On the properties of additives for strength reduction in ice

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SUBJECT ON THE PROPERTIES OF ADDITIVES FOR STRENGTH REDUCTION IN ICE

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For an accurate scale model testing of icebreakers and stationary platforms in a test tank facility, it is important that the physical properties of the ice sheet be properly scaled from those of sea ice. Basically, the important physical properties for the test tank ice may be summarized as follows[1]:

1) The ultimate strength (σ) of the ice must be reduced by the geometric scaling factor (λ) of the tests. Thus for a 30:1 test of an icebreaker in sea ice (say), the ultimate strength of the ice should be on the order of 17 kPa.

2) The value of Young's modulus (E) for the ice must similarly be reduced by the same amount λ. Again for $\lambda = 30$, $E \sim 34$ MPa.
This implies that the E/σ ratio must remain constant and greater than $\sim 2{,}000$.

3) The shear (rigidity) modulus (G) must also be reduced by the scaling factor λ.

4) Both the dynamic and static frictional coefficients of the ice must be the same as that for sea ice.

5) Poisson's ratio must be the same as that for sea ice.

6) The density of the ice should be the same as sea ice. Implied in this is that the ice must be structurally homogeneous.

To date, there is no known method for producing an ice sheet which fits all of these criteria. In most of the major test tank facilities presently in operation, a saline ice sheet is used. However, to some extent, this compromises both (1) and (2) of the above. Thus, it is of interest to investigate the possible ways of producing an ice sheet which better fits the required criteria. One approach to this problem is to investigate the physical properties of ice produced by adding a variety of dopants to the melt solution before the freeze. With a suitable dopant material(s), it may then be possible to produce an ice sheet which either has the required physical characteristics or, at least, better meets the above criteria than saline ice.

It is well known, however, that the ice lattice is a very selective one, accepting only a few substitutional ions[2]. To date, little has been reported in the literature on the mechanical properties of impurity doped ice. Moesveld[3] reported that if minute quantities of certain organic materials having long carbon chains are added to the surface of still water before the freeze, an ice sheet with negligible shear strength results. Truby[4] and Jones and Glen[5] have reported that the introduction of fluorine ions in ice alters the microstructure, thereby leading to a softening effect. Pounder[6] has carried out a systematic investigation on the effects of doping with a number of organic materials (alcohols, ethers) and reported that ice frozen from water solutions containing small amounts of these materials is much weaker than

normal ice. In addition, Pounder's work points out important guidelines regarding the type of dopant which might prove most useful for strength reduction in ice.

In brief, some of the essential features of an "ideal" solute for doping ice for a test tank facility may be summarized as follows:

1) The ice frozen from the doped water solution must produce an ice sheet whose physical properties match those discussed above.

2) The dopant material must be soluble in (cold) water. Pounder[6] has noted that the strength reduction was greater for substances which are infinitely soluble in water.

3) The solute should readily mix with water to form a homogeneous solution. Moreover, the solution should remain well mixed in spite of repeated temperature cycling.

4) The dopant should be non-volatile with a low vapour pressure so that it does not evaporate before the ice sheet forms to trap it. A volatile dopant would present problems with maintaining a constant solution concentration and consistent ice sheet.

5) The dopant, if it is a member of a homologous series, should be at the lower end of the series. Pounder[6] observed that within individual series (alcohols, ketones) there is a definite decrease in strength reduction of the ice towards the higher molecular weight members. This result seems reasonable since the depression of the freezing point varies proportionally with the number of solute particles per unit volume. Thus, for equal masses of solute, the lower members of the series should produce a greater strength reduction.

6) The melt solution should be non-corrosive.

7) The material should show positive adsorption characteristics (i.e. tend to concentrate in the surface layer) in water[6]. This would enhance the concentration of the solute in the surface layer of the water, thereby providing more impurities at the growth interface. This would lead to constitutional supercooling which would make it possible for pockets or layers of solution to exist whose freezing point is lower than that of the surrounding ice.

8) Any fumes given off by the solute must certainly be non-toxic. Also, the solution itself should be non-toxic and preferably non-irritating to the skin, eyes, etc.

9) The dopant should be either biodegradable, non-polluting or be readily separatable from solution (for disposal purposes).

10) The dopant should be relatively economical to use.

In looking for a dopant which meets all (or most) of the above criteria, it is necessary to investigate several possibilities. Clearly, the basic approach is simply to add an additive to the melt before the freeze, and measure the physical properties of the resulting solid phase. At first glance it would seem that there are an "infinite" number of possible additives to try; that is, additives that at least meet criteria (2) - solubility in water. However, from the microscopic viewpoint, it is possible to divide all additives into only four groups (or freezing mechanisms), according to size and/or bonding type. With increasing particle size, the types of additives may be divided into the following four categories:

1) free atoms (ions) in solution (ex: dissociated salts, acids),

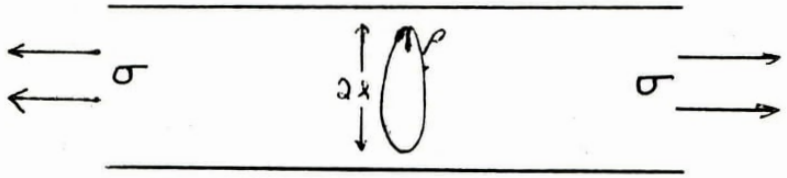
2) free molecules (non-bonded or very weakly bonded with H_2O) in a molecular dispersion in solution (ex: alcohols, glycols),

3) molecules which form hydrogen bonds with H_2O in solution (ex: molecules with ethylene oxide groups, detergents),

4) microscopic particles suspended in solution (ex: colloidal suspensions, emulsions).

Each of these basic categories can be further subdivided as outlined in figure 1 (for solid additives) and figure 2 (for liquid additives). Although at this stage it is difficult to predict which of the above categories would produce the greatest strength reduction in ice, some guidelines may be obtained from the literature. It is known, for example, that a water solution containing additives of either a low molecular weight salt (sodium chloride)[2] or a high molecular weight salt (sodium stearate)[3] when frozen produce a structurally weakened ice. Which of these two salts produces the weaker ice is not known. The action of starch as the sole additive in water has been reported to produce a strengthened (reinforced) ice[7], whereas it produces a weakened ice when added to an alcohol-water solution[6]. Pounder[6] has reported that if a small amount of a long chain, organic substance such as sodium carboxymethyl cellulose is added to an alcohol-water mixture, the weakening effect on the resulting ice is greater than that due to alcohol alone. These latter two results are of particular interest since they suggest a mechanism whereby it may be possible to reduce considerably the strength of ice. Consider the following:

It is known from crack theory that at the tip of an elliptical (Griffith) crack

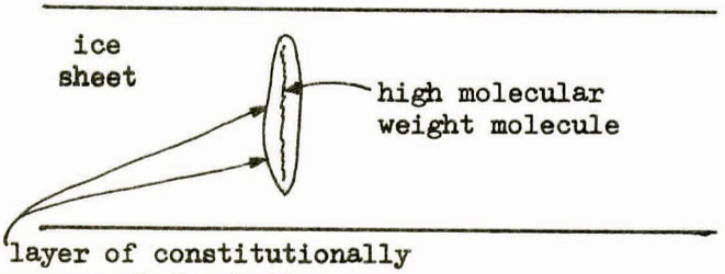


the local stress (σ_m) is given by[8]

$$\sigma_m \sim 2\sigma\sqrt{\ell/\rho} \qquad \text{.....(1)}$$

where ρ = radius of curvature of tip
σ = applied tensile stress normal to the crack surface
ℓ = length of semi-major axis

Thus, for cracks with $\ell \gg \rho$, the stress magnification factor $2\sqrt{\ell/\rho}$ can be very large, the cohesive strength of the material can be locally exceeded, and failure can occur well below the theoretical cohesive strength of the material. Thus, if it is possible to randomly distribute a large number of stress raiser "cracks" of this type throughout the ice, the ultimate strength of the ice would be considerably reduced. Pounder's[6] work in conjunction with that of Coble and Kingery[7] suggests that this may be possible. Their results indicate that if a large molecule (such as starch) is introduced into the ice sheet as the sole additive, the strength of the ice is reinforced. On the other hand, if the large molecule is introduced with other much lower molecular weight molecules, the situation is reversed. In this case the dopants would form "cracks" in the ice sheet as shown below:



During freezing, both of the solutes would be rejected from the growing (selective) ice lattice, and thereby they would form ("brine") pockets throughout the ice sheet. Since the concentration of the lower molecular weight solute would be high in these pockets, the solution would be constitutionally supercooled, and therefore it would act as a lubricant between the higher molecular weight solute and the ice lattice. The higher molecular weight molecule, on the other hand, would be instrumental in shaping the pocket inclusions. Since ice typically grows with long vertical columnar grains, nature would aid in aligning these pockets vertically, i.e. in the direction that would enhance the stress raiser properties of the pockets. Clearly, since the stress concentration factor varies as $2\sqrt{\ell/\rho}$, it would be advantageous to use a long-chain linear molecule as the high molecular weight solute. Moreover, since the depression of the freezing point is proportional to the number of particles per unit volume, it would seem that low molecular weight molecules should be used as the 'lubricant'. Of particular importance may be those which show a positive adsorption coefficient. Of course, the H_2O - low molecular weight solute - high molecular weight solute bonding mechanism would play an extremely important role in this process, and thus different solutes would lead to different results.

In order to provide a quantitative comparison of the effectiveness of various additives, it is necessary to test them under identical experimental conditions. However, these tests necessarily must be performed on ice grown in large test tanks in order to ensure that the same type of chemical rejection and convection will occur in these tests as will occur in a large test tank facility. Experiments in this laboratory have repeatedly shown that the results of tests on doped ice grown in shallow test tanks are not comparable with those on ice grown from the same solution concentration in deeper test tanks. This important requirement places a severe limit on the number of additives which can be tested in a given time span. Nevertheless, a systematic experimental investigation of a few representative examples from each of the aforementioned categories (both alone and in conjunction with additives from other categories) may present some further guidelines for future experimental work.

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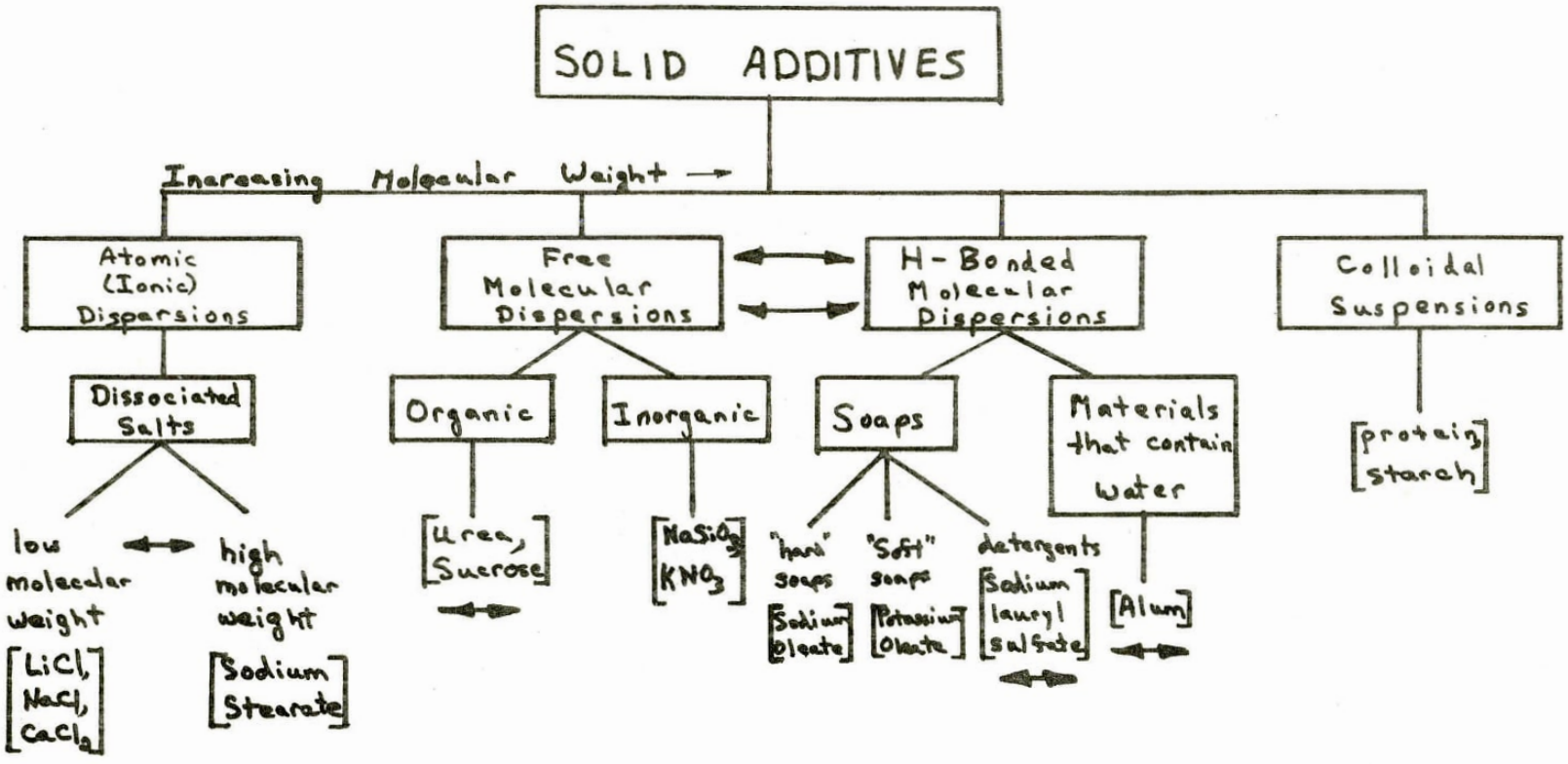

FIGURE 1: SCHEMATIC REPRESENTATION OF VARIOUS TYPES OF SOLID ADDITIVES FOR DOPING WATER. THE STRAIGHT DOUBLE-HEADED ARROWS INDICATE THAT A RANGE OF MOLECULAR WEIGHTS ARE POSSIBLE IN THAT CATEGORY.

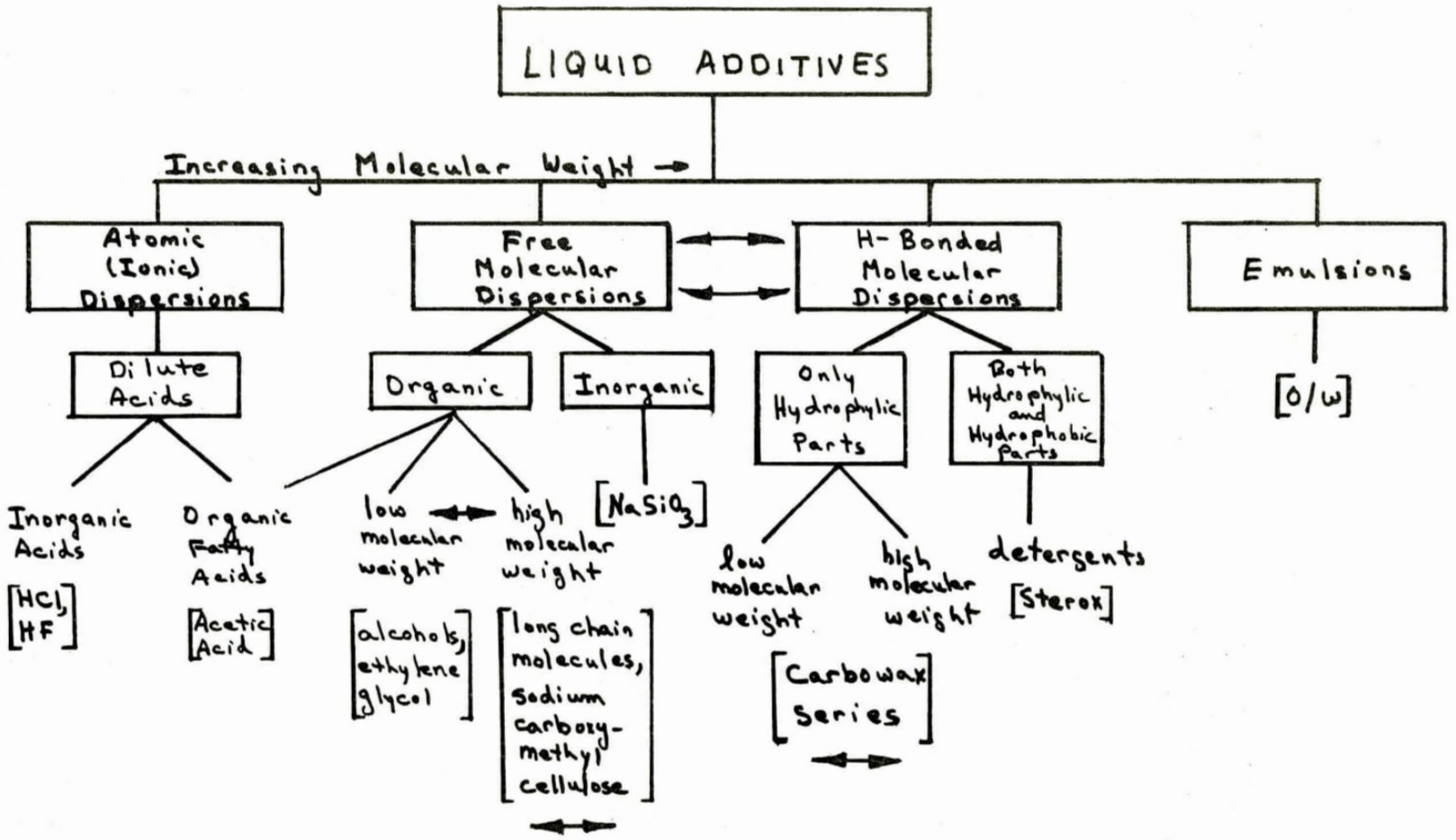

FIGURE 2: SCHEMATIC REPRESENTATION OF VARIOUS TYPES OF LIQUID ADDITIVES FOR DOPING WATER. THE STRAIGHT DOUBLE-HEADED ARROWS INDICATE THAT A RANGE OF MOLECULAR WEIGHTS ARE POSSIBLE IN THAT CATEGORY.