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Purity and mechanical strength of naturally frozen ice in wastewater basins

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Abstract

A fairly clean ice cover can form over a contaminated water pond when the air-cooled surface of water freezes and impurities are efficiently expelled to the remaining water underneath. Natural freeze crystallization has recently been studied as a potential wastewater purification method with aqueous solutions on a laboratory scale. The effect of impurity inclusions on ice strength has been researched in model ice basins over the past few decades. It is of interest to discover how efficiently natural freeze separation works under real weather conditions before freezing can be utilized for wastewater treatment application. Herein, understanding the mechanical strength properties of naturally frozen wastewater (ice) is important when planning ice breaking and harvesting devices.

This research implemented in-situ measurements of the flexural and compressive strength of ice in natural ice-covered environments of a freshwater lake, two peatlands and three mining site basins, and compares the determined strength with analyzed impurities of the ice. The results showed that despite varying ice growth conditions and initial water constituents, it was possible to deduce an evident yet simple relationship between mean ice strength and ice impurities: the more impure the ice is, the lower the value of strength is. Based on this exploration, it was concluded that separation efficiencies, i.e. the impurity removal ratio between basin water and ice, from 65% up to 90% can be achieved by natural freezing.

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Keywords: Compressive strength; Flexural strength; Ice impurity; Natural freezing; Wastewater treatment

1 Introduction

The major industries in raw material production and final product manufacturing produce large quantities of wastewaters, which also more often contain toxic heavy metals and other inorganic constituents in low concentrations. For instance, millions of cubic meters of water can be consumed annually in a mine during the extraction and processing of minerals. This is likely to pollute fresh water sources in the mine environment through acid mine drainage, leaks and the disposal of tailings (Akcil and Koldas, 2006; García et al., 2014). Thus, the large quantities of industrial wastewaters have generated a need to develop energy efficient wastewater treatment methods.

A naturally cold climate could be utilized as a sustainable cooling energy source to purify wastewaters in basins by means of freezing. Several studies have proved that the purification of aqueous solutions and wastewater by natural freezing is a simple, efficient and cost-effective method (Lorain et al., 2001; Hasan and Louhi-Kultanen, 2015; Shirai et al., 1998), which makes natural freezing a potential purification technique to treat huge volumes of wastewaters. The conventional industrial wastewater purification methods based on biological and physico-chemical treatment, such as adsorption, chemical precipitation, electrolytic treatment, flotation, ion exchange and membrane filtration, have some limitations (Fu and Wang, 2011; Kurniawan et al., 2006). In contrast, in wastewater freezing these can be turned to advantages:

- Devoid of adding chemicals (Lorain et al., 2001),
- No waste product generation as in chemical precipitation and adsorption (Babel and Kurniawan, 2003),
- No high operational costs caused e.g. by fouling and cleaning of membrane filters or high energy consumption in electrodialysis (Kurniawan et al., 2006),
- High separation efficiency and non-selectivity in impurities are achievable, as ice is naturally highly intolerant to impurities (Bogdan et al., 2014; Lorain et al., 2001).

Sustainable wastewater management includes efficient water purification and provides the possibility for the recovery of valuable materials as well. Particularly with certain industrial wastewaters, natural freezing provides these both, as ice and salt can be crystallized simultaneously in eutectic condition (Hasan et al., 2017). Ice and salt can be separated due to gravity, when salt settles down and ice floats (Randall et al., 2011). If the purity of the ice layer is high, it could be recycled as process water or utilized further as a cold storing material for cold heat storage (Shirai et al., 1999).

Figure 1 presents a conceptual design of wastewater freezing in a basin with downstream processing of the naturally frozen ice layer. At first, the surface of the wastewater is frozen naturally in the basin. This ice layer is broken into pieces, which could be collected and separated from the concentrated wastewater in the subsequent steps. For ice breaking device design and the optimization of the ice harvesting process, it is of great importance to have knowledge of the mechanical properties of the ice layer, such as bending and compressive strength, the influence of freezing conditions (consequently the purity of the ice) and wastewater composition. The ice strength, together with the ice thickness, determines the design requirements of the ice breaking device, i.e. the strength defines the force needed to break the ice. This research assays the variability on ice strength in the studied wastewaters and gives an overview of further device planning.

Figure 1. Principled process of water purification by natural freezing.

Natural ice consists of ice crystals whose orientation, shape and size determine the structural characteristics of the ice as well as impurity inclusions due to the formation of aqueous solution pockets and veins and gas bubble voids in the ice cover. Ice properties such as temperature and structure are considered to affect the physical and mechanical properties of the ice (Light et. al, 2003; Timco and Weeks, 2010). Bogdan and Molina (2010, 2017) investigated the impacts of a freeze-concentrated solution on complex phase transformations (such as ice crystallization) during the cooling and warming of bulk solution droplets in emulsions in a highly controlled manner in a temperature range between 133 K and 278 K. They evidenced that the processes yielded mixed-phase particles formed of an ice core with a freeze-concentrated solution coating. The effects of impurities on sea ice in the form of brine (salt) have been studied to a great extent in the past. The studies have shown that increasing the brine content in ice weakens the ice significantly; see Timco and Weeks (2010) for a review study.

The effects of chemicals on the mechanical properties of ice have been studied to some extent already decades ago. These studies have focused on scaling down the mechanical properties of the ice to a suitable strength for model testing in ice basins by weakening the ice (Borland, 1988). Hirayama (1983a) showed a clear decreasing trend in the ice flexural strength and elastic modulus with increased urea concentration; the top layer of the urea doped is thicker than what is observed in sea ice (Hirayama 1983b). Timco (1981) tested various salts, alcohols, acetates, amides and sugar and came to similar conclusions regarding the reduction in flexural strength with increasing impurities. Timco (1981) reported that the lower the molecular weight of the doped substance is, the lower the concentration required to reduce ice strength is. The same applies for the saturation point, i.e. the point whereafter the ice strength does not decrease (Timco, 1981). Some interaction between various chemicals that intensify the weakening of the ice has also been postulated between aliphatic detergent and ethylene glycol (Lehmus, 1988).

However, studies focusing on purification by freezing have not clearly addressed the effect of impurities on the mechanical properties of ice. Studies focusing on the effect of doped

substances on the mechanical properties have considered the concentration of the initial solution, but the purification has not been studied precisely. Furthermore, studies on purification by freezing have been conducted in laboratory conditions where the environment and the initial impurities have been controlled. In contrast, real wastewater is a complicated mixture of various impurities, as it contains constituents that the water accumulates through different processes. When the wastewater is exposed to the open environment conditions, the freezing process is hardly controlled. To use natural freezing for wastewater purification in practice and to be able to break and harvest the purified ice, a few issues need to be clarified: 1) how efficiently the natural freezing purifies the wastewater in the open environment; 2) what the mechanical properties of the ice are; 3) how impurities affect the mechanical properties of ice and 4) how the purity and strength of ice could be assessed.

In this study, the flexural and compressive strength tests for ice were carried out and ice and water samples were collected for chemical impurity analyses from several locations in different types of natural water and wastewater environments. As a result, the effects of impurities on the mechanical properties of ice were analyzed and the parameters that could indicate the impurity level and the strength of ice were identified. The study outlined separation efficiencies of freezing in the studied ice-water basin systems and evaluated how well legislative requirements can be met.

2 Materials and methods

2.1 Measurement sites

The measurements were performed in six different locations in Finland, northern Europe, in winter conditions in March 2017. Figure 2 presents the geographic locations of the measurement sites. The site characteristics observed during the measurement survey are further presented below.

Figure 2. Locations of the measurement sites in Finland: 1. Lake, 2. Peat I, 3. Peat II, mining site, 4. Pond, 5. Pit, 6. Gypsum. Points A, B and C show the locations of the national recording weather stations near the measurement sites.

On the first exploration day, 1 March 2017, Maavesi was chosen as the experiment and sampling site, referred to here as *Lake*. Maavesi is a small 17.9 km² lake area isolated from the larger freshwater Lake Saimaa in Southeast Finland. This naturally eutrophic lake is located next to the peat extraction area Suursuo and close to forestry and agricultural areas with draining ditches. Water in the lake is very shallow with a 1.9 m mean depth and low water flow circulation (Sääksjärvi et al., 2016). The ice samples are taken ca. 80 m from the shoreline.

The second (8 March 2017) and third (9 March 2017) sites were situated on peatlands called Suursuo (*Peat I*) and Konnunsuo (*Peat II*) in Southeast Finland. Peat has been extracted from both of these peat bogs for decades. Leachate water from peat production fields flows in a controlled manner along ditches and is channeled to multiunit sedimentation ponds. The water contains suspended solids and nutrients and is treated with the overland flow method and chemical purification before it is released into the environment. The amount of flowing water

and water levels in the system are changing due to precipitation and meltwater. During winter, less water flows under ice covered channels and basins. Rain water and trickling leachate from the soil embankment may flow to the ice surface and cause colorful ice layering. (Kuokkanen, 2017). Real water depths were difficult to determine due to mushy sludge sediment layers on the pond bottoms. Ice blocks studied in this research were cut from the center of the ice cover of the sedimentation ponds, areas of $\sim 1700 \text{ m}^2$ (*Peat I*) and $\sim 500 \text{ m}^2$ (*Peat II*).

The fourth, fifth and sixth ice samplings and in-situ experiments were performed in a mining territory in Sotkamo in Northern Finland in 28-30 March 2017. The mining company produces nickel, zinc, cobalt and copper by open pit mining and bioleaching. Water cycles within the wide surface area and water purification processes are distributed to several purification units due to water being used in production and the requirement of controlling rain and meltwaters. The main purification methods are lime milk neutralization for all wastewaters and reverse osmosis for production water. The annually collected or treated total water amount is about 6-10 million m^3 . In every studied pond, water flow fluctuated under the ice cover due to varied pumping and piping actions during the ice layer generation. The temperature of the pumped water may also vary. (Terraframe, 2018). Accordingly, the total influence of circulating water is difficult to assess.

Experiment site no. 4 called *Pond* was a dammed flood pond (area $\sim 160\,000 \text{ m}^2$), which has been deployed to secondary settling and water storage use. Most of the incoming waters can be considered as a type of natural leachate or drain water from the surroundings. Intensive pumping was causing a curving unfrozen stream through the pond surface, so presumably water flow and circulation is high in the mid-section of the pond. Experiment site no. 5 *Pit* situated in an open mining pit from which around half (area $\sim 180\,000 \text{ m}^2$) was dammed for water storage. The other half was in ore mining process use at the moment. Experiment site no. 6 *Gypsum* was located in a gypsum pond (area $\sim 200\,000 \text{ m}^2$), which is used for the sedimentation and settling of chemically treated water in lime purification. Ice samples were

cut from the ice surface over the end part of the multiunit water pond flow system, so water was assumed to be quite pure already.

The water ponds or basins in this study are open to air and enfold naturally or are built up in soil walls and the ground. Only the base of the gypsum pond is isolated with a special membrane. Weather conditions (air temperature, humidity, wind and precipitation) as well as water level, the temperature and the flow fluctuation in the water system during the ice cover formation affect the natural freezing process. These conditions have effects on the ice layer growth rate, the characteristics of forming ice and the separation efficiency of impurities (Leppäranta, 2015; Light et al., 2003; Shirai et al., 1998). As the test sites consist of settling basins in real processes designed for different uses, changes in conditions were not possible to determine locally near the ice sheets or under the ice.

2.2 Ice strength measurements

The flexural and compressive strength tests were conducted in-situ next to the ice sampling location. The ice samples for strength tests were extracted by sawing a 120 cm x 20 cm block with a chain saw and then pulled off the ice cover, as Figure 3a shows. The mobile bending test device can handle a maximum height of 20 cm beams. In the measurement locations, the ice thickness exceeded 40 cm and was sliced into two or three horizontal beams; see Figure 3b. Each ice beam was then tested individually. For the compression test (see Figure 3c), a 10 cm x 10 cm x 10 cm cube was cut with a band saw. The temperature of the ice beam during the test was measured by drilling a small hole for the temperature probe.

Figure 3. Setup for in-situ measurements: (a) ice sample extraction before cutting the sample into horizontal slices (*Peat II* ice), (b) the flexural strength test (lake ice) and (c) the compressive strength test (lake ice).

The flexural strength test was performed in a similar manner as in previous work (Suominen et al., 2013) with a three-point bending device, where the ice beam was seated on two supports. The loading was executed with a piston which was coupled with a recording force sensor. The geometry of each beam and the span were measured after the test. The flexural strength was taken as the tensile axial stress on the bottom surface of the beam. Here, it is assumed that the failure starts on the surface as the axial stress over the cross-section of the beam is the highest on the beam surface. Assuming the beam behaves as an Euler-Bernoulli beam, the flexural strength σ_{Flex} (Pa) was calculated from Equation (1) (Suominen et al., 2013).

$$\sigma_{Flex} = \frac{3x}{WH^2} [F + (L - x)g\rho WH] \quad (1)$$

In Equation (1), L (m) is the length of the span, x (m) is the distance from the support to the location where the ice failed, W (m) is the width of the beam, g (m/s²) is the gravity, H (m) is the height of the beam, F (N) is the force and ρ (kg/m³) is the density. The density was determined after the test by cutting a sample of the beam and measuring the dimensions and weight of the cube. It should be noted that the beam theory applied assumes a homogeneous and isotropic material, which ice is not. However, the flexural strength is taken as an index value to estimate the force needed to break the ice by bending.

The uniaxial compressive strength test was produced with a hydraulic piston coupled with a force recording load sensor as in the previous study of Suominen et al. (2013). After the dimensions and the mass of the ice cube were determined, the cube was placed between two metal plates and pressed until it broke. The loading was applied from the vertical direction of the original ice layer, i.e. it was parallel in the growth direction of the ice layer thickness. The compressive strength σ_{Comp} (Pa) was calculated from Equation (2) (Suominen et al., 2013).

$$\sigma_{Comp} = \frac{F + m_p g}{W D} \quad (2)$$

In Equation (2), D (m) is the depth of the beam and m_p is the mass of the plate (here 1.852 kg) which was placed on top of the sample; see Figure 3c.

2.3 Impurity analysis

The guidance on sampling of the European Standard EN ISO 5667 Water quality was followed, where applicable, to be able to obtain representative samples under quite different fieldwork conditions around the sampling locations. A sampling point at a ca. 10 m distance from the hole sawn with a motor saw was chosen to avoid contamination from the motor saw (oil, exhaust fumes and metals). The ice sampling started by removing the loose snow and slush with a shovel. Four holes were drilled in a square form with an auger, and a cubic ice block was extracted with an ice saw and pulled off. The ice block was sliced in sections and composite samples were collected from the whole ice layer and different horizontal layers. Snow ice was not collected within the ice layer samples to avoid air mediated contamination (dust from production areas).

Water samples were collected from the free water under the ice cover through the sampling hole. The temperature and pH of the water were measured. For the water samples, a manually closable pipe sampler with an arm was used to collect 10 x 1 dl subsamples about 0.5 m under the ice. Only from *Peat I*, a water sample was collected from the flowing effluent, as there it was possible to do so in winter. All water and ice samples were collected into polyethylene bottles and closed tightly to be kept cool in a cooler box during transportation to the laboratory.

The samples were stored in a freezer room at -18 °C temperature and melted at room temperature for analyses in the laboratory.

In this case, the studied water quality parameters were defined and chosen based on previous data collected in past years and decades at sites for obligatory pollutant monitoring by authorities and companies. This data provided general characteristics of the waters and also showed that the pollutants in the water remain rather constant over long periods. The electrical conductivity (probe with cell constant 1.0 cm⁻¹, range 0.001 to 100 mS/cm) and pH were measured with a Consort C3040 Multi-parameter analyzer. The apparent color (PtCo) and turbidity (FTU) were measured with a colorimetric method using a Hach DR/2000 spectrophotometer (455 nm, 450 nm). The chemical oxygen demand (COD, mg/L) was determined by a dichromate oxidation method with a spectrophotometer (420 nm, 620 nm) using COD reaction cell tests. Anions – sulphate, nitrite, nitrate and chloride – were analyzed with IC Ion Chromatography, Thermo Scientific Dionex ICS-1100. For IC analysis, samples were prepared with a 0.45 µm syringe filter and Dionex OnGuard II H cartridge filter for metal removal. Chosen elements (Ag, As, Ca, Cd, Co, Cr, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Tl, U, V, Zn) were analyzed with inductively coupled plasma mass spectrometry, Agilent 7700 ICP-MS. For ICP-MS analysis, samples were prepared with a 0.45 µm syringe filter and diluted with a mixture of 1% HNO₃ and 0.5% HCL.

3 Results and discussion

3.1 Ice characteristics

Figure 4 presents the visual characteristics of the ice from the different sites. All ice at the sites seemed to grow in layers. The lake ice also exhibits bubbles appearing as layers of pearls; see Figure 4a. These can be assumed to be gas bubbles that floated up from the bottom of the lake sediment and were trapped inside the ice. The bubble size increases towards the ice bottom. In the peatland, the ice samples have layers with brown coloring, which may indicate that water rich in humus flows onto the existing ice cover. The *Peat I* ice also exhibits liquid inclusions and the *Peat II* ice showed a very clear column like bottom ice layer; see Figures

4b and 4c. The mine site ice – in particular the *Pond* ice (see Figure 4d) – showed clear colorings almost all the way through. The ice was so weak that sampling for flexural tests was often very difficult as the beams would collapse under their own weight or when lifting. Ice from *Pit* (Figure 4e) and *Gypsum* (Figure 4f) also showed distinct layering, where several layers can be considered separate instead of a solid beam. This ice layering with loose grain like ice caused the ice to shatter easily in small ice hails with a diameter of a few millimeters, even when squeezed in the hand.

Figure 4. Ice cross-sections from sites: a) Lake, b) Peat I, c) Peat II and from mine sites d) Pond, e) Pit and f) Gypsum.

Table 1 depicts the ice thickness and water temperature under the ice as well as the water depth under the ice and air temperature at the sampling location. Ice layers at the mining site are somewhat thicker than in the lake and peatland due to more freezing degree days and a

lower average air temperature. Nevertheless, at the mining site, the difference in thicknesses is 10 cm between pond ice (thickness 0.50 m) and gypsum ice (0.60 m), although the weather conditions during winter are similar. Also lake ice and Peat I ice have a 3 cm difference in thickness, although the distance between these locations is only a few kilometers. It is noticeable that based on the measurement, the water temperature right under the ice cover seemed to be below 0 °C in all wastewater ponds as the waters are undercooled and the freezing point is depressed. As Table 1 shows, the temperatures of the ice were close to 0 °C with in the lake and peatlands and slightly below 0 °C at the mine site, where the weather was also colder during tests. The temperature difference in the ice is so small that the effect on strength measurement results can be considered negligible when compared with other factors, i.e. the direct effect of impurities and structure can be supposed to be more significant here.

Table 1.

Observations during on-site measurements at different sites: ice cover thickness, temperature of ice, water depth, temperature of water under the ice, and air temperature during the test day. In addition, freezing degree days (FDD) / total days of monitored winter period and average temperatures recorded by weather stations (locations in Figure 2) during the winter so far are shown (Data © Finnish Meteorological Institute 04/2018 CC by 4.0.).

Site name	Ice thickness	Ice temp.	Water depth	Water temp.	Air temp.	FDD	Average temp.
	(m)	(°C)	(m)	(°C)	(°C)		(°C)
Lake	0.45	0.0	1	0.0	2.5	100/128	-3.68
Peat I	0.42	0.0	2	-0.3	0.0	100/128	-3.68
Peat II	0.41	0.0	2	-0.3	0.0	96/128	-3.74
Pond	0.50	-0.4	6	-0.7	-2.0	124/151	-5.34
Pit	0.55	-0.6	15	-0.7	-7.0...-2.0	124/151	-5.34
Gypsum	0.60	-0.6	3	-0.5	-12.5...-2.0	124/151	-5.34

3.2 Ice strength results

Figures 5 and 6 show the calculated results from Equations 1 and 2 for the flexural and compressive strength tests. The measured and calculated results are presented in supplementary material (Supplementary material, Table A.4 and Table A.5). In some tests (particularly in compressive strength; see Figure 6), differences in strength values between

the individual layers were observed. The statistical significance of possible differences in strength between different ice layer measurements from individual sites was tested using ANOVA (Supplementary material, Table A.2). The mean values of flexural and compressive strengths were calculated for different ice layers, and the mean value for the whole ice layer of the site was determined. The strength test devices were selected on the basis of the loading rates causing brittle failure in both flexural and compressive strength tests. The flexural strength measuring device has a nominal loading rate of 11 mm/s and a nominal loading capacity of 4 kN. The compressive strength measuring device has a nominal loading rate of 24.2 mm/s and a nominal loading capacity of 69 kN. However, despite the applied loading rate, some samples failed, clearly in a ductile manner. To keep the results more comparable, these measured ductile results were excluded from the calculations.

Figure 5. Flexural strengths of all test site ice samples, ice layers: t - top, m - middle and b - bottom.

Figure 6. Compressive strengths of all test site ice samples, ice layers: t - top, m - middle and b - bottom.

Figure 7 presents the overall mean values of the flexural and compressive strengths of ice samples for all test sites. The lake ice exhibits a much higher flexural strength mean value (1469 kPa) than the peat ice (638 and 518 kPa), whereas the mine site ice has the lowest values (239 to 373 kPa). The results of the freshwater lake ice are at the same level as presented by Timco (1981), 1200 to 1400 kPa, and Timco and O'Brien (1994), 1760 kPa. For the sea ice, the values vary from 1000 kPa to as low as 100 to 150 kPa depending on the salinity and temperature (Timco and Weeks, 2010). Ice is an anisotropic material; thus, variation in the structure causes differences in results when the ice is exposed to different loadings, as in flexural and compression strength tests. This variation can be seen in the results of compressive strength in this study as well as in literature. Timco and Weeks (2010) give a variation on values between 500 and 5000 kPa for sea ice.

Figure 7. Average ice flexural and compressive strength results, all sites.

3.3 Water and ice impurities

The definition for pollution is interrelated with the environment of the water system, and for that reason, some comparisons are made here only from the viewpoint of the freezing process in general. Some constituents in the studied samples could not be determined at all, as they were below the detection limit. However, the differences in water composition and quality between the sites can be seen clearly in the results presented in Table 2. The lake water quality is almost at the same level as the peatland water quality when measured with the chosen indicators. Obviously, the waters of the mine site contain a great number of pollutants, but COD levels as high as 400 mg/L in *Pond* and *Pit* waters were not expected. Tchobanoglous et al. (2003) give similar concentrations for untreated domestic wastewater. *Pond* water can be considered as the richest with impurities of these three mine sites, although color and turbidity are at a very high level in *Pit*. The same trend can also be seen with ice samples; see Table 3 for the average results of ice layers of different sites. The results of analyzed constituents are presented in supplementary material (Supplementary material, Table A.6).

Table 2.
Analysis results of water samples, relevant parameters shown.

	Conductivity ($\mu\text{S}/\text{cm}$)	pH	COD (mg/L)	Color (PtCo)	Turbidity (FTU)	SO ₄ (mg/L)	Ca (mg/L)	Fe (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)
Lake	82.4	6.65	27	73	14	19	7.83	0.07	1.85	2.49	0.07	4.97

Peat I	78.1	6.46	27	125	22	10	6.94	0.11	2.03	2.72	0.14	3.82
Peat II	85.8	6.05	24	194	34	26	8.38	0.25	2.20	3.34	0.36	2.20
Pond	6410	5.74	473	484	94	5580	254.40	40.77	23.64	831.40	268.31	602.88
Pit	4240	3.02	339	1884	346	3236	302.37	126.13	16.81	268.74	192.55	304.65
Gypsum	5390	10.64	<3	30	4	3340	379.88	<0.005	44.62	7.15	<0.005	1330.09

Table 3.

Analysis results of ice samples, relevant parameters shown.

	Conductivity ($\mu\text{S/cm}$)	pH	COD (mg/L)	Color (PtCo)	Turbidity (FTU)	SO ₄ (mg/L)	Ca (mg/L)	Fe (mg/L)	K (mg/L)	Mg (mg/L)	Mn (mg/L)	Na (mg/L)
Lake	2.54	5.55	<3	2	1	<1	0.05	<0.005	0.98	0.02	<0.005	0.68
Peat I	4.41	5.83	7	55	10	<1	0.35	0.03	0.79	0.12	<0.005	0.42
Peat II	24.4	6.05	10	80	14	7.7	2.54	0.02	0.70	0.88	0.01	0.49
Pond	1083	5.75	55	393	68	694	63.53	0.01	2.41	76.50	22.32	54.47
Pit	575	3.61	45	176	31	316	34.73	6.81	1.89	19.33	13.33	23.42
Gypsum	1259	6.60	<3	25	4	727	214.79	0.03	3.23	3.26	0.10	101.65

In this dataset, a strong correlation was found between many contaminant variables. On the one hand, this limits statistical multivariate analysis due to collinearity problems, but on the other, knowing one impurity allows predicting other impurity values. (Supplementary material, Table A.1).

The ice purity levels of the collected samples were relatively high in terms of effluent regulations, when the analyzed impurities in the ice were compared with concentration levels regulated by the mining company's environmental permits (TerraFame, 2018). For example, the maximum concentration limit for the main emission sulphate is 4 000 mg/L (for a single sample) in the discharge water pipe, whereas about 2000 mg/L has been reached. In the future, the recommended target will be as low as 1000 mg/L. The sulphate concentrations in every ice of three mine basins were below that: in Pit ice the sulphate concentration was the lowest, i.e. 316 mg/L, and in Gypsum ice the highest, 727 mg/L; see Table 3. It was also positive that the ice of peatlands is cleaner than that of lake water, as their effluents are usually led to natural water systems, such as lakes and rivers.

3.4 Effective distribution coefficient

The effective distribution coefficient K describes the relative impurity constituent in the ice when compared with impurity in basin water. This gives the separation efficiency of the

freezing process with this particular constituent as well. The effective distribution coefficient K is determined as $K = C_i / C_w$, where C_i is the concentration (or other measured value indicating water quality) of the constituent in ice and C_w is concentration (or value) of the constituent in basin water.

Figures 8 and 9 show the calculated effective distribution coefficient K values of relevant constituents for all sites. An approximated average K value of all constituents gives an overview of the total separation efficiency for a process of a certain site. As the COD and turbidity results for *Gypsum* water and ice are very low, the values were excluded from the calculation. The average effective distribution coefficient is the highest, $K = 0.10$, for the *Pit* site, meaning a 90% separation efficiency, while the *Gypsum* site had the lowest one, 65% ($K = 0.35$). The impurity separation process is highly efficient in every pond despite very different water composition concentrations.

There is very little variation in the K values of various constituents at the *Pit* site, whereas other sites have considerably more variation. For example, the K values of two significant constituents, calcium and magnesium, are 0.25 and 0.09, respectively, for the *Pond* site. It is important to be aware of the reasons behind this variation. Most likely, the changes in conditions (initial water flow and quality) are causing impurity inclusions during ice layer growth. As expected, the best separation and the smallest variation in coefficients can be found in the open pit pond where the steadiest state conditions were observed.

Figure 8. Effective distribution coefficient K determined by organic (COD) and physical (color, turbidity, conductivity) characteristics and calculated average of all constituents for all sites.

Figure 9. Effective distribution coefficient K , determined by inorganic characteristics: sulphate, calcium, potassium, magnesium and sodium for all sites.

3.5 Combined ice strength and impurity analysis

The ice strength as a function of the analyzed impurities was evaluated by fitting various models (linear, polynomial and exponential) to the data, both for the averaged flexural and

compressive strengths. This was done at three levels: the individual sample, the layer means and the test site means.

As Figures 5 and 6 indicate, some of the ice samples show significant scatter in strength – both between some of the layers and between different samples taken from the same ice layer right next to the previous sample. To avoid contamination, the ice samples for impurity tests could not be taken directly from ice samples for the strength tests. This means that there will inevitably be some measurement uncertainty, as the impurity content of the ice varies. Thus, mean impurities are compared with mean strengths. The plotting of the mean impurity values by layers vs. mean strength values by layers, or the plotting of individual strength values vs. layer per average impurity values did not show a significant relation (see Supplementary material, Figures A.1, A.2 and A.3). This is reflected in the analysis of the ice strength as a function of various impurities: utilizing the mean values for each of the six sample sites, several meaningful mathematical relationships were found. When the comparison was done on a mean layer by layer, the values for R^2 (the coefficient of determination) decreased. Only mathematically meaningful relationships are presented here, as the quantities of different constituents in samples vary on a wide scale (a 1000 times from $\mu\text{g/L}$ to mg/L). Elements with relatively small concentrations can be assumed to have a negligible effect on strength.

The average strength and average impurity values for all relevant samples of a test site (six in total) were analyzed. These calculations can be considered the most reliable, as the measurement uncertainty described earlier can be eliminated, but then we have a quite low $N = 6$. For the flexural strength, meaningful potential relationships were found between strength and calcium, magnesium, sodium and sulphate (see Figure 10a). Of these, the strongest R^2 with flexural strength was found for calcium ($R^2 = 0.92$). A potential relationship was found between strength and color as well as turbidity, but with COD, R^2 is quite low (see Figure 11). For the compressive strength, the results were different, providing meaningful results for sodium ($R^2 = 0.824$), sulphate ($R^2 = 0.813$), calcium ($R^2 = 0.669$) and magnesium ($R^2 = 0.638$) (see Figure 10b).

Figure 10. Mean (a) flexural and (b) compressive strength values of test sites as a function of mean sulphate, calcium, sodium and magnesium concentrations.

Figure 11. Mean flexural strength values of test sites as a function of mean color, turbidity and COD values.

The most promising single relationship to ice strength as a function of impurity was found to be with conductivity, which can be considered an overall metavariable for other impurities and was shown to correlate strongly with many pollutants. The relationship between conductivity and ice strength is well modelled with $R^2 > 0.85$ (with equation $y = 1231.2 \cdot x^{-0.221}$) for the

mean flexural strength and $R^2 > 0.72$ (with equation $y = 1872.7 \cdot x^{-0.203}$) for the compressive strength (Figure 12). The R^2 values were even better (0.91 and 0.83) when excluding the freshwater lake ice samples, which barely contain any impurities (Supplementary material, Figures A.4 and A.5).

432

433 **Figure 12.** Mean flexural strength and compressive strength as a function of mean conductivity.

434 Conductivity measurement is based on the conducted electric current due to ionic
 435 transportation in a solution; the more concentrated the ionic solution is, the higher the electrical
 436 conductivity value is. Based on analyses of the present research, electrical conductivity
 437 correlates strongly ($R^2 = 0.9899$) with total ionic concentration, as expected, when all analyzed
 438 ionic concentrations for ice samples are simply summarized ($N = 14$) (see Supplementary
 439 material, Figure A.6).

440 Electrical conductivity is a commonly used water quality indicator in environmental analysis.
 441 The conductivity of water is used to estimate the concentration of total dissolved solids (TDS)
 442 where the correlating constant numeric value depends on the type of water, i.e. is the ratio of
 443 organic and inorganic solid content. In agricultural irrigation, the suitability of effluent from a
 444 wastewater treatment plant is determined by applying TDS based on electrical conductivity
 445 (Tchobanoglous et al., 2003). The salinity of seawater has been determined by conductivity
 446 measurement (see e.g. Timco and Weeks 2010). Leppäranta (2015) gives a direct method for

salinity calculation with lake waters by estimating the dissolved matter concentration by multiplying the conductivity value directly.

Within an electrolyte solution, conductivity can be calculated if all ionic concentrations in the solution are known. Natural or waste waters contain various impurities and the relation of conductivity and concentration is much more complicated. The methods for such calculations have been studied with a comprehensive range of different water types from ground water to mine water and with wide-ranging analysis (McCleskey et al., 2012; Marandi et al., 2013). As a correlation between the electrical conductivity and strength of ice was found, it is of interest to explore the potential of using this easy and quick measurement method further in the evaluation of ice strength.

3.6 Emerged remarks

As the ice layers were grown under non-controlled conditions presented above, the ice layer samples were not homogenous and showed variation between layers and between various layer samples, as was expected. The ice layers exhibited clearly different degrees of transparency and ice structures (e.g. bubbles). In lake ice, there were layers with large bubbles, whereas peatland ice showed brownish middle or top layers and the mine site samples had layers practically detached (fractured) from one another. Due to this, a limitation of the study is the calculation of mean ice flexural and compressive strength, which is calculated here as a pure average of the samples in the ice beams that were cut horizontally. There are methods for calculating the flexural strength for composite beams that could be utilized here. However, these methods should firstly be validated for ice: one of the main open questions is whether the ice in question should be treated as a composite or as loose layers.

The problem of variance in flexural strength in-situ measurements has been demonstrated in other experiments, such as with first year sea ice brine content (Timo and Weeks, 2010). Thus, this variation could be expected. Using the mean strengths and mean impurity values yields much better results, as some of the measurement uncertainty, such as the effect of temperature and fractures or micro cracks inside the ice layer, can be diminished. The results

were unexpectedly positive for the mean values despite several limitations. Variation in layers could be investigated more in depth by more controlled experiments with samples of a wide range including also accurate ice crystal structure observations.

In this study, conductivity showed to be the best parameter explaining and comparing the quality of ice or water from different water sources. Lake ice was clearly the cleanest (2.54 $\mu\text{S}/\text{cm}$) and mine pond water the most contaminated (6410 $\mu\text{S}/\text{cm}$). However, the results show that other factors also affect the ice strength. None of these determined constituents can really explain as significant a difference in ice strength as was noticed between lake ice and peatland ice. The average flexural strength of peatland ice showed to be 57-65% smaller than the strength of freshwater lake ice. Nevertheless, a notable difference can be found in color and turbidity, as peatland ice looked partly very colorful and opaque. This can be due to humus and other organic matters which were determined here based on COD analyses only. It would be interesting and important to conduct similar research with wastewaters containing more organic constituents to be better able to define the combined effect of different types of impurities on ice structure and mechanical strength.

4 Conclusions

- The results highlight how much ice is weakened by the presence of impurities in ice: the mean flexural strength value decreased from 1450 kPa to 250 kPa between freshwater lake ice and the more impure ice from a mining site. This is important from the perspective of ice removal: pure ice is quite strong, whereas purified ice still containing some impurities can be broken easily with less force and energy. The results presented here can be utilized towards evaluating how much energy would be needed to break the ice formed from wastewater.
- A strong relationship between mean flexural strength and ice impurity was found. This relationship is surprisingly well modeled with a single variable, electrical conductivity, with $R^2 > 0.8$. This easy measurement may prove to be a feasible parameter in controlling ice harvesting operations.

- The natural freezing of wastewater systems was proved to achieve a 65–90% separation efficiency with different wastewater concentrations. In this study, the purity of ice (water) of the mining site was at a very good level and could also fill the requirements of the environmental permit. When the method is utilized in a designed wastewater treatment process, the efficiency can be expected to be much higher. Therefore, the natural freezing method is applicable to practice in wastewater purification.

The results obtained in this research were consistent with the hypothesis of correlation between impurity and strength: the purer the naturally frozen ice is, the harder it is to break mechanically. This research also showed that the natural freeze separation will work with wide-scale concentrations of wastewaters. This poses challenges in freeze separation process design and optimization. As the production of extremely pure ice will consume more energy in harvesting, finding the optimal thickness and sufficient purity of ice for harvesting operations will be essential in future studies.

Appendix A. Supplementary material

Supplementary material related to this research can be found at <http://....>

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