CHEMICAL RESEARCH IN ICE MANUFACTURE

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In considering the industrial growth of the country during the past twenty years it is interesting to discover that one of the major industries which developed during this period was the production of artificial ice. It is only possible to gain an accurate conception of the true proportions of this development by considering the fact that during 1929, 54,000,000 tons of ice were produced, the retail value of which was approximately $400,000,000. As, in addition to its size, the industry is intimately connected with the efficient maintenance of public health, its problems deserve particular attention in the form of effective research. In the past this attention has been centered in studies concerned with the efficient operation of the mechanical units comprising the refrigerating cycle. During a recent investigation conducted at the University of Illinois, however, problems more intimately concerned in the production of artificial ice itself have been made the basis of extensive research.

From a mechanical standpoint the manufacturing process does not include an extremely involved procedure. A gaseous refrigerant, usually ammonia, is compressed to a liquid by means of mechanically operated compressors and is then allowed to boil at the expense of heat absorbed from a concentrated salt solution containing either sodium or calcium chloride, commonly called a brine, the freezing point of which is below that of pure water. Heat exchange is effected in an apparatus which effectively separates the two liquids by means of a metal wall. The ammonia vaporized during the process is again compressed, cooled in a water condenser, and returned as a liquid to the evaporator, thus operating as a continuous, closed system. The net effect of using the refrigerant is to remove heat from the brine and to deliver the heat thus extracted to the condenser water used to cool the ammonia gas following its compression.

The brine, cooled by the removal of heat in the ammonia evaporator, is rapidly circulated past steel cans containing the water to be

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[1] This article is based on data previously published in Engineering Experiment Station Bulletin No. 219, "The Treatment of Water for Ice Manufacture," by Professor Dana Burke, Jr., Chemical Engineering Division, University of Illinois.

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frozen. Ice is formed at the sides and bottom of the cans thus leaving the unfrozen water confined in a core bounded by the growing walls of ice. When the water is completely frozen the cans are removed from the brine and placed in a thawing tank which is filled with warm water. Here a thin layer of ice is melted from the sides and bottom of the cans, thus allowing the ice to be removed. The ice removed, the cans are refilled with water and returned to the freezing tank.

The production of ice is thus seen to result from the expenditure of mechanical energy, the total work required being equivalent to that used by the compressors to return to its original liquid state the ammonia vaporized during the extraction of heat from the brine. In the original plants the only economical motive power available was that obtained from coal burned to produce steam, a procedure which fortunately served a double purpose, as the steam after being passed through the compressors was condensed to produce distilled water. When this water was quietly frozen in cans immersed in the freezing brine the ice produced was invariably transparent, due to the almost complete absence of dissolved salts. The effect of this practice was destined, however, to play an important rôle in the future economic development of the industry itself, for the consuming public finally arrived at the point where it demanded the transparency that it had been early educated to expect.

The full effect of this demand for transparent ice became apparent with the next major development affecting the industry. With general industrial growth it gradually became evident that power could be produced more economically in central power stations as electrical energy than in small individual steam installations. It was determined in the case of the ice industry, for example, that a ton of coal burned in a steam-driven ice-plant would produce from 4 to 6 tons of ice, whereas the same amount of fuel burned in a central power station would generate sufficient electrical energy to produce from 16 to 18 tons of ice when the plant was electrified. Electrification afforded savings in ice production cost of from $0.40 to $1.00 per ton.

In the electrified ice-plant, however, distilled water was no longer available for the ice and natural water supplies had to be used in its place. Such water always includes varying amounts of dissolved salts and when quietly frozen, according to the procedure giving transparent ice from distilled water, the product is completely opaque, as indicated in figure 1.

The reason for the production of opaque ice from solutions containing dissolved salts will be readily understood upon reviewing the conditions to which such solutions are subjected on being cooled. As the temperature is lowered, a point is finally reached at which solid water or ice forms, and as heat continues to be absorbed from the solution, the formation of ice continues. With the separation of water as ice, however, the salts in the unfrozen solution are more and more concentrated, until a point is finally reached at which either of two conditions occasioning the formation of opaque ice results.

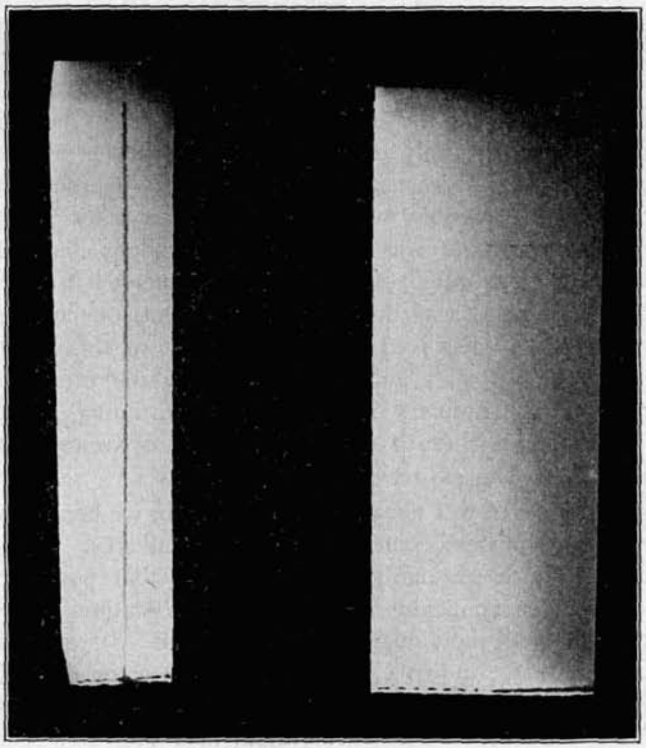

FIG. 1. Ice frozen from a solution containing dissolved salts under conditions that invariably produce highly transparent ice when the solution being frozen is distilled water and therefore free from salts. This ice is completely opaque, opacity having resulted from the fact that its optical properties have been materially affected by the presence of the dissolved salts in the water from which the ice crystals formed.
(Courtesy Engineering Experiment Station, University of Illinois.)

If the composition of the original solution is such that an insoluble compound may be formed as the result of concentration, solid salt will eventually separate with the ice as an eutectic mixture. Due to the fact that an eutectic generally possesses optical properties which differ from those of pure ice alone, the solid will appear opaque. A further disadvantage of the separation of an eutectic mixture lies in the fact that when the ice melts the salt does not redissolve but remains behind as an insoluble sludge which either clogs up the drain in the domestic ice-box or coats the produce which it is used to cool during shipment to market. The separation of salt with the ice may be prevented, however, by treating the water chemically before it is frozen so that the salts of low solubility are converted into more soluble compounds. This may be effected, for example, by neutralizing the carbonates of calcium and magnesium to the corresponding sulphates, a process commonly accomplished by means of aluminum sulphate.

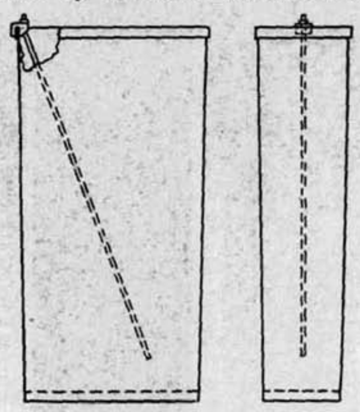

Fig. 2. A typical method of applying air to obtain agitation of the solutions being frozen according to procedure which has become standardized in the ice industry. The air enters the solution at a single point, and maximum agitation results in the center of the solution. When the initial salt concentration and the rate of crystallization are high such agitation is ineffective in preventing the formation of opaque ice at the freezing surface where the dissolved salt has a tendency to concentrate locally.

The second condition occasioning the formation of opaque ice results when the dissolved salts become sufficiently concentrated to affect the physical characteristics of the individual ice crystals themselves. The environment in which a crystal forms exerts a decided effect on both its habit and orientation. When these properties become materially altered, light passing through the solid is sufficiently scattered to cause the mass to appear opaque. The general phenomenon is quite common. For example, a large transparent crystal on being pulverized is reduced to a mass which appears opaque, even though the individual crystal units themselves remain perfectly transparent.

To overcome the formation of opacity from this cause any localized salt concentration at the surface of the growing crystal must be prevented and the unfrozen solution must be removed whenever the salts become concentrated to the point where the orientation and habit of the ice crystals are affected. Removal of the unfrozen core water obviously necessitates refilling the core cavity with a fresh supply of the water originally used.

When the salt solution is first subjected to freezing, extremely rapid cooling takes place at the sides of the metal can. This results from the fact that the heat conductivity of steel is comparatively high

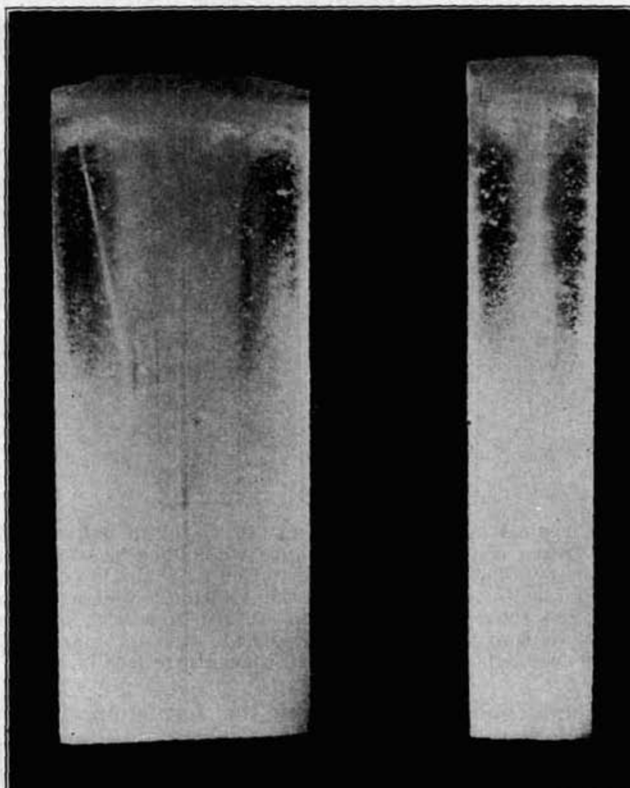

Fig. 3. Ice from a solution containing a high concentration of dissolved salt frozen under conditions resulting from air agitation applied according to the method illustrated in Figure 2. The opaque shell encasing the ice cake and the thick opaque core are typical results of ineffective agitation. Ice of this quality is thoroughly unmarketable. In the past the only remedy for this condition has been to distill the water to remove the salts. Such procedure prevents the electrification of the manufacturing process and materially increases the cost of production.

(Courtesy Engineering Experiment Station, University of Illinois.)

and that the freezing brine in the average plant is maintained at a temperature 16° F. below that at which ice initially forms.

This layer of ice which forms first is of course surrounded by all of the unfrozen solution. Actually, however, it may be considered to be bounded by only a thin film of the salt solution. The conditions existing in this fluid film not only affect the physical characteristics of the crystal but also determine the physical characteristics of the final cake of ice. As growth of the ice surface depends upon its continued ability to remove water from this fluid film, there is a decided tendency for the salts present in the film to become locally concentrated, the extent of this tendency being dependent upon the initial concentration of the salts in the solution and the rate at which ice is formed at the crystal face. Unless local concentration of the salt is prevented, the

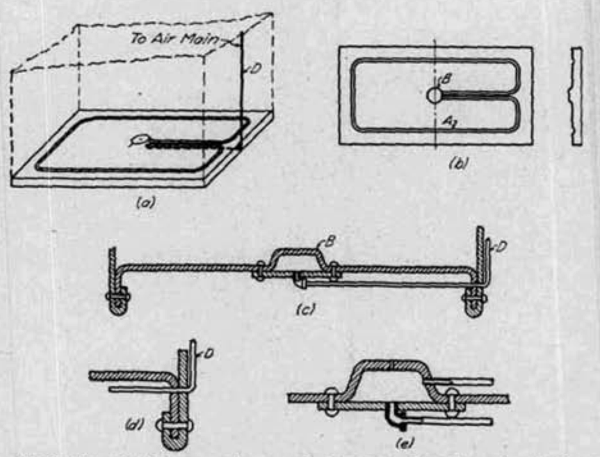

Fig. 4. Details of the new type of ice-can developed at the University of Illinois. The air for agitation is forced to enter the solution through a series of small holes in a header located at the extreme sides of the can as indicated in *(a)*. The ice which initially forms while the rate of crystallization is high is thus effectively agitated. When the rate of crystallization is materially reduced by the formation of a sufficiently thick layer of ice through which heat must be removed by the brine, a much smaller amount of air applied from a point located centrally in the can as at B in *(b)* is sufficient to prevent the formation of opaque ice. When the air supply is reduced, ice forming in from the sides of the can effectively plugs the holes in the outer header and allows the final air to enter only from the hole at B. Details of the can's construction are indicated in *(c)*, *(d)* and *(e)*.

critical concentration affecting crystal orientation may be reached in the film long before the concentration of the salts in the main body of the unfrozen solution is materially altered.

The best way to prevent local concentration in the surface film is to agitate the solution as it is being frozen, thus mixing the concentrated salt solution formed in the fluid film with the main body of the solution which is more dilute. In common practice agitation is accomplished by expanding air under pressure into the bottom of the cans of water. The air in rising to the surface imparts a certain motion to the liquid which in turn results in the desired mixing. In the past, however, the agitation developed by means of air has been relatively inefficient. The air was delivered to a single point located near the center of the bottom of the can (fig. 2) resulting in the effective movement of the liquid being limited to the form of an inverted cone whose apex corresponds to the point of entry of the air. The maximum agitation results, not at the sides of the can, but in the center. It is at the sides,

FIG. 5. Ice from the same water which produced the unmarketable product shown in Figure 3 frozen in the new type of ice can shown in Figure 4. In order to judge the quality of this ice from the standpoint of transparency, reference should be made to Figure 6, which indicates the ice produced from distilled water agitated by air during the freezing operation.
(Courtesy Engineering Experiment Station, University of Illinois.)

however, that the most effective agitation is needed, especially during the initial freezing. An example of inefficient agitation where the initial salt concentration of the water being frozen is high is shown in figure 3. As a result of such procedure it has formerly been considered impossible to produce marketable ice from raw water sources containing salts in excess of six hundred to seven hundred parts per million.

During the course of the present investigation a new type of freezing can has been developed whereby the efficiency of the air agitation imparted to the solution is greatly increased. The construction of the new can is indicated in figure 4. The air is forced to enter at the extreme sides of the can, thus causing maximum agitation to

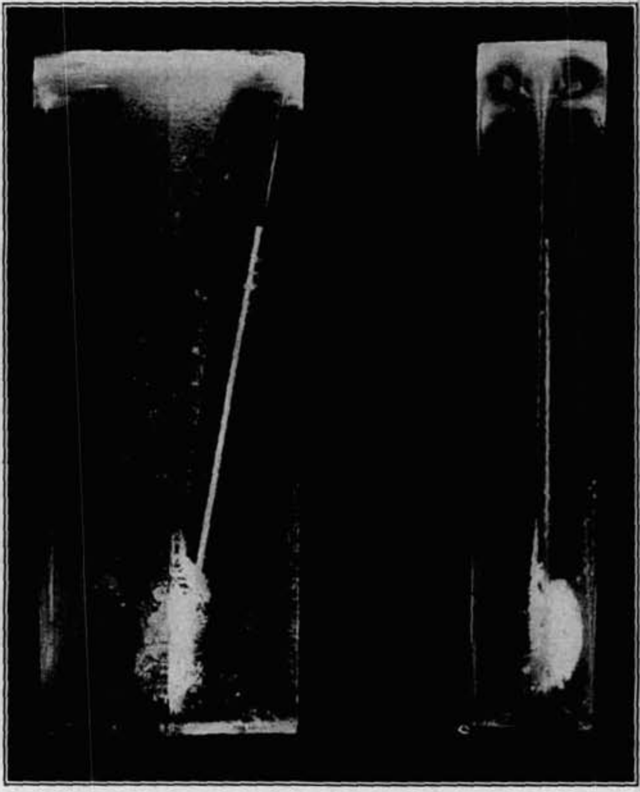

Fig. 6. Ice frozen from distilled water agitated by means of air throughout the freezing operation. Opacity in this case results from the fact that the final water which freezes is whipped into and freezes as an air foam, the optical properties of which differ sufficiently from those of ice alone to cause light passing through the ice cake to be materially scattered.
(Courtesy Engineering Experiment Station, University of Illinois.)

exist always at the surface of the ice. In figure 5 is shown the result of using the new can in freezing the water which produced, under standard freezing procedure, the thoroughly unmarketable product shown in figure 3. For comparison, ice frozen from distilled water is shown in figure 6.

As a result of this investigation it has been determined, on the basis of both laboratory and plant scale operations, that thoroughly marketable ice can be made from any natural water source which may be considered as an industrial supply, so that it is no longer necessary to distill water in order to render it suitable for the production of marketable ice. Approximately one-third of the ice produced is still being manufactured in steam plants in spite of the lower operating

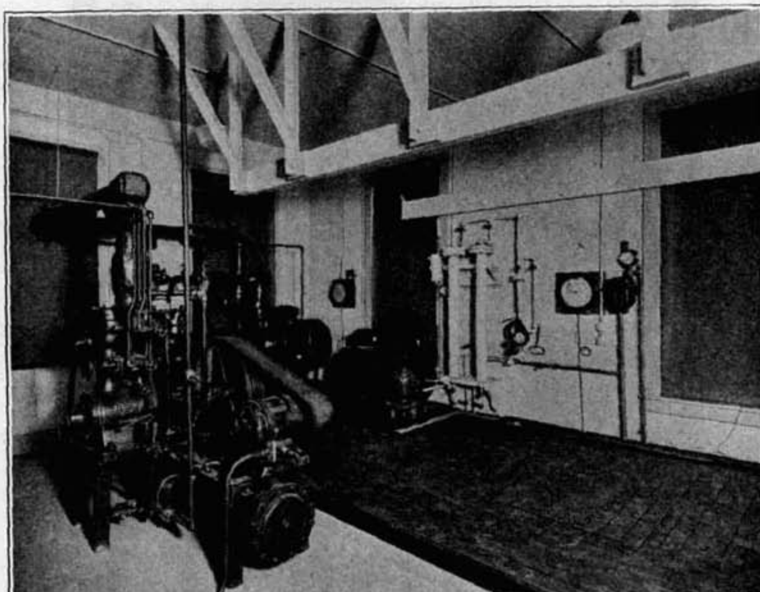

FIG. 7. Details of the experimental ice plant recently installed at the University of Illinois to facilitate further investigation of problems involved in the efficient manuıacture of artificial ice.

cost which electrification offers. Undoubtedly factors other than the inability to produce marketable ice in electrified production exist in many steam installations. The steam generating equipment, for example, may have been so recently installed that the depreciation loss incurred by its removal cannot yet be economically absorbed. As the result of the present investigation, however, control of the physical and chemical conditions at the surface of the growing ice crystal has been shown to be sufficient to produce clear, transparent ice in electrified plants, whenever desired, from any natural water found in the United States.