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STUDIES OF THE REACTION OF CRYSTALLINE CALCIUM CARBONATE WITH AQUEOUS SOLUTIONS OF NH_4F, KF and NaF

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SUMMARY

The reaction between solid calcium carbonate and the aqueous fluorides NH_4F, KF, and NaF has been completely investigated. The reaction of $CaCO_3$ (solid) is completely independent of the dimensions of its polycrystalline particles and gives calcium fluoride. The calcium fluoride is formed in the same form and size as the grains of the original calcium carbonate. A course crystalline fluorite is formed at a satisfactory rate and with a sufficiently high mechanical strength to be of industrial interest.

The course of the reaction appears to involve penetration of the fluoride solution into the body of a grain through voids which develop in the solid material owing to the formation of polycrystalline CaF_2 with a different molar volume as compared with $CaCO_3$. Data were obtained on the rate of formation and nature of the fluorite formed.

The fluorite which is formed around the dissolving calcite was shown by X-ray diffraction and electron microscopy to have a polycrystalline aggregated structure and an estimate is made of crystallite size.

The fluorite grains are pseudomorphs of the calcite crystals and there is crystallographic orientation of the product with respect to the parent phase.

INTRODUCTION

In a patent literature [1-4] the reaction of calcium carbonate with solutions of NH_4F, NaF and KF which gives CaF_2 and the corresponding carbonates [$(NH_4)_2CO_3$, Na_2CO_3 and K_2CO_3] has been mentioned but without consideration of any theoretical aspects of the reaction. The reaction may be expressed as follows :

$$CaCO_3 + 2F^- \longrightarrow CaF_2 + CO_3^{2-}$$

During the reaction the hexagonal calcite (d 2.711) is converted into cubic fluorite (d 3.180) with a 27% volume change.

We examined the reaction between calcium carbonate and solutions of NH_4F and KF with the aim of developing a method for the manufacture of synthetic fluorite and potassium carbonate. During our investigations we encountered the interesting phenomenon of the transformation of calcite into fluorite occurring deep inside fairly large granules. It was shown that a carbonate granule is converted into a fluorite granule whilst preserving the original shape and volume and that under the same conditions the rate and manner of the reaction are favourable from a technical viewpoint.

We, therefore, set out to make a complete investigation of this reaction. We made the basic assumption thatfor the reaction to occur there must be free penetration of the fluoride salt solution into the interior of the solid.

As the grain volume remains constant during the reaction and as the molar volume of fluorite is much smaller than that of calcite, it could be inferred that the reaction product is of high porosity. A fast reaction rate suggested that the voids in the fluorite product are best characterised as channels of sufficient permeability for the reaction solution to reach calcite phases situated deep inside the grains. As a basic condition for the formation of voids, a polycrystalline character was assumed for the fluorite phase.

EXPERIMENTAL

The course of the reaction with time

The rate of the conversion of calcium carbonate into fluorite was followed by analytical determination of fluoride ion concentration in the solution at intervals.

The reaction was carried out by using two different calcite materials, viz. (a) a precipitated $CaCO_3$ (Anal. grade) having a particle size smaller than 0.03 mm, and (b) a very fine limestone mineral with a grain size of 0.4 to 0.6 mm (impurities SiO_2 0.25%, Al_2O_3 + Fe_2O_3 0.15%).

For the reaction of precipitated calcium carbonate, solutions of 0.55 M KF, NH_4F and NaF were used. Reactions were carried out in thermostatted 0.5 dm^3 round-bottomed flasks using 0.25 dm^3 portions with mechanical stirring. The reactions were held at 20^o and were complete in several hours.

For the study of the limestone reactions particles with a grain size of 0.4 - 0.6 mm were used and solutions of 6 M KF or NH_4F, or solutions containing 1:2 KF and NH_4F were applied. The reactions were conducted in round-bottomed flasks fitted with a stirrer, and a reflux condenser. The flasks were immersed in a bath of boiling water and the water in the reflux condenser was maintained at ca. 80^oC. Under these conditions evaporation of water from the system was negligible whilst ammonium carbonate was practically completely removed. The experiments were started by introducing into a flask 76 g calcium carbonate and 0.25 dm^3 solution at 90^oC. As in the first series the conditions employed ensured a slow decrease in fluoride ion concentration over several hours.

The reaction between mineral $CaCO_3$ and a KF solution was run at 100°; the reaction with NH_4F solutions was carried out by varying the temperature continuously from 75 to 98°C.

Observations on the formation of fluorite in particular grains

In experiments completed in this field particular monocrystals of calcite with dimensions up to 10 mm were processed under reflux conditions with a 6 M solution of NH_4F mol/dm^3 at about 98°C for many hours. Particular granules, after removal from the reaction solution, were cut and then etched with hydrochloric acid in order to decompose unreacted calcium carbonate and to form fluorite material free from calcite.

Examination of the fluorite-phase

The surface of the fluorite phase formed in the reaction was examined by using a scanning electron microscope (JEOL type ISN-33) at magnifications of 20 to 60000. Material obtained from 3 to 5 mm calcite crystals reacted with 6 M NH_4F solution for 10 hours were examined. Material prepared by the action of NH_4F solutions for 15 hours on a 20 mm calcite monocrystal were examined by X-ray diffraction. The monocrystal of calcite was partly immersed in HCl solution so that one half of its surface was freed of calcite.

The X-ray analysis of both the reacted and unreacted part was performed with a Rigaku-Denki Model D-3F diffractometer with a Cu-anode and a Ni-filter. A monocrystal was set in the goniometer in such a way that the diffraction surface was the plane (1011).

RESULTS AND DISCUSSION

The course of the reaction with time

The experiments described here were carried out for the two systems both under slow running conditions at 20°C and fast running conditions at ca. 100°C. Either active precipitated calcium carbonate with a grain size of about 0.03 mm or high purity mineral limestone with 0.4 to 0.6 mm grains was used. The concentration of the fluoride solutions and temperatures were selected so that the whole reaction took place over several hours. The courses of the reactions between precipitated calcium carbonate and 0.55 M solutions of KF, NaF and NH_4F at 20°C are shown in Fig.1.

Curve 1 relates to the ammonium fluoride, while curve 2 describes the course of the reaction in two systems, the first containing NaF and the second containing KF. The reaction rates of KF and NaF are basically the same, whilst with NH_4F

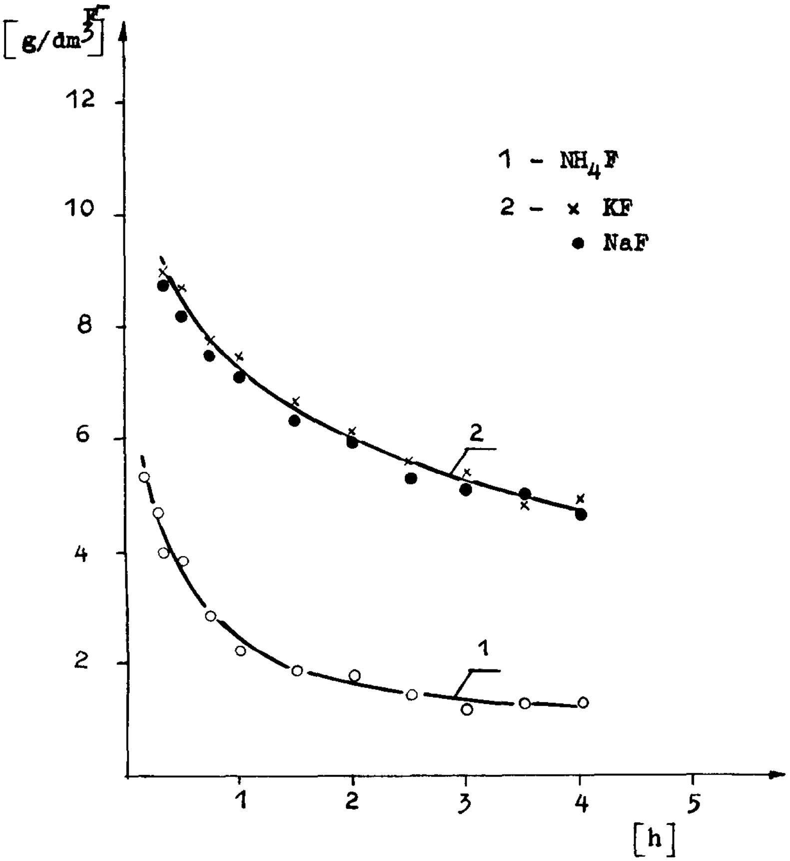

Fig.1. The course of the reactions of $CaCO_3$ with NH_4F (1), KF (2) and NaF (2) solutions. $CaCO_3$ grain size <0.03 mm.

the rate is much greater. Curves 1 and 2 tend ultimately to the fluoride concentrations of 0.3 and 1.0 g/l, respectively. These values were determined by adding to the systems amounts of calcium carbonate which according to stoichiometry exceeded by 20-fold the final concentration of fluoride ion remaining in solution. The values of fluoride ion concentrations in solution, given above, were taken as determining the static limits of the reaction.

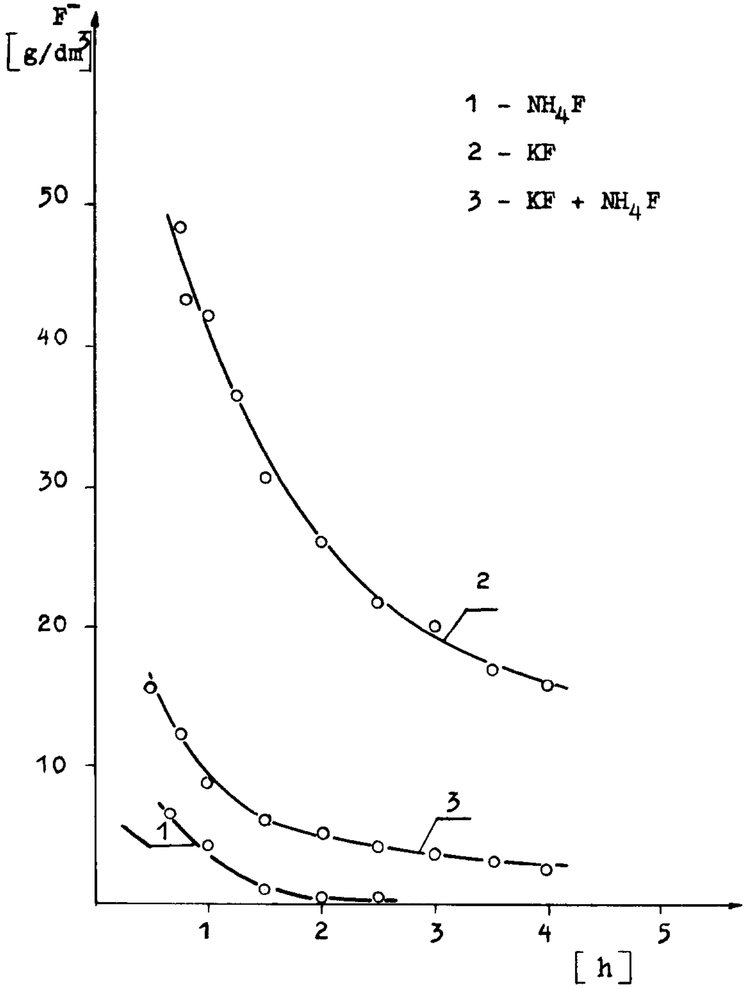

Fig.2. The course of the reactions of $CaCO_3$ with NH_4F (1), KF (2) and NH_4F + KF (3) solutions. $CaCO_3$ grain size, 0.4 - 0.6 mm.

The results for mineral $CaCO_3$ at 100^o are given in fig.2. Curve 1 relates to the system containing NH_4F, curve 2 to KF and curve 3 to the 2:1 mixture of NH_4F and KF.

By comparison with runs from fig.1, the greatest differences are observed in the reaction rates for the NH_4F system (curve 1) and the KF (curve 2). It is noteworthy that this is in spite of the fact that the reaction in the first system was run at a lower temperature than the second. It can be assumed that the reason for an especially fast reaction in the NH_4F systems is not only dependent upon the cation but also because of evaporation of $(NH_4)_2CO_3$ from the solution. The curves presented in fig.2 show technical possibilities and conditions for carrying out, within several hours, the reaction of NH_4F and KF with mineral coarse-grained calcium carbonate using solutions of fluoride salts at realistic strengths and calcium carbonate grains of sizes ranging from 0.4 to 0.6 mm which are favourable for the separation of fluorite from solution. The best conditions involve use of NH_4F in the reaction but conditions are also good with a 2:1 mixture of NH_4F and KF which is easily attained by hydrolysis of K_2SiF_6 with ammonia.

The transition of calcium carbonate into fluorite

The gradual transition of calcite into fluorite is demonstrated in fig.3, which shows three partially reacted grains after their removal from the reaction solution, cutting and digesting with hydrochloric acid. The white layer, resistant to hydrochloric acid, is the fluorite phase while the voids correspond to calcite which had not yet reacted with fluoride solution and was dissolved in hydrochloric acid. The thickness of the fluorite layer is dependent on the time that the grain was held in fluoride solution, its concentration, and temperature. With a longer operating time the calcium carbonate finally disappears.

The fluorite grains formed in the reaction are very strong although less so than calcite. If the process is continued with strong stirring after completion of the reaction, fluorite

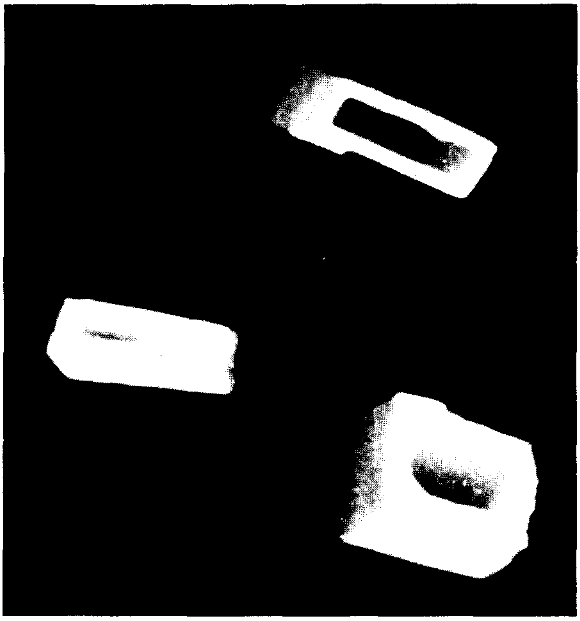

Fig.3. Image of the fluorite phase in a partially reacted calcite monocrystal of dimensions several mm.

undergoes abrasion and is converted into a rather stable suspension which is only filtered with difficulty. For such reasons the best way of carrying out the reaction would be to pass the fluoride solution through a bed of calcium carbonate grains under which conditions the fluorite will not disintegrate to fine material.

The nature of the fluorite phase

The views of fractures of the partially reacted calcite monocrystals obtained with a scanning electron microscope are shown in figs.4a-d.

Fig.4a presents, at low magnification, a fracture showing clearly the division boundary between the calcite phase (the dark area) and the fluorite phase (the light area). 2000 Times magnification (fig.4b) shows a polycrystalline fibrous

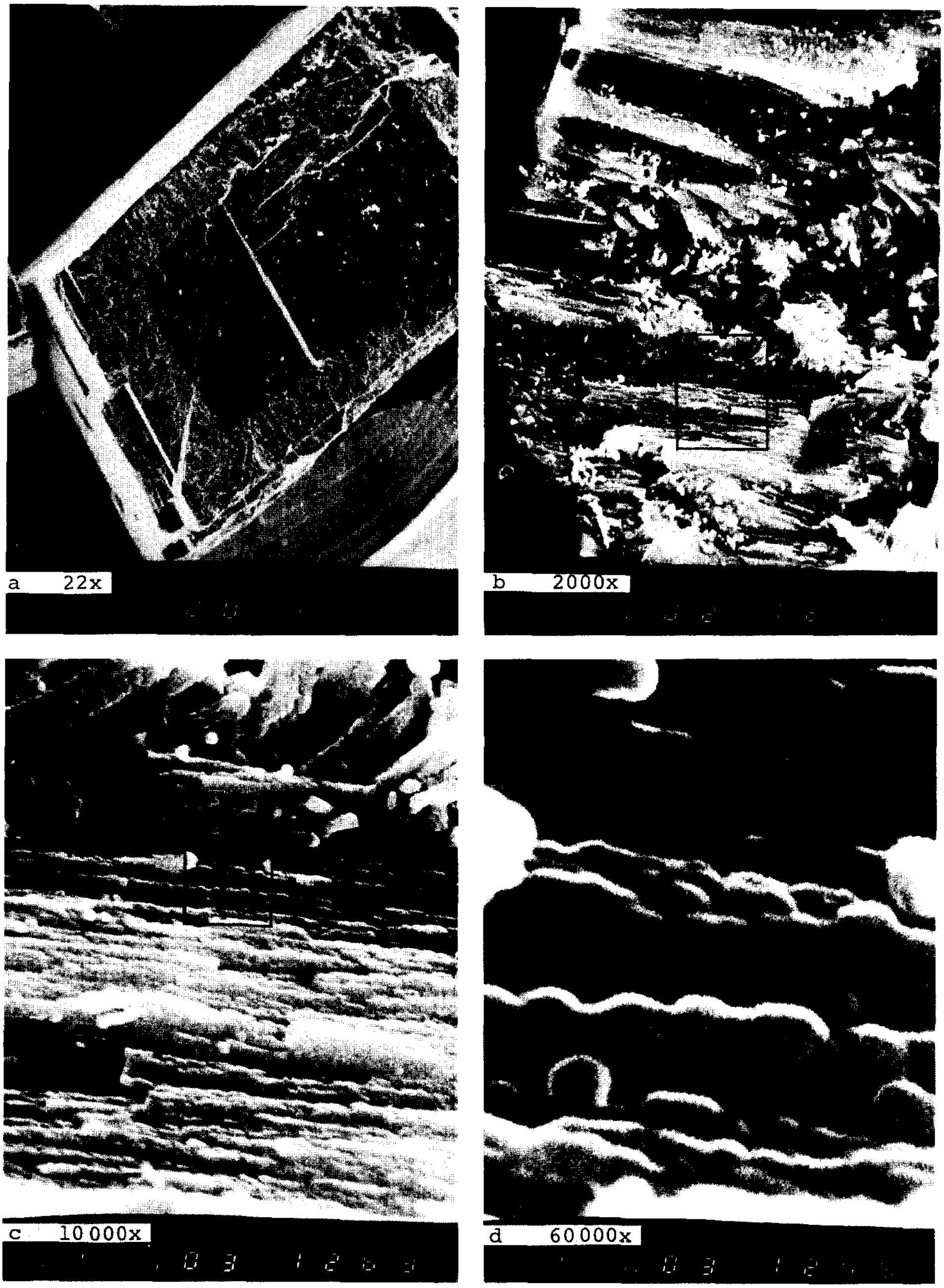

Fig.4. Image of the fracture of a partially reacted calcite monocrystal. Scanning microscopy. Magnification a - 22 x, b - 2000 x, c - 10000 x, d - 60000 x.

texture in which the fibre orientation is perpendicular to the calcite cleavage plane. Greater magnifications (fig.4c and 4d) reveal details of the polycrystalline structure of fibrous aggregates of CaF_2 grains forming the calcite pseudomorphs.

The arrangement of the fibrous aggregates of the fluorite crystallites observed, points to crystallographic orientation of the fluorite lattice related to the calcite parent lattice (observed also from the X-ray diffraction pattern of the calcite pseudomorph).

The fluorite fragment shown in fig.4a was observed parallel to the polycrystalline fibrous aggregates (also parallel to the direction of the reaction developing inside a grain) (figs.5a and 5b at 10000 and 26000 magnification).

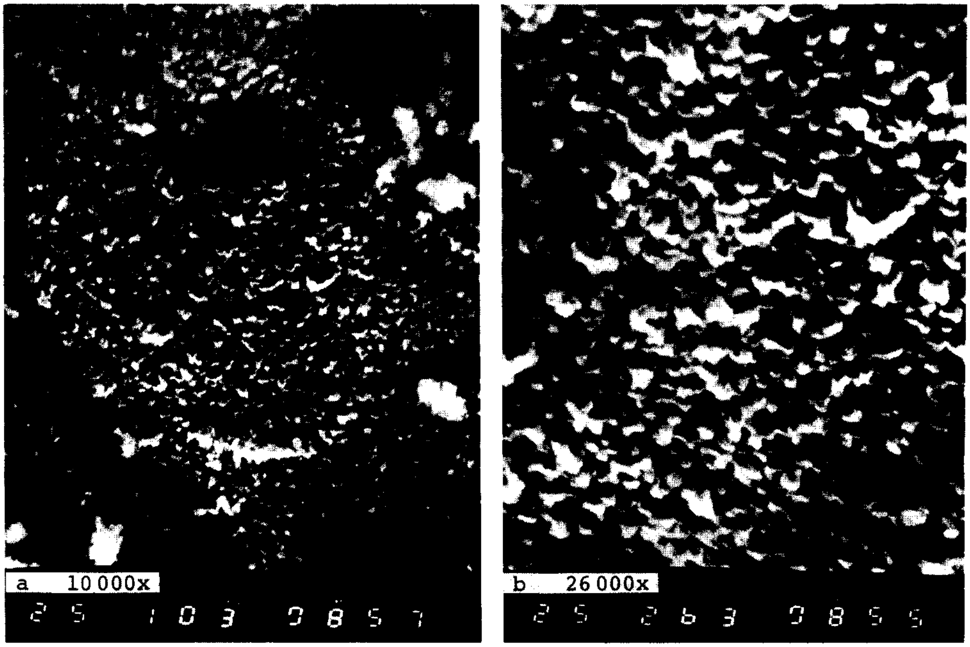

Fig.5. Image of the surface of the fluorite phase perpendicular to the surfaces presented in Fig.4. Scanning microscopy. Magnification a - 10000 x, b - 26000 x.

There can be seen separate frontal sections of the polycrystalline fibrous cubic fluorite aggregates as well as free spaces between them ensuring a permanent solution contact with the carbonate phase.

The X-ray diffraction patterns of the partly reacted calcite monocrystals are shown in fig.6. The diffraction

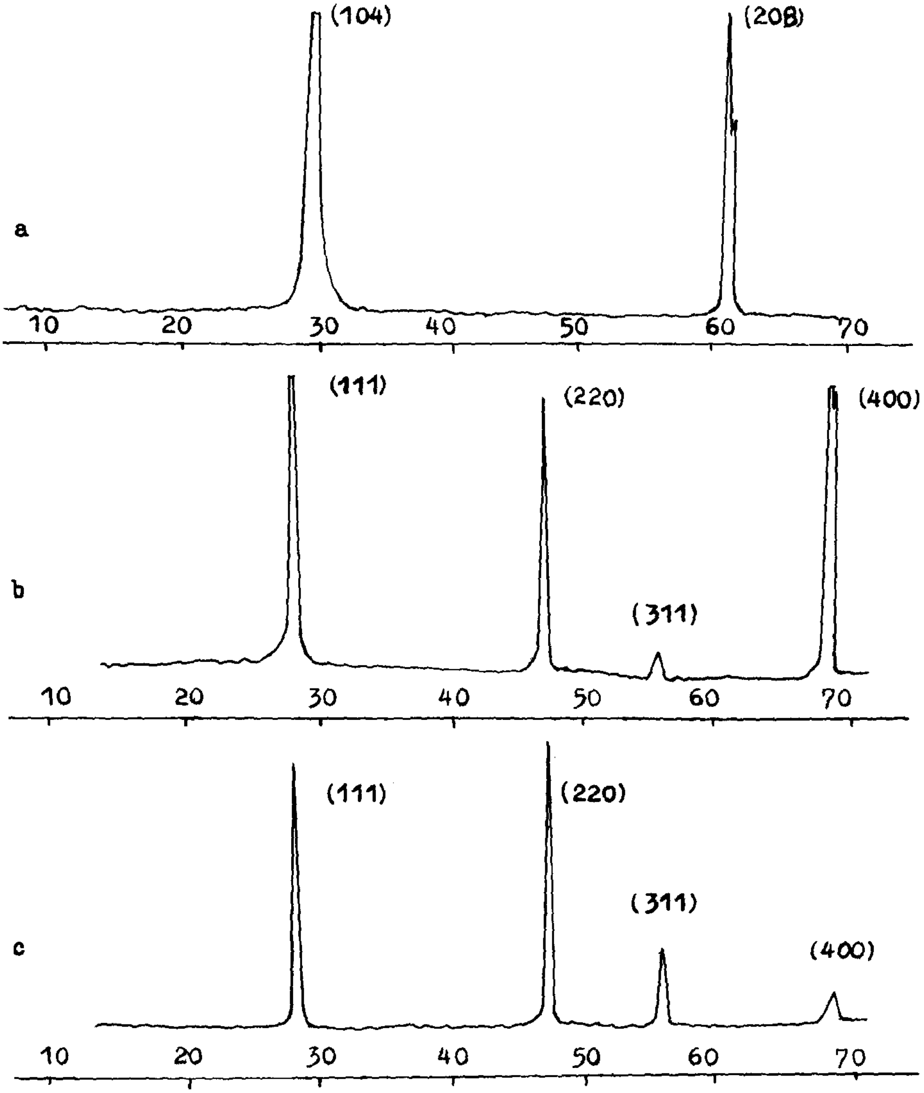

Fig 6. The X-ray diffractograms. a) calcite monocrystal, b) pseudomorphosic CaF_2 with a texture effect, c) standard CaF_2.

pattern of the unreacted face (fig.6a) is a typical monocrystal image. The crystallographically identical reactive fluorite face shows the polycrystalline material with a strong textured effect (fig.6b) indicating the relation between the product structure and that of the parent phase.

The broadened (220) diffraction line allowed determination of the size of the calcium fluoride crystallites. Crystallite sizes were determined using the approximation method of a diffraction line and a function of the $(1 + k^2x^2)^{-2}$ type. They were found to be within the range 300 to 350 Å (0.030 to 0.033 μm).

The formation of phases of particular structural orientation in these aqueous reactions does not parallel the similar formations of ordered phases in thermal decomposition reactions.

REFERENCES

1 US Patent 1,776,064
2 US Patent 3,357,788
3 Germ. Patent 568,207
4 USSR Patent 109043.