Efficiency of Landfill Leachate Treatment by Freeze Crystallization and Natural Process of Snow Metamorphism

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ABSTRACT

The purpose of this study is to draw attention to the possibility of the implementation of natural processes of snow metamorphism for the treatment of landfill leachate. An experiment with Freeze Crystallization of landfill leachate was performed on a laboratory-scale. An elution of anions and cations, as well as conductivity and selected other parameters were monitored during the melting process. A high concentration of contaminants was reported in the initial runoff of melt water. The concentration of compounds in melt water reached a level of raw wastewater after melting of 20 to 30% of the total volume of snow, and has progressively decreased. Most toxic elements and organics were concentrated in the range of 85-95%. It was concluded that metamorphism occurring in the man-made snow, created by the freezing of landfill leachate in a cold atmosphere, could be successfully used as a treatment process.

KEYWORDS

Landfill Leachate, Freeze Crystallization, Concentration, Wastewater Treatment

1. INTRODUCTION

An application of freeze crystallization for purification and concentration of wastewater has been investigated by many researchers. The traditional research and use of the freeze crystallization process has been a two-phase process. Liquid and ice were present simultaneously. In such processes the ice crystals grow in solution, incorporating molecules of water, and the contaminants are concentrated in the remaining water. Such an approach has a long research history and has been applied in studies of concentration and purification of municipal wastewater and other fluid wastes “Taft, (1965); Baker, (1967, 1967a); Muller and Sekoulov, (1992)”.

It is now known that most solute compounds, as well as solid particles, are rejected from the growing ice crystals. Furthermore, it is known that growing ice crystals more easily incorporate some ionic compounds than others “Hobbs (1974)”.

Various attempts have been made to apply, in full scale, the beneficial effect of the freeze crystallization phenomenon. However, in most of the studies, the process has not been widely accepted because of the high energy consumption of the refrigeration system, or, in the case of freezing in natural conditions, because of the problem with distribution and freezing of large volumes of wastewater. Two-phase concentration devices with the refrigeration system are currently available but are not widely accepted.

The above problems can be avoided by freezing the wastewater in the form of man-made snow “White, (1985)”. Atomizing the wastewater in cold air with complete and rapid freezing of droplets is a new concept and was studied for the purpose of wastewater storage during the winter months “Wright, (1976)”. “Huber and Palmateer (1985)” in a joint project with “White (1985)” performed extensive studies on properties of wastewater after freezing by atomization in cold ambient air. Particular emphasis was placed on the bacteriological aspects of atomizing freeze crystallization and chemical properties of municipal wastewater converted to snow. Similar studies of freeze crystallization, done by “Zapf-Gilje et al. (1985)” also referred to municipal wastewater. The phenomenon of chemical compound segregation in the man made snow pack profile was noted.

Experimental studies in full-scale operations “White (1990, 1994)” brought the development of the atomizing freeze crystallization technology. As a result, the first atomizing freeze crystallization facility for treatment of municipal wastewater was built in Carrabassett Valley, Maine, U.S.A. To date five atomizing freeze crystallization treatment plants have been designed and built. One of them processes wastewater from a potato processing plant in Mars Hill, Maine, U.S.A.
In the following paper, a different approach of the utilization of freeze crystallization is presented – the concentration of contaminants by snow metamorphism and recycling relatively clean effluent into the environment.

2. CONCENTRATION EFFECT OF SNOW METAMORPHISM

The process responsible for segregation of chemical elements and nutrients in the snow pack, as well as its concentration, is snow metamorphism. The effect of metamorphism in natural snow is known but the mechanism of this segregation is still being investigated by many researchers. The concentration of impurities in first runoff from natural snow, which contributes to acidification of surface water during the spring, still remains of particular concern of scientists “Johannes et al., (1975); Brimblecombe et al., (1987); Bales, (1989); Tranter, (1992); Cragin, (1993)”.

Analyses of melt water from a solute rich natural snow pack revealed “Johannensen et al. (1975)” that the initial 20-30 % of runoff contained up to 80% of solutes.

Furthermore, it was shown that there is a preferential elution of ions from the snow pack. Some compounds are released earlier and with higher concentration than others. Previous studies suggested, for example, that sulfate and nitrate are removed in preference to chloride and the cations such as Potassium and Magnesium, as well as Calcium, are released easier than Sodium “Brimblecomble et al. (1987)”. “Cragin et al. (1993)” noted that preferential chemical elution during snow pack melting is strongly influenced by preferential chemical exclusion during snow crystal growth. The author concluded that less soluble chemical impurities, such as sulfates, are excluded more efficiently and therefore appear sooner and in higher concentrations in the melt water than more soluble species, such as chloride.
“Droste and Johnson (1993)” analyzed various pollutants in the snow and snowmelt from four snow dumpsites in the Ottawa-Carleton Region. They also noted a high concentration of contaminants in the first melt water coming from the natural snow pack.

Snow, as a thermodynamically unstable material, has the ability to change its physical characteristic even at very low temperatures. Fresh man-made snow is a composition of frozen droplets and in macro scale, is dissimilar to natural snowflakes.
However, the process of metamorphism is governed by the same mechanisms.

Based on this process, as well as the phenomenon of ions elution and its concentration in melt water, authors of this report hypothesized that the snow metamorphism process could be applied to treat landfill leachate and industrial wastewater.

After wastewater atomization, the ice crystals first form from the pure water at the surface of each droplet, and trap dissolved compounds such as salts and gases, as well as solid particles in the ice globule. Growing further ice crystals, incorporate water molecules and concentrates compounds in the remaining liquid inside the droplet. As the ice crystal grows, the free space for liquid decreases and the concentration at the growing ice front is higher than in the bulk water. When the solubility of the gaseous compounds reaches the maximum and oversaturation takes place, gas bubbles nucleate and are trapped between the growing ice crystals. An analogous situation occurs with other compounds and some salts may precipitate. The pressure of liquid inside the ice droplet increases with the decreasing volume of remaining liquid. The ice globule may fracture and the concentrate could be released outside. This gives additional benefit for further concentration because the concentrate is removed from the inside of the droplets to the surface. At that moment, the separation and concentration is in macro scale of each droplet and the contaminants are equally distributed in the snow pack profile.

However, immediately after the frozen droplets are deposited on the ground as “snow”, creating stable conditions below the snow pack surface, formation of bonds at the contact points takes place. Ice is transferred from the surfaces of the grains to the “contact points” by sublimation and partially by surface diffusion. The necks between droplets are created. Their growth minimizes the surface to volume ratio and, as a result – free surface energy. The mechanism of this phenomenon still fascinating and is a topic of many research dissertations.

Soon after the man-made snow is deposited on the ground, the temperature gradient is established in the snow pack profile. The mechanism of snow metamorphism is altered and is based on vapor pressure gradient “Colbeck, (1981)”. Thermodynamically, the snow is still in an unstable state and the high ratio of free surface to grain volume is far from its minimum. Since the gradients of temperature and vapor pressure have been established, the transfer of mass through sublimation is significantly enhanced “Perla and Ommanney, (1985); Perla and Summerfeld, (1986)”. Some ice grains or portions sublimate and the water vapor condenses as pure ice on the surface of the ice grains located in the area with lower vapor pressure. Small grains have a higher surface energy and their sublimation is naturally favorable. Furthermore, dislocation in the ice structure, caused by impurities and grain boundaries that are strictly related to higher system energy, also create favorable conditions for sublimation. As a result, solid particles and ionic compounds, as well as gas bubbles (volatile compounds of wastewater/leachate) are easily excluded and released from the ice grains. The majority of the snow volume is transferred to a vapor state and back into a solid state. Most of the contaminants are deposited on the surface of the ice grains in the pores of the snow pack. Furthermore, when the snow pack or its portion has reached the freeze/thaw temperature, other mechanisms of concentration take place. Fluctuations in the ambient temperature around the freezing point repeatedly thaw and freeze the ice crystals and the contaminants are rejected from the ice structure.

Solid particles, such as colloids undergo natural agglomeration and are easily separated from water. The freeze/thaw cycle significantly enhances the process of separation during the storage period. Longer storage periods and more frequent and higher variations in temperature during winter give a higher efficiency of concentration. When the melting begins, the rejected and accumulated soluble impurities on the ice crystals are similarly washed down as "cake" is washed in a filtration process. Solid particles and their agglomerates stay on the snow pack surface.

3. EFFICIENCY OF CONCENTRATION - DEFINITION

The efficiency of concentration for non-volatile compounds is defined "Szpaczynski, White (2000)" as follows:

$$E_{(i)} = \frac{m_{C(i)}}{M_{0(i)}} = 1 - \frac{m_{E(i)}}{M_{0(i)}}$$

where:

$E_{(i)}$ – efficiency of concentration [-],
$m_{C(i)}$ – mass of compound "i" in the concentrate [kg],
$m_{E(i)}$ – mass of compound "i" in effluent [kg],
$M_{0(i)}$ – mass of compound "i" in landfill leachate (wastewater) [kg].

Figure 1 shows a graphical interpretation of the efficiency of concentration. The concentration curve reflects changes in discharged contaminants of the runoff.
The area under the curve in Figure 1 in the range from V=0 to $V=V_c$ represents the mass of compound (i) in concentrate. Thus, in non-dimensional quantities, as shown in Fig. 1, the efficiency of concentration is given as:

$$E_{(i)} = \int_0^1 f_{(i)}(V)dV - \int_{V_C}^1 f_{(i)}(V)dV = 1 - \int_{V_C}^1 f_{(i)}(V)dV;$$

V – ratio of discharge melt water volume to total volume [-],
V_c – ratio of concentrate volume to total volume of wastewater [-],
C - Concentration ratio $C=C_{M(i)}/C_{0(i)}$ [-],
$C_{M(i)}$ - Concentration of compound (i) in melt water [mg/l],
$C_{0(i)}$ - Concentration of compound (i) in raw waste water [mg/l],
$f_{(i)}(V)$ – concentration function for compound "i".

Results from experiments indicated that the efficiency of the concentration process could be described by the exponential function:

$$f(V) = a + b\exp(-V/d).$$

Therefore,

$$E_{(i)} = 1 - a(1 - V_c) - bd(e^{(-V_c/d)} - e^{(-1/d)});$$

where:

a, b, d = coefficients of concentration (based on experimental data).

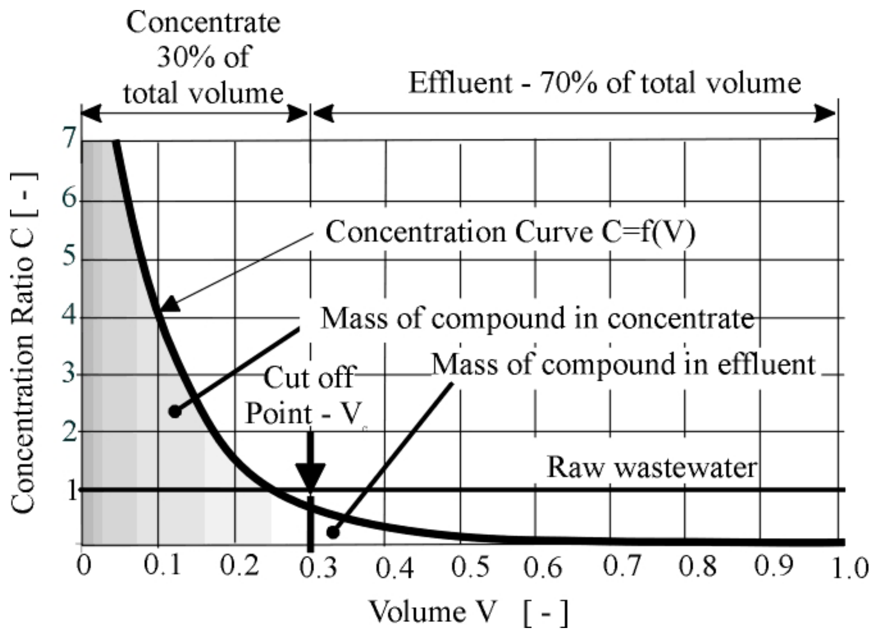


FIGURE 1. Concentration of contaminants in melt water

Concentration of compound "i" in the effluent melt water and in the concentrate can be calculated as follows:

$$C_{E(i)} = \frac{1 - E_{(i)}}{1 - V_c} C_{0(i)} \qquad C_{C(i)} = \frac{E_{(i)}}{V_c} C_{0(i)}$$

Where:

$C_{E(i)}$ = Average concentration of compound (i) in effluent [mg/l];
$C_{C(i)}$ = Average concentration of compound (i) in concentrate [mg/l];

4. EXPERIMENTAL STUDIES

The raw leachate sample was withdrawn from the drainage system of the Trail Road Waste Facility in Ottawa. The weather conditions at that time did not allow the atomization of the leachate in a cold atmosphere to produce a laboratory sample of snow. It was decided to supercool the sample of leachate in small cubes, then freeze samples with natural ice crystals as a nucleator. Then, the snow was made by double stage crushing of the ice cubes with a laboratory ice crusher "White, Szpaczynski (1998)". However, it was realized that the releasing of volatile compounds could be more efficient during leachate atomization.

The volume of 9 l of snow was produced and placed in the jar for further observation. The jar was located outside, buried in the natural snow pack. Variations of ambient temperature created favorable conditions for snow metamorphosis and concentration of contaminants at the surface of ice crystals. The snow was kept outside for a period of 4 weeks in temperatures ranging from -15°C to -1°C. When the temperature in the snow pack increased to the melting point, the jars were temporarily placed in the laboratory freezer. During the storage of the sample of snow, the temperature gradient metamorphosis took place and the contaminants were slowly rejected from the ice crystals and concentrated at crystal surface. Some soluble compounds gradually gravitated to the bottom of the jar. At the same time, the small precipitated solid particles were also carried down and concentrated at the bottom of the jar. The contaminants were also rejected from the ice crystals and accumulated at the bottom of the jar. During the melting, samples of melt water were collected and the volume of each sample was measured. Compared to raw leachate, the first samples of melt water were darker in color when examined visually. The chemical composition of the samples was analyzed, accordingly to the Standard Method for the Examination of Water and Wastewater, at Accutest Laboratories of Ottawa.

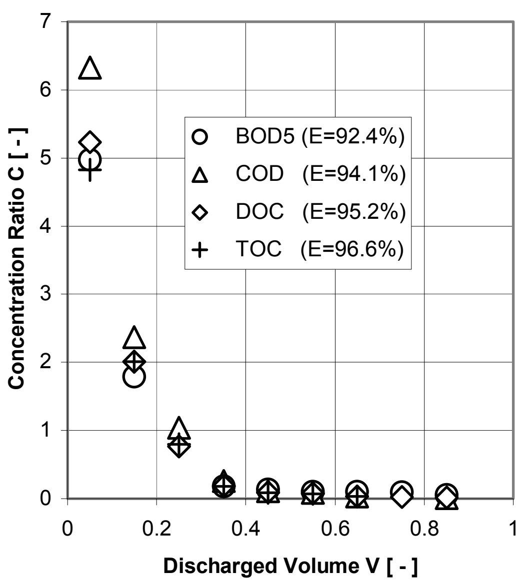
The results from the concentration of contaminants are presented in Figures 2 a, b, c, d, e, f.

The efficiency of the process was different for different elements. Sulfate was generally not detectable in the melt water effluent. Very effective removal was also noted for chloride (Cl) and such compounds as Boron (B), Potassium (K) and Sodium (Na). More than 95% of these elements were removed from the snow sample.

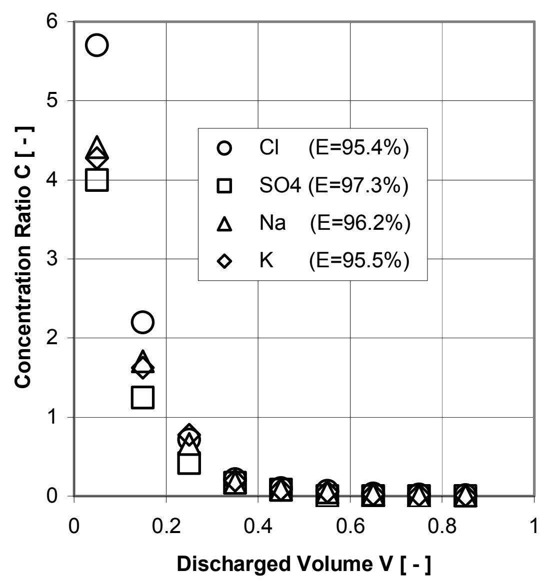
An increase in concentration of BOD, COD, DOC and TOC, in the first melt fraction was also very high, and reached values of 92%, 94%, 95% and 97%, respectively. Satisfactory concentration efficiency of Barium (Ba) was also reported (94%). Other elements such as Aluminum (Al), Chromium (Cr), Nickel (Ni), Zinc and Iron (Fe) were concentrated to 93%, 90%, 93%, 89% and 92%, respectively. Mercury, in raw leachate was 0.0007mg/L and was concentrated in the first 20% of melt to the value of 0.003 mg/L .In further samples of effluent, Mercury (Hg) was below Method Detection Limit. The concentration efficiency of Copper (Cu) was at the range of 77%. Lower concentration of 21% was reported for Fluoride F. Fluoride is easy incorporated into the ice structure and thus its concentration was restricted. Generally, more than 92 % of all contaminants were concentrated and discharged in the first 30% of sample volume.

FIGURE 2 a, b, c, d, e, f
Concentration of selected compounds in melt water

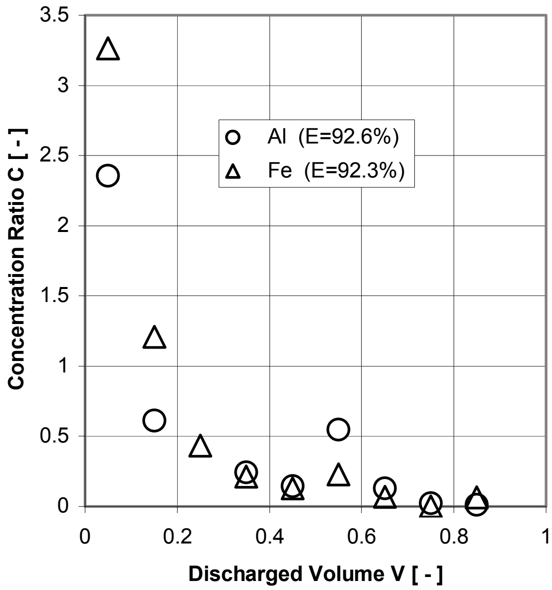
a)



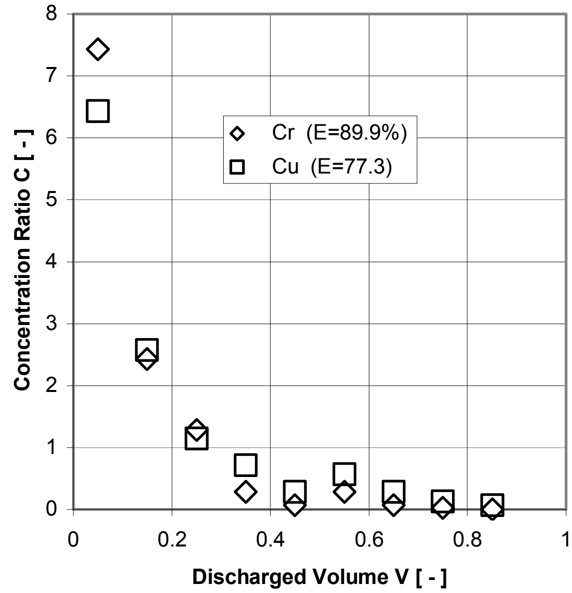
b)



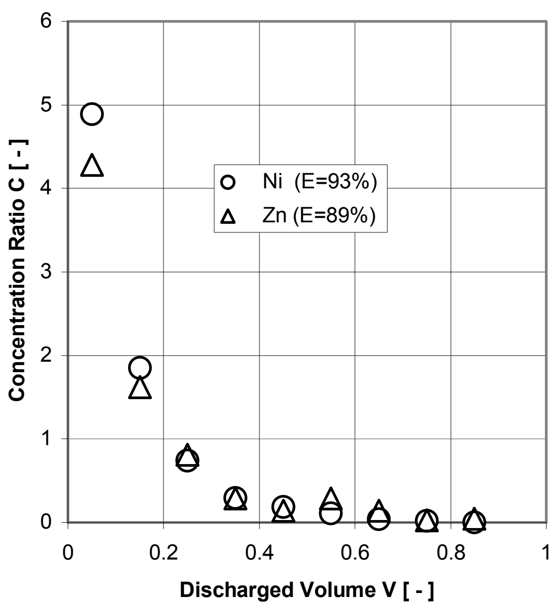
c)



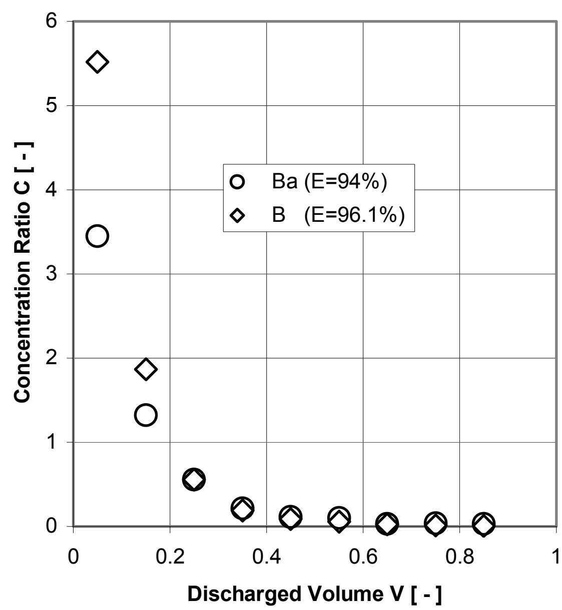
d)



e)



f)



5. PROPOSED PROCESS LAYOUT

In Figure 3 the proposed processed layout is presented. Wastewater is pumped at high pressure to specialized nozzles, where, using the compressed air it is atomized and projected into the cold ambient air. After atomization, the droplets are frozen and deposited on the adequately prepared lined ground. In northern latitudes, processing of wastewater can start as early as November, and the snow can be stored until July. During this period, the metamorphism processes separate the contaminants, and rainwater or melt water washes them down and discharges them in the first runoff. This highly contaminated concentrate has to be collected and separated from the subsequent effluent stream. Continuous measurement of conductivity could help to set the "cut off" point for runoff. Conductivity of melt water can be used as an indicator of concentration.

The size of the snow pack extends the melting period to the beginning of July. Higher conductivity at the beginning of melting is well documented in other studies done by the authors of this paper, and reflects the concentration effect of snow metamorphism. Based on the characteristic of this data, it is easy to decide where the flow stream should be directed; to the storage pond or to the discharged system of natural or constructed wetlands. Generally, during the first 20 days of melting the conductivity decreases significantly and then stabilizes at very low level. The "cut off" point" for stream redirection could be set up at the point of stabilization.

One of the benefits from the application of the atomizing freeze crystallization system is the concentration of most nutrients and contaminants in small volumes of melt water, and postponement of the polishing treatment of effluent to late spring and summer.
The selection of the discharge method for freeze crystallization effluent depends upon the characteristics of the wastewater and should be considered separately for each specific wastewater.

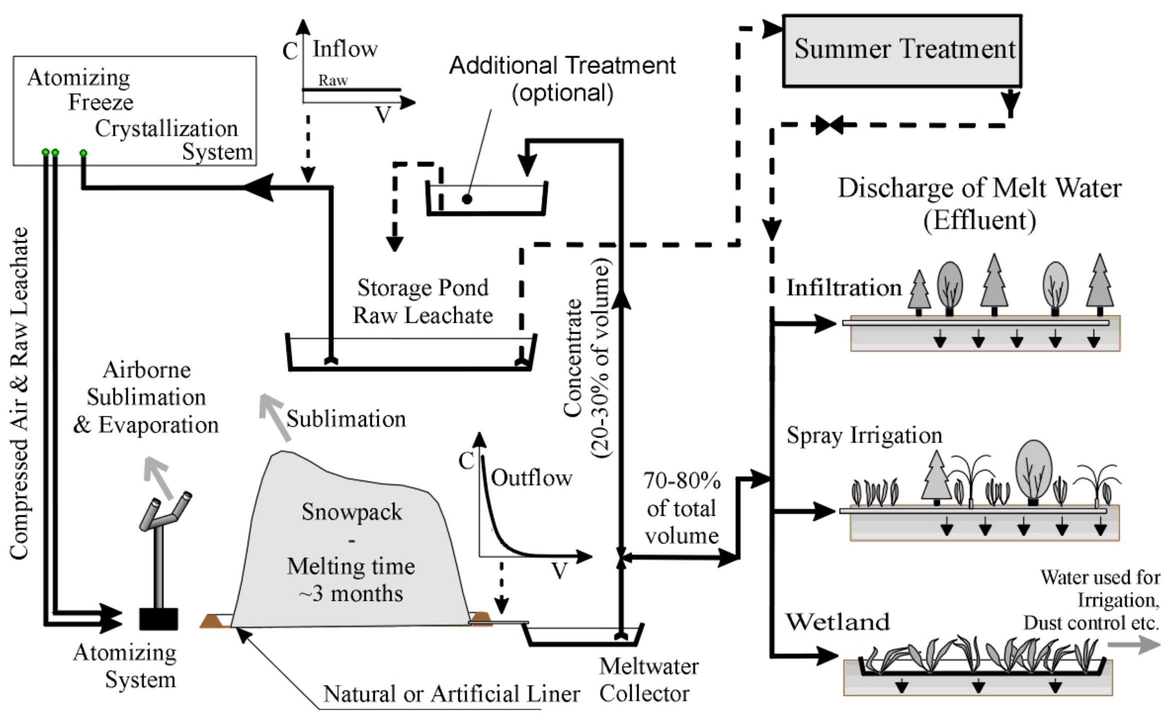


Figure 3 Proposed process layout

6. CONCULSION

The following points summarize the findings of the study.

- The application of the atomizing freeze crystallization process can be successful in the treatment of landfill leachate

- The atomizing freeze crystallization process can be an excellent pretreatment unit system in winter operation or can work as a separate independent unit.

- The freeze crystallization process improves clarity of effluent. The colloidal particles undergo natural agglomeration and are easily separated from the melt water stream.

- High efficiency of concentration was reported for heavy metals, chloride and sulfate as well as for nitrogen compounds (nitrate, nitrite and ammonia). BOD and COD in effluent were significantly reduced.

- Volatile compounds are stripped away during atomization and/or separated in frozen droplets as gas bubbles, and slowly released during snow metamorphism and melting.

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