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IRON SULFIDE CRYSTAL GROWTH: A LITERATURE REVIEW

by

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Croissance de cristaux de sulfure de fer: Examen de la littérature*

par

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* Étude effectuée sous contrat pour l'EACL

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Résumé

On trouve souvent de la pyrite de fer (FeS_2) sur les plateaux et dans les échangeurs de chaleur des usines GS (Girdler-Sulfide) employées pour extraire l'eau lourde de l'eau douce. On a procédé à un examen critique de la littérature afin de déterminer:

(i) ce que l'on sait au sujet de la croissance des cristaux de FeS_2;

(ii) quelles techniques pourraient être employées pour étudier expérimentalement la croissance des cristaux de FeS_2;

(iii) les additifs chimiques possibles pouvant être utilisés en quantités minimes pour empoisonner les cristaux de FeS_2 et réduire leur taux de croissance dans les usines GS.

L'Energie Atomique du Canada, Limitée
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*IRON SULFIDE CRYSTAL GROWTH: A LITERATURE REVIEW**

by

*E.J. Dewar***

ABSTRACT

Iron Pyrite (FeS_2) is often found on trays and in heat exchangers in Girdler-Sulfide (G.S.) plants used to extract D_2O from fresh water. A critical review of the literature was made to find:

(i) what is known about FeS_2 crystal growth.

(ii) which techniques could be used to study FeS_2 crystal growth experimentally.

(iii) potential chemical additives that could be used in trace amounts to poison FeS_2 crystals and reduce their growth rate in G.S. plants.

* Work performed under contract for Atomic Energy of Canada Limited

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1. INTRODUCTION

The Girdler-Sulfide (G.S.) process is used extensively in Canada to extract D_2O from fresh water. In this process, water and hydrogen sulfide gas (H_2S) are contacted counter-currently, with the water being heated by the gas from 30°C at the contactor inlet to 130°C at the outlet. As well, some water side-streams are heated to at least 160°C. After one year's operation, some of the sieve trays in the contactors, and some of the heat exchanger tubes have deposits of iron pyrite (FeS_2). The deposits can reduce D_2O production rates, for example, by reducing the heat transfer rates in heat exchangers. Consequently, the deposits must be removed periodically.

Little is known about the crystal growth of FeS_2 from aqueous solutions of iron and hydrogen sulfide. The solubility of pyrite is apparently very small at G.S. conditions. Yet large quantities of pyrite do accumulate on non-corroding surfaces such as the stainless steel trays. The situation is often similar in many chemical process industries but little is known about the mechanisms for growth of various foulants encountered. A common solution to fouling in such plants is the use of crystal growth inhibitors. For example sodium polyacrylate is used in boilers to limit the deposition of calcium hydroxyapatite (Kelen, 1974).

A critical review of the crystal growth literature is given here. The review had three goals:

(i) to find what is known about crystal growth of FeS_2, in particular, growth from aqueous solutions

(ii) to evaluate different techniques for studying FeS_2 crystal growth

(iii) to explore the potential of trace amounts of additive to control the crystal growth of FeS_2 in G.S. plants.

A brief review of crystal growth is given first. Then, each of the above three areas is discussed.

2. MECHANISMS FOR GROWTH

Crystalline solids (crystals) are characterized by a rigid lattice of molecules, atoms or ions. The regularity of the internal structure of this solid results in the crystal having a characteristic shape, with smooth faces parallel to atomic planes in the lattice. This orderly arrangement of molecules during the initiation and growth of the crystal is complex and affected by many variables.

The three basic stages in the process of producing crystals are:

1) achievement of supersaturation

2) formation of crystal nuclei (nucleation)

3) growth of the crystals.

However, having a supersaturated solution does not necessarily result in nuclei nor does the appearance of nuclei guarantee further growth to produce larger cyrstals.

The exact mechanism of nuclei formation is not known although there are a number of hypotheses on how the molecules in a homogenous system arrange themselves into clusters to form stable nuclei. Nucleation from a solution or melt can be affected by impurities which may inhibit or accelerate their production. The presence of other solids in the system can also act as nucleation centers in what is known as heterogeneous nucleation.

The growth of ionic crystals from solution according to diffusion theories involves a number of steps which are as follows (Mullin, 1972):

(1) Mass transport of the ions to the outside of the stagnant film of liquid surrounding the crystal.

(2) Diffusion across the stagnant surface film.

(3) Adsorption of the elements onto the crystal faces.

(4) Surface diffusion to the growing step or ledge.

(5) Integration into the crystal lattice at kinks in the ledges which is accompanied by dehydration of the ions. There may also be a reaction involved in the integration.

(6) Counter-diffusion of released water (or solvent).

In theory, any one of these steps can control the rate of crystal growth. It is easy to postulate how solution conditions could influence one or more of these steps. For example, an impurity which adsorbs onto the crystal faces could easily prevent adsorption of an element required for further crystal growth and thus stop crystal growth. The amount of impurity required to form a monomolecular barrier to the diffusion process obviously can be very small as is found in practice.

One of the well-known examples of the effect of impurities is prevention of $CaCO_3$ scale formation with a few parts per million of sodium hexametaphosphate. There are many other examples as will be seen later.

3. LABORATORY TECHNIQUES FOR CRYSTAL GROWTH STUDIES

Many articles describe methods for studying crystal growth mechanisms and kinetics. There are two basic techniques; one uses a single crystal while the other uses a large number of small crystals in suspension. Growth of single crystals was described by Mullin, 1972; Holden, 1949; Fehlner, 1956; and Torgensen, 1962. Phillips, 1975, described a method for observing growth layers on adjacent faces of a crystal. Fluidized bed techniques were described by Bajac, 1969 and Mullin, 1969; 1972. Each technique has its advantages as shown by Davey and Rutti, 1974, and Konak, 1974. The single crystal is better for study of face growth, and mechanisms. The fluidized bed is preferred for study of kinetics, particularly for kinetic data used in engineering design which must apply to the average growing crystal. Single crystal studies are also more difficult as damage or contamination of crystal faces is very easy and can have dramatic effects. In both cases contamination can cause major inexplicable changes in rates and shape.

Methods for measuring crystal size for fluidized bed studies were described by Mullin and Ang, 1974. Garside, 1973, demonstrated the importance of seed crystal shape factors when determining crystal growth rate. As well he discussed the problem of eliminating volume diffusion so that the surface integration kinetics can be measured (Garside, 1974).

The use of time-lapse photomicrography for study of crystal growth rates on specific faces was described by Michaels, 1964.

Randolph, 1970, described a method and apparatus for producing narrow crystal size distributions which can be used for measurement of the kinetics and nucleation rates.

4. EFFECT OF ADDITIVES ON CRYSTAL GROWTH

The effect of impurities on crystal growth rates, nucleation rates and shape (morphology) are so varied that it is difficult to predict the response to an impurity although attempts have been made to explain specific cases. Classification of impurities into groups giving a particular response also is not possible at the present. The complexity of impurity effects has often made crystallization processes an art based on trial and error.

Models proposed to account for impurity effects are summarized first, then specific effects of impurities are considered for different crystals.

4.1 Models for Impurity Effects

A brief but good review of the mechanisms of adsorption of impurities was given by Davey in 1975. The mechanisms are as follows:

(1) Model of Sears, 1958: the number of growth sites along a step decreases with increasing adsorption of impurity which results in a step velocity which is insensitive to impurity adsorption until monostep coverage is achieved.

(2) Model of Albon & Dunning, 1962: This is a quantification of Sears model in which the probability of a solute molecule finding a free step length is evaluated.

(3) Model of Cabrera & Vermilyea, 1958: This model assumes step motion is not impeded due to direct adsorption at the step but rather due to the step encountering impurity species which are adsorbed on the ledges ahead of the step.

Davey concluded that the work reported by Davey and Mullin, 1974 was consistent with Sear's model but not with the other two models unless some assumptions were made regarding adsorption of the impurity on the crystal surface.

Burrill, 1971, presents a detailed discussion of the mechanisms of impurity effects and includes a modification of the adsorption-diffusion model of crystallization to account for the presence of impurities.

Although most papers on mechanisms include some mathematical interpretation, Ohara, 1973, dealt specifically with mathematical modelling of crystal growth rates from solution. Nielsen, 1969, described mathematically the rate-determining steps and the influence of physical parameters. Sears, 1958 presented a model for "monostep adsorption of growth poisons" at the growth steps.

Although the mechanisms for action of impurities are not well understood they can be classified into two categories: (a) those that affect the solution properties such as equilibrium saturation, and (b) those that affect the adsorption at the crystal face, most likely by disrupting the two-dimensional diffusion of ions across the crystal growth steps.

4.2 Impurity Effects on Specific Crystals

One of the earliest articles that reviewed the effect of impurities on crystal growth mechanisms was by Yamamota, 1939. More recently, Cabrera, 1958, described growth mechanisms and the effect of impurities. Davey, 1975, discussed models for impurity adsorption in crystal growth. Garrett, 1959, and Mullin, 1964, reviewed the use of crystal shape modifiers and mechanisms. Sheftal, 1968, edited a collection of papers on the growth of crystals including impurity influences.

One of the major uses of crystallization theory is in the design of industrial crystallizers. Larson, 1971, and Mullin, 1971, dealt with the applications or engineering use of crystallization theory and data. It was pointed out in several articles that much of the design data has come from trial and error, particularly where the effect of trace impurities is concerned. Blakadder, 1964, presented a good survey of crystallization including design factors, scale-up, agitation, shape modifiers and seeding. He advocated research in the area of crystal shape modification as well as nucleation and growth.

Randolph, 1970, related nucleation and growth rates to crystal size distribution. However, McCabe, 1951, showed that the rate was proportional to the velocity between crystal and solution and is not directly affected by crystal size. Recent work by Garside and Mullin, 1974, showed that the surface integration kinetics of potassium sulfate were size dependent in the range 0.4 to 1.6 mm.

Crystals tend to grow preferentially at different faces under different environments which accounts for shape modifications of similar crystal lattices. Ansheles, 1957, presented a concept of "physically impossible faces" and impurity effects. Kern, 1969, reviewed equilibrium shapes and the prediction of which crystal face will grow. Davey and Mullin, 1974; 1974; 1975; 1976 and Davey and White, 1975, conducted many experiments on the growth rates of the various faces of ammonium dihydrogen phosphate and of triglycide sulfate. They studied physical effects such as supersaturation and the influence of other ionic species in the solution. They also derived a mechanism for shape modification. Their work was one of the most extensive found in the current literature. Portnov, 1970, studied the rate of growth of the (010) face of Rochelle Salt.

Whetstone, 1955; 1955, has studied the mechanism of integration of dyes onto the crystal planes of inorganic salts and the resulting shape modification. The effect of dye was dependent on the nature of the anionic or cationic polar substituent groups and the crystal planes. Rainstrick, 1949, and Sarig, Glasner and Epstein, 1975, discussed the relation between the effectiveness of an impurity on crystal growth and the fit between molecular structure of the additive and the crystal lattice.

Michaels, 1960; 1961; 1964, has published his adsorption theory based on work with the effect of impurities on adipic acid crystals. A second growth theory is the filament theory of Price, 1958, which explains the growth of whiskers.

The work of Nancollas and associates: Nancollas, 1973; Nancollas and Gardner, 1974; Nancollas, Reddy and Tsai, 1973; Nancollas and Tomazic, 1974; Nancollas and Wefel, 1972; Reddy and Nancollas, 1972, and Tomazic and Nancollas, 1975, on the crystal growth of sparingly soluble salts has helped explain the mechanism of growth of deposits in aqueous systems and the effect of impurities or scale inhibitors such as polyphosphates and phosphonates. Calcium sulfate, calcium carbonate and calcium phosphate or hydroxyapatite were three of the scaling materials studied.

Sarig, 1973; 1974, and Sarig and Tartakovsky, 1975, have studied the effect of surface active agents and chelating agents on the growth rates, nucleation rates and crystal shape and have presented mechanisms to explain the observed effects of impurities.

Other fairly recent work in this area includes Mullin, 1973, who studied nickel ammonium sulfate nucleation and observed both homogeneous and heterogeneous nucleation under different conditions, and Smith, 1970, who postulated that polymeric additives acted as immobile impurities on $CaSO_4.2\ H_2O$ crystal faces, and Sroczynski, 1974, who found the effect of impurities on glucose crystals was a function of concentration and not the nature of the impurity.

The following table (Table 1) lists the crystals where impurity effects were noted in the literature reviewed for this study, with the exception of the lists given in Industrial and Engineering Chemistry Annual Reviews: Botsaris, Parts I, II, III, 1969; Palermo, 1964, 1966, 1968; Reid, Parts I, and II, 1970. Many references to impurity and additive effects are given in short notes and in industrial chemical processing articles.

CRYSTAL GROWTH OF IRON SULFIDES

A search was made for information on iron sulfides, particularly their growth from solution and the effect of impurities or additives. In general very little useful information was found. Most of the iron sulfide work concerned solid state properties, geological phenomena, preparation from melts, and corrosion of iron exposed to H_2S. Although they are not given in this report, much of the literature reported in Chemical Abstracts on these related topics, particularly corrosion, has been indexed and copies are available from Nova Scotia Research Foundation.

.1 Iron Sulfide Growth and Properties

The only published studies located on iron sulfide growth from solution were by Korolev, 1965; Rickard, 1975; Wikjord, Rummery and Doern, 1975; Zotov, 1969. No work using G.S. plant conditions or demonstrating

TABLE 1
Impurity effects on various crystals

Material Crystallizing	Impurity and Effect	Reference
Sucrose	Raffinose (shape in modifier)	Albon, 1962
KH_2PO_4	$AlNO_3.9H_2O$, KOH (decreased (100) face growth)	Belyustin, 1973, 1974
$3CaO.SiO_2$	$CaCl_2$, CdI_2, $CrCl_3$ (all accelerated hydration)	Ben-dor, 1975
Th-oxylate	$Ce^{3+} > Ca^{2+} > Ba^{2+} > Mn^{2+} = Zn^{2+} > Mg^{2+}$ (delay growth in above order, K^+ has no affect)	Bykhovskii, 1974
$CuSO_4$ and $CdSO_4$	Gelatin (reduces size)	Cabrera, 1958
$NH_4H_2PO_4$	$CrCl_3.6H_2O$, $FeCl_3$, $AlCl_3$ (growth rate reduction)	Davey, 1975; Davey and Mullin, 1974, 1974, 1975
$CaCO_3$, $CaSO_4$ (seawater)	Tripolyphosphate, sodium polyacrylate, N_2-amino trimethyl phosphonic acid and lignin sulfonic acid (retard scaling).	Elliot, 1970
NH_4NO_3	Acid dyes (shape modifier)	Garrett, 1959
NaCl, KCl, NH_4Cl	Pb^{2+} (produces larger crystals)	Garrett, 1959
$CaCO_3$	Na-metaphosphate (growth inhibitor)	Garrett, 1959
$Na_2SO_4.10H_2O$	Alkyl aryl sulfonates and others (shape modifiers)	Garrett, 1959
$(NH_4)_2SO_4$	Surfactants, pH (shape modifiers)	Garrett, 1959
$CuSO_4.5H_2O$	H_2SO_4 (shape modifier)	Garrett, 1959
$Na_2CO_3.NaHCO_3.2H_2O$	Organic compounds (shape modifier)	Garrett, 1959
Borax	Oleic Acid, Fe^{2+}, Mg^{2+} Zn^{2+}, Al^{3+} (shape modifiers)	Garrett, 1959
$Na_2CO_3.H_2O$	Na_2SO_4 (shape modifier)	Garrett, 1959

TABLE 1 (continued)
Impurity effects on various cyrstals

Material Crystallizing	Impurity and Effect	Reference
NaCl	$CdCl_2$, urea, $NH_2CH_2CO_2H$, $Fe(CN)_6^{4-}$ (shape modifiers)	Kern, 1969
$CaSO_4.2H_2O$	Ionic Polyacrylamide based polymer, Sepran AP-273 (shape modifier)	Konak, 1976
$CaSO_4$	Fe^{3+}	Kopylev, 1969
KNO_3	Cr^{3+} (increases size) surfactants dodecylamine, methylamine and fluorocarbon FC-98 (decrease size and rates)	Larson, 1971; Shor, 1971
$CaSO_3.2H_2O$	Phosphonic Acids, EDTA, Na-benzoate, gelatin, (scale retarders and shape modifiers)	Liu, 1975; 1973
$BaSO_4$	Phosphonic acids, metaphosphate (shape modifiers)	Liu, 1975
NaCl	Pb^{2+} (shape modifier)	Liu, Yih-An and Botsaris, 1973
$CaHPO_4.2H_2O$	Na-pyrophosphate (growth inhibitor)	Marshall, 1969
$Ca_5(OH)(PO_4)_3$ (hydroxyapatite)	Organic phosphonates (reduced crystal growth)	Meyer, 1973
Adipic Acid	Cationic and Anionic surfactants (growth rate and shape modifiers)	Michaels, 1960; 1964; 1961
NaCl, $(NH_4)H_2PO_4$	Potassium ferrocyanide, Fe^{3+}, pH (shape modifiers)	Mullin, 1971
$(NH_4)_2SO_4$	$CrCl_3$ (shape modifier, nucleation suppression)	Mullin and Garside, 1974
$CaSO_4$, $CaCO_3$	Phosphonates, (inhibit crystal growth)	Narcollas, 1973
Ca-Oxalate	Phosphates, Polyelectrolytes, organic dyes (affects growth kinetics)	Nancollas and Gardner, 1974
$BaSO_4$	Polyphosphates, phosphonates (growth inhibitors)	Nancollas and Liu 1975

TABLE 1 (continued)
Impurity effects on various cyrstals

Material Crystallizing	Impurity and Effect	Reference
$CaSO_4$, $CaCO_3$, $BaSO_4$	Phosphonates (growth inhibitors)	Nancollas and Reddy, 1974
Calcite, $Mg(OH)_2$, $CaHPO_4.2H_2O$	Phosphates, phosphonates (scale inhibitors)	Nancollas and Reddy, 1974
$Ca_5(OH).(PO_4)_3$ (Hydroxapatite)	NaCl, KCl	Nancollas and Tomazic, 1974
$Ca_2H_2(PO_4)_2 .2H_2O$	SnF, SnCl, NaF	Nancollas and Wefel, 1974
K,Na-tartrate (Rochelle Salt)	Sky Blue Dye	Portnov, 1970
glucose	Disaccharides, inorganic salts (growth inhibitors)	Portnov, 1970
K_2SO_4	Na_2SO_4, $MgSO_4$ (shape modifiers)	Pokhodenko, 1975
$CaCO_3$	O-P-O-P-O type molecules (shape inhibitor)	Reddy, 1972
$SrSO_4$	Polyvinyl sulfonate (shape modifier, growth retarder)	Sarig, 1974
NaCl, KCl	Nitrilotriacetamide, nitrilotripropionamide (shape modifier)	Sarig, 1975; 1975
Ca-oxylate	$P_2O_7^{4-}$, Cationic impurities (shape modifier, growth retarder)	Sarig, 1973
$CaSO_4.2H_2O$	Anionic and cationic polyelectrolytes (decreased growth rate)	Smith, 1970
Sucrose	Glucose, raffinose (shape modifiers, influence on growth rate)	VanHook, 1969
NaCl, KCl	Ca^{2+} (shape modifier)	Yacaman, 1975

TABLE 1 (continued)
Impurity effects on various crystals

Material Crystallizing	Impurity and Effect	Reference
Chlorides	Heavy Metal Cations (shape and growth modifiers)	Yamamoto, 1939
$Al(OH)_3$	Phosphates and silicates	Hsu, 1975

the effect of impurities on growth rates and shape of iron sulfide crystals was noted. Rickard concluded that pyrite was formed according to the reaction:

$$Fe^{2+} + S_5S^{2-} + HS^- \rightarrow FeS_2 + S_4S^{2-} + H^+$$

Korolev showed that pH, redox potential and the ratio of iron to sulfur were important factors in producing pyrite.

One of the most important factors in crystallization is the extent of supersaturation of the ions in solution. Data on solubility of iron sulfides are scarce. The most comprehensive report is by Pohl, 1962. Other references with some solubility data were Rafalskii, 1966, and Ol'Shanskii, 1958. Tewari, 1975, is currently measuring iron sulfide solubilities at G.S. plant conditions.

The structure and properties of iron sulfides, other than pyrite* and marcasite*, were reviewed by Ward, 1970. Several other references were found on the thermodynamics and properties of iron sulfides: Nakazawa, 1971; Marquart, 1963; and Berner, 1967. Articles on reactions of gaseous H_2S with iron included those by Turkdogam, 1968, Worrell, 1968; and Narita, 1973.

5.2 General Considerations for Crystal Growth Studies

The well-defined morphology of pyrite crystals found in the G.S. towers and heat exchangers indicates that the pyrite may result from the crystalization of Fe^{++} and $S_2^=$ from solution. There is some doubt as to the source of the $S_2^=$. For example, the quantity of oxygen entering the system is probably insufficient to oxidize H_2S to $S_2^=$. The results of a study of pyrite growth rates could shed light on the mechanisms postulated to explain the growth of pyrite. Information on the rate of growth of pyrite crystals and the effect of additives on this growth relate to the deposition process in the towers and not to the sources of the iron or sulfur.

* Pyrite has a cubic unit cell; marcasite is also FeS_2, but with an orthorhombic unit cell.

If $S_2^=$ is essential to the formation of pyrite then the rate of buildup may be controlled by reactions that produce the $S_2^=$. Consideration should be given to additives or conditions that reduce the $S_2^=$ availability, which could reduce the rate of pyrite formation.

The rate of crystal growth is normally a strong function of the supersaturation of the ions in solution and growth rates are determined as a function of supersaturation. In the case of iron sulfides very little solubility data are available, particularly for pyrite which is the least soluble of the iron sulfides. This means that the degree of supersaturation will not be known for growth rate studies.

Seed crystals of pyrite are available commercially but are often of poor quality. It is desirable to produce the required crystals by reaction of pure iron and sulfur in a sealed glass ampule according to the well-established techniques of Bouchard, 1968; Ripley, 1972; Stafford, 1969; Yamada, 1974.

As shown earlier, impurities or additives even at trace concentrations (<1 mg/ℓ) can have a marked effect on the nucleation rate, growth kinetics and morphology of crystals. There are many references to these effects and many compounds used commercially to control crystal growth rates and morphology.

Both inorganic ions and organic compounds have an effect. Multivalent ions such as Al^{3+}, Cr^{3+} are often shape modifiers or growth inhibitors. Polar organic polymers such as starch, lignin, synthetic polyelectrolytes, and organic surfactants have been found to be effective for inhibiting crystal growth rates. For example, low molecular weight polyacrylic acid can inhibit the growth of calcium and magnesium scale in water evaporators or boilers. In some cases the additives retard nucleation, whereas in others they prevent adherent deposits from forming on the walls which permits the precipitates to flow through the system.

6. CONCLUSION

The review has shown that little information has been published that directly relates to iron sulfide deposition in G.S. heavy water plants. However, there is sufficient evidence to indicate that trace additives have good potential as agents to control the deposition of iron sulfide. The difficulties associated with studying low solubility crystals combined with a lack of solubility data make it difficult to conduct a rigorous study of the kinetics of iron sulfide growth. However, in this case it may be preferable to observe empirically the effect of various additives, impurities and system conditions since a solution to an industrial problem is the desired end result. Elucidation of mechanisms can follow actual plant trials.

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