Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Freeze Purification of Water Utilizing a Cold Plastic Surface and Ice-Liquid Separation with a Centrifuge

Ehsan Ul Haq[a]
[a] PROCESS GROUP PAKISTAN INSTITUTE OF NUCLEAR SCIENCE & TECHNOLOGY, ISLAMABAD, PAKISTAN

To cite this Article Haq, Ehsan Ul(1996) 'Freeze Purification of Water Utilizing a Cold Plastic Surface and Ice-Liquid Separation with a Centrifuge', Separation Science and Technology, 31: 14, 1971 — 1977
To link to this Article: DOI: 10.1080/01496399608001023
URL: http://dx.doi.org/10.1080/01496399608001023

SEPARATION SCIENCE AND TECHNOLOGY, 31(14), pp. 1971–1977, 1996

TECHNICAL NOTE

Freeze Purification of Water Utilizing a Cold Plastic Surface and Ice–Liquid Separation with a Centrifuge

EHSAN UL HAQ
PROCESS GROUP
PAKISTAN INSTITUTE OF NUCLEAR SCIENCE & TECHNOLOGY
P.O. BOX 1356, ISLAMABAD, PAKISTAN

ABSTRACT

Freeze purification utilizing a cold plastic surface rather than a metallic surface may be advantageous. Plastics are more inert and weaker ice crystal nucleating agents, and possess low ice–plastic adhesion. Batch experiments were performed to test the viability of a freeze purification technique. One-liter samples of an aqueous feed solution containing 20 g/L sodium chloride were contacted with a 350-cm^2 area of polyethylene terephthalate surface at 256 K for 10 minutes. About 200 mL of ice-liquid mass was obtained. A centrifugal technique was utilized to separate solid ice crystals from adhering liquid. An average of 60 mL of solid ice containing 1.9 g/L salt was recovered. Ice crystal grain characteristics and conditions to improve efficiency of the freeze purification technique are discussed. A brief comparison with alternate freeze purification techniques is also mentioned.

INTRODUCTION

Liquid water is a very good solvent for a wide variety of substances, but in its solid form it does not retain its solvent nature. Freezing of aqueous solutions results in segregation of pure solid ice. The phenomenon is an alternate to well-known evaporation (1). The process is applicable in a range from extreme dilution to eutectic concentrations and is considered economic from medium to low values within this range.

The simplest way to freeze an aqueous solution is to bring it in contact with a cold surface. It may also be conducive to planar growth of a layer of pure crystal ice if heat dissipation can be channeled from a growing ice–liquid interface toward solid ice. The temperature gradient in that

condition is believed to avoid the onset of conditions where a planar ice front is transformed into a rugged one (2). Though growth of a planar ice front may be possible, all practical freeze purification systems with a supercooled liquid, high initial solute concentrations, and small values of solute to heat diffusion coefficient ratios in liquid give rise to rugged fronts. Here some sections of an ice front outgrow others to form spikes or grains perpendicular to the surface. Significant amounts of liquid at a rugged front are entrapped during its creation. Ice spikes, with their low thermal conductivity and liquid entrapped in their thin spaces where little convective current can exist, collectively have a very high resistance to heat dissipation. Thus, once a layer of ice covers a cold surface, heat dissipation toward a cold surface requires very large temperature gradients and heat transport becomes slow, rendering further freezing less economical. Continuing growth by providing higher temperature gradients or maintaining the same gradient for longer times increases the dimensions of any already present grains and also gives rise to new grains. Ice spikes growing alongside each other continue to become closer, and a fraction touchs and adheres to each other, forming a larger lump of frozen mass. Sooner or later a stage arrives where a thicker layer of tightly packed grains with a quantity of entrapped liquid in thin, long spaces covers the cold surface, virtually stopping further growth. The main problem with the lumped frozen mass is that it is unsuitable for further purification with the help of the available solid–liquid separation techniques (3).

Freezing aqueous solutions in a manner that results in a collection of separate grains is the preferred method. A mass of separate grains is more amenable to ice–liquid separation and grain washing operations. These operations are an integral part of any freeze purification technique. Without efficient ice–liquid separation, freezing brings about little purification on a macro scale. One technique used to harvest ice as individual grains is to utilize moderate temperature gradients between a cold surface and the initial impure solution and to remove sparsely growing grains from the surface well before they adhere to each other and are transformed into a large lump of solid frozen mass.

Metallic surfaces have the best ice crystal nucleation properties but may increasingly promote lumped frozen masses. The processing of chemically active solutions utilizing metallic containers is also not preferred. Additionally, ice sticks to metallic surfaces so strongly that its removal is both difficult and energy consuming (4).

The weak adhesion of ice to plastic can save energy. A cheaper plastic material may also lead to a lower capital cost in a commercial freeze purification plant. The thermal inefficiency effect could also be reduced by mounting a very thin plastic film on a metallic base.

Mixing and agitation in the liquid during freezing improves the purity of solid ice. Agitation with ultrasonic vibrations has been found very effective (5). A complete freeze purification technique with a plastic surface requires an agitating device. A laboratory shaker has been utilized in this investigation. The separation of ice grains by a centrifugation technique has also been investigated.

EXPERIMENTAL

A round-bottomed cylindrical bottle (85 mm O.D. and 0.5 mm wall thickness) of transparent polyethylene terephthalate contained 1 L of coolant as an aqueous solution containing 20% by weight NaCl (freezing point 256 K). The bottle was placed in a thin, transparent polyethylene bag and kept in a freezer until it was frozen. It was then removed from the freezer and left outside until melting of the coolant was observed. The coolant container was then taken out of the polyethylene bag and immersed in a 1-L sample of impure solution containing 20 g NaCl/L at a temperature of 277 ± 1 K. The impure solution was contained in a flat-bottomed cylindrical container of 145 mm I.D. All the above apparatuses were placed inside a thick-walled heat-insulating box of expanded polystyrene. The box was fixed in a laboratory shaker that moved in a horizontal plane with a sweep of 1.5 in. at a frequency of 4 to 5 Hz. The coolant bottle was kept immersed in the impure solution for ice growth on its outer surface for a fixed time interval of 10 minutes. A part of the coolant remained solidified inside the bottle throughout. The shaker was then stopped, and the coolant holding the plastic container was removed from the impure solution along with a layer of frozen mass (pure ice grains and adhering liquid) sticking on its outer surface. The frozen mass was gently scrapped from the surface. The mass was transferred to a fine filter cloth bag which was then inserted in 100 mL capacity centrifuge glass tubes. A coarse filter screen was fixed inside the tube at approximately 20 mm from its bottom to provide room (about 25 mL) for separated the liquid during centrifuging. Two sets of cloth bags and tubes were utilized. The tubes were thermally insulated by wrapping five layers of plastic tape around them, and a heat insulating plastic lid was fixed at their tops. The centrifuge was operated at 3000 rpm for 2 minutes. The filter cloth bag holding the solid mass was then taken out of the tube, and the separated liquid was poured into a separate container. The filter cloth bag with the ice was again placed in the tube for another 2 minutes of centrifugal separation at 3000 rpm. Three liquid samples were thus collected after three centrifugal liquid separation stages subsequent to each freezing run. The solid ice left in the cloth bag at the end of third stage of centrifugal

separation was left in a separate container to thaw. The volumes of the initial solution left after removal of the frozen mass after 10 minutes of freezing, the three samples of liquid separated from the ice at each stage of centrifugal separation, and the solid ice (after melting) left at the end were measured. The salt concentrations in the solutions and samples were analyzed by the electrical conductivity method. The liquid sample results and their time sequences were utilized to determine the average concentration of impurities in the solid mass at each stage of centrifugal separation.

Five additional freezing experiments at similar conditions were performed to observe individual ice crystals. The frozen mass scrapped from the cold plastic surface at the end of each freezing run was transferred to a loose bag made up of several cold and dry tissue paper layers. Shaking and mild pressing of the bag placed in thermal insulation was continued for 5 minutes. The tissue paper layers were sufficient to absorb all adhering liquid.

RESULTS AND DISCUSSION

It was observed that a crop of sparsely separated spike-like ice grains holding a large amount of liquid in its spaces grew in the experimental time span. The mass stuck to the PET bottle surface only lightly and was easily scrapped off. That indicates the viability of a plastic freezing surface for devising a continuous freezer. For instance, a cylindrical cold surface could be continuously exposed to a fresh, impure solution in order to freeze its water content in the form of ice that a wiper removes regularly.

The first batch of liquid separated after 2 minutes of centrifuging had a significantly higher concentration of salt (Table 1) than the unfrozen

TABLE 1
Average Values of Results from Four Typical Experimental Runs at Similar Conditions

Streams analyzed		Volume (mL)	Impurity concentration (g NaCl/L)
Initial impure solution		1000	20.0
Isolated unfrozen liquid left after frozen mass was removed		817	21.4
Batches of liquid separated after one, two, and three consecutive centrifuging operations on the frozen mass at 3000 rpm for 2 minutes each:	One	47	25.9
	Two	42	19.0
	Three	32	10.2
Purified solid product		60	1.9

liquid left after removal of the frozen mass at the end of freezing. This indicates that the agitation imparted by the shaker to disperse the accumulation of salt growing near the ice front is not enough. The higher concentration of salt in the liquid in the ice grains impedes the growth of ice crystals in the direction of their thickness, i.e., parallel to the cold surface. Better mixing during freezing was expected to result in thicker, purer ice spikes. The second and third batches of liquid had salt concentrations lower than the initial solution, indicating melting of pure ice crystals during centrifugation. The thermal insulation was insufficient, especially during removal of separated liquid batches.

A common trend shown in Fig. 1 is that liquid separation from a frozen mass increases the purity of the frozen mass, which indicates that the ice

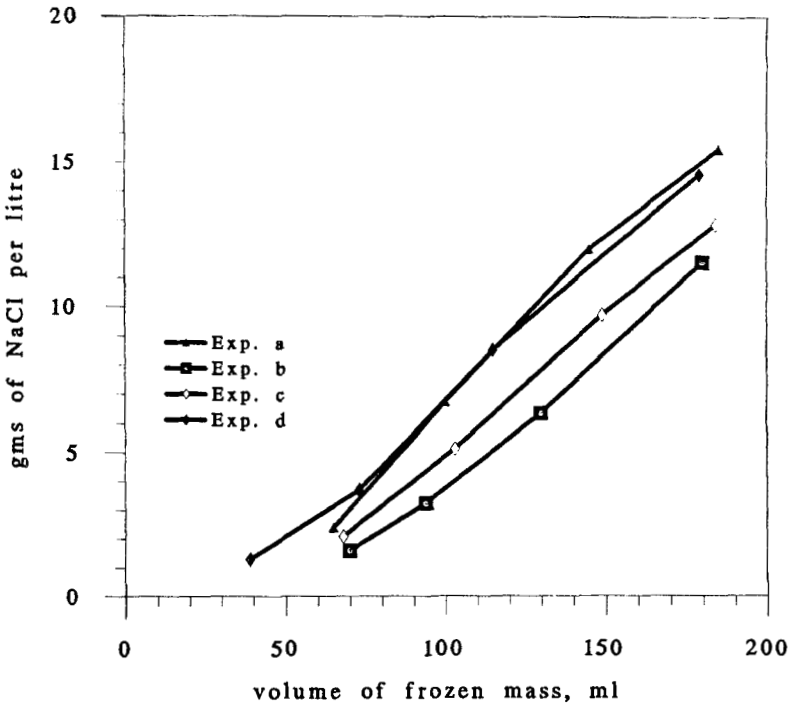

FIG. 1 Conditions of frozen mass as obtained at the end of freezing and during its subsequent centrifugal deliquification. The centrifuge was operated in three stages, with each stage at 3000 rpm for 2 minutes. The rightmost value of each experiment represents the initial frozen mass obtained at the end of freezing, and the leftmost value represents the final purified solid product left at the end of the third stage of centrifugation.

grains themselves were almost pure solidified water. Centrifuge operation at more than 3000 rpm gave an ice product that was a single porous hard lump in which the ice grains were stuck to each other. This is believed to be due to recrystallization. A strong centrifugal pressure lowers the melting point, initiating melting of ice grains. When the centrifugal pressure is removed, the melting point rises and the liquid among the ice grains solidifies. Thus at higher rpm values all liquid should be removed in a single centrifugal operation operating for a longer time.

The scatter in the results of the different experiments in Fig. 1 under similar conditions is typical of all freezing operations where little control over the nucleation of crystals and convective flow patterns during liquid agitation is possible.

Liquid removal from a frozen mass by cold, dry tissue papers left white, shining, pure ice crystals in a dry and free-flowing state for at least 10 seconds. Visual observation revealed the average individual ice crystal resembled a strip about 6 mm long, 1 mm wide, and thin to the point of being indistinct to the naked eye (a value of 0.1 mm was assumed). Ice crystals that grow while suspended in an impure solution have been reported to be spherical in shape. Desalination Plants Ltd.'s vacuum freezing technique (6) produces crystals 0.8–1 mm in diameter, and Freezing Technologies Corporation's direct contact technique (7) produces spherical crystals 0.25 mm in diameter. These spheres have surface to volume ratios of 6 and 24, respectively, while in this investigation the ratio value for the crystal dimensions was 22. The frozen mass sent to the centrifuge contained more than 35% solid ice. The FTC freezer produces a mass with 15% solids.

The low thermal conductivity of ice could only support the dissipation of a very small fraction of the total heat of fusion through such thin and long grains toward the cold surface during their growth. That means that the growth of such long grains is only possible by the dissipation of significant quantities of heat to the surrounding supercooled liquid. Thus, the growth of crystals with heat dissipation into the liquid also produced very pure ice grains.

CONCLUSIONS

Sparsely separated strip-like ice crystals grew on a cold plastic surface. They were easy to remove from the surface. The surface to mass ratio of the ice crystals obtained was comparable with that reported for the alternate freeze purification techniques of suspension crystal growth configurations. The frozen mass collected contained a comparatively larger ratio of solid ice to adhering liquid. Agitation during freezing was insufficient

to dissipate the solutes rejected by the growing pure ice. The centrifugal separation technique separated solid ice grains from the adhering liquid satisfactorily. The purified product ice had an impurity content 90% less than the initial impure solution after a single freezing. The investigation was carried out under constant conditions. It is expected that at optimum freezing, liquid agitation, and centrifuge conditions a continuously operating technique with considerably improved efficiency can be devised.

ACKNOWLEDGEMENTS

The author acknowledges Dr. M. Zafarullah and Ashraf Hameed for supporting the work and allowing staff, Zafar Khan, Zulfiqar Alvi, and Sardar Mohammad, to assist during the experiments.

REFERENCES

1. A. E. Synder, "Freezing Methods," in *Principles of Desalination* (K. S. Spiegler, Ed.), Academic Press, New York, 1966, pp. 291–343.
2. B. Chalmers, *Principles of Solidification*, Wiley, New York, 1964, p. 157.
3. H. M. Hendrickson and R. W. Moulton, *Research and Development of Processes for Desalting Water by Freezing* (Report No. 10), Office of Saline Water, New York, 1958.
4. R. W. Hartel and L. A. Espinel, "Freeze Concentration of Skim Milk," *J. Food Eng.*, *20*, 101–120 (1993).
5. E. Ul Haq and D. A. White, "Freeze Decontamination Process: Modeling in a Simplified Case of Completely Mixed Aqueous Phase and Observations with Ultrasonic Agitation in the Liquid during Freezing," *Sep. Sci. Technol.*, *30*(5), 719–730 (1995).
6. R. Martz, "Desalination of Sea and Brackish Water: The Present State of the Art in Isreal," in *Proceedings, 1964 International Symposium on Fresh Water from the Sea, Milan, Italy April 20–21, 1964*, p. 93.
7. J. Chowdhury, "CPI Warms Up to Freeze Concentration," *Chem. Eng.*, p. 29 (April 25, 1988).

Received by editor July 25, 1995