

The Inhibiting Effect of Scandium Ions upon the Dissolution of Calcium Fluoride

I. NESTAAS and S. G. TERJESEN

Chemical Engineering Laboratory, Technical University of Norway, Trondheim, Norway

This paper describes the results of experiments carried out in order to investigate the inhibiting effect of Sc^{3+} upon the rate of dissolution of fluorite.

Sc^{3+} added in concentrations as low as 2.42×10^{-8} M was found to inhibit the dissolution. Simultaneous addition of F^- strongly increased the inhibition. The adsorption of Sc^{3+} on the surface of the fluorite was measured by means of the radioactive isotope ^{46}Sc . Less than 4.5 % of the solid surface were covered by Sc^{3+} , indicating that the adsorption takes place on particular surface sites controlling the rate of dissolution. The reduction in rate of dissolution caused by the inhibitor was, at low concentrations of CaF_2 , found to be proportional to the amount of Sc^{3+} adsorbed.

The experiments described in a previous paper¹ have shown that the inhibiting effect of several ions upon the dissolution of fluorite is connected with adsorption of the inhibitors on the surface of the dissolving mineral, or in the stagnant liquid layer very close to it. A deeper understanding of the nature of the inhibiting effect thus requires knowledge of how this adsorption takes place. The purpose of the current paper is to describe the results of experiments where fluorite was dissolved in presence of ScCl_3 containing ^{46}Sc . Sc^{3+} is a highly efficient inhibitor of the dissolution of fluorite, and the radioactive isotope ^{46}Sc is very convenient as a tracer.

Sc^{3+} and F^- in aqueous solutions form stable complexes of the type $\text{ScF}_n(\text{H}_2\text{O})_{6-n}^{3-n}$ with n ranging from 0 to 6. The stability constant K_n of these complexes is defined as

$$K_n = \frac{[\text{ScF}_n(\text{H}_2\text{O})_{6-n}^{3-n}]}{[\text{ScF}_{n-1}(\text{H}_2\text{O})_{6-(n-1)}^{3-(n-1)}][\text{F}^-]}$$

where [] denotes concentration. The total stability constant β_6 for the system is defined as

$$\beta_6 = K_1 \cdot K_2 \dots K_6$$

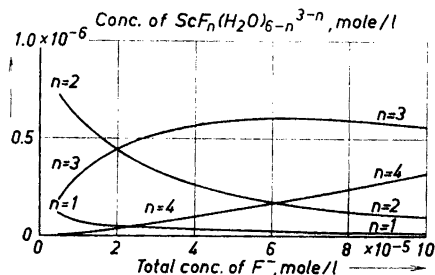


Fig. 1. The concentrations of different complexes of the type $\text{ScF}_n(\text{H}_2\text{O})_{6-n}^{3-n}$ as functions of the total concentration of F^- . The total concentration of Sc^{3+} is 10^{-6} M.

According to Bjerrum *et al.*² the stability constants at 25°C and infinite dilution are $K_1=1.2 \times 10^7$, $K_2=6.3 \times 10^5$, $K_3=2.8 \times 10^4$ and $K_4=3 \times 10^3$. The values of K_4 are considered uncertain. Assuming that $K_5=10^2$ and $K_6=10$, it is possible to calculate the equilibrium concentrations of the different complexes present in aqueous solutions of CaF_2 containing Sc^{3+} .

Fig. 1 shows that when 10^{-6} M ScCl_3 is added to the solution, practically no free Sc^{3+} is present. At a total fluoride concentration of 10^{-4} M, 97 % are present as F^- . In a solution containing 10^{-5} M ScCl_3 and 2×10^{-5} M fluorides, only 15 % of the fluorides are F^- . The results of the calculations are relatively insensitive to the values assumed for K_5 and K_6 . It should, however, be noted that according to Wilson *et al.*,³ some metal ions forming complexes with F^- need weeks to reach equilibrium.

The relative concentrations of Ca^{2+} and F^- in a solution of CaF_2 may thus be significantly changed by addition of Sc^{3+} ions. This change causes unpredictable effects in the kinetics of dissolution of fluorite and in the electrical conductivity of the CaF_2 -solutions. To avoid these complications, all experiments were carried out with addition of 10^{-6} M ScCl_3 or less.

EXPERIMENTAL

Dissolution of fluorite. Particles of fluorite were dissolved in distilled water in a cylindrical vessel equipped with a stirrer, 4 baffles and a thermostat. The concentration of CaF_2 as a function of time was determined partly by removing liquid samples and titrating with EDTA and partly by measuring the electrical conductivity of the solution. No changes in experimental conditions, procedures or methods of calculation were made from those described in the previous paper.¹

Adsorption of Sc^{3+} . The material used in the experiments was prepared from spectroscopically pure $\text{ScCl}_3 \cdot 6 \text{H}_2\text{O}$, subjected to a flux of 10^{12} neutrons per square centimeter per second for 133 h. A gamma spectre of the activated material showed no contamination from other radioactive isotopes. The concentration of Sc^{3+} in a standard solution made from the activated material was determined by titration with EDTA according to a procedure described by Welcher.⁴

Known amounts of the standard solution were added to the distilled water in the vessel prior to the introduction of fluorite particles.

The amounts of Sc^{3+} adsorbed on the fluorite were determined by sucking small samples of particles and solution from the vessel into a pipette. Its contents were then distributed between two small test tubes, a mixture of particles and solution in one and a clear solution in the other. The amounts of radioactivity in the test tubes were determined by placing them in the well of a thallium-activated NaI crystal, mounted in a lead tower and attached to a scintillation counter. By a procedure of weighing and drying

it was possible to correct the radioactivity of the fluorite particles in the tubes for the error arising from the small amounts of Sc^{3+} contained in the solution clinging to them. Knowing the specific surface of the particles, the number of moles of Sc^{3+} adsorbed per square centimeter of fluorite surface was then readily calculated.

RESULTS

Kinetics of dissolution. Fig. 2 shows the concentration of CaF_2 as a function of time for experiments with varying amounts of ScCl_3 added. Concentrations measured later than 250 min after the beginning are not shown because of the very low rates of dissolution in this region. The rate of dissolution as a function of the concentration of CaF_2 for the same experiments is shown on Fig. 3. The values have been corrected for variations in area of particles caused by the removal of samples. The curves differ from the corresponding curves of the previous paper¹ in that they are drawn to fit the points representing the lower rates, not as straight lines ending at the apparent equilibria. When drawing the curves it was assumed that the initial rate of all experiments is unaffected by the presence of inhibitor.

An experiment with 2.57×10^{-7} M ScCl_3 and 9.6×10^{-5} M CaCl_2 added showed slightly lower rates of dissolution than an experiment with 2.66×10^{-7} M ScCl_3 ; the initial rate was not affected. The results of this experiment are not shown.

Simultaneous addition of 2.56×10^{-7} M ScCl_3 and 5×10^{-5} M BaF_2 inhibited the dissolution far more than did any of the two agents added separately. It reduced the initial rate of dissolution to approximately 4 % of the value

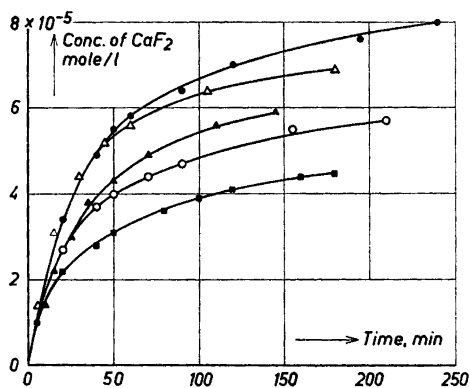


Fig. 2. The concentration of CaF_2 as function of time.

●: Pure water. Δ : 2.42×10^{-8} M ScCl_3 . \blacktriangle : 1.03×10^{-7} M ScCl_3 . \circ : 2.66×10^{-7} M ScCl_3 . \blacksquare : 1.02×10^{-8} M ScCl_3 .

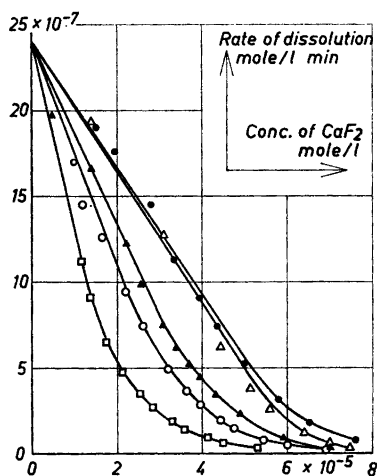


Fig. 3. The rate of dissolution as a function of the concentration of CaF_2 .

●: Pure water. Δ : 2.42×10^{-8} M ScCl_3 . \blacktriangle : 1.03×10^{-7} M ScCl_3 . \circ : 2.66×10^{-7} M ScCl_3 . \square : 1.02×10^{-8} M ScCl_3 .

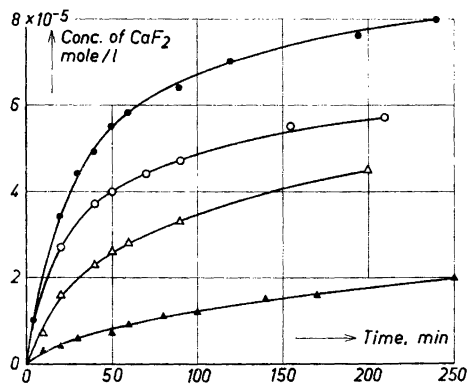


Fig. 4. The concentration of CaF_2 as a function of time.

●: Pure water. ○: 2.66×10^{-7} M ScCl_3 .
 △: 5×10^{-5} M BaF_2 . ▲: 2.56×10^{-7} M ScCl_3
 and 5×10^{-5} M BaF_2 .

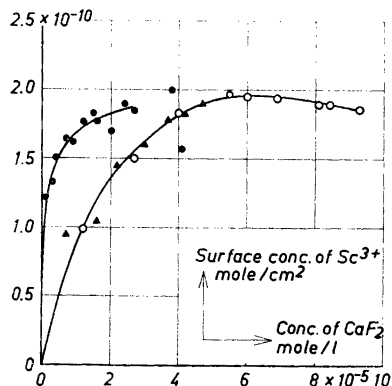


Fig. 5. The reproducibility of the adsorption experiments and the influence of BaF_2 upon the adsorption of Sc^{3+} .

○: 2.66×10^{-7} M ScCl_3 . ▲: 2.61×10^{-7} M ScCl_3 . ●: 2.56×10^{-7} M ScCl_3 and 5×10^{-5} M BaF_2 .

obtained in an experiment with pure water. The concentration of CaF_2 for these experiments is plotted as a function of time on Fig. 4.

Adsorption of Sc^{3+} . The surface concentration of Sc^{3+} is conveniently expressed as moles Sc^{3+} per cm^2 of fluorite surface. The lower curve on Fig. 5 shows a plot of the surface concentration of Sc^{3+} as a function of the concentration of CaF_2 for two experiments. They were carried out at identical experimental conditions except for a small difference in the amount of ScCl_3 added. The difference is, however, small enough to allow a comparison of the two experiments, indicating a satisfactory reproducibility.

The accuracy of the measurements may be checked by making a material balance on Sc^{3+} ; this is shown on Fig. 6 for an experiment with 2.66×10^{-6} moles ScCl_3 added. At lower concentrations of CaF_2 , the amount of Sc^{3+} found is too small. A possible explanation is that the adsorption of Sc^{3+} on the walls of the vessel is reduced by an increasing concentration of CaF_2 . At higher concentrations of CaF_2 , more Sc^{3+} than the amount actually added is sometimes detected. This discrepancy might be explained by the presence of very small fluorite particles, formed by mechanical wear of the larger ones, in the test tubes supposed to contain clear, decanted solution only. The relatively high radioactivity of these particles causes a positive error in the measured concentration of Sc^{3+} in the solution.

An increased concentration of CaF_2 reduces the rate of adsorption as shown on Fig. 7. The upper curve represents an ordinary dissolution experiment started with water containing no CaF_2 . The lowest of the fully drawn curves shows the effect of the presence of 15×10^{-5} M CaF_2 at the time of introduction of the particles. No change in the concentration of CaF_2 was observed during this experiment. The two points on the dotted

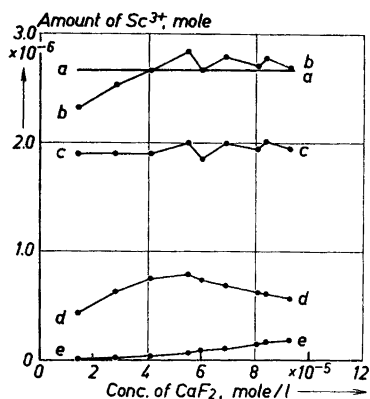


Fig. 6. The material balance for Sc^{3+} at different concentrations of CaF_2 in an experiment with 2.66×10^{-7} M ScCl_3 added.

- a—a: The total amount added, 2.66×10^{-6} moles Sc^{3+} .
 b—b: The amount of Sc^{3+} found, equal to $c + d + e$.
 c—c: The amount of Sc^{3+} in the solution.
 d—d: The amount of Sc^{3+} adsorbed on the particles.
 e—e: The amount of Sc^{3+} removed with previous samples.

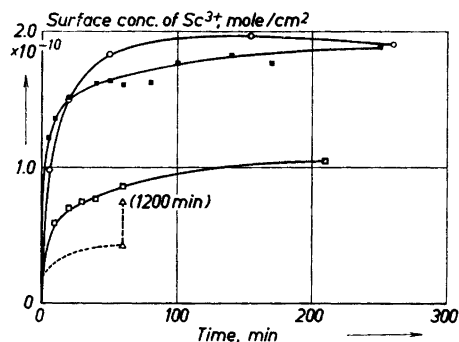


Fig. 7. The surface concentration of Sc^{3+} as a function of time.

- : 2.66×10^{-7} M ScCl_3 . Increasing concentration of CaF_2 .
 □: 2.50×10^{-7} M ScCl_3 .
 △: 2.47×10^{-7} M ScCl_3 .
 ■: 2.56×10^{-7} M ScCl_3 .
 —: 5×10^{-5} M BaF_2 .

curve show the significantly reduced adsorption of Sc^{3+} from a saturated solution of CaF_2 .

Fig. 8 shows a plot of the surface concentration of Sc^{3+} as a function of the concentration of CaF_2 for the dissolution experiments previously shown on Figs. 2 and 3. The curves representing the experiments with 1.02×10^{-6} and 2.66×10^{-7} M Sc^{3+} are seen to have maxima at about 6×10^{-5} M CaF_2 . This effect is thought to be caused by mechanical wear of the particles. The parts of the surface recently formed by wear will have a lower surface concentration of inhibitor than those which have been exposed to the solution for a long time. This is because of the reduced rate of adsorption at higher concentrations of CaF_2 . The maxima could then be interpreted as the points where an equilibrium exists between rate of adsorption and the rate of desorption plus the effect of mechanical wear. In the experiment with 2.66×10^{-7} M ScCl_3 , 28.4 % of the Sc^{3+} present in the system were adsorbed on the particles at a concentration of 6×10^{-5} M CaF_2 .

The surface concentration of Sc^{3+} is plotted on Fig. 5 as a function of the concentration of CaF_2 for the dissolution experiment with combined addition of ScCl_3 and BaF_2 . The surface concentrations are very high when compared with an experiment without addition of BaF_2 .

In order to examine the strength of the adsorption, 40 g of particles having a surface concentration of 10^{-10} moles Sc^{3+} per cm^2 were washed with distilled water. After 15 washings, each consisting of 3 min stirring with 0.5 litres of distilled water, the surface concentration was still 0.56×10^{-10} moles Sc^{3+} per cm^2 .

DISCUSSION

The difficulty of removing the Sc^{3+} ions from the particles by washing with water, indicates that they are adsorbed on the surface and not in the liquid layers close to it. Only a small fraction of the surface is covered with inhibitor, 10^{-10} moles Sc^{3+} per cm^2 covers 1.4 % in the form of unhydrated Sc^{3+} ions. This indicates that the inhibition is caused by the adsorbed inhibitor interfering with a limited number of "active spots" on the surface of the dissolving crystal. Ives⁵ has investigated the inhibiting effect of Fe^{3+} ions upon the rate of dissolution of LiF . He suggests that these "active spots" are the kinks on the surface ledges where crystalline material enters into solution. An ion adsorbed at a kink is supposed to put it out of action as a source of dissolving material, thus inhibiting the process of dissolution. The mechanism of inhibition will be discussed in more detail by the authors of this article in a future paper on the kinetics of dissolution of calcite.

Some properties of the inhibiting effect are clarified by plotting the rate of dissolution as a function of the surface concentration of Sc^{3+} , using the concentration of CaF_2 as a parameter. This plot is made by combining Figs. 3 and 8 and is shown on Fig. 9 for the experiments with varying amounts of ScCl_3 added. The straight, dotted lines are drawn for each experiment to fit points representing different concentrations of CaF_2 . The concentration interval between the points is 10^{-5} M CaF_2 starting at 10^{-5} M. The dotted

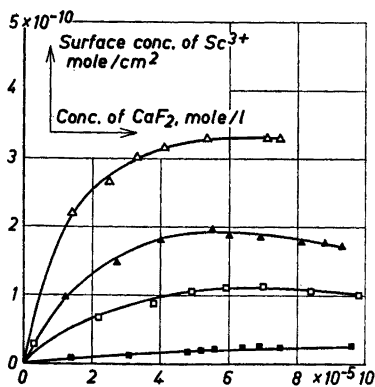


Fig. 8. The surface concentration of Sc^{3+} as a function of the concentration of CaF_2 .
 Δ : 1.02×10^{-6} M ScCl_3 . \blacktriangle : 2.66×10^{-7} M ScCl_3 . \square : 1.03×10^{-7} M ScCl_3 . \blacksquare : 2.42×10^{-8} M ScCl_3 .

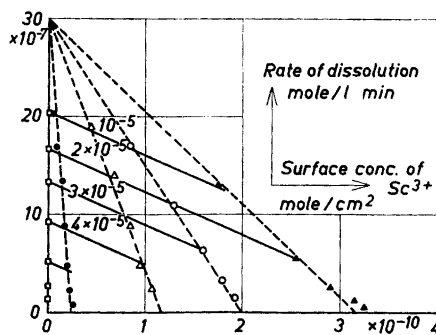


Fig. 9. The rate of dissolution as a function of the surface concentration of Sc^{3+} with the concentration of CaF_2 as a parameter.
 \square : Pure water. \bullet : 2.42×10^{-8} M ScCl_3 . Δ : 1.03×10^{-7} M ScCl_3 . \circ : 2.66×10^{-7} M ScCl_3 . \blacktriangle : 1.02×10^{-6} M ScCl_3 .

lines are when extrapolated converging towards a common initial rate of dissolution of 30×10^{-7} moles CaF_2 per litre per minute. Extrapolation of the curves on Fig. 3 showing the rate of dissolution as a function of the concentration of CaF_2 for the same experiments, indicates that the initial rate of dissolution is 24×10^{-7} moles CaF_2 per litre per minute. The explanation of this discrepancy is probably the difficulties involved in determining accurately the values of the rate of dissolution at concentrations below 10^{-5} M CaF_2 . The dotted lines are described by equations of the form

$$\frac{dC}{dt} = \left(\frac{dC}{dt} \right)_{t=0} - k_1(C, \bar{C}) \times \bar{C} \quad (1)$$

In eqn. (1) C = the concentration of CaF_2 , t = the time and \bar{C} = the surface concentration of Sc^{3+} . $k_1(C, \bar{C})$ is a function of corresponding values of C and \bar{C} , measured at the same time, having the property of being a constant within each experiment.

The points plotted along the ordinate of Fig. 9 represent the rates of dissolution for an experiment carried out with pure water. They correspond to concentrations of 10^{-5} M CaF_2 , 2×10^{-5} M CaF_2 , and so on. They are selected as starting points for the fully drawn parallel lines. These lines are drawn to fit points on the dotted lines all representing the same concentration of CaF_2 . The points falling reasonably well along the lines are confined to a region of low concentrations of CaF_2 and low surface concentrations of Sc^{3+} . This region is also the one in which the rates of dissolution as functions of the concentrations of CaF_2 may be approximated by first order rate equations. The parallel lines are described by the equation

$$\frac{dC}{dt} = \left(\frac{dC}{dt} \right)^* - k_2 \times \bar{C} \quad (2)$$

The first term is the rate of dissolution at a particular concentration of CaF_2 for an inhibited experiment, the second refers to the uninhibited experiment at the same concentration of CaF_2 . By rearrangement of eqn. (2) and insertion of data from the experiments, the slope of the parallel lines, k_2 , is calculated to be 4.39×10^3 in the actual units. The physical meaning of eqn. (2) is that the reduction in rate of dissolution caused by the inhibitor is within this region proportional to the amount of inhibitor adsorbed on the surface of the fluorite.

Acknowledgements. The experiments described in this paper were carried out with financial support from *Norges Teknisk-Naturvitenskapelige Forskningsråd* and *Norges Tekniske Høgskoles Fond*.

REFERENCES

1. Nestaas, I. and Terjesen, S. G. *Acta Chem. Scand.* **22** (1968) 2101.
2. Bjerrum, J., Schwarzenbach, G. and Sillén, L. G. *Stability Constants of Metal-Ion Complexes*, The Chemical Society, London 1958.
3. Wilson, A. S. and Taube, H. *J. Am. Chem. Soc.* **60** (1952) 3509.
4. Welcher, F. J. *The Analytical Uses of Ethylene-Diamine-Tetraacetic-Acid*, Van Nostrand, New York 1958.
5. Ives, M. B. *Ind. Eng. Chem.* **57** (1965) 34.

Received December 21, 1967.