SOLUTE REDISTRIBUTION DURING NORMAL FREEZING

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Abstract. Mathematical models used in metallurgy to describe solute partitioning are applied to solute distribution in ice crystals. Results demonstrate that the model developed under the assumption of ideal directional freezing can be used to estimate distribution coefficients from experimental data. The deviation of experimental results from normal freezing theory is consistent with the Burton-Slichter film theory model.

1. Introduction

In northern areas where snow precipitation is abundant in winter time, laboratory and field experiments indicate that 50 to 80% of the pollutants accumulated in the snowpack are released when the first 30% melts (Seip, 1980). The very first meltwater may have concentrations 5 times the values found in the bulk. This meltwater can cause dramatic changes in the chemistry of rivers and lakes and may have profound environmental impacts (Seip, 1980).

A thorough understanding of snow and ice pack chemistry and melting is necessary to predict the chemical composition and delivery rates of meltwater to aquatic systems. Snow and ice packs are complicated systems and are difficult to model because of the dynamic nature of the profile formation and the uncertain transport properties within the pack. A less complex subset of this system is ice formed by direct freezing of either polluted water or meltsnow.

In this paper an investigation of segregation of solutes and their transport properties in ice layers is reported and techniques for estimating solute redistribution resulting from normal freezing processes are presented.

2. Theory

The process of freezing water containing impurities represents a practical application of phenomenon of solute rejection during the solidification of a multi-component system. The theory of such solute redistribution has been the subject of considerable study in recent years due to its importance in the field of semiconductor technology. In principle, one should be able to calculate the growth rate of ice crystallites, the morphology, and the degree of impurities rejection starting with only basic theory. In practice a general analysis is complicated and for many purposes, empirical methods provide the only means for determining the behavior of a real system.

The effective distribution coefficient, $k$, is defined as the ratio of the solute content of the solid to the initial or average solute content of the liquid. The $k$ values can be either larger or smaller than unity. In most of the substances encountered in the pollution field,
The $k$ values are smaller than one and this can be presumed throughout the discussion. Theoretically, if the interface distribution coefficient is known, then the solute concentration profile in the solid phase can be calculated from solutions of the appropriate transport equations. Three approaches are discussed in this study.

2.1. THERMODYNAMIC APPROACH – FREEZING DEPRESSION

If a small amount of solute (gas, liquid, solid) is added to a liquid solvent and the temperature of the mixture lowered, a temperature, $T_f$, is reached at which the solvent begins to separate out as a solid. The temperature is lower than the freezing (or melting) point of the pure solvent, $T_m$. The general relationship between the composition of a liquid solution and that of a solid solution with which it is in equilibrium is given by the following formula, which is strictly valid only when both phases are perfect solutions (Hayes and Chapman, 1939):

$$
\ln N_1_{\text{liq}} - \ln N_1_{\text{solid}} = -\frac{\Delta H}{R} \left( \frac{1}{T_m} - \frac{1}{T_f} \right),
$$

where $N_1$ is the mole fraction of the solvent in the respective phases at the absolute temperature $T_f$, $\Delta H$ is the heat of fusion in transferring one mole of solvent from the solid solvent to the liquid, and $R$ is the gas constant.

Equation (1) can be simplified for systems in which the amount of dissolved substance is relatively small (i.e., not more than a few percent). If the mole fraction of the dissolved substance in the two phases is designated by $N_2(s)$ and $N_2(liq)$, the distribution coefficient can be defined as

$$
k = \frac{N_2(s)}{N_2(liq)}.
$$

Combining Equations (1) and (2) yields

$$
N_2(liq) = \frac{\Delta H \Delta T}{RT_m^2(1 - k)},
$$

or

$$
k = 1 - \frac{\Delta H \Delta T}{RT_m^2N_2(liq)},
$$

where $\Delta T$ is the freezing point depression.

The distribution coefficient can be easily found by Equation (4) provided $\Delta T$ is known.

2.2. IDEAL DIRECTIONAL FREEZING

The freezing of water in ponds, rivers or lakes can be represented ideally by the freezing of a vertical bar unidirectionally as shown in Figure 1. If it is assumed that: (1) the