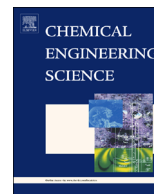




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## Ice growth kinetics modeling of air-cooled layer crystallization from sodium sulfate solutions

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## HIGHLIGHTS

- Natural freezing as a novel separation method is replicated experimentally.
- Natural freezing was epitomized by ice crystallization from  $\text{Na}_2\text{SO}_4$  (aq) solutions.
- Robust model was developed to depict the influence of different factors.
- Natural freezing of solution was found to be heat transfer controlled.
- This process has adaptability in cold climate countries at wastewater pond regions.

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## ABSTRACT

Natural freezing has the possible use to be used as a purification technique to treat wastewater. Natural freezing was simulated experimentally for ice crystallization from unsaturated  $\text{Na}_2\text{SO}_4$  (aq) solutions to assess the feasibility of such a technique for being used to purify wastewater. The influence of solution concentration and different growth conditions, such as ambient temperature, freezing time and freezing rate, on the efficiency of the purification process was investigated by analysis of the effective distribution coefficient ( $K$ ) of the solute between the ice and the solution. A calculation method is introduced to estimate the concentration of solution at the advancing ice–solution interface in terms of the limiting distribution coefficient ( $K^*$ ) from experimental  $K$  values at different growth conditions. The heat transfer controlled growth rate of the ice limited by the free convective heat transfer coefficient of air ( $h_{\text{air}}$ ) rather than the thermal conductivity of the ice ( $k_{\text{ice}}$ ) and the heat transfer coefficient of the solution ( $h_{\text{sol}}$ ) found to prevail over the mass transfer of rejected solute molecules from the ice–solution interface to the bulk solution. Advancement of the thermal ( $\delta_T$ ) and concentration boundary layer ( $\delta_C$ ) at the ice–solution interface was proportional to the square root of freezing time. A simplified model is developed to estimate the thickness of the ice layer formed from solutions at different freezing conditions and the model is validated with experimental results.

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## 1. Introduction

Crystallization of water as ice from aqueous solutions by freeze crystallization has an extensive range of applications, especially in solute concentration and wastewater purification processes (Huige and Thijssen, 1972). High product quality, good separation efficiency (Kapembwa et al., 2013) and low energy requirement (Liu et al., 1997) have made freeze crystallization a promising method to address the treatment of wastewater (Lorain et al., 2001). If it is possible to form a single ice layer by natural freezing, ice crystallization treatment of wastewater would become a simple and cost

effective approach, because separation of the ice layer is relatively easy as a result of the density difference between the ice and solution.

Redistribution of solute occurs during ice crystallization from a solution and the extent of redistribution is greatly influenced by the ability of the solute to diffuse away from the ice–solution interface (Butler, 2002). During ice crystallization from solution, usually solute molecules/ions are not able to incorporate into the ice crystal lattice owing to constraints of their size/charge (Petrich and Eicken, 2009). These ions are rejected by the advancing ice–solution interface. If the growth rate of the ice layer by natural freezing were low enough then only a small portion of the solute is incorporated into the ice layer and most of it is rejected and purity of the ice layer would be very high. Hence, almost pure water would be obtainable by separation of the ice layer formed on the

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surface of wastewater ponds in cold climate countries where the temperature goes below 0 °C during winter. In Finland, the mining industries produce significant amount of wastewater. Thus huge volume of wastewater (more than 1 million tons per year) need to be treated in an energy efficient manner. Mining operations are a potential source of seriously contaminated water that is difficult to treat. For example, sulfuric and nitric acid, commonly used as leaching agents in the mining and metallurgical industries, produce effluents containing sulfate ( $\text{SO}_4^{2-}$ ) (Silva et al., 2010) and nitrate ( $\text{NO}_3^-$ ) (Primo et al., 2008) ions. Both of these compounds are considered threats to the environment if present in high level.

Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) is common in effluents emanating from the use of detergents, the textile, glass and mining industries, kraft pulping, (Garrett, 1998) and the ash of marine fossil fuels (Lin and Pan, 2001). This work introduces ice crystallization from  $\text{Na}_2\text{SO}_4$  (aq) solution, as a model solution, with varying concentrations and ambient temperature imitating natural freezing of saline sea water. Separation efficiency is investigated in terms of a distribution coefficient as a function of solution concentration and different growth conditions. Concentration of the solution at the ice–solution interface and parameters describing the growth kinetics of the ice layer are estimated from experimental results. A model is derived to quantify the ice layer by natural freezing of  $\text{Na}_2\text{SO}_4$  (aq) solutions. The model can also be used to study the dependency of the growth rate on the initial solution concentration, heat and mass transfer, difference between the solution's freezing point and ambient temperature and freezing time.

## 2. Theoretical considerations

At any solid–liquid equilibrium (SLE) the chemical potential of the solvent and the corresponding solid phase is equal (Hasan et al., 2014). Solidification of melt is associated with the release of heat from the crystallization and rejection of solutes from the ice–solution interface to the bulk solution. These effects create temperature and concentration gradients in the liquid phase adjacent to the solid–liquid interface, which in turn generate thermal and mass boundary layers. The temperature and concentration profile of natural freezing of a solution and the corresponding boundary layers are illustrated in Fig. 1.

The purity of the ice crystals formed in ice crystallization is dependent on the growth rate (Butler, 2002). If the ice growth rate is low enough for the solute to diffuse away from the advancing ice front, pure ice is formed and the solution becomes more concentrated. On the other hand, if the growth rate is so high that all solutes are entrapped in the ice, this leads to impure ice crystals and no enrichment of the solution.

When a melt solidifies, the distribution of solute in the solid phase,  $C_s$  (wt%), relative to that present in the bulk liquid phase,  $C_b$  (wt%), is referred to as the effective distribution coefficient,  $K=C_s/C_b$ , which is predominantly determined by the ability of the solute to diffuse away from the solid–liquid interface. A higher solute rejection rate of ice compared with the diffusion of solute from the ice–solution interface to the bulk solution results in a higher concentration of solute in the interface,  $C_i$  (wt%) than in the bulk solution,  $C_i > C_b$ . The limiting distribution coefficient ( $K^*$ ) is a specific form of distribution coefficient at the solid–liquid interface, defined as  $K^*=C_s/C_i$  (Weeks and Lofgren, 1967).

Knowledge of a diffusion model is necessary to describe the movement of rejected solute from the advancing solid–liquid interface into the bulk. In water crystallization, surface kinetics is very fast due to its small molecular size. This is the reason why amorphous ice can only be formed at extreme conditions, i.e., below  $-143.15$  °C (Kouchi et al., 1994). Pronk et al. (2006) investigated ice crystallization with a freezing system equipped

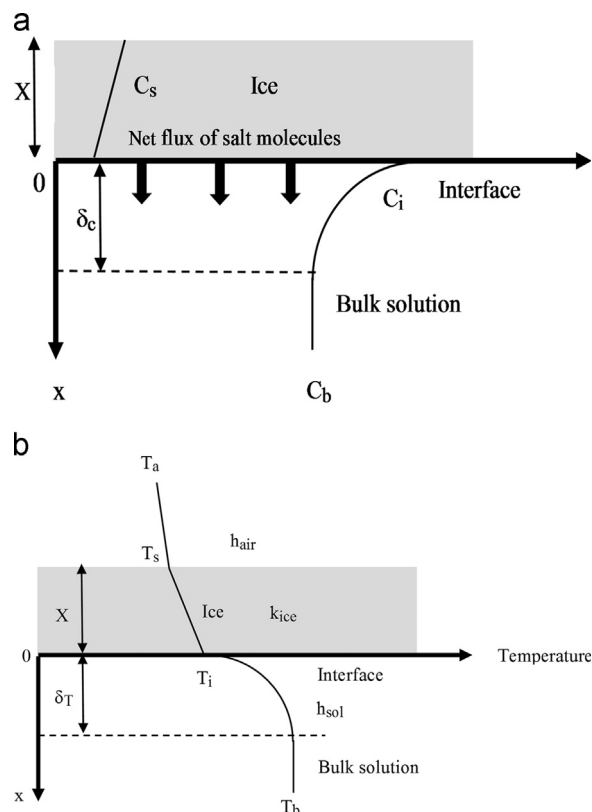


Fig. 1. Schematic depiction of (a) the concentration profile and (b) temperature profile of ice crystallization by natural freezing from solution.

with a cooling heat exchanger. They investigated the factors dominating the ice crystal growth with the salt solutions. According to Pronk et al., at salt concentration higher than 1 wt%, the resistance of ice growth rate due to surface integration kinetics is ignorable compared with heat and mass transfer resistance. In the present work, the solution concentration was 1 wt% or above, so the surface kinetics was ignored.

### 2.1. Differential mass transfer model (DMTM)

The extent of the concentration gradient in the locality of the advancing solid–liquid interface during growth of the crystal from melt depends upon several factors, e.g., the solidification rate, the effective distribution coefficient,  $K$  and the nature of the fluid flow (Weeks and Lofgren, 1967). The mass transfer of solute molecules between a single crystal and the melt is commonly studied using a differential mass transfer model (DMTM) presented by Burton et al. (1953) and assuming that the solution concentration in the radial direction perpendicular to the growth condition is uniform, and that the fluid is incompressible and uniform beyond the boundary layer. It is assumed that the coordinates move at the same rate as the growing ice layer for being fixed to the solid–liquid interface, i.e., at  $x=0$ , and extends in a positive direction into the melt.

At the solid–liquid interface, there is no fluid velocity with an exception of the flow normal to the interface produced by crystal growth. Therefore, at the interface the flow is laminar and the fluid velocity is small enough for molecular diffusion to be the main means of transporting the rejected solute molecules away from the growing crystal (Weeks and Lofgren, 1967). According to BPS (Burton–Prim–Slichter) theory, the governing diffusion equation

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