The thio silane appears to be superior to both the fluorocarbon and the octadecyl mercaptan although if promoter cost is important the latter might be a reasonable compromise.

It is quite likely that had the fluorocarbon been of considerably longer chain length, rather than $C_8$, it might have indeed proved to be of superior quality.

The problem of cleaning and repromotion in industrial situations still remains unsolved.


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# Secondary Nucleation Due to Fluid Forces Upon a Polycrystalline Mass of Ice


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Recent developments are making possible the use of small-scale laboratory experiments to design full-scale suspension crystallizers including accurately accounting for nucleation. The single crystal experiments of McCabe et al. (1971, 1972, 1974), Strickland-Constable and coworkers (1966, 1969, 1972), Denk and Botsaris (1972), and Larson and Bauer (1974) have revealed much of the fundamental character of collision breeding which is likely to be the dominant secondary nucleation process in many systems. The population balance methods of Randolph and Larson (1962, 1972) and others permit the experimental determination of the nucleation characteristics in a more gross but realistic sense, namely, in a stirred-tank configuration. Attempts to couple these independent approaches (Ottens et al., 1972; Evans et al., 1974) in order to describe nucleation kinetics due to collision breeding have met with some success.

Recently, Evans, Margolis, and Sarofim (1974) have conjectured that as much as 25% of the nucleation which occurred in their ice-brine experiments using a mixed suspension crystallizer was due to fluid shear. Also Sung, Estrin, and Youngquist (1973) demonstrated that fluid shear can induce secondary nucleation in the magnesium sulfate-water system. The object of this work was to determine the secondary nucleation characteristics of polycrystalline ice as brought about by the action of a fluid mechanical disturbance at the ice surface. A jet of brine solution of finite duration was employed as the disturbance. The number of nuclei generated due to the jet action was observed primarily as a function of solution subcooling at the ice seed.

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### EXPERIMENTAL APPARATUS AND PROCEDURE

Figure 1 is a schematic diagram of the apparatus and Figure 2 shows the jet system used. Details are available in the thesis of Wang (1974). The temperature-controlled test chamber was divided into two compartments separated by a check valve, the upper compartment containing 3% and the lower 2% brine solution. The jet was a 2 mm Pyrex tube drawn to a tip diam-

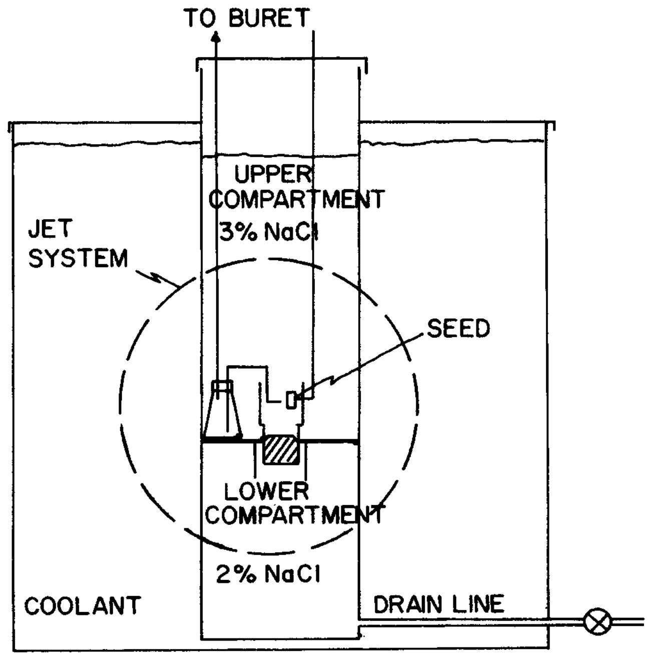


**Fig. 1. Schematic diagram of apparatus.**

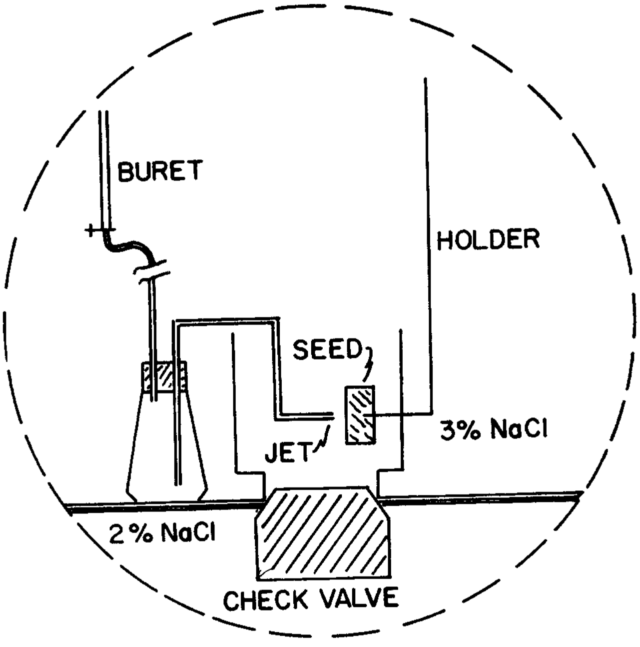


Fig. 2. Jet system.

eter of 0.4 mm. The polycrystalline ice seed, prepared by freezing distilled water, was 3.5 cm in diameter by 1.25 cm thick. Temperatures were determined using a Beckmann thermometer. The freezing point of the 3% brine solution was determined by observing the temperature at which the first dendrite of scallop shape appeared on the edge of the ice disk after it was inserted into the brine solution which was being cooled slowly from an undersaturated condition. Dendrites appeared suddenly and reproducibly. The difference between the temperatures at which first dendrites appeared and the accepted freezing point was found to be 0.02° in an independently conducted test. In carrying out the experiments, the ice seed was pretreated to avoid initial breeding by immersion in 3% brine solution at room temperature. The seed was then introduced to the subcooled solution of the upper chamber. When desired temperatures were reached upon further cooling, solution was drawn into the jet reservoir. The buret was opened to discharge solution from the jet, and simultaneously the drain line valve was opened to draw solution from the vicinity of the seed past the check valve and into the lower chamber. Since the subcooling of the lower chamber was greater, the nuclei produced at the seed and transferred to the lower chamber grew rapidly and were readily observed and counted visually at the transparent plate separating the two chambers.

## RESULTS AND DISCUSSION

The experiments showed that fluid shear can induce secondary nucleation of ice. Table 1 shows the experimental results in the order in which they were obtained. Runs 1 through 14 were preliminary and carried out by an assistant; the higher numbered runs were carried out by one of the authors using the same apparatus and procedure except somewhat more developed in several details.

The secondary nucleation which occurs may be considered to involve the detachment of dendrites or other entities from the surface of the ice seed crystal, or the detachment of contiguous liquid containing an embryo species, by the jet. These mechanisms are suggested by the work of McCabe et al. (1971, 1972, 1974), Denk and Botsaris (1972), and Sung, Estrin, and Youngquist (1973). In all cases, the crystals observed in the lower compartment were thin platelets and obviously very fragile. Breakage of such fragile particulates may well be the mechanism responsible for the large rates of nucleation observed at early times in batch crystallizations (Omran and King, 1973; Wey and Estrin, 1974).

To confirm that the nuclei observed originate at the ice seed, control experiments (runs 34, 35, 37) were conducted using a dummy seed of hard rubber. No nuclei were observed in the absence of the ice seed. Furthermore, there was no effect on the number of nuclei observed due to changes in subcooling in the lower compartment (runs 56 and 57, 58, and 59) and volume of solution used (runs 38 to 48) (so long as solution drained exceeded about 350 ml). The intensity of fluid shear, as it varied due to changes in distance between jet and seed (runs 2, 28, 54, 55) and jet velocity (340 cm/s for run 55, 225 cm/s for other runs), did not affect significantly different numbers of nuclei. These results are quite different from those obtained by Sung et al. (1974) who performed similar experiments for the magnesium sulfate-water system and found strong dependence for the number of observed nuclei on these variables. Growth (regeneration) limited nucleation is suggested by the lack of dependence on jet intensity and duration. Smaller subcooling in the lower chamber had no effect on the number of nuclei observed but caused these nuclei to develop more slowly. Possibly the species removed at the seed are quite large so that critical size considerations are unimportant for the conditions investigated. Runs 21 and 22 indicate that the embryos do not survive in undersaturated solution.

The number of nuclei observed was strongly dependent on the subcooling at the ice seed as is indicated by Figures 3 and 4. The data of Figure 3, which include early runs carried out before the details of the procedure were completely developed, show dependence on subcooling to the 1.74 power. Figure 4, showing the data of later runs only, exhibits somewhat less scatter and dependence on subcooling to the 1.69 power. These results are surprisingly consistent with those of Evans et al. (1974) who found 1.7 power dependence on subcooling for nuclea-

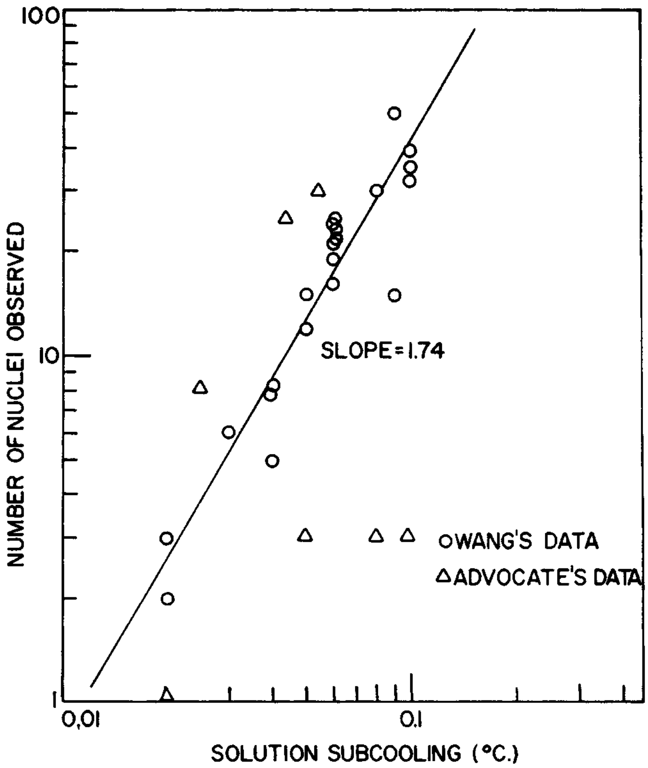


Fig. 3. Number of nuclei observed in the lower compartment as a function of subcooling.

tion rate in ice-brine suspension crystallizer studies. The dependence is much weaker, however, than that observed by Sung et al. (1973, 1974) for magnesium sulfate.

Actually the $\Delta T$'s indicated as the abscissa variable in Figures 3 and 4 should be properly labeled cooling below the temperature of first dendrite appearance. If these are modified by adding 0.02°, a straight line, whose slope is 2.40, displays comparable correlation results.

Sung, Estrin, and Youngquist (1973) applied classical nucleation theory to a similar process but one which involved the magnesium sulfate water system. They employed a region of greater supersaturation to detect the nuclei, the intended purpose for the 2% solution used in this work. In this work involving the ice brine system, it is not clear that the more supersaturated region is where the nuclei stabilize. The face of the ice mass upon which

Table 1. Experimental Operating Conditions and Results

| Run no. | F.P./3 wt. % brine sol. (°C) | Distance between jet and slab of ice, mm | Vol/brine sol. drained from jet, ml | Vol/brine sol drained from lower comp., ml | Run temp. °C | S-cooling (−) U-cooling (+) | No. nuclei observed in lower comp. |
|---|---|---|---|---|---|---|---|
| 1 | −1.81 | No jet | 0 | 0 | −1.81 | 0 | 0 |
| 2 | −1.75 | 2 | 4.5 | 205 | −1.79 | −0.04 | 8 |
| 3 | −1.715 | 2 | 4.1 | 293 | −1.74 | −0.025 | 8 |
| 5 | −1.772 | 1.5 | 4.5 | 102 | −1.87 | −0.098 | 3 |
| 7* | −1.78 | No jet | 0 | 245 | −1.86<br>−1.885 | −0.08 | 3 |
| 8* | −1.78 | No jet | 0 | 213 | −1.895<br>−1.875 | −0.115 | 0 |
| 9* | −1.78 | No jet | 0 | 185 | −1.870<br>−1.885 | −0.09 | 0 |
| 11 | −1.78 | 2 | 4.5 | 170 | −1.83 | −0.05 | 3 |
| 12 | −1.78 | 1 | 4.5 | 234 | −1.80 | −0.02 | 1 |
| 13 | −1.816 | 2.5 | 4.5 | 183 | −1.86 | −0.044 | 25 |
| 14 | −1.816 | 2.5 | 4.5 | 363 | −1.87 | −0.054 | 30 |
| 21** | −1.82 | 2 | 5.0 | 325 | −1.96<br>−1.75 | −0.14<br>+0.07 | 0 |
| 22** | −1.82 | 2 | 5.0 | 290 | −1.99<br>−1.74 | −0.17<br>+0.08 | 0 |
| 23△ | −1.82 | 2 | 5.2 | 265 | −1.92 | −0.10 | 35 (1st min.)<br>1000 |
| 28 | −1.89 | 2 | 5.7 | 450 | −1.93 | −0.04 | 8 |
| 29 | −1.89 | 2 | 6.2 | 455 | −1.91 | −0.02 | 3 |
| 30 | −1.89 | 2 | 6.2 | 400 | −1.93 | −0.04 | 5 |
| 31 | −1.89 | 2 | 6.8 | 480 | −1.98 | −0.09 | 15 |
| 32 | −1.92 | 2 | 7.2 | 475 | −1.94 | −0.02 | 2 |
| 33 | −1.92 | 2 | 7.6 | 500 | −2.01 | −0.09 | 50 |
| 34*** | −1.91 | 2 | 7.2 | 455 | −1.96 | −0.05 | 0 |
| 35*** | −1.91 | 2 | 7.5 | 520 | −2.04 | −0.13 | 0 |
| 36 | −1.81 | 2 | 7.6 | 465 | −1.86 | −0.05 | 15 |
| 37*** | −1.81 | 2 | 8.0 | 455 | −1.86 | −0.05 | 0 |
| 38 | −1.81 | 2 | 6.3 | 490 | −1.87 | −0.06 | 19 |
| 39 | −1.81 | 2 | 6.4 | 500 | −1.87 | −0.06 | 21 |
| 40 | −1.81 | 2 | 6.2 | 458 | −1.87 | −0.06 | 23 |
| 41 | −1.81 | 2 | 6.1 | 470 | −1.87 | −0.06 | 24 |
| 42 | −1.81 | 2 | 3 | 475 | −1.87 | −0.06 | 23 |
| 43 | −1.81 | 2 | 3 | 460 | −1.87 | −0.06 | 25 |
| 44 | −1.81 | 2 | 3 | 150 | −1.87 | −0.06 | 2 |
| 45 | −1.81 | 2 | 6.0 | 330 | −1.87 | −0.06 | 16 |
| 47 | −1.81 | 6 | 3 | 460 | −1.87 | −0.06 | 23 |
| 48 | −1.81 | 2 | 6.5 | 490 | −1.87 | −0.06 | 22 |
| 49 | −1.805 | 2 | 4.0 | 400 | −1.905 | −0.10 | 39 |
| 50 | −1.805 | 2 | 6.0 | 485 | −1.905 | −0.10 | 32 |
| 51 | −1.78 | 2 | 6.5 | 470 | −1.86 | −0.08 | 30 |
| 52 | −1.78 | 2 | 6.1 | 460 | −1.83 | −0.05 | 12 |
| 53 | −1.78 | 2 | 6.1 | 480 | −1.81 | −0.03 | 6 |
| 54 | −1.83 | 7 | 5.6 | 425 | −1.87 | −0.04 | 8 |
| 55△△ | −1.83 | 4 | 6.5 | 435 | −1.87 | −0.04 | 9 |
| 56▲ | −1.82 | 2 | 6.9 | 425 | −1.87 | −0.05 | 16 |
| 57▲ | −1.82 | 3 | 6.6 | 435 | −1.87 | −0.05 | 14 |
| 58▲ | −1.82 | 3 | 6.5 | 430 | −1.89 | −0.07 | 27 |
| 59▲ | −1.82 | 3 | 6.5 | 420 | −1.89 | −0.07 | 25 |

The volume of lower compartment contents was 2525 ml; the upper compartment contents, 4200 ml. Except for Run 14, no nuclei were observed at the free surface of the solution in the upper compartment at all operating temperatures.

* Run 7: The ice crystal was held for 10 min. in the crystallizer at the lowest temperature, −1.86°C. Five min. after removing the seed, at temperature −1.885°C, the run was initiated. The same procedure was used for Runs 8, 9.

** Run 21: The jet was used at −1.96°C, the solution was heated to −1.75°C for 5 min.; then the solution was drained.

** Run 22: The jet was used at −1.99°C, the solution was heated to −1.74°C for 1 min.; then the solution was drained.

*** Run 34, 35, 37: A dummy crystal (hard rubber) was used in place of a polycrystalline ice mass.

△ Run 23: The solution was agitated in the lower compartment. 35 Nuclei were observed 1 min. after draining the solution. More than 1,000 were observed 2 min. after draining the solution.

△△ Run 55: The head of liquid in the buret was raised 60 cm above the standard 80 cm. The velocity of jet was 340 cm/s.

▲ Runs 56-59: The lower compartment was filled with 2.5 wt % brine solution instead of the standard 2.0 wt %.

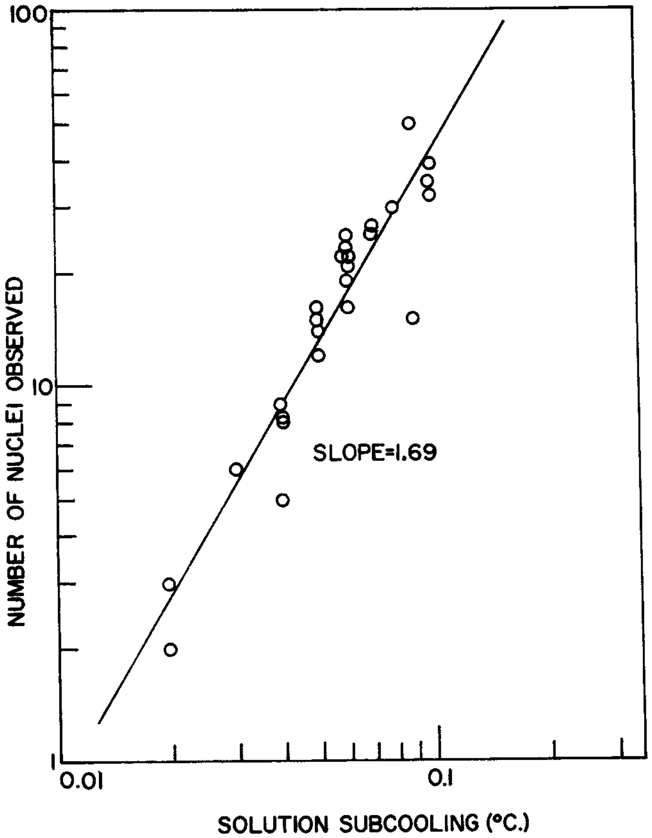


**Fig. 4. Number of nuclei observed in the lower compartment as a function of subcooling.**

the jet impinged were largely nonbasal planes as observed through crossed polarizers. Thus the face was fast growing in the sense that growth was probably heat and mass transfer controlled. Therefore equilibrium prevailed, very nearly, at the solid-solution interface and the more supersaturated region in which nuclei at least stabilized probably was the bulk solution in the upper chamber. Experimentally, this was made clear by the ineffectiveness in changing the number of nuclei generated when the bottom chamber solution was less supercooled. Thus the general configuration is much more complicated than the system employed by Sung et al. (1973).

An attempt was made to use the theory of Sung to interpret the present results. The size of the critical nucleus was calculated to be about $10^{11}$ molecules or radius 1 $\mu$m. This is many orders of magnitude larger than that obtained by Sung and than that generally encountered in classical nucleation theory. This size was calculated using a surface free energy of 33 ergs/cm$^2$, and a supercooling of 0.05°C representing bulk upper chamber supercooling. The existence of such large entities is highly unlikely.

Hence we speculate that the shearing of irregular growth protuberances is involved. Quite possibly dendrites which may be growing at the surface of the polycrystalline ice mass are sheared abruptly from the crystal face. It is too early to speculate further concerning the nucleation process except that the nucleation mechanism is likely different from that observed recently by Garabedian and Strickland-Constable (1974). These investigators described experiments in which a single crystal of ice displayed breeding only when rigid body contacts or crystal breakage was involved. Their supercooling values extended to about ½°C, five times the range employed in this work, yet their numbers of resulting crystals were of the same order of magnitude as observed here. There are several reasons which may account for these differences in results. They investigated the pure water system; the work here involved brine. Their level of cleanliness was no doubt greater than existed in the rather complicated apparatus employed here. The velocities of liquid relative to the ice mass were greater here than in Garabedian and Strickland-Constable's experiments. A polycrystalline ice seed rather than a single crystal was used here which may lead to polycrystalline breeding. Finally, their single crystal grew into the velocity field and had no opportunity to develop any necessary features of surface irregularities as was true here, where the seed developed in stagnant conditions.

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