Gross Imperfections and Habit Modification in Salt Crystals

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ABSTRACT

The term gross imperfection refers to micro- and macro- scale defects as opposed to lattic defects. Mother liquor inclusions (brine cavities in this paper) represent one type of gross imperfection. The effect of crystal size and shape on the number of brine cavities is shown. Laboratory tests show that additives such as heavy metals and carrageen moss extract reduce brine cavities. Brine cavities, which may be responsible for salt caking under some conditions, can be removed by heating to high temperatures.

Inclusions of solid particles, principally calcium sulfate and calcium carbonate, within crystals represent another type of gross imperfection discussed. The number of inclusions is shown to be a function of salt crystal size, concentration of solid particles in suspension in the brine, an particle size of the inclusions. Laboratory tests show that soluble phosphates added to brine markedly reduce inclusions.

A well-known example of habit modification is the effect of ferrocyanide, which causes formation of dendritic salt. Lesser known is the effect of carboxymethyl cellulose, which produces octahedral crystals.

Any additive which affects brine cavities or crystal habit is invariably found tied up in the crystal in some fashion. This suggests that in producing these effects the additive is adsorbed by the growing crystal.

INTRODUCTION

This paper deals with three aspects of crystal growth from solution. These are: cavities, inclusions and habit modification.

A cavity is defined for the purposes of this discussion as a hole or imperfection in the crystal filled with mother liquor from which the crystal grew. Cavities are probably formed by the crystal growing around an imperfection in the surface of the growing crystal and trapping mother liquor in the imperfection. They vary in size from microscopic to fractions of an inch. Often inside the cavity one can see a bubble which will move back and forth as the crystal is tipped like the bubble in a spirit level. This bubble may be actually a vacuum formed by differential contraction of the cavity space and the mother liquor in it on cooling.

Inclusions in this paper mean solid particles other than salt inside crystals. Since salt is normally crystallized in the presence of other crystalline solids in suspension in the mother liquor, these may be trapped inside the crystal as it grows. The commonly observed inclusions in vacuum pan salt are calcium carbonate and calcium sulfate in one of its forms such as, gypsum, anhydrite or hemihydrate. Inclusions are difficult to observe except with the polarized light microscope.

Habit modification means a change in the external geometric configuration of the crystal without a change in the crystal lattice. Under most conditions salt crystallizes in the form of cubes. Under certain conditions growth is relatively more rapid on the edges and corners than on the centers of the cube faces and a dendritic shape results. Under other conditions growth is more rapid in the centers of the faces than on the edges and corners and an octahedron shape results.

Cavities and inclusions are designated "gross" imperfections because they can be seen with the eye or with a microscope. Thus, they are distinguished from imperfections on a smaller scale, such as dislocations. Dislocations are imperfections in the lattice and are usually observed by indirect means such as etching.

Gross imperfections and habit modification affect market qualities of salt. Cavities affect purity because of the moisture and mother liquor impurities contained in them. Also, they may be a cause of caking in storage when some of the trapped moisture slowly comes to the crystal surface. Inclusions affect quality mainly by decreasing purity. Habit modification in the form of dendrites is today finding an increasing sales market.

The results reported here apply mainly to vacuum pan salt. They have been accumulated over a period of years at various plants of Morton Salt Company and from laboratory experiments.

CAVITIES

Cavities have been found to vary with the type of salt crystal and conditions in the evaporator. Cube-shaped crystals with square edges and corners usually have a small number of cavities of relatively large size. These are usually formed in an evaporator with relatively low agitation rate and low salt suspension. Typical crystals of this type are shown in Fig. 1. These crystals were immersed in a liquid of nearly the same index of refraction as salt. This makes the crystal outside surface almost invisible and enables a view inside the crystal. Clove oil is a suitable liquid for this purpose. In Fig. 1 the cavities appearing as rectangles with a heavy black line around them are filled with brine. In some of these a bubble is visible. Cavities appearing as solid black irregular shapes have lost their liquid during drying of the salt and are now filled with air. Either they were close to the surface or had a crack running through them so that the moisture could escape during drying.

Crystals grown under conditions giving a rounded shape usually have a large number of small size cavities, and these cavities are usually concentrated in a shell near the crystal surface. Conditions for growing rounded crystals are high agitation and high salt suspension. Crystals of this type are shown in Fig. 2. For looking inside the crystals these were also immersed in a liquid having an index of refraction close to that of the salt. In this case the cavities appear as the numerous small white spots in the thick shell representing about one third of the radius of the crystal.

Figure 1. Square vacuum pan salt crystals showing brine cavities as dark areas and light rectangles outlined by a heavy dark line. Bubbles show in some cavities.

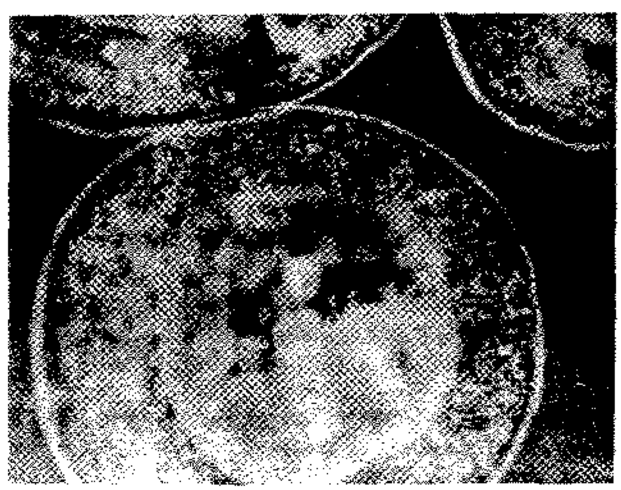

Figure 2. Round vacuum pan salt crystals showing brine cavities as light spots concentrated in crystal shell.

The crystals shown in Figs. 1 and 2 were grown in the laboratory from the same pure brine but under different conditions. The square crystals were made with moderate agitation and low salt suspension (about 10%). They contained 0.23% brine cavities. The rounded crystals were made with high agitation and salt suspension (about 30%). They contained 0.45% brine cavities. I is suggested that high agitation and salt suspension cause abrasion and roughening of the crystals, and inclusions are formed by trapping mother liquor as growth proceeds on this rough surface. Concentration of cavities in the shell is the result of increasing abrasion as the crystal grows larger and its mass and force of impact increase. Although grown in the laboratory, the crystals shown in Figs. 1 and 2 are typical of vacuum pan salt from different pans.

The number of cavities in salt from commercial vacuum pans varies with crystal size as shown by Fig. 3. The increasing percentage of cavities with increasing screen size fraction suggests that the rate of formation of cavities increases as the crystal grows in size. This is consistent with the above mentioned idea that abrasion is a cause of cavities, and that abrasion increases as size and mass increase. The variation in results from plant to plant is a warning to be cautious in trying to quantitatively apply to one plant the results obtained at another. Each plant must be considered individually. In addition to degree of agitation there are other factors, such as impurities in the brine, which vary and contribute to plant-to-plant differences.

Cavities are affected by some additives, and typical effects are shown in Table I. Of all additives tested the most cavity reduction was found with lead chloride, cadmium chloride and carrageen moss extract. This effect of heavy metals in giving clear crystals is well known, but the effect of carrageen moss extract is not well known. Practical use has not been made of these additives because they end up as impurities in the salt. Salt made with cadmium chloride contained 30 to 270 parts per million of cadmium depending upon evaporating conditions. Salt made with either lead, cadmium or manganese darkened on heating, and so did salt made with carrageen moss extract.

Most additives have no appreciable effect on cavities, and one has been found to increase cavities. It is sodium ferrocyanide and at the same time it produces dendrites as will be discussed later.

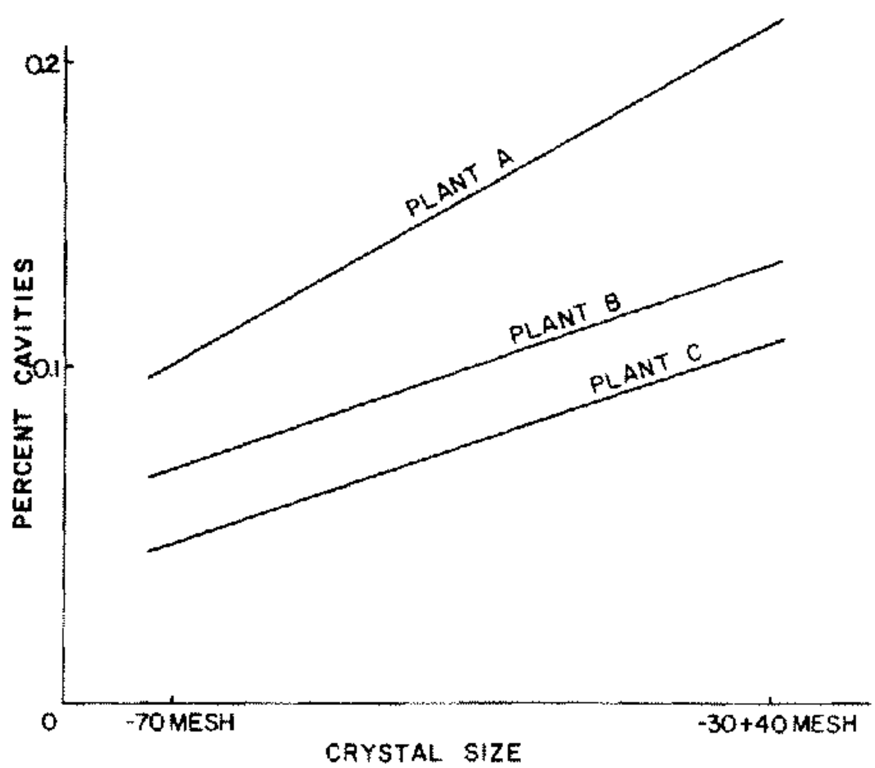

Figure 3. Relationship between percent cavities and salt crystal size for different plants.

Table I

Effect of Some Additives on Brine Cavities

Additive	Amount Added p.p.m. in brine	Cavities % in salt
Control brine -- no additive	---	0.29
Lead chloride	500	0.02
Cadmium chloride	500	0.02
Manganese sulfate	500	0.05
Carrageen moss extract	200	----*
Sodium citrate	250	0.21
Methyl cellulose	250	0.23
Gelatin	250	0.31
Citric acid	250	0.24
Gum Arabic	250	0.20
Urea	100,000 (10%)	0.32
Sodium ferrocyanide	250	0.64**

* Amount could not be determined because of weight loss due to absorbed organic matter. Microscopic examination showed amount of cavities was very low.

** Crystals formed were dendritic.

The effect of cavities on market quality of salt has not been well established. Naturally they decrease the purity of salt because of the impurities contained in the entrapped mother liquor, however, for most uses of salt this is of minor importance. It has been suggested that in storage some of the moisture from cavities leaks through microcracks to the crystal surface where it contributes to caking, especially when salt is stored hot. Salt caking of this type is sometimes of considerable importance to the salt industry, and positively associating it with brine cavities would be a strong incentive to find ways of eliminating cavities.

Cavity moisture can be removed by heating. The rate of moisture evolution at three different temperatures is shown in Figure 4. While some moisture is evolved at moderate temperatures, heating close to the melting point (1474°F, 801°C) is necessary to evolve close to 100% of the moisture in a time of one hour or less.

The analytical method for percent cavities measures the loss in weight of the salt sample heated for one hour at 1155°F, 624°C. The percent cavities is the percent weight loss in the sample. This measures moisture loss from the cavities and, of course, is limited to samples containing no other volatiles or organic matter decomposable at this temperature.

INCLUSIONS

The principal inclusions in vacuum pan salt are calcium sulfate and calcium carbonate. Calcium sulfate occurs in several forms including gypsum, hemihydrate and anhydrite. In the high temperature vacuum pans anhydrite is the predominating form. In the low temperature pans gypsum predominates. Gypsum inclusions are usually large as illustrated by the single inclusion in a single salt crystal in Fig. 5. Anhydrite inclusions are sometimes distributed throughout the salt crystal as illustrated in Fig. 6. In this case they are needle-shaped crystals oriented parallel to the surfaces of the salt crystal. Usually anhydrite occurs as a cluster of inclusions at the center of the salt crystal with the rest of the crystal relatively free from inclusions. This common occurrence of anhydrite inclusions is shown in Fig. 7. A cluster of inclusions at the center of the crystal suggests that the inclusions act as seeds or nuclei for salt crystallization.

Inclusions are best observed with a polarized light microscope. Since the inclusions are optically anisotropic and salt is optically isotropic, the inclusions appear either as light particles inside the dark salt crystal or as yellow- or blue-colored particles inside the pink-colored salt

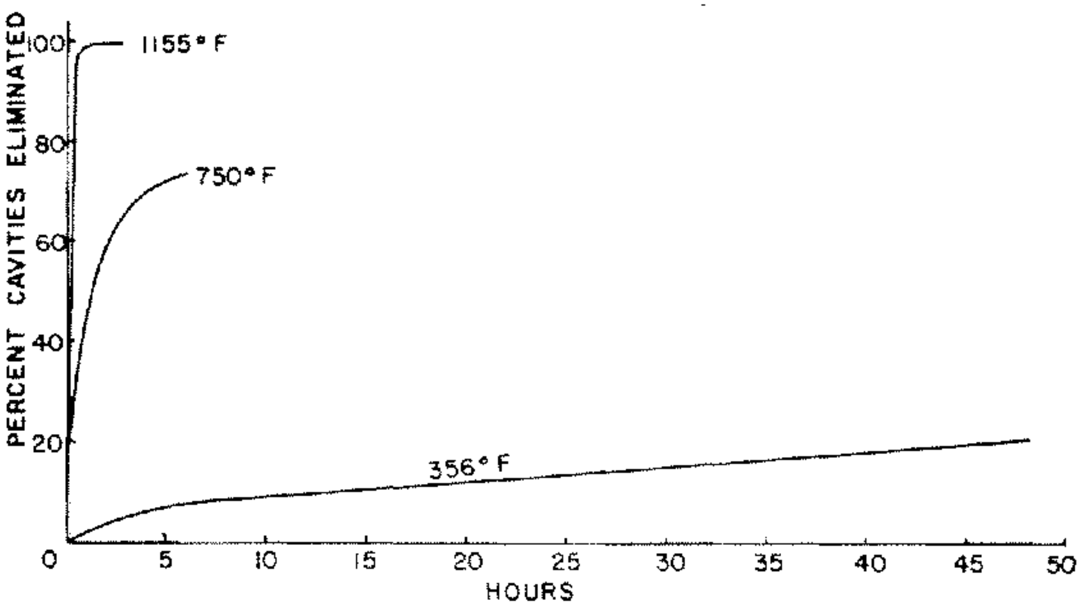

Figure 4. Rate of moisture release from brine inclusions in salt heated to various temperatures.

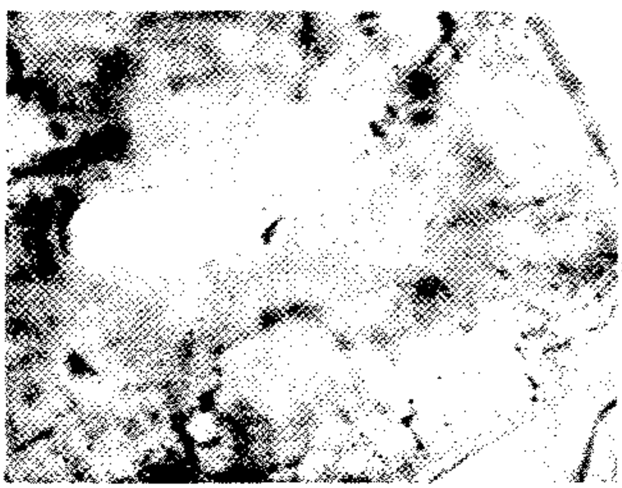

Figure 5. Polarized light photomicrograph of a gypsum inclusion inside a salt crystal.

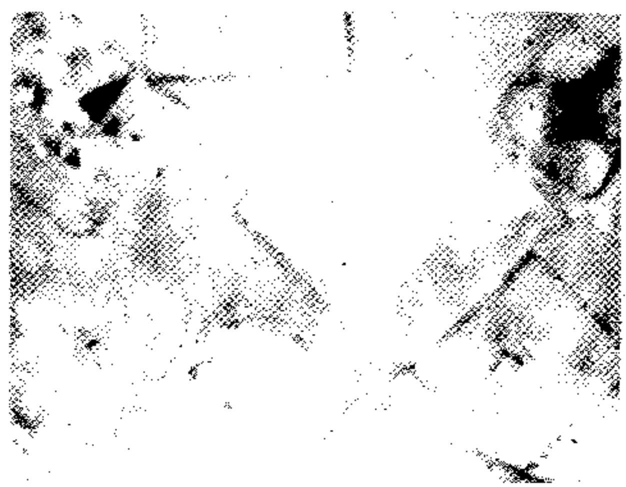

Figure 6. Polarized light photomicrograph of needle-shaped anhydrite inclusions oriented parallel to surfaces of salt crystals.

crystals. The photographs in Figs. 5, 6, and 7 were made with a polarized light microscope with the crystals immersed in clove oil.

Calcium sulfate crystallizes out of brine during evaporation, and these crystals being small in comparison to the salt crystals remain in suspension in the mother liquor. Their concentration commonly builds up to 100 G.P.L. (grams per liter) of the brine or 8.3% by weight. These are the crystals which are included in salt crystals. The amount of included calcium sulfate has been found to be proportional to the concentration of suspended calcium sulfate.

In a given set of vacuum pans percent inclusions decrease as the size of the salt crystals increase, but the amount of inclusions varies from one set of pans to another. This relationship is shown in Fig. 8 for three different plants. The very sharp decrease in percent inclusions for sizes just larger than 70 mesh is consistent with the commonly observed condition of inclusions concentrated at the center of the crystal as shown in Fig. 7.

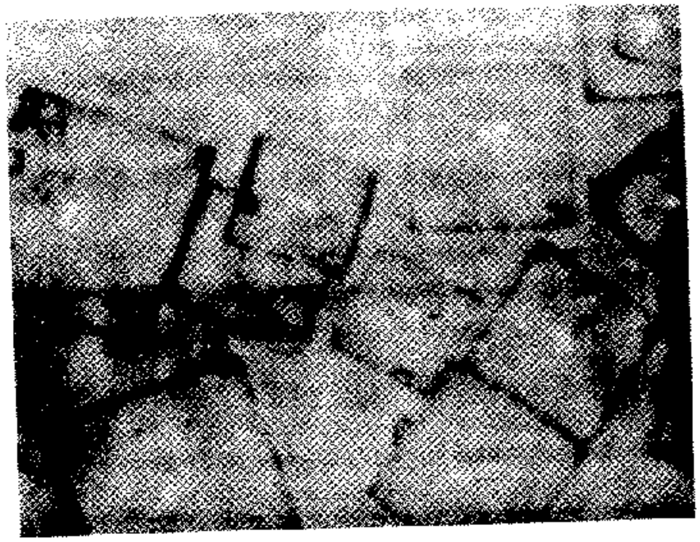

Figure 7. Polarized light photomicrograph of anhydrite inclusions located at the center of salt crystals.

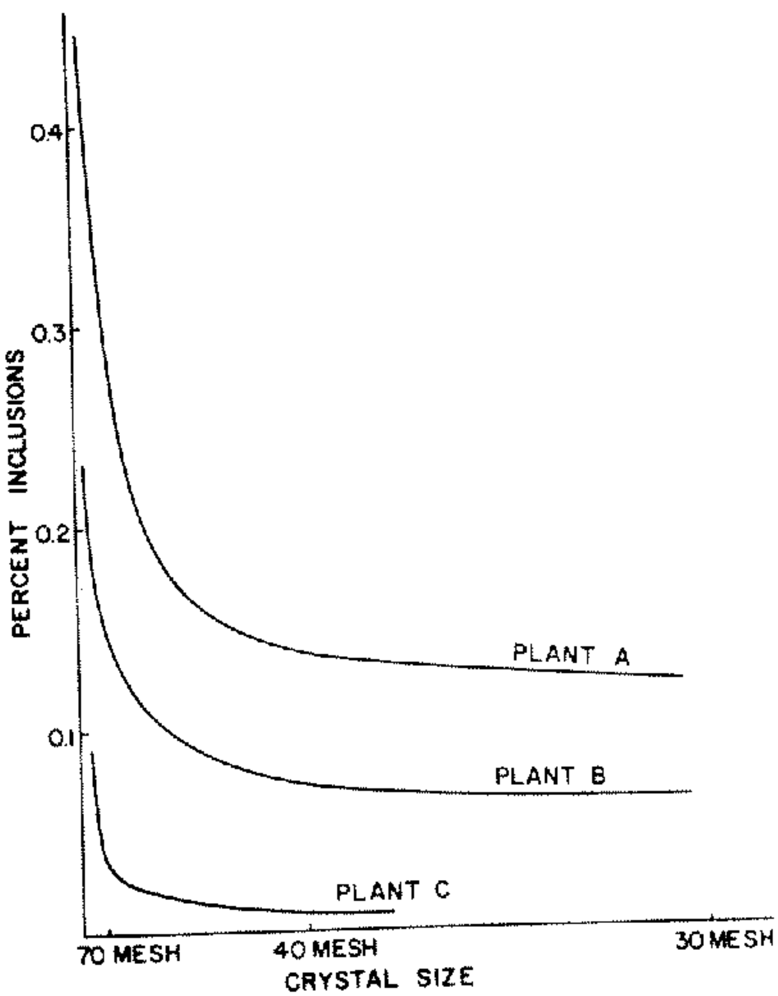

Figure 8. Relationship between percent inclusions and salt crystal size for different plants.

High salt suspensions and high agitation tend toward low inclusions. Two theories are offered in explanation. One is that the small particles of salt knocked off by abrasion under these conditions act as seeds for further salt crystallization and reduce the incidence of seeding by calcium sulfate particles. This idea of seeding by calcium sulfate particles is consistent with the observation that calcium sulfate inclusions are commonly located at the center of the salt crystals. Another is the so-called "bumping theory." As agitation and salt suspension are increased the salt crystals bump each other more vigorously and knock off particles of calcium sulfate or calcium carbonate which normally tend to stick to the salt crystal faces and be included. This theory accounts for inclusions located only at the center of the salt crystal, because small crystals do not have enough mass or force to prevent the calcium sulfate and carbonate particles from sticking and being included. It is not known definitely which of these theories is correct.

Certain additives have been found to reduce inclusions. Soluble phosphates are effective and one of the most potent additives is sodium polyphosphate as shown in Fig. 9. It is effective against calcium sulfate and carbonate and at all levels of calcium sulfate suspension, however, at high levels of suspension more phosphate is required than at low levels. It is believed that polyphosphate acts by reacting with the surface of the calcium sulfate or carbonate particles, thereby altering them in some way as yet unexplained to make them less subject to inclusion. Other additives which form insoluble calcium compounds were tried and found ineffective. These included sodium fluoride, oxalate, molybdate and silicate.

Crystallization is well known as a method of purification. Vacuum pan salt is an outstanding example of this. Salt crystallized from brine containing as much as 8.3% fine calcium sulfate particles in suspension contains only 0.4% calcium sulfate inclusions and this is reduced to less than 0.06% by phosphates as shown in Fig. 8.

Inclusions affect market quality of salt because they decrease purity and are not capable of being removed by classification or washing. Inclusions of gypsum are especially objectionable because each inclusion is large in size.

Determination of inclusions is usually made by analyzing the salt for calcium and calculating the result in terms of calcium sulfate. Before analysis the salt is washed with hydrochloric acid solution saturated with sodium chloride to remove calcium sulfate particles which might be adhering to the crystal surfaces.

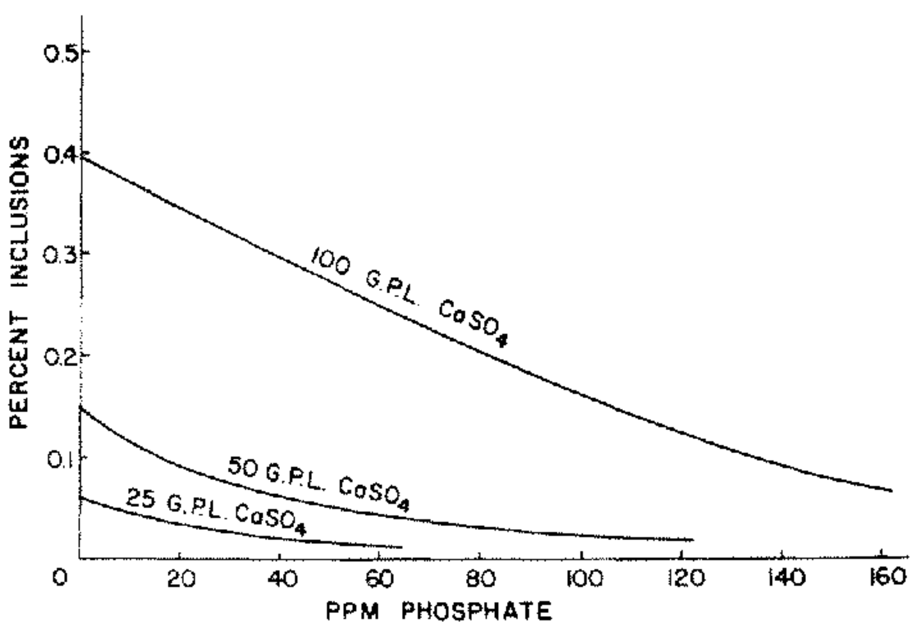

Figure 9. Effect of polyphosphate in reducing inclusions at various levels of suspended calcium sulfate. G.P.L. $CaSO_4$ stands for grams of suspended calcium sulphate per liter of brine.

HABIT MODIFICATION

Habit modification has been discussed so much in many publications that it will be treated here only briefly. However, a discussion of imperfections in vacuum pan salt would not be complete without a mention of dendritic salt. This modification has found many uses because of its unique physical properties, such as low bulk density and high surface area.

Dendritic salt is formed by addition of very small amounts of sodium ferrocyanide to brine. A dendritic crystal of sodium chloride produced by sodium ferrocyanide addition is shown in Fig. 10. This type of crystal is produced by preferential growth at the cube corners causing the corners to grow out from the crystal.

The opposite of preferential growth at the corners is preferential growth at the cube face centers. The result of this type of preferred growth is an octahedron shape. It is possible to control additives in such a way as to obtain crystals intermediate between a cube and an octahedron. Examples of such shapes would be a cube with the corners cut off and an octahedron with its points cut off.

An additive very effective in forming octahedron shapes is carboxymethyl cellulose (CMC). An illustration of octahedral salt formed by this additive is shown in Fig. 11.

All additives effective in modifying habit are retained in varying degrees by the crystal. The same is true of additives affecting cavities. This suggests that the effects are brought about by adsorption of the additive on the growing crystal and perhaps a retention of the additive in the lattice. The same is not true of the use of phosphates in affecting inclusions, because here the effect is believed to be on the particle subject to inclusion rather than on the salt crystals.

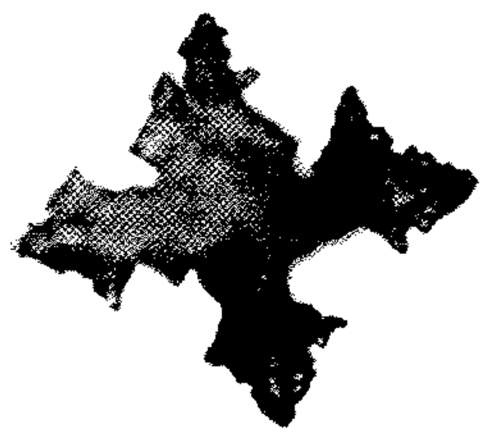

Figure 10. Dendritic type of salt crystal produced by addition of sodium ferrocyanide to brine.

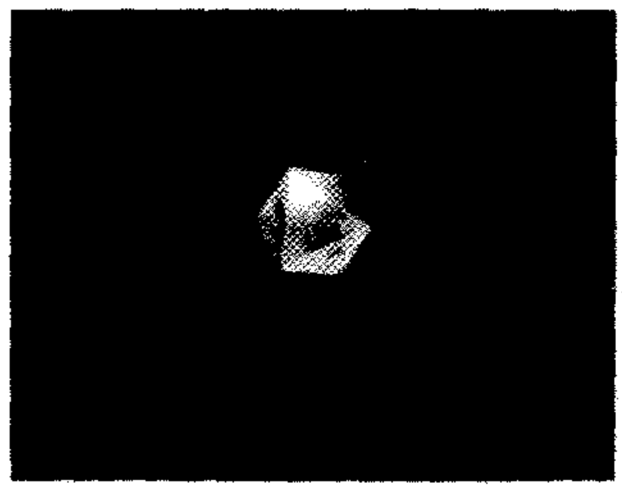

Figure 11. Octahedral type of salt crystal produced by addition of carboxymethyl cellulose (CMC) to brine.