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SEPARATION OF CONTAMINANTS IN THE FREEZE/THAW PROCESS

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These studies examined the concept of concentration and purification of several types of wastewater by freezing and thawing. The experiments demonstrated that freezing of contaminated liquid contributed to concentration of contaminants in solution as well as significant concentration and agglomeration of solid particles.

A high degree of purification was achieved for many parameters. The results of comparative laboratory tests for single and multiple freezing are presented. It was found that there was a higher degree of concentration of pollutants in wastewater frozen as man-made snow than in bulk ice. Furthermore, the hypothesis that long storage time of liquid as snow and sufficient temperature gradient metamorphism allows for high efficiency of the concentration process was confirmed.

It was reported that the first 30% of the melted liquid volume contained over 90% of all impurities. It gives great opportunities to use this method to concentrate pollutants. The results revealed that the application of this process in full scale is possible. Significant agglomeration of solid particles was also noted. Tests with clay slurry showed that repeated freezing and thawing processes significantly improve the characteristics of slurry for sedimentation and filtration.

Keywords: freeze crystallization, snow metamorphism, landfill leachate, wastewater, sludge dewatering

1. INTRODUCTION

Conventional methods for treatment of municipal and industrial fluid waste are costly, particularly if large volumes have to be processed. Professional engineers and scientists are looking for economical alternatives for methods that are currently in use. In recent decades, with particular emphasis, the process of freezing of wastewater has been investigated. Several different approaches have been studied and the process has gained new interest for industrial and municipal wastewaters.

In the 1960's, research studies were intensified at the two-phase concentration process. In such an approach, ice grows in solution by adding to its structure water molecules. If ice incorporates to its structure impurities, internal stresses appear. Therefore, ice crystals try to collect only molecules of water and reject dissolved and solid compounds. In this approach, impurities are concentrated in the remaining unfrozen liquid. Such method was studied by Baker (1967; 1967a; 1969), Taft (1965) and recently by Wakisaka et al. (2001) and Gay et al. (2003). Researchers focused on issues of trapping and rejection of solid particles during freezing of contaminated water and migration of particles in front of a growing ice plane (Cisse and Bolling, 1971; Corte, 1962; Halde, 1979). The authors reported that the best particle migrations as well as the best concentration effect were obtained at a low freezing rate.

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This fact was also noted by Chian et al. (2002). However, Parker (1999), for higher concentration of solids, noted satisfactory results after experiments with ultra-rapid freezing of alum sludge.

Muller and Sekoulov (1992) used a falling film reactor to examine the potential of freeze concentration to reuse municipal wastewater. Pure water was removed from the solution as ice. Impurities were concentrated in the remaining water. The authors noted efficiencies of up to 99% of conductivity, TOC, DOC and NH_4-N in a single stage freezing of municipal wastewater. For wastewater with higher concentration of impurities the efficiency was about 91%.

Cragin (1995) studied an exclusion of sodium chloride from ice during freezing. He reported that for a given freezing rate, the salt incorporation mechanism depends upon the solution concentration. Later, Geo et al. (2009) noted that mixing of the freezing liquid reduces the influence of the initial feed water impurity concentration on the efficiency of separation.

Various attempts have been made to apply, in full scale, the beneficial effect of the freeze crystallization process. For example, the process has been successful in food industry for concentration of fruit juices and pre-concentration of wine (Kyprianidou-Leodidou and Botsaris,1990). Recently Montusiewicz et al. (2010) examined the effect of freezing and thawing effects on anaerobic digestion of mixed sewage sludge from municipal WWTP. For treatment of industrial or municipal wastewater, in most cases, the traditional freeze and thaw process with application of the refrigeration system has not been accepted for full scale application because of its high energy consumption. The concept of freezing wastewater in natural weather conditions, with ambient temperature below zero, dramatically changes the situation and creates favourable circumstances for industrial applications.

Large volumes of wastewater, such as mine tailings, create serious environmental problems. The wastewater, from Canadian Athabasca Oil Sands, is a well known example. Treatment of fine tailings from Athabasca Basin has been the subject of many theoretical and experimental studies in the last several decades. Many different methods and technologies, including freezing, were tested (FTFC, 1995). Sego (1996) used freezing for impurity removal from recycle water from the extraction of bitumen from oil sands. The author reported achieving separation of over 95% of original chloride and sodium concentration in field tests. Gao et al. (2004) used spray freezing for concentration of oil sands tailings pond water and the pulp mill wastewater. In the experiments, the wastewater froze partially with run off production or completely during the operation. The authors concluded that to achieve higher efficiency of impurity removal, the wastewater should be only partially frozen. It could be assumed that the method of partially frozen spray is similar to conventional two phase concentration process. Most probably, part of wastewater in the form of droplets was frozen as a bulk ice on the ground and the concentrated run off was created. Beier et al. (2007) as well investigated the feasibility of using freeze separation process for reducing salinity of oil sands process water from Athabasca Basin in Northern Alberta. Experiments revealed that during freeze-thaw cycle, the majority of salts were concentrated into less than one quarter of the original frozen volume. Moreover, Gao and Shao (2009) used progressive freeze concentration process for removal of five commonly used pharmaceuticals (ibuprofen, gemfibrozil, acetylsalicylic acid, metoprolol and sulfamethoxazole). By freezing only 80% of feed water and without washing the ice, about 84-92% of the drug content reduction in ice was achieved in single unidirectional downward freezing (UDF). In two stage UDF about 99% reduction was achieved. With a few exceptions, which will be discussed later in this paper, freeze-thaw concept has been applied for treatment of several different industrial wastewaters but only in small scale experimental studies.

At the same time, parallel to research of wastewater freezing, independent studies were carried out in the field of separation of impurities present in the natural snow. Johannessen et al. (1975; 1978) reported that 20 to 30 % of the first run off from a natural snow pack contained up to 80% of dissolved compounds absorbed to snowflakes and deposited on the ground. This phenomenon, called "ionic pulse" or "first flash", is partially responsible for acidification of surface water during spring. The process of ion elution from natural snowpack still remains of particular concerns of scientists (Bales, 1989; Brimblecombe et al., 1985, 1987; Tranter, 1992). Recently, Meyer et al. (2006; 2009), based on experiments, reported that even though conductivity of melt indicated a preferential early elution of ions, in the first meltwater fraction, no "first flash" phenomenon was observed for soluble PAHs. Furthermore, the authors noted that water soluble organic chemicals, such as atrazine, are preferentially released at an early stage of melting. Authors concluded that such chemicals were accumulated at the surface of snow particles and dissolved in downward percolating meltwater. Therefore, they were released with first meltwater. Furthermore, the author stated that hydrophobic substances attached to particles such as larger polycyclic aromatic hydrocarbons, are often released at the end of melting because of particle coagulation and its trapping in pores of the snow pack. Recently, Meyer and Wania (2011) developed a snowmelt model to simulate and predict the elution of organic substances from melting snow.

The process responsible for segregation of chemical compounds in the natural snow pack, as well as its concentration is different than the standard processes in freeze and thaw operations. Segregation of impurities in natural snowpack and ion elution as well as ionic pulse are created by the snow metamorphism phenomenon (Sommerfeld, LaChapelle, 1970). The effect of metamorphism in natural snow is known but the mechanism of this segregation is still investigated by many researchers (Christon et al. 1994; Colbeck, 1980; Marbouty, 1980; Pinzer et al. 2012). Brimblecombe et al. (1985; 1987) revealed that some compounds are released earlier and with higher concentration than others. The authors established the following sequence of ion elution from the natural snowpack:

$$SO_4^{2-} > NO_3^- > NH_4^+ > K^+ > Ca^{2+} > Mg^{2+} > Na^+ > Cl^-$$

Sulphate and nitrate are removed in preference to chloride and the cations such as sodium, magnesium, calcium as well as potassium. Preferential chemical elution was also noted by Cragin et al. (1993). The authors noted that preferential chemical elution during snow melting is influenced by preferential rejection of ions during snow crystal growth. The author also stated that less soluble chemical impurities, such as sulphates, are rejected more efficiently and therefore appear sooner and in higher concentrations in the meltwater than more soluble species, such as chloride. Droste and Johnson (1993) analysed various pollutants in snow and snowmelt from four snow dumpsites in the Ottawa-Carleton Region. They also noted a high concentration of contaminants in the first meltwater coming from the snow pack. Tatarniuk et al. (2009) also reported "ionic pulse" in the first melt from snow at municipal storage facilities. The salt concentration in the first meltwater was 10 times higher than average concentration in the bulk snow. The authors reported that about 90% of the chloride and sodium was released from experimental cores within the first 19% of meltwater.

Several studies were done to use man-made snowmaking techniques and freeze/thaw process for treatment of wastewater. The first trial was done in 1974. The Upper Yampa Water Conservation District of Colorado and Wright-McLaughlin Engineers performed trials of sewage effluent storage as snow. The purpose of the study was to evaluate the use of sewage for snowmaking on ski slopes. A limited monitoring program was conducted. Pollutants in effluent, snow and snow melt were examined. Significant reduction of BOD_5 in the snowpack was noted. Huber and Palmateer in a joint project with White of Delta Engineering (1985) performed extensive studies on properties of secondary treated effluent converted to man-made snow. Particular emphasis was placed on the bacteriological aspects of atomizing freeze crystallization (AFC) and chemical properties of snowpack and meltwater. The results were very promising. The authors stated that ponded meltwater was of better quality than the tertiary effluents. Similar studies of freeze crystallization, done by Zapf-Gilje et al. (1985) also referred to municipal wastewater. The phenomenon of chemical compound segregation in man-made snow pack profile was reported. In 1995, Delta Engineering built the first full scale AFC plant for treatment of secondary effluent in Carrabassett Valley, Maine, USA. Shortly after, the second AFC plant, also for secondary effluent from wastewater treatment plant, was built in Westport, Ontario, Canada.

Numerous research projects were conducted to investigate possible application of AFC for treatment of municipal and industrial fluid waste (White, 1998). White and Lefebvre (1997) presented pilot scale field experiment with treatment of agricultural and hog manure wastes. Szpaczynski and White (2000a) presented results from experiments with freeze/thaw treatment of boiler and cooling water system from a fertilizer plant. The wastewater was converted into ice crystals (man-made snow) by atomizing wastewater in cold ambient temperature. To simulate the natural condition of temperature fluctuations and the temperature gradient metamorphism - TGM, the container with ice crystals was kept outdoors and buried in natural snowpack. In March, when the ambient temperature in the snowpack reached melting point, the snow gradually melted (48 hours) and samples of discharged meltwater were analysed for selected contaminants. The calculated efficiency of nitrate concentration was 94%. High concentration was also reported for nitrite – 89.7 % and phosphorous – 87 %. About 80% by weight of sodium, chloride and sulphate were concentrated in the first 30% of melt. Additionally, the authors presented the results of experiments with acid mine drainage. The samples originated from a drainage pond at the Inco Copper Cliff Mill Site in Sudbury, Ontario. The experiment was done by White in 1989. The wastewater was converted to snow by two-phase atomization. The snow was made in February and deposited in several insulated containers (about 100 l. each), then stored for five weeks outdoors, and melted at room temperature in 48 hours. Progressively during the melting, the samples of meltwater were collected and analyzed in the professional laboratory. Preferential elution of ions was noted. However, the results for SO_4 did not support results of research work done by Brimblecombe et al. (1985) for natural snowpack. In White's project, elution of sulphate ions was less efficient than other measured parameters (Fig. 8, Szpaczynski and White, 2000a). Nevertheless, the concentration of metals in the first melt was very impressive. Application of freeze and thaw processes and phenomenon of ice crystal metamorphism for treatment of landfill leachate in small scale experiments were investigated in late 1990's and presented by Szpaczynski and White (2000b). The leachate samples were converted into ice crystals (snow). As expected, leachate was highly contaminated with organic and inorganic compounds. During the storage of leachate in the form of man-made snow, the temperature gradient metamorphism took place. After several weeks of storage and simulating the presence of temperature gradient, the samples of meltwater were collected and the volume of each sample was measured. Significant concentration of organic and inorganic contaminants took place during the metamorphosis of snow. Most of the pollutants were concentrated and removed in the first 30% of the melt. Compared to raw leachate, the first samples of meltwater were darker in colour. This illustrated the efficacy of the concentration by freeze and thaw process.

Several more studies were done by different authors. Recently, spray freezing technology has been promoted. In fact, the base of action of spray freezing is similar to regular two phase freezing with falling film reactor. The authors (Gao et al., 2004) stated that to achieve higher efficiency of impurity removal, the wastewater should be only partially frozen. In our opinion, temperature gradient metamorphism (TGM) of ice crystals can assure very high efficiency of impurity concentration in the first part of melt and the complete freeze out by atomization of fluid waste in cold ambient temperature guarantee a high efficiency of treatment. Furthermore, it creates favourable condition for precipitation of dissolved compounds inside the droplet. These precipitates are later released because of TGM actions. However, sufficient time of snow storage is required to insure proper condition for metamorphism. Periodical thawing and refreezing in warm days and cold nights in spring can significantly improve efficiency of concentration of contaminants in the first "ionic pulse".

2. EXPERIMENTS OF FREEZE/THAW OF FLUID WASTE

2.1. Materials and methods

In the following experiment, the authors of this work present the comparison of two different freeze and thaw processes for treatment of landfill leachate. The first one is based on TGM of ice crystals. The second one, the decantation test, concerns complete freeze out of the same volume of leachate sample but frozen as a bulk ice. For the best results, to simulate melting and refreezing in natural condition, the second sample (B) was frozen and thawed 5 times. Schematic of the experimental setup used in the snowmelt experiments is presented in Fig. 1.

For the first container (A), the sample of landfill leachate was frozen in small droplets (dia. ~5 mm). Then, the droplets were crushed in a laboratory ice crusher to make man-made snow (dia. < 1 mm). The column was filled with about 9 litres of snow for further processing by TGM. The "A" container was located outdoors and buried in the natural snow pack. Variations of ambient temperature created favourable conditions for TGM and concentration of contaminants at the surface of ice grains. The snow was kept outdoors for a period of about 4 weeks in temperatures ranging from -15 °C to -1 °C. The temperature of the snowpack was controlled by thermocouples. When the temperature in the snowpack warmed up to the melting point, the container was temporarily placed in the laboratory freezer. The TGM was further simulated for about 4 weeks by changing the temperature of the container from -15 °C to -1 °C. Although the temperature was kept below 0 °C some liquid and soluble compounds were present at boundaries and in pores of snow particles and could gradually flow down because of freezing point depression. Therefore, some dissolved compounds (salts), with a low eutectic point, accumulated at the bottom of the container. Before melting, the container was placed in the second, larger container with ice cubes that insured slow melting of snow. The samples were collected from the bottom.

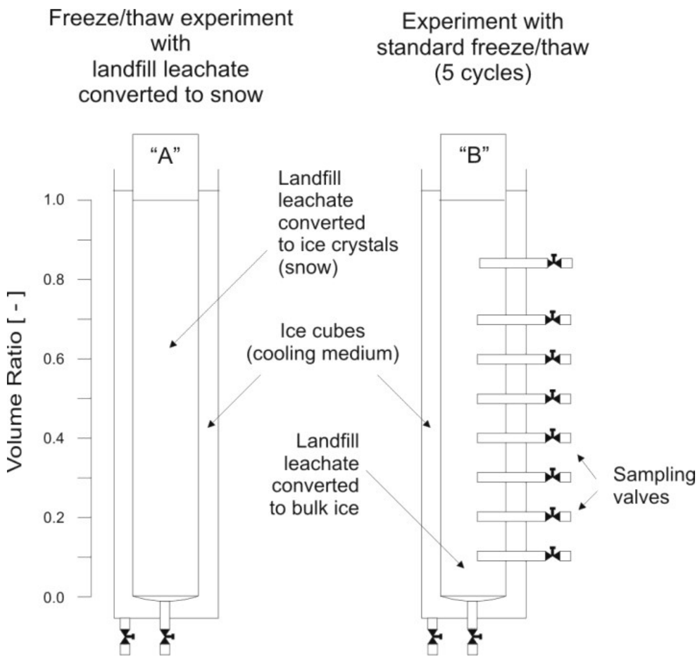

Fig. 1. Schematic of the experimental setup for snowmelt experiment

The second column "B" was filled out with raw landfill leachate. The container was placed in a vertical position in a large size freezer, where leachate was completely frozen at a temperature of about -25 °C. Then, the container was removed from the freezer and the ice was slowly melted at room temperature. To simulate the natural conditions of freeze, melt and refreeze during winter the process of freeze and melt was repeated 5 times. Because small particles of colloids that precipitate during freezing were noticed, care was taken not to disturb the meltwater in the container before the next cycle of freezing. As soon as five cycles of freeze/thaw were finished, when all ice melted, the meltwater was discharged by the special valves.

The first volume of sample was withdrawn from the top valve, the last one at the bottom. Although, there were several sampling valves, for comparison purposes, the melt water was collected only from

4 valves. Four composite samples were prepared from it. The top sample represents the cleanest water - the effluent. The closer to the bottom, the more pollutants were found in the samples. The bottom one, with some colloids and particles that precipitated during freezing and were suspended in leachate or settled, represents the most contaminated part of melt - the concentrate.

The results are presented in Figs. 2 – 5 and in Tables 1 and 2. The chemical composition of the samples from containers was analysed, accordingly to the standard method for the examination of water and wastewater, at the professional laboratory with accreditation.

3. RESULTS AND DISCUSSIONS

3.1. Landfill leachate

The efficiency of the process was different for different elements. Not like with tests with acid mine drainage (Szpaczynski and White, 2000a), the efficiency of concentration of sulphate in the first flash of 30 % of meltwater was very high (93.2%), and after that, in the rest of meltwater, was generally not detectable. Very high efficiency of the treatment with presence of TGM was also noted for chloride (92.3%) and such compounds as boron (93.8%), potassium (92.9%) and sodium (93.7%). An increase in BOD_5, COD, DOC and TOC in the first melt was also very high and reached values of 90.2%, 90.5%, 92.2% and 93.3%, respectively. Other elements such as chromium, nickel, zinc and iron were concentrated to 86.9%, 90.9%, 88% and 91.2%, respectively. The concentration efficiency of copper was at the range of 73%. Very low efficiency of concentration was reported for fluoride. Fluoride is easily incorporated into the ice structure and thus its efficiency of concentration was limited. Over 90% of analysed elements were removed from the snow sample of container "A" in the first 30% of meltwater. In the graphs (Figs. 2 – 5), continuous lines represent concentration of compounds in meltwater from this container. The area under each curve represents the mass ratio of a compound in a sample. For example, if we assume that the first 30% of melt is the concentrate, the mass ratio of a compound in this concentrate is represented by the area under the curve in the range of V/V_0 from 0 to 0.3. Dashed lines represent meltwater from the decantation test, where the landfill leachate was frozen as bulk ice.

It is clear, that the concentration efficiency of contaminants in the first melt is higher if the dominant process of separation is snow metamorphism (container "A"). Moreover, the concentration curve of TGM is steeper. Therefore, the sharpness of the TGM separation is higher.

The separation of contaminants in complete freeze out of leachate, even with five cycles of freeze and thaw does not give the same quality of treatment as for snow samples with the presence of TGM. The efficiency of concentration in decantation test is noticeably lower.

Based on these small scale experiments, it was established that the relative concentration of a compound in meltwater can be described very well by the following exponential equation:

$$\overline{C} = a + b \cdot \exp\left(-c \cdot \overline{V}\right) \tag{1}$$

where: $\overline{C} = \dfrac{C}{C_0}$; $\overline{V} = \dfrac{V}{V_0}$.

Efficiency of concentration E_{30} was defined as the relative mass of compound in the first 30% of meltwater. Results for selected parameters are presented in Tables 1 and 2.

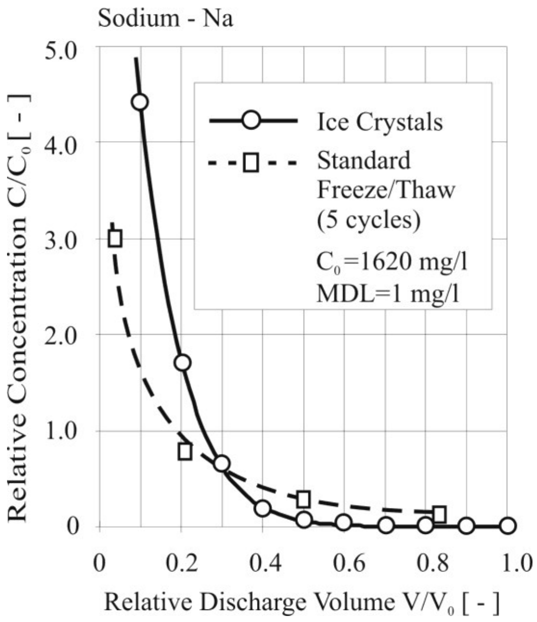

Fig. 2. Concentration of Na in meltwater of landfill leachate

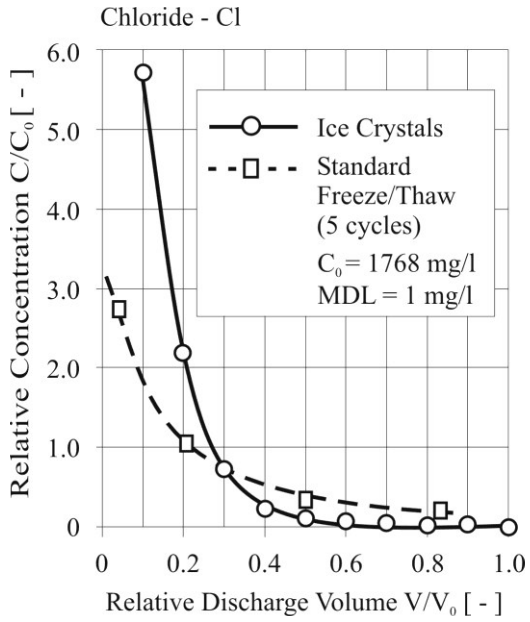

Fig. 3. Concentration of Cl in meltwater of landfill leachate

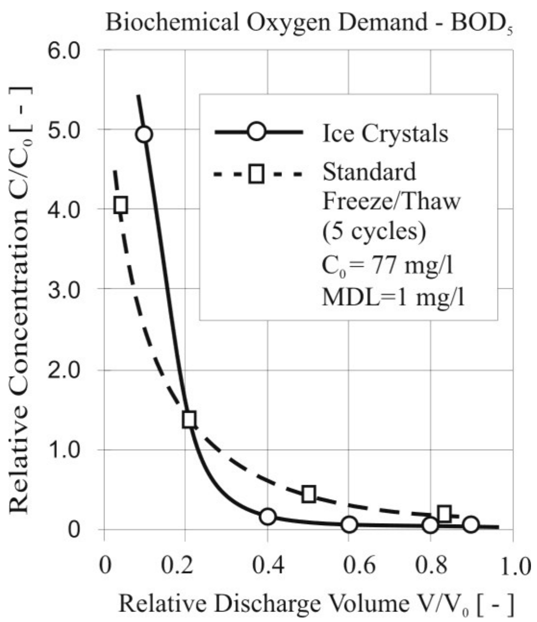

Fig. 4. Concentration of BOD_5 in meltwater of landfill leachate

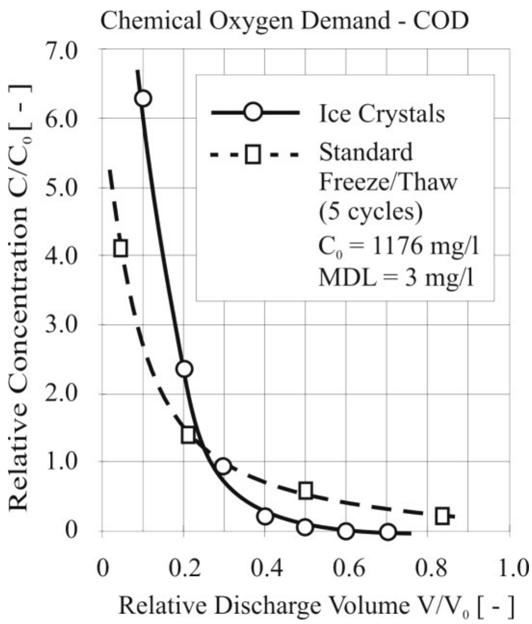

Fig. 5. Concentration of COD in meltwater of landfill leachate

Because of relatively a small volume of sample that was collected for the analysis, it was not possible to describe the concentration of compounds in the first few percent of meltwater. In order to eliminate the influence of the concentration peak at the beginning of melting on the calculation result, the efficiency of the concentration was determined based on Equation (2).

$$E_{30} = 1 - \int_{0.3}^{1} a + b \cdot \exp\left(-c \cdot \overline{V}\right) d\overline{V} \tag{2}$$

Table 1. Coefficients of Eq. (1) and efficiency of landfill leachate concentration with ice crystal metamorphism (container A)

Parameter	C_0 [mg/l]	MDL [mg/l]	a	b	c	Adj R^2	E_{30} [%]	$C_{e,70}$ [mg/l]
Na	1620	1	-0.0051	11.5668	9.6199	0.999	93.7	145.8
Cl	1768	1	-0.0034	15.4280	9.9228	0.999	92.3	194.5
Cr	0.07	0.01	0.0659	21.0392	10.5402	0.994	86.9	0.01
Ni	0.27	0.01	0.0265	12.7652	9.6625	0.999	90.9	0.04
K	758	1	0.0011	10.8516	9.3489	0.998	92.9	76.9
Fe	3.77	0.01	0.0721	9.0564	10.4370	0.996	91.2	0.47
Zn	0.21	0.01	0.0772	10.8381	9.4969	0.994	88.0	0.04
BOD_5	77	1	0.0609	14.2007	10.6092	0.999	90.2	10.8
COD	1176	3	-0.0017	16.5535	9.6196	0.998	90.5	159.6
B	9.91	0.01	0.0110	16.7219	11.0928	0.999	93.8	0.88
Cu	0.07	0.01	0.2512	16.0806	9.5871	0.994	73.0	0.03
SO4	12	3	0.0502	12.6729	11.6736	0.998	93.2	1.2
TOC	520	1	-0.0353	11.8871	8.9139	0.998	93.3	49.8
DOC	470	1	0.0015	13.8701	9.7342	0.999	92.2	52.4

Table 2. Coefficients of Equation (1) and the efficiency of landfill leachate concentration with standard freeze-thaw (container B)

Parameter	C_0 [mg/l]	MDL [mg/l]	a	b	c	Adj R^2	E_{30} [%]	$C_{e,70}$ [mg/l]
Na	1620	1	0.1966	4.1157	9.0174	0.997	83.9	372.6
Cl	1768	1	0.2109	3.3545	6.4016	0.998	83.5	416.7
Cr	0.07	0.01	0.3002	3.0230	6.8979	0.998	77.8	0.02
Ni	0.27	0.01	0.2244	3.3173	7.3389	0.995	82.4	0.07
K	758	1	0.2018	3.4414	7.2959	0.996	83.7	176.5
Fe	3.77	0.01	0.2045	2.3043	8.3421	0.999	84.7	0.82
Zn	0.21	0.01	0.6704	3.9514	6.6350	0.993	50.7	0.15
BOD_5	77	1	0.2752	5.0638	6.8153	0.998	78.8	23.3
COD	1176	3	0.3255	5.1231	7.0827	0.988	74.2	433.4

3.2. Tannery effluents

Unit operations at tannery factory include the use of a number of chemicals such as surfactants, acids, dyes, tanning agents, salts etc. (Di Iaconi et al., 2002). Because of low biodegradability of such chemicals, effluents from tannery wastewater treatment plants create a serious problem. Moreover, in many cases effluents after conventional biological treatment do not meet the required limits for parameters such as COD, salinity, ammonia and surfactants.

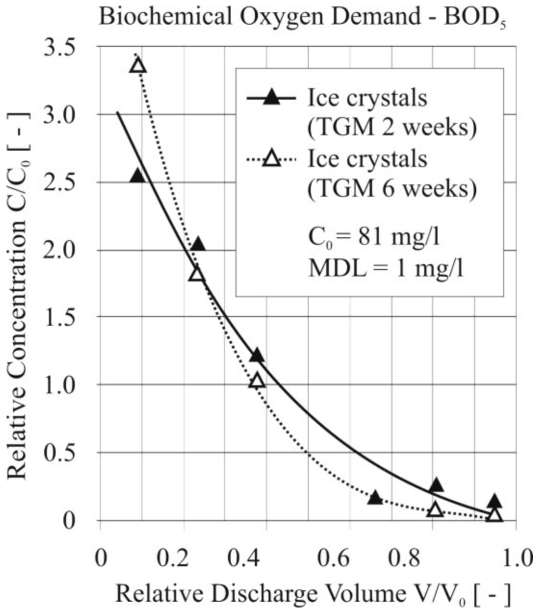

Fig. 6. Concentration of BOD_5 in meltwater (wastewater from tanneries)

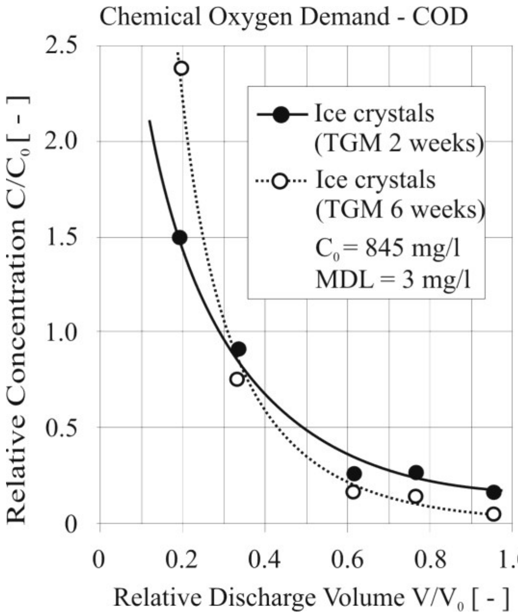

Fig. 7. Concentration of COD in meltwater (wastewater from tanneries)

The authors of this work performed preliminary research into the possibility of application of freeze/thaw process for treatment of effluents from tanneries. The effluent samples used in this study were collected from the plant after partial treatment. In Figs. 6 and 7, examples of concentration curves for BOD_5 and COD for freeze/thaw experiment with effluents from tanneries are illustrated. The effluent was converted to man-made snow and divided into two equal volumes. The first was placed in a container and kept for 2 weeks at temperature from about –15 °C to –1 °C and then slowly melted. The samples of melt were analysed for concentration of several compounds. The second part of man-made snow was placed in the same container but kept for 6 weeks at temperature from –15 °C to –1 °C. The temperature in the freezer was controlled and the TGM was simulated and intensified by changing the temperature inside the freezer. Examples of experimental data, for BOD_5 and COD are presented in Figs. 6 and 7 and in Table 3.

Table 3. Coefficients of Equation (1) and the efficiency of tannery effluent concentration with ice crystal metamorphism

Parameter	C_0 [mg/l]	MDL [mg/l]	a	b	c	Adj R^2	E_{30} [%]	$C_{e,70}$ [mg/l]	TGM [weeks]
BOD_5	81	1	-0.5026	3.6832	1.9897	0.902	58.6	47.9	2
			-0.1269	4.7696	3.8198	0.996	71.9	32.5	6
COD	845	3	0.15694	3.2148	4.5583	0.975	71.8	340.4	2
			0.13433	12.5251	9.0022	0.994	81.3	225.7	6

Higher impurity removal from the first 30% of meltwater was observed for the snow with longer storage time (6 weeks) when the TGM had time to “process” the whole volume of the snow sample. Efficiency of contaminants concentration E_{30} after 2 weeks of ice crystals metamorphism for BOD_5 was only 58.6 %. However, after increasing time of metamorphism to 6 weeks, the efficiency increased to 71.9 %. A similar situation was noted for the efficiency of concentration of COD. It was reported that the efficiency was as high as 71.8 % and 81.3 % for 2 weeks and 6 weeks of TGM, respectively. This confirms hypothesis that long storage time and sufficient TGM allows for high efficiency of the concentration process.

3.3. Full-scale treatment of municipal wastewater

An additional test was done at the full scale AFC plant in Westport, Ontario, Canada. At the beginning of melting season, the conductivity of ponded meltwater in close range from the main snowpack was measured. The results are shown in Fig. 8.

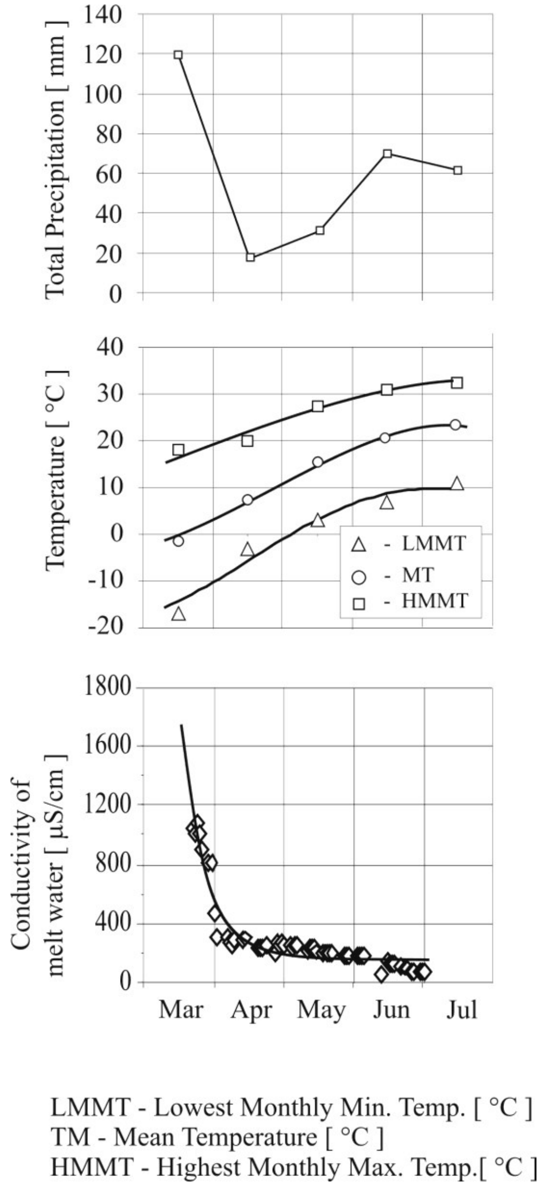

Fig. 8. Conductivity of meltwater, precipitation and temperatures during the melting season

The average conductivity of the wastewater was about 800 μS/cm. The graph also presents total precipitation as well as the lowest and the highest monthly temperatures and the mean temperature for each month of melting season. Because of the size of the snowpack (height ~ 10 m, length ~ 50m) the volume of meltwater discharge was not recorded. However, based on the graph presented in Fig. 8, it can be noticed that fast melting started in March after a significant precipitation event. Ionic pulse took place at the beginning of March but, unfortunately, it was recorded only in part.

The first fraction of the meltwater is observed to have significantly higher conductivity than later fractions. Elevated concentration of salts (high conductivity) was reported in the second half of March and dropped at the turn of March and April. After that, until the beginning of June, conductivity was dropping slowly and ranged from about 300 μS/cm to about 200 μS/cm. The next substantial drop was noticed in June after heavy rain.

The full scale experimental data for conductivity, revealed that concentration of compounds in meltwater can also be described by an exponential function (1) with adj $R^2 = 0.91$. However, it should be noted that the rate of melting of man-made snow in natural condition is influenced by a number of factors, including: precipitation, solar radiation, ambient temperature, the size and the shape of snowpack etc. Therefore, minor inaccuracies of the predicted concentration curve may occur in practice.

3.4. Agglomeration of solid particles in freeze and thaw process

If the rate of freezing is sufficiently small, most of fine solid particles are rejected by ice and push in front of growing crystals. It is well known fact that freeze/thaw process can improve efficiency of agglomeration of particles and dewatering. Significant work in the field of freezing of solid-liquid mixture was done by Corte (1962); Dawson et al. (1999); Halde (1979); Martel et al. (1998); Nakamura and Okada (1976); Reed et al. (1986); Vesilind et al. (1990); Volkhin and Ponomarev (1965) and recently by Gao (2011); Tao et al. (2006 a, b).

Agglomeration of solid particles in man-made snow crystals made from municipal sludge or mineral suspension is more complex. It starts from liquid droplets that have to be super-cooled and nucleated to freeze out in cold ambient air. At the first moment, after nucleation, the development of ice is fast. The surface of droplet is covered with a thin shell of ice but inside there is liquid and its temperature rises to about 0 °C. Then, because the droplet is still exposed to low ambient temperature, the liquid inside the droplet cools down. At this stage, ice crystals grow inside the droplet. It is a slow process and depends on the ambient temperature. The volume of liquid within the drop is reduced and the pressure increases. Because ice absorbs only pure water molecules, the concentration of dissolved compounds increases. Some of them, such as dissolved salts exceed the limits of its solubility and precipitate. If gases exceed its solubility range, it nucleates and inside the droplet bubbles of gas are created. That gas is later released during the TGM. If the temperature is sufficiently low, the droplet can freeze out completely in the air and hits the ground entirely frozen. Solid particles that are inside the droplet, such as colloids, undergo natural agglomeration and are easily separated in the next step. Particles are pushed to each other and create clusters that are dehydrated because water molecules can diffuse in the direction of ice. These clusters are also released if the TGM take place in the snowpack or are released during melting and refreezing processes in spring. Meltwater percolates down and the particles remain in the pores of snow and further agglomerate to form relatively large granules. At the end, most solids remain on the surface. In Fig. 9, the photograph of the full scale snowpack surface from atomizing freeze crystallization plant in Westport, Ontario is presented. These precipitated solids can be easily removed if liner is installed under the snowpack and/or it can be used as fertilizer. The freeze and thaw cycles significantly enhance the process of separation during the storage period. At a time when there is a high TGM in the snowpack, the majority of the snow volume is transferred to a vapour state and back into a solid state. Longer storage time and more frequent and higher variations in temperature during winter give a higher efficiency of concentration and more efficient process of agglomeration. Most contaminants are deposited on the surface of the ice grains in the pores of the snow pack. Moreover, fluctuations in the ambient temperature around freezing point repeatedly thaw and freeze the ice crystals and the solid particles are rejected from the ice structure.

The authors of this work carried out an experiment to see the difference in the characteristics of the clay slurry that was once and five times frozen. In order not to distort the characteristics of the sludge, the sample of sludge was not filtered, but freeze-dried. Frozen water in the pores of the sludge sublimated and the undisturbed structure of sludge was revealed.

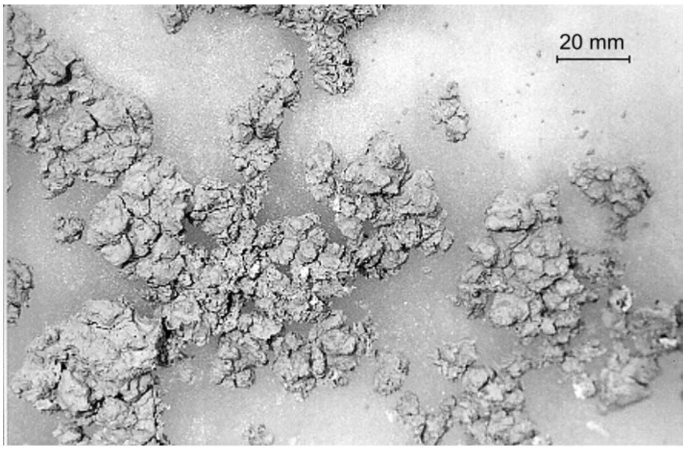

Fig. 9. The surface of the full scale of man-made snow-pack from secondary effluent of municipal wastewater processed by atomizing freeze crystallization (AFC). End of melting season in June, Westport, Ontario, Canada

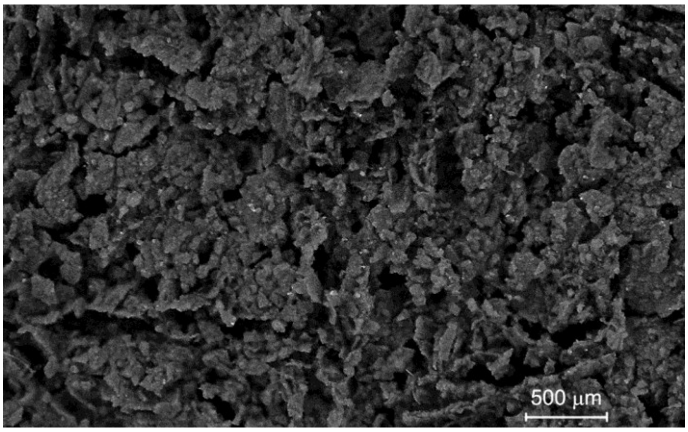

Fig. 10. Microscopic view of the surface of clay slurry with one cycle of freeze and thaw process

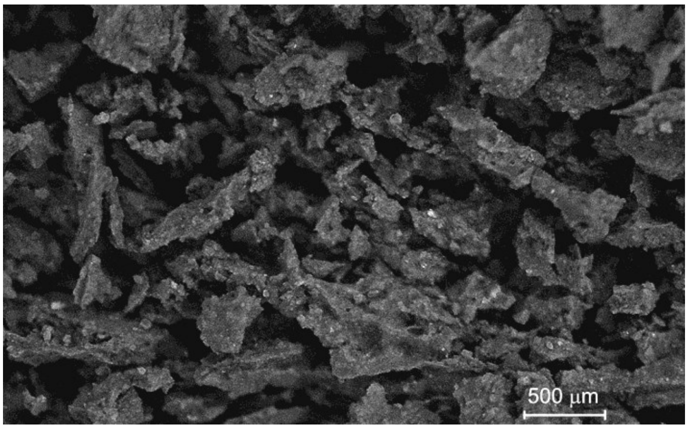

Fig. 11. Microscopic view of the surface of clay slurry with five cycles of freeze and thaw process

Clay slurry such as, for example, mine tailings from Athabasca Oil Sands cannot be filtered because the resistance of filtration is very high and filtration is not economical. After freezing one time, the agglomerates of clay particles are created (Fig. 10) and solid-liquid separation is enhanced. Even better results can be achieved if the slurry is frozen five times (Fig. 11). It can be hypothesised that during the TGM the snow particle volume is transferred to a vapour state and back into a solid state several times. Therefore, the efficiency of agglomeration and subsequent separation of solid particles is so high in atomising freeze crystallization plant (Fig. 9).

4. CONCLUSIONS

Very high efficiency of the freeze/thaw leachate treatment with presence of TGM was noted for chloride and such compounds as boron, potassium and sodium. It was reported that about 93 % of these elements were removed in concentrate from the snow sample. An increase in BOD_5, COD, DOC and TOC, in the first melt was also very high. The efficiency of concentration reached values of 90.2, 90.5%, 92.2 % and 93.3 %, respectively. Chromium, nickel, zinc and iron were concentrated in the first 30% of melt to 86.9 %, 90.9%, 88% and 91.2 %, respectively. The concentration efficiency of copper was in the range of 73 %. Generally, more than about 90 % of all contaminants were concentrated and discharged in the first 30 % of the melt water volume.

The effluent concentrations of Na, Cl, Cr, Ni, K, Fe and Zn in the last 70% of melt water from container "A", where TGM was present, were: 145.8 mg/l, 194.5 mg/l, 0.01 mg/l, 0.04 mg/l, 76.9 mg/l, 0.47 mg/l and 0.04 mg/l, respectively. The concentrations of the same compounds after five cycles of standard freeze/thaw were higher and reached the following values: 372.6 mg/l, 416.7 mg/l, 0.02 mg/l, 0.07 mg/l, 176.5 mg/l, 0.82 mg/l and 0.15, respectively.

Freezing of landfill leachate by converting it to man-made snow and its storage with presence of TGM before melting, resulting in an improved efficiency of concentration of pollutants. For such compounds as sodium, chloride, chromium, nickel, potassium, iron and zinc, the application of TGM gives, from 6.5 % for Fe to 37.3% for Zn, higher efficiency of concentration than that in five cycles of the standard freeze-thaw process. The method of freeze/thaw with presence of TGM proved to be better than the standard freeze-thaw and decantation option also for BOD_5 and COD. Increase in BOD_5 efficiency of concentration was by about 11.4% higher for TGM than that for five cycles of standard freeze/thaw. Even better results of increase, in the range of 16.3% were achieved for COD. The average concentrations of BOD_5 and COD in effluent for TGM option were as low as 10.8 mg/l and 159.6 mg/l, respectively. With the application of five cycles of standard freeze/thaw the average concentrations of these compounds in effluent were higher and reached the values of: 23.3 mg/l and 433.4 mg/l, respectively.

A significant concentration effect of BOD_5 and COD was also reported for tannery effluent. Higher impurity removal from meltwater was observed for the snow with longer storage time (6 weeks) – longer exposer to TGM. The results show about 13% and 10 % higher efficiency of concentration of BOD_5 and COD, respectively. This proves the hypothesis that TGM has influence on the efficiency of the freeze crystallization process. Moreover, TGM and spring melting and refreezing improve agglomeration of particles and the characteristics of the sludge.

The effect of the freeze/thaw process as well as TGM can be observed in full scale operations. The measurements of conductivity of melt water that was discharged from the full size operation, where about 70,000 m^3 of wastewater were converted to man-made snow, revealed a significant decrease of salt concentration with the passage of time during the melting process of a large snowpack.

SYMBOLS

a, b, c	constants in both, equations (1) and (2)
$\overline{C}$	relative concentration
C	current concentration of compound in a sample, kg/m^3
$C_{e,70}$	average concentration of compound in the last 70% of melt water, kg/m^3
C_0	concentration of the feed water, kg/m^3
E_{30}	efficiency of concentration in 30% of meltwater volume, %
$\overline{V}$	relative discharged volume

V	discharged volume of meltwater, m^3
V_0	total volume of meltwater, m^3

Abbreviations

AFC	Atomizing freeze crystallization
BOD_5	Biochemical oxygen demand, mg/l
COD	Chemical oxygen demand, mg/l
DOC	Dissolved organic carbon, mg/l
MDL	Method detection limit, mg/l
PAH	Polycyclic aromatic hydrocarbons
TGM	Temperature gradient metamorphism
TOC	Total organic carbon, mg/l
UDF	Unidirectional downward freezing

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