

# The Effect of Additives on the Crystal Form of Sodium Chloride

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## ABSTRACT

*The crystal structure of sodium chloride is face-centered cubic, and under normal circumstances pure salt crystallizes from aqueous solution in the form of well-defined cubes. The external form of a sodium chloride crystal depends, however, on the conditions obtaining while crystallization is taking place, and a number of non-cubic shapes have been produced simply by using, for example, extreme conditions of supersaturation.*

*By far the most profound effect on crystal shape of salt is, however, produced by the presence in the brine of foreign substances, often at extremely small concentration. The chlorides of cadmium, zinc, lead and manganese are particularly active and organic substances such as urea, glycine, pyridine, betaine,  $\beta$ -alanine, nitrilotriacetic acid, polyvinyl alcohol, certain polycarboxylic acids and sodium glutamate are known to have effects. A number of other examples are reported. By far the most potent additive is the ferrocyanide ion, and to a lesser extent the ferricyanide ion. Their effects have been studied extensively by a number of workers in the last few years, particularly in relation to the formation of dendrites and effects on growth and dissolution rates. It has been shown that conditions such as temperature, agitation and supersaturation have a marked effect on the extent and nature of the modification produced by the ferrocyanide ion.*

*These phenomena can have far-reaching consequences on the production and application of salt. For example, changes in product size distribution, bulk density, solubility rate and caking tendency can be brought about by the use of a particular additive and suitable control of the evaporation process.*

## INTRODUCTION

In this short paper I am going to try to give some idea of the ways in which the shape of the salt crystal can be altered by the use of substances added to the brine from which it is made, and to introduce some views about the mechanism whereby these impurities produce the quite profound and sometimes quite specific effects. What we are certain of is that these phenomena are very useful to the saltmaker in determining some of the properties of his product. He no longer has to be content with what emerges naturally from his evaporator.

It should be made clear that I am describing entirely salt made by evaporation in which crystallization takes place in the body of the brine such as occurs in vacuum evaporation. Irregularly-shaped salt can be produced by forming it at the brine/air interface, for example, in open pans and in solar evaporation, but I am not including these effects in the scope of this paper, although that is not to say that some of the agents I describe will not have a value in affecting growth in these methods.

The crystal structure of sodium chloride is face-centered cubic and Fig. 1 shows the space lattice in which each sodium ion is surrounded by six chloride ions and each chloride ion

surrounded by six sodium ions. The naturally-formed external faces of a crystal are related (and I stress related) to the regular internal arrangement. When the faces of sodium chloride have equal chances they grow at the same rate and the crystal eventually becomes a perfect cube. It is a matter of common experience that salt produced from pure brine in a vacuum evaporator at normal rates of make is in the form of regular cubes.

But Fig. 2 shows that a number of different planes are possible in the crystal lattice. If any of these are preferred to the normal faces -- (100) in the case of NaCl -- habit modification will occur, that is, the external morphology of the crystal will change.

However, this change of habit in no way changes the symmetry and crystal class and the internal spatial relationships of the ions remain the same. Thus it is possible to move from a cube to an octahedron by increasingly cutting away the corners of a cube as shown in Fig. 3.

### HABIT CHANGE BY SUPERSATURATION

Changes in habit can be brought about by radical alteration of the conditions used during crystallization. High supersaturations are particularly likely to produce non-cubic forms of salt. Kern (1953) showed that, while the (100) habit was produced just above saturation, (111) faces appeared at a supersaturation of 8.2 g/100 g water and dendritic forms appeared.

So we see that it is possible to modify the shape of salt by evaporation conditions alone, but these conditions are really too extreme to be of practical use in ordinary production.

### HABIT MODIFIERS FOR SALT

The external shape and size of salt is much more readily altered by the presence in the brine of foreign substances. There is no doubt that many hundreds, possibly thousands, of chemical species have been evaluated for their effect on the crystal growth of sodium chloride. Certainly in my Company the number runs into many hundreds. The literature describes the effects of a fair number of very diverse materials possessing varying activity. Much of the work has, however, been done under particular (often unspecified) conditions of crystallization and it is likely that many useful effects have been missed for this reason. Table 1 shows a selection of the published habit modifying materials. It is probable that much of the work done has remained unpublished.

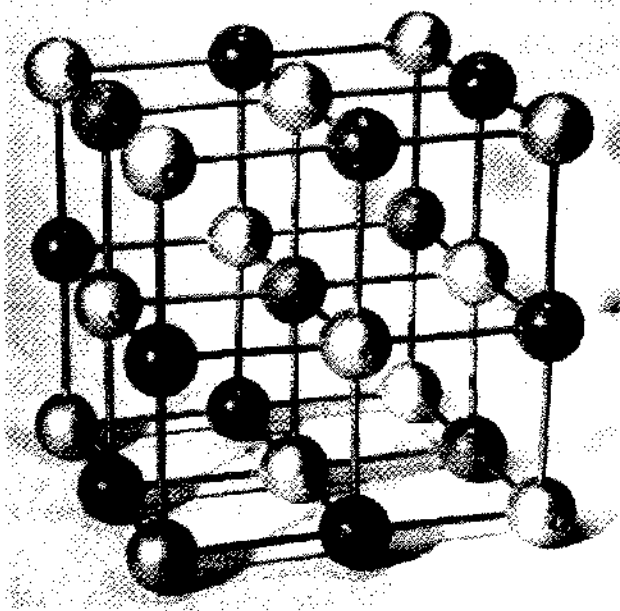


Figure 1. Space lattice of sodium chloride.

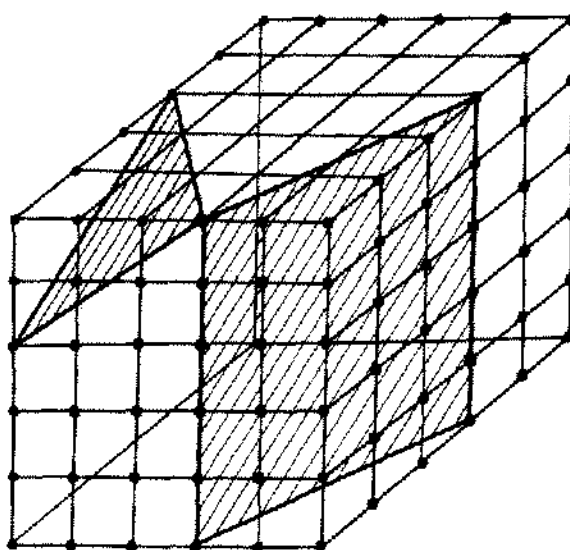


Figure 2. Some theoretically possible planes in NaCl lattice.

It is seen that both inorganic and organic substances can produce changes of habit. Urea was probably the first substance to be recorded as having a habit modifying effect on salt (Rome de l'Isle, 1783) and the system has been extensively studied. The amount of urea required to produce

a strong effect is very large. At high concentrations of urea, growth is slowest on the (111) face, and octahedral crystals are produced. As can be seen from the table, many different shapes are produced, for example, octahedra, rhomboidal dodecahedra, whiskers, dendrites and tetrakaidecahedra. Figures 4, 5, 6 and 7 show some forms which have been produced in our laboratories. Figure 4 shows needles produced by the action of polyvinyl alcohol. Figure 5 shows highly branched dendrites obtained by the use of ferrocyanide. Figure 6 is of spiky salt produced by precipitating salt by the use of alcohol in the presence of potassium ferrocyanide, and Fig. 7 is of octahedral salt produced by a complex phosphate.

These different forms are produced either by different substances or in the case of one substance, different concentrations and crystallizing conditions. The importance of the latter is illustrated by the investigations carried out by Kern and Tillman (1953) on the influence of supersaturation on the extent of modification of the (100) faces to (111) by differing amounts of the additives urea, magnesium chloride, manganese chloride, lead chloride, cadmium chloride and sodium carbonate. They showed that for each salt/additive combination an increase in the concentration of the additive progressively reduced the supersaturation required to effect the change of face. This seems to the author to point to the key to the effect of impurities -- they make it easier to bring about those crystallographic changes which very high super-

saturation could probably bring about if this were not normally limited by practical difficulties such as excessive nucleation.

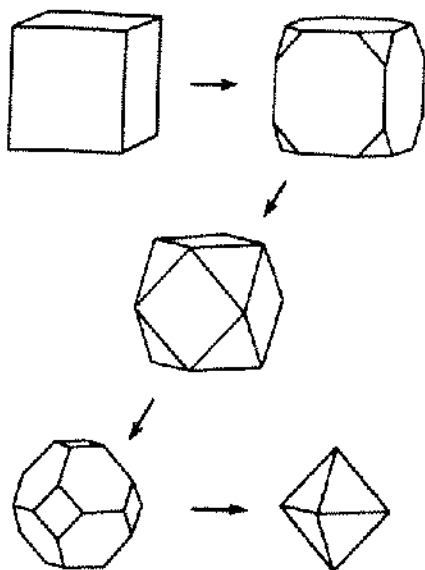


Figure 3. Progressive change from cube to octahedron.



Figure 4. Needles of sodium chloride (x20).

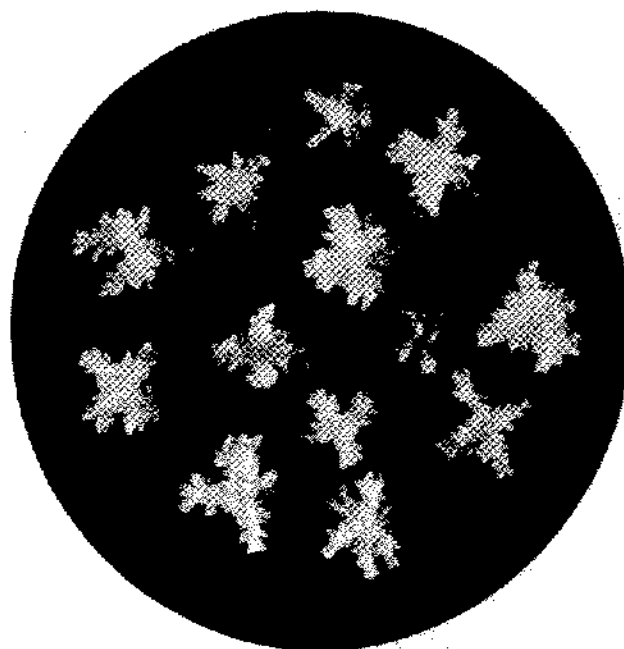


Figure 5. Highly branched dendrites of sodium chloride (x20).

TABLE 1  
Habit Modifying Agents for Sodium Chloride

Additive	Crystal Change
<u>Inorganic</u>	
Manganous sulphate	
Manganous chloride	Octahedra
Cadmium chloride	Octahedra
Zinc chloride	Octahedra
Magnesium chloride	(110)
Bismuth chloride	Pyramidal and starlike
(Complex cyanides)	Dendrites, octahedra, etc.
<u>Organic</u>	
Urea	Octahedra
Glycine	Rhombic dodecahedra
Formamide	Octahedra
Nitrilotriacetic acid	Octahedra
Copolymers of vinyl acetate and maleic anhydride	Hollow-faced cubes
Polyvinyl acetate	Needles
Cysteine	Octahedra
Creatinine	Octahedra
Papain	Octahedra
Monosodium glutamate	Octahedra
Sodium hexametaphosphate	Octahedra
Sodium hexametaphosphate plus an aluminium salt	Tetrakaidecahedra
Polyvinyl alcohol	Needles

By far the most potent additives, however, are a number of complex cyanides, especially ferrocyanides, and much research work has been done on the action of these additives in the past few years. Since the introduction of dendritic salt as a commercial product by ICI a number of years ago, much background work on habit modification of salt by ferrocyanides has been done, and I will describe this in a little more detail.

#### INHIBITION OF GROWTH AND DISSOLUTION BY FERROCYANIDE

Several years ago, one of our research workers measured the growth and dissolution rates of salt granules in a bed fluidized by supersaturated and undersaturated brine with and without potassium ferrocyanide. A summary of his results is given in Fig. 8. There is complete suppression of growth and dissolution below certain values of supersaturation and undersaturation, the extent of the effect being dependent upon the amount of ferrocyanide used. It can be seen that even at a concentration as small as 1 ppm no growth occurred until a supersaturation of 4.6 g/litre had

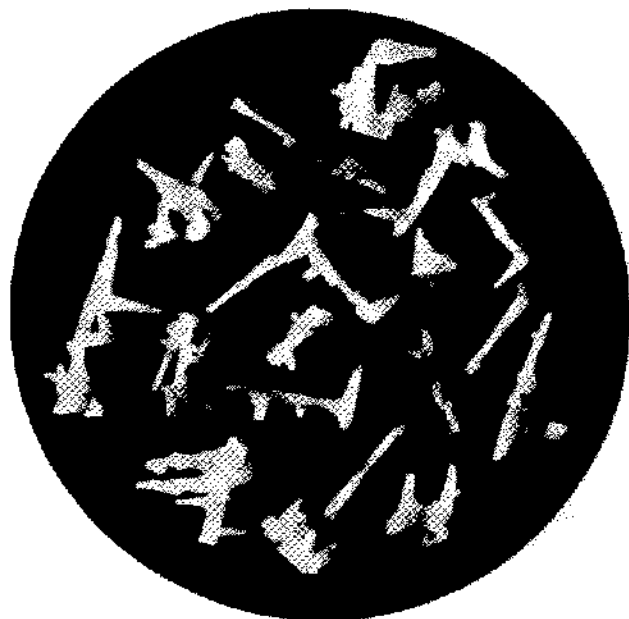


Figure 6. "Spiky" crystals of sodium chloride (x10).



Figure 7. Octahedral crystal of sodium chloride (x100).

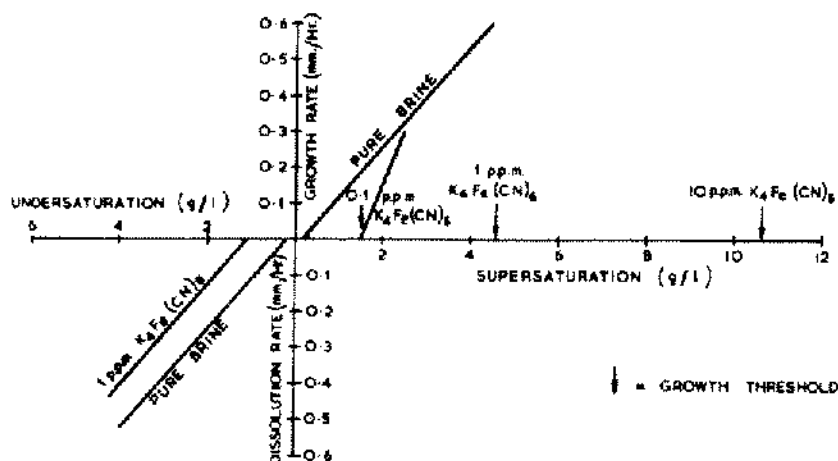


Figure 8. Growth and dissolution of granular salt crystals in brines containing  $K_4Fe(CN)_6$  -- 42° C.

been exceeded. Other workers, notably Steinike (1962) and van Damme (1963), have reported similar results although the former's work was concerned with potassium chloride not sodium chloride. These effects are of relevance when we come to consider the mechanism of habit change and applications below.

#### GROWTH OF SALT IN THE PRESENCE OF COMPLEX CYANIDES

We now come to consider what happens when growth does start in the presence of ferrocyanide in concentrations insufficient to cause complete suppression of nucleation.

Birchall (personal communication 1964) working in our laboratories at Winnington, has carried out an extensive study of this subject. In one set of experiments he produced various supersaturation conditions by cooling sodium chloride brines containing various amounts of potassium ferrocyanide to a certain temperature at which growth occurred. He studied both stirred and

unstirred conditions, and repeated his experiments at three different temperatures. He expressed his results in the form of a morphogram in which crystal habit was entered between co-ordinates of initial supersaturation and initial ferrocyanide concentration. When the solutions were gently agitated a morphogram represented by Fig. 9 was obtained. Three distinct regions are drawn on the diagram. Thus at any particular supersaturation a certain minimum amount of ferrocyanide was required before normal cubic growth ceased and excrescences developed at the corners of the crystal. By adding more ferrocyanide increasingly skeletal character was produced until growth and nucleation were suppressed at least for the duration of the experiment. The salt produced as these stages were gone through is illustrated by Figs. 10, 11 and 12. Figure 10 shows crystals in the cubic region, Fig. 11 is of salt produced just inside the skeletal region, and Fig. 12 demonstrates the maximum modification produced at a particular supersaturation and ferrocyanide content.

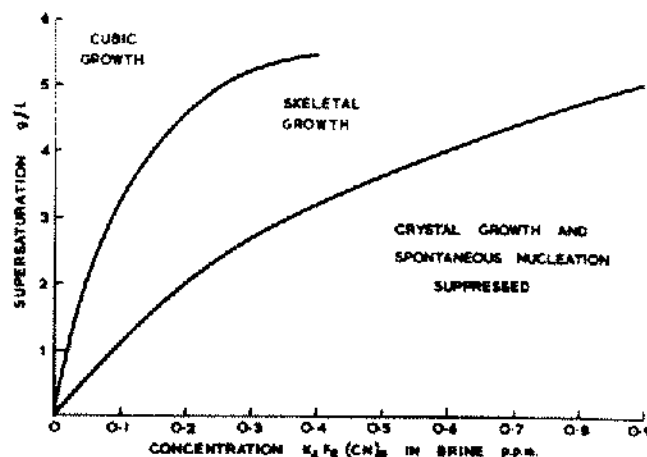


Figure 9. Morphogram for the system  $K_4Fe(CN)_6 : NaCl : H_2O$ . Stirred crystallization at  $45^\circ C$ .

These results were not very much affected by speed of stirring provided the crystals were kept in suspension. In quiescent conditions, however, a different situation existed. Very much higher ferrocyanide concentrations and supersaturations were required to produce excrescence growth and normally only cubes or hollow-faced cubes were seen.

The effect of increasing temperature from  $13^\circ C$  to  $60^\circ C$  was generally to decrease the supersaturations required to produce dendrites at a particular ferrocyanide concentration.

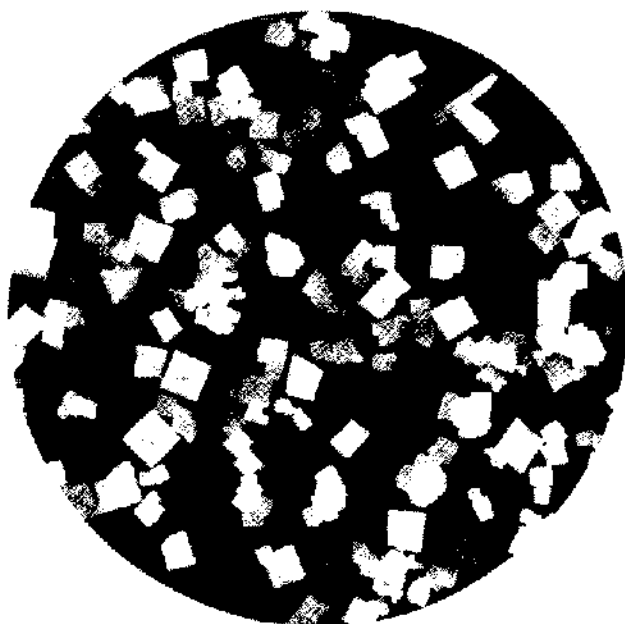


Figure 10. Crystals from "cubic" region of morphogram.



Figure 11. Crystals from just inside the "skeletal" region of morphogram.

Kern (1963) and his collaborators have also studied the influence of ferrocyanide ions on the exterior form of sodium chloride under different conditions of supersaturation. They apparently grew their crystals in relatively quiescent conditions and found that concentrations of ferrocyanide of at least 25 ppm were required to distort the cubes and 60 ppm were required before dendrites appeared. The importance of supersaturation on the effectiveness of the additive was also shown. These figures are in qualitative agreement with Birchall's results obtained under unstirred conditions, and show that concentrations required to produce an effect are higher than in stirred conditions by a factor of several hundred.

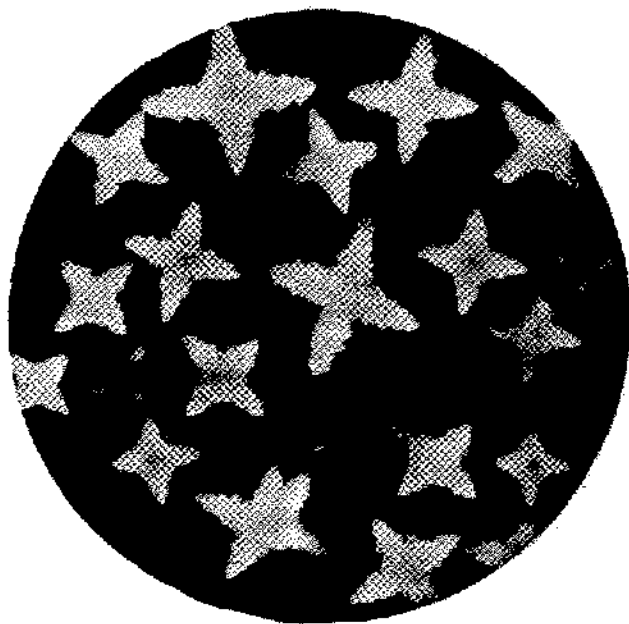


Figure 12. Crystals showing maximum modification in "skeletal" region of morphogram.

A number of other complex cyanides have been investigated and it appears that compounds with the ion grouping  $[M(CN)_5X]$  are active in varying degrees depending upon M, which may be iron, cobalt, manganese, chromium or ruthenium, etc., and on X, which may be CN, CO, NO,  $NO_2$ ,  $NH_2$ ,  $NH_3$ ,  $H_2O$ , etc. The  $[Fe(CN)_6]^{-4}$  ion remains the most powerful, however. Where less or more than six groups are attached to M, for example, in  $K_2Ni(CN)_4$  and  $K_4W(CN)_8$ , the effects are considerably diminished. The valency of the complex ion is also very important. Kern and his collaborators have shown that the ferricyanide ion,  $Fe(CN)_6^{-3}$ , behaves very differently from the ferrocyanide ion  $Fe(CN)_6^{-4}$ . In general,

higher concentrations of the ferricyanide are required to produce habit modification, and the transformation with increasing ferricyanide concentration and supersaturation is from the cube (100) to the octahedra (111) via intermediate forms.

#### MECHANISM OF HABIT MODIFICATION

So much for the facts known about habit modification of sodium chloride. How are we to explain these interesting and diverse phenomena? Unfortunately there is not as yet a really comprehensive and unifying theory to explain all the facts, but attempts have been made from time to time to explain particular examples of the general effect.

Royer (1934) attempted to explain the action of  $CdCl_2$ ,  $MnCl_2$  and  $ZnCl_2$  in producing octahedral (111) faces on NaCl by pointing out that these divalent chlorides have (111) faces with dimensions very close to the (111) face of NaCl. He supposed that this encouraged the development of the (111) faces in the salt crystal and thus brought about an octahedral form.

Bunn (1933) explained the habit modifying action of urea on salt by postulating that an unstable mixed crystal of the materials formed on the affected face. Being unstable it tends to redissolve, so that the net result is a reduction in growth rate. Conditions for the strong absorption necessary for the formation of the mixed crystal are similarity of lattice structure and interatomic distances on specific planes only; the rest of the structure can be quite dissimilar. Recently Palm and McGillavry (1963) have produced evidence to suggest that it is the compound  $NaCl/urea/H_2O$  which is absorbed and is responsible for the habit modification. Hille and Jentsch (1963) have concluded that urea produced its effect by encouraging the adsorption of water molecules onto the (111) face.

Speidel (1961), in attempting to explain the different effects of glycine, acetic acid, alanine and formamide on salt, introduces the concept that charge distribution in the molecule plays a part as well as the "fit" of the molecule on to a lattice in determining its adsorption onto the surface of a crystal.

Clearly strong adsorption plays a dominant part in deciding whether a substance will influence the growth of a crystal. Cabrera (1958) considers that impurity is strongly adsorbed on the relevant face of the crystal and forms a "jacket," which encloses the growth steps. The growth rate will fall if the mean distance between impurity particles is comparable with the size of the two dimensional nucleus for the prevailing supersaturation. Clearly this mechanism is only possible if the lifetime of the absorption is longer than the time needed for a growth step to move the distance between impurity particles. This implies that for the impurity to be effective absorption energy must be particularly high.

But what makes one substance, say sodium ferrocyanide, so much more active than others? Undoubtedly a certain degree of "fit" of the ion on the lattice is necessary. But it is also very likely that the charge on the ion plays an important part and probably explains the quite distinctly smaller effect shown by the trivalent ion  $[\text{Fe}(\text{CN})_6]^{-3}$ .

It is no doubt significant that the length of the Fe-CN distance in the  $[\text{Fe}(\text{CN})_6]^{-4}$  ion is of the same order as that of the Na-Cl distance in the sodium chloride lattice, and the central Fe is surrounded by six CN groups, a remarkably similar situation to the spatial arrangement of the Na and Cl ions around each other.

At the beginning of this paper the effect of ferrocyanide in suppressing growth altogether was referred to. This can be regarded as being due to the complete poisoning of available growth sites, in which case growth can take place only via the formation of two dimensional nuclei. This method of growth is very dependent upon supersaturation. It is suggested by Birchall that dendritic growth brought about by the presence of ferrocyanide occurs solely by two-dimensional nucleation, so that the orientation of growth is very sensitive to the distribution of supersaturation around the growing crystal. The fact that dendritic growth occurs only within certain limits of supersaturation is also explained.

It has been shown that the supersaturation over the face of a polyhedral crystal is higher at the corners than at the face-centres (Berg 1938, Bunn 1949, Humphries Owen 1949). When a salt crystal is growing under quiescent conditions in the presence of ferrocyanide, under some conditions it is possible for the supersaturation above the centre of the face to fall below the critical value for growth and hollow-faced cubes will be formed. This, it has been shown, was observed by Birchall. Even when the salt crystals are moving in their brine, a similar supersaturation gradient will exist and also the corners of the crystal will tend to protrude through the stagnant layer into regions of higher supersaturations still. If, as is postulated, growth can proceed only by two-dimensional nucleation owing to the poisoning of growth steps by ferrocyanide, the supersaturation gradient would starve the centre of the face and bring about rapid development of the corners. The supersaturation difference would then be further accentuated by the formation of a hollow face and extended corners. Chernov (1963) has calculated that a crystal cannot maintain a polyhedral form beyond a certain critical size and that due to the supersaturation gradient, skeletal growth from the corners will then occur. Apparently ferrocyanide is capable of providing the conditions whereby this critical size is very considerably reduced.

It is clear from Birchall's work that dendritic salt originates from a small cubic seed. It is evident that the position and number of excrescences developed will depend on the geometry of this original seed. Figure 13 shows the

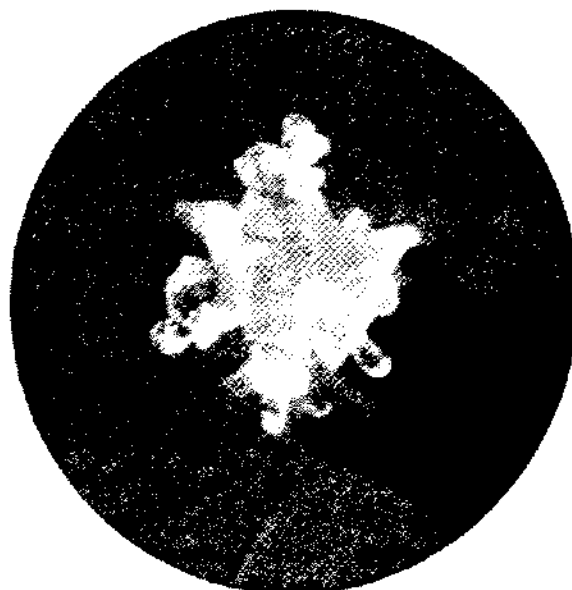


Figure 13. Excrescence growth from corners of an octahedral salt seed.



growth of excrescences from the six corners of a small octahedral salt seed when it was grown further in the presence of ferrocyanide.

Unfortunately not enough is yet known about the precise relationship between the crystal and the growth poison to do very much in the way of tailor-making molecules to produce specified effects. Intelligent application of analogy helps to increase the chance of finding a better material than that already known, but the discovery of active agents still remains largely empirical, although some useful guesses for starting materials can be made from structural data.

#### APPLICATIONS OF HABIT MODIFICATION AND GROWTH POISONS

It is important to consider the uses to which habit modification and growth poisons can be put.

The well-known use of ferrocyanide as an anti-caking agent is probably the most widely used and economically important example. When salt is subjected to varying humidities as it is in storage the presence of ferrocyanide on the surface of the grains inhibits solution and recrystallization so that caking bridges are not formed. When complete drying out occurs the sodium chloride crystals separate in the form of fragile dendrites, so that the bridges are weak and caking is much reduced.

The application of habit modification to salt technology has been the subject of several patents (see Bibliography). Dendritic salt, made by adding ferrocyanide to the evaporator, has a number of advantages over cubic salt for many applications. Its highly branched shape ensures that it does not readily segregate from mixtures with other materials such as one finds in fluxes and seasoning preparations. This shape also allows the salt to cling better to skins, etc., during curing and provides better handling properties. Its higher rate of solution makes it more useful for such processes as buttermaking. Its increased bulking properties make it go further for the same weight, an important point in applications where the salt is required to be spread over a large area. It will hold more than twice as much weight of water as cubic salt of equivalent size, which makes it especially useful in such applications as sausage casing curing, where a "blotting" action is required. This ability to physically absorb up to about half its weight of water means that it will not drip brine when stored in a humid atmosphere for a considerable time.

The addition of nitrilotriacetic acid and sodium carboxymethyl cellulose to the evaporator is claimed to give larger, sharper crystals than normal.

A recent patent (Ploss 1964) assigned to the International Salt Co. describes the preparation of low bulk density salt in the form of cyclic tetrakaidecahedra. The active material used is a mixture of sodium hexametaphosphate and an aluminium salt.

#### CONCLUDING REMARKS

This paper attempts to give some insight into the types of habit modification possible with sodium chloride and to what uses such phenomena can be put. Our knowledge of precisely how these effects are produced is still far from complete, but I would like to emphasize that studying the effect of an additive at one set of crystallizing conditions is quite inadequate to give a picture of its usefulness. It is important to remember that supersaturation itself plays a very important part in deciding the final shape of the crystal.

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