystals became plate-like and gradually decreased in size. An interesting confirmation was that there were uncovered areas on the surfaces of insoluble apatite particles which remain when unsieved apatite is treated with 60% sulphuric acid where the solubility is at its maximum. The X-ray diffractograms revealed that the conversion of hemi-hydrate to anhydrite occurred at the surface of the apatite during the major part of the time when the apatite was dissolved at the highest rate, whereas this transition occurred either very rapidly or not at all when the solubility of apatite was low and when the apatite was covered with a dense layer of calcium sulphate crystals. In the latter case only one crystalline modification of calcium sulphate occurs during the greater part of the reaction period.

Mr. A. DAVISTER (Belgium) : In the superphosphate industry, the basic reaction is that of sulphuric acid with phosphate rock, to obtain either phosphoric acid or superphosphate. But, in fact, all those who are well acquainted with this industry know that attention is being increasingly directed to the production of calcium sulphate, which is only a by-product of this reaction, rather than to the primary finished product, which produces itself. Present in the solid state, and capable of assuming three different forms of hydration and crystallisation, this calcium sulphate does, indeed, deserve our attention. The study of its various forms, its mutations from one to the other and the equilibria which are established certainly constitute the essential basis of a better comprehension of the reactions

which we exploit. European superphosphate producers, who are represented fairly well in this meeting, are not greatly concerned with these problems in relation to the production of single superphosphate, for they generally use phosphate rocks which are easily dissolved. Our Finnish hosts, on the contrary, are used to dealing with Kola apatite to manufacture single super, and all those among us who have tried to do this know that it raises delicate problems. This is the reason for the work of Mr. Aalto and Dr. Vahervuori. They have not hesitated to attack the problem by the most powerful means at the disposal of scientific research, namely electronic microscopy and X-ray diffraction. Their well-designed paper will, I am sure, have an honoured place in the library of all who are concerned with finding better working conditions for the industrial operation of the reaction between sulphuric acid and phosphate rock.

I should like to put the following questions to Mr. Aalto. Have you been able to make practical use of the main conclusion in your paper, namely the fact that maximum solubility of the apatite is obtained in the presence of a 60% sulphuric acid?

Have you been able to satisfy yourself that the crystals present on the surface of the apatite grains are, indeed, calcium sulphate and not another salt possibly containing calcium sulphate?

You have proved that the calcium sulphate evolves from the semi-hydrate state in which it is precipitated to the anhydrite state. Have you observed any correlation of this phenomenon with the superphosphate setting period? In connection with this, what are the durations of the mixing stage, on the one hand, and the denning stage on the other?

One final question: what is the duration of the curing period in storage, which is normally adopted for superphosphate produced from Kola rock, and, after this curing, what is the average water-soluble or water-and-citrate-soluble P_2O_5 analysis of this superphosphate, according to your own sales basis?

Mr. AALTO : We have not yet been able to apply the 60% acid giving maximum apatite solubility. We are currently using 65% acid, because if we use a more dilute acid we obtain a product with poor physical properties. However, we hope to be able to use more dilute

acid considering the direct ammoniation of the acidulation slurry.

With regard to the crystals deposited on the surface of the apatite particles, we can see from the X-ray diffractograms the characteristic diffraction maxima of the pure forms of calcium sulphate, as is shown in Appendix 10 of the paper. We have tried these diffractograms of undecomposed apatite in the whole range of 10° - 50° and established the same diffraction maxima. Secondly, we can exclude the possibility of, for example, monocalcium phosphate, because free sulphuric acid is present in the early stages of the reaction. Similarly, we can exclude the possibility of the double salt of calcium sulphate and dicalcium phosphate for the same reason.

The third question concerned the setting of superphosphate. I think the main cause of setting is the crystallisation of monocalcium phosphate, because superphosphate crystallises after all free sulphuric acid has been consumed. I do not think calcium sulphate has much to do with this aspect. The mixing time in our Moritz-Standaert mixer is half a minute, and the reaction time in our Moritz-Standaert den is about 60 minutes. The curing time of our superphosphate is 4 - 6 weeks, and after this period 95% of the P_2O_5 is in water soluble form, and about 97% is soluble in ammonium citrate.
