Progressive Freeze Concentration of Naphthenic Acids

By

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Abstract

Canada's oil reserves are among the largest in the world with over 1.7 trillion barrels of bitumen in place with confirmed measurements indicating there are 173 billion barrels of recoverable oil under current economic conditions and technology. These oil sands are unlike traditional oil reserves, they are typically composed of sand or clay, water, and bitumen. As a result, the oil sands must be heavily processed to separate the bitumen from the sand and clay before further refining may occur. This process requires tremendous amounts of water; as much as 4.2 m^3 of water per m^3 of bitumen, an astounding 7% of Alberta's total water use. As a result large volumes of oil sands process affected waters (OSPW) are formed containing high concentrations of suspended and dissolved organic and inorganic contaminates. These waters have been reported to be toxic to a wide range of aquatic and terrestrial organisms. Evidence suggests that Naphthenic acids (NAs) are the primary cause of toxicity. Current investigated treatment options have shown mixed results for treatment. This investigation examines the potential for progressive freeze concentration as an alternative method for the treatment of NAs in OSPW.

Two methods of freezing were investigated, power ultrasonic and mechanical progressive freeze concentration. Laboratory experiments were carried out to examine the effect of freezing temperature, the initial feedwater NAs concentration, chemical nature of NAs, mixing intensity and the freezing methods on treatment efficiency of freeze concentration. Behaviour of NAs during freeze concentration was also examined by calculating the partition coefficients to predict the incorporation/ rejection of NAs during formation of ice crystals based on the experimental conditions. Synthetic wastewater samples with various NAs (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic acid, cyclohexanepentanoic acid and a synthetic NAs mixture) were used as a feedwater for the freeze concentration processes.

Experimental results showed that both ultrasonic and mechanical freeze concentration methods were equally effective for the removal of NAs at concentrations of 20mg/L to 120mg/L. An average 98% reduction of chemical oxygen demand (COD) concentration, 95% total solids (TS) and 99% conductivity were observed in the ice samples. A lower freezing temperature (-25^0C) reported higher contamination in the solid phase as compared to a warmer freezing temperature (-15^0C). Overall, the experimental results suggest that progressive freeze concentration has great potential as an effective treatment method for OSPW.

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Chapter 1 – Introduction

1.1 Problem Statement

The Alberta oil sands provide a valuable asset for the Canadian economy. In fact, Canada's oil reserves are among the largest in the world with over 1.7 trillion barrels of bitumen in place with proven measures indicating there are 173 billion barrels of recoverable oil under current economic conditions and technology (Government of Alberta, 2008). These oil sands are unlike traditional oil reserves. Typical oil reserves are present as crude oil deep underground. Oil sand reserves on the other hand typically composed of sand or clay, water, and bitumen (Government of Alberta, 2008). As a result, the oil sands must be heavily processed to separate the bitumen from the sand and clay before further refining may occur. This process requires tremendous amounts of water with some accounts being as much as 4.2 m^3 of water per m^3 of bitumen and an astounding 7% of Alberta's total water use (Griffiths et al., 2006). The effluent of this process is comprised of a variety materials including water, solids, a small amount of unrecovered bitumen, soluble organic compounds and solvents, in varying percents (Motta Cabrera et al., 2009, Government of Alberta, 2011). This resulting oil sands process affected water (OSPW) is then stored onsite in large tailings ponds. These tailing ponds are a considerable size and are thusly a significant environmental concern. Presently, tailings ponds in Alberta cover an area of over 170 km^2 and are considered among the largest manmade structures in the world (Government of Alberta, 2011).

This OSPW is of particular concern, not only because of the sheer volume being produced on a daily basis, but also due to the great potential for significant environmental consequences. In fact, polycyclic aromatic hydrocarbons associated with oil processing have been in found lake

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sediment as far away as 90km from major oil sands development areas (Kurek et al., 2013). As well, numerous researchers have reported that OSPW is toxic to a wide range of organisms (Colavecchia et al., 2004, Gentes et al., 2006). It is becoming increasingly evident that naphthenic acids (NAs) are the primary cause of toxicity within OSPW (Verbeek et al., 1993).

Considerable research has been done for potential treatment options for OSPW and the NAs contained within. Both bioremediation and ozonation have been investigated with mixed results. Scott et al. (2008) and Perez-Estrada et al. (2011) both applied a method of ozonation to treat NAs contained within OSPW and resulted in a significant reduction in concentration of NAs. Although this reduction was selective, favouring NAs of larger molecular size. Biodegradation of materials within OSPW is currently occurring, Holowenko et al. (2000) reported significant production of methane in tailings ponds containing OSPW. NAs have specifically been shown to be biodegradable, both aerobically (Herman et al., 1994) and anaerobically (Holowenko et al., 2002). This is a particularly slow and selective process favouring smaller molecular size NAs (Holowenko et al., 2002).

It is clear that the extraction of Canada's vast bitumen deposits is having substantial impact on the surrounding environment. As well, current potential treatment options have considerable downsides. Therefore an alternative approach may be required. Progressive freeze concentration is one potential such approach worth investigation. Progressive freeze concentration has been extensively researched in the food industry for the successful concentration of food stuffs (Liu, et al., 1997, Liu et al., 1999, Miyawaki et al., 1998). It has also shown considerable success for treatment of simulated wastewater in a laboratory setting (Jusoh et al., 2008).

1.2 Research Objectives

The research objectives of this investigation are as follows:

1. Determine the potential of progressive freeze concentration as a means for removal of NAs in solution.

2. Examine the effectiveness of progressive freeze concentration methods mechanical and ultrasound.

3. Investigate the influence of NAs identity and NAs concentration of efficacy of progressive freeze concentration.

4. Determine the influence of agitation level of both mechanical and ultrasound on treatment efficiency for NAs.

5. Examine the effect of the inorganic contaminates sulfate and chloride on progressive freeze concentration of NAs.

6. Calculate and assess the partition coefficient of various NAs solutions.

Chapter 2 – Background and Literature Review

2.1 Bitumen Extraction and Processing

The bitumen present in bituminous sands requires processing for removal from the other constituents, that being primarily clay and sand. The separation process that is commonly used is called Clark Hot Water Extraction. During this process vast amounts of water are employed in a displacement and flotation process which ultimately destroys the bonds holding the ore components together. The process consists of the digesting the raw tar sands with hot aqueous solutions containing a caustic wetting agent such as sodium hydroxide, sodium carbonate, or sodium silicate (Sepulveda & Miller, 1977). This results in strong surface hydration and shearing forces at the sand-bitumen interface which gives rise to the displacement and subsequent disengagement of the bitumen by the aqueous phase.

The water extraction process therefore requires an insurmountable amount of water. Sources of water used by oils sands operations include the adjacent Athabasca River, ground water, and recycled water (Allen, 2008). To reduce the demand for fresh water a considerable amount of the water recycled water is used during the extraction process. Syncrude Canada Ltd. (2005) reports that it recycles 80 to 88 percent of total water used during the bitumen extraction process. Even after considering the large volume of recycled water used during the extraction process vast amounts of fresh water are still required. Syncrude Canada Ltd. (2005) operations alone extracted 30.6 million m^3 of water from the Athabasca River during the 2004 calendar year. The process water that is not recycled for further processing is stored onsite in tailings ponds.

2.2 Oil Sands Process-Affected Water Properties

The tailings ponds used for storage of effluent wastewater contain enormous amounts of contaminated water which is commonly termed oil sands process-affected water (OSPW). The extraction process, while being highly effective for the separation of bitumen by promoting the dispersion of clay particles, results in wastewater effluent that is extremely difficult to treat. The resulting effluent is typically composed of 55wt% solids, which is about 82wt% sand, 17 wt% are fines smaller than 44μm and 1wt% residual bitumen (Chalaturnyk, 2002). The slurry also contains residual soluble organic compounds and solvents. Upon discharging into the tailings ponds the coarser particles settle promptly while, due to the composition of the slurry, the finer particles remain in a stable slurry structure for decades (McKinnon, 1989). The actual water quality of OSPW depends on a variety of factors including; the properties of the crude bitumen, bitumen extraction process, chemicals used during extraction, treatments performed on the OSPW before entry into the tailings ponds, and the age of the tailings pond (Allen, 2008). Mackinnon and Sethi (1993) state that OSPW is typically alkaline, slightly brackish and acutely toxic to aquatic biota due to high concentrations of organic acids leached from the bitumen during extraction.

2.2.1 Inorganic Water Quality of OSPW

There is considerable knowledge on the water quality properties of oil sands tailings water. Allen (2008) compiled an extensive table of present knowledge on inorganic water quality of oil sands affected water and surrounding bodies of water. As shown in

Table 2-1, OSPW has significantly higher values of water quality parameters total dissolved solids and conductivity, as well as, increased values of inorganic constituents calcium, sodium, magnesium, chloride, sulphate, and ammonia.

Table 2-1: Inorganic water chemistry of OSPW from a variety of locations within the Canadian oil sands region (Allen, 2008).

Variable (mg/L unless otherwise noted)	Syncrude MLSB (2003)[a]	Syncrude de-monstration ponds (1997)[b]	Suncor TPW (2000)[c]	Suncor CT release water (1996–97)[d]	Suncor CT Pond seepage (1996–97)[d]	Athabasca River (2001)[e]	Regional lakes (2001)[e]
TDS	2221	400–1792	1887	1551	1164	170	80–190
COND ($\mu S \cdot cm^{-1}$)	2400[f]	486–2283	1113–1160[f]	1700	1130	280	70–226
pH	8.2[g]	8.25–8.8	8.4	8.1	7.7	8.2	7–8.6
Sodium	659	99–608	520	363	254	16	<1–10
Calcium	17	15–41	25	72	36	30	2–25
Magnesium	8	9–22	12	15	15	8.5	1–8
Chloride	540	40–258	80	52	18	6	<1–2
Bicarbonate	775	219–667	950	470	780	115	9–133
Sulphate	218	70–513	290	564	50	22	1–6
Ammonia	14[g]	0.03–0.16	14[f]	0.35	3.4	0.06	<0.05–0.57

Note: MLSB, Mildred Lake Settling Basin; TPW, tailings pond water; CT, consolidated tailings; TDS, total dissolved solids; COND, conductivity; data represent mean values from samples collected during the year indicated; ranges indicate mean values for multiple sites.

2.2.2   Organic Water Quality of OSPW

Oil sands process-affected water generally has high concentrations of organic materials. This is predominantly dominated by the presence of naphthenic acids which will be discussed in a proceeding section. Allen (2008) collaborated on some present knowledge on the organic concentrations and properties of some oil sands process affected waters. These sites include Syncrude Mildred Lake Settling Basin, Syncrude demonstration ponds, Suncor tailings ponds, Athabasca River, and Regional lakes. A summary of this data may be seen in Table 2-2. As shown, both the Syncrude MLSB and Suncor tailings reported increased values of the water quality parameters DOC, BOD, and COD compared to that of the Athabasca River. NAs were also higher in all the tested OSPW compared to that of the Athabasca River and local Regional Lakes.

Table 2-2: Organic chemistry of oil sands process affected water (Allen, 2008).

Variable (mg/L)	Syncrude MLSB (1985–1998)	Syncrude demonstration ponds (1996–97)[a]	Suncor tailings ponds (1982–1998)	Athabasca River (2001)[b]	Regional lakes (2001)[b]
DOC	58[c]	26–58	62–67[c]	7	14–27
BOD	25[d]	-	<10–70[e]	<2	-
COD	350[d]	-	86–525[f] 260–973[e]	40[d]	-
OG	25[d]	-	9–31[f] 92[e]	<0.5	-
NA	49[g]	3–59	68[g]	<1	1–2
Phenols	0.008[h]	0.001–0.003	0.03–1.8[f] 0.03–1.4[e]	<0.001	0.002–0.004
Cyanide	0.5[d]	-	0.01–0.04 [e]	0.004[d]	-
PAHs	0.01[h]	-	-	-	-
Toluene	-	-	1–3[e]	-	-
Benzene	-	-	<0.6–6[e]	-	-
BTEX	<0.01[h]	-	-	-	-

Note: DOC, dissolved organic carbon; BOD, biochemical oxygen demand; COD, chemical oxygen demand; OG, oil and grease; NA, naphthenic acids; PAH, polycyclic aromatic hydrocarbon; BTEX, benzene, toluene, ethylbenzene, xylene; MLSB, Mildred Lake Settling Basin; data represent mean values from samples collected during the year indicated; ranges indicate mean values for multiple sites.

2.2.3 Toxicity of OSPW

There have been numerous investigations into the resulting toxicity of OSPW. Colavecchia et al. (2004) reported acute toxicity to fathead minnows during early life stages, with increased mortality, malformations and reduced size. Gentes et al. (2006) reported higher mortality and reduced weights of nestlings of nestling tree swallows (*Tachycineta bicolor)* on reclaimed wetlands affected by oil sands process material. Due to the varying contaminants contained within the tailings ponds it is crucial to indentify the main constituents responsible for the high toxicity. There is escalating evidence that suggests naphthenic acids are one of the primary sources for toxicity associated with tailings ponds water (Verbeek et al., 1993).

2.2.4 Naphthenic Acids

Naphthenic acids (NAs) are naturally occurring organic acids encompassing a wide variety molecular weights and structures. NAs in fact are found in natural surface waters in the Athabasca region in concentrations of 1 – 2 mg/L (Albert Environmental Protection, 1996). At

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higher concentrations naphthenic acids can be acutely toxic to a wide range of organisms.

Unfortunately, one consequence of the present bitumen extraction process is the release of high

concentrations of naphthenic acids in the OSPW. This is attributed to the alkalinity during the

hot water extraction process (with water pH = 8) promotes the solubilization of NAs, which have

a acid dissociation constant of approximately 5, thereby concentrating them as mixtures of

sodium salts in aqueous tailings (Rogers et al., 2002).

2.2.4.1 Composition

NAs compose of a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic

acids. A visual representation of several structures of NAs may be seen in Figure 2-1.

$$CH_3(CH_2)_mCO_2H$$

$$Z = 0$$

$$R-\text{(ring)}-(CH_2)_mCO_2H \qquad R-\text{(ring)}-(CH_2)_mCO_2H$$

$$Z = -2$$

$$Z = -4$$

$$Z = -6$$
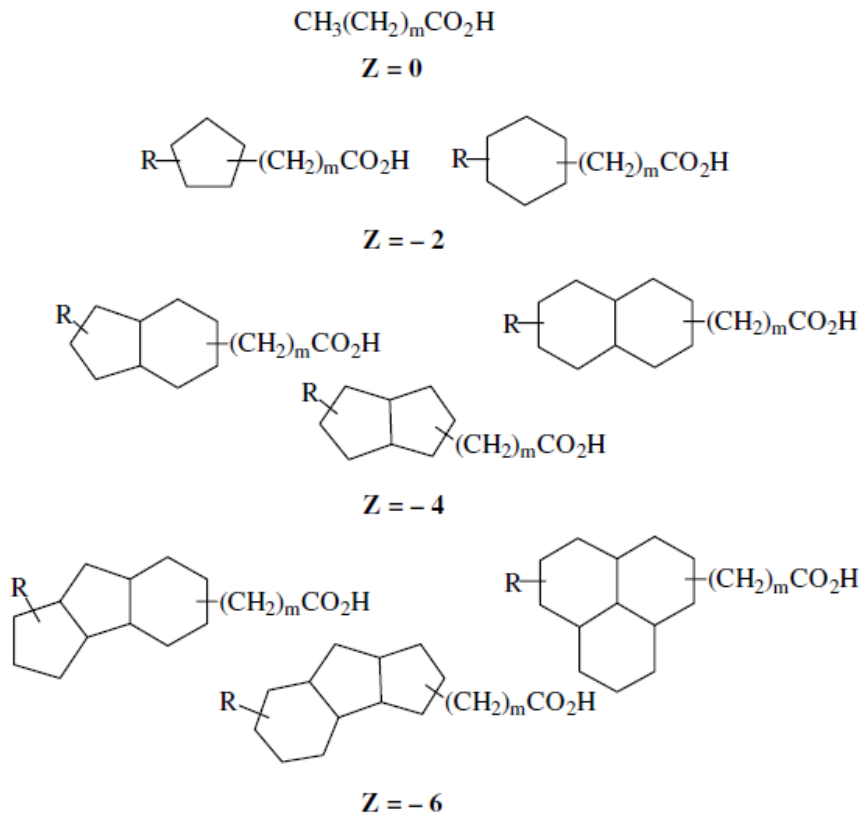
Figure 2-1: Sample naphthenic acid structures where R is an alkyl chain, Z describes the hydrogen deficiency, and m is the number of CH_2 units (Clemente & Fedorak, 2005).

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A general chemical formula of naphthenic acids is represented by the following equation:

$$C_nH_{2n+z}O_2$$
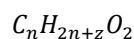
Where n represents the carbon number and z is either zero or a negative integer that specifies the hydrogen deficiency resulting from ring formation (Clemente & Fedorak, 2005). Identifying exact naphthenic acid compounds is a difficult and complex process and this can be accredited to their similar chemical and physical attributes. Holowenko et al. (2002) outlined that their acid character, the small range of in molecular weights, polarity, and volatility can attribute to no analytical method for the separation of individual acids from the complex mixture of NAs. They characterized NAs into two distinct clusters; "C22+ cluster" that is, molecules with 22 or greater carbons, and those with less carbons and a corresponding smaller molecular weight. St John et al. (1998) developed a method for the characterization of naphthenic acid mixtures. This method entails gas chromatography – mass spectrometry to determine the composition of NA mixtures in regards to their NA isomer abundance.

There has been recent evidence suggesting that the applying of the term naphthenic acids to describe all toxic organic acid-extractable compounds within OSPW may not be entirely correct. Drewer et al. (2010) investigated the composition of three commercial NA preparations, acid-extractable organics from eight OSPW, and from six surface fresh water extracts. Their findings conclude that toxic organic acid-extractable compounds within OSPW comprise less than 50% of naphthenic acids with the remaining percentage consisting of other organic compounds. They suggest the adoption of oil sands tailings water acid-extractable organics (OSTWAEO) to replace the usage of naphthenic acids.

2.2.4.2   *Toxicity*

The toxicity of naphthenic acids has been studied significantly and has been reported to negatively influence a wide variety of aquatic and mammalian organisms. Rogers et al. (2002) reported significant toxic effects on Wistar rats when repeatedly exposed to a variety of levels of naphthenic acid concentrations; causing liver and heart damage and brain hemmoraging in high doses, while weight lose and liver enlargement from chronic exposure. Anderson et al. (2012) reported reduction in survival, growth pupation and emergence of *Chironomus dilutus* when exposed to OSPW containing NA. He et al. (2012) reported significant influence on the endocrine-disrupting effects on fathead minnows when exposed to OSPW.

Also, supporting the position of the toxicity and numerous negative consequences of naphthenic acids upon terrestrial organisms, there have been attempts to amend databases for the addition of naphthenic acids. A proposal was submitted by Environmental Defense, and environmental lobby group, to add naphthenic acids to the National Pollutant Release Inventory (Environment Canada, 2010). The National Pollutant Release Inventory (NPRI) is a database of pollutants and contaminants, that when released into the environment by facilities, are required to be reported on. The potential addition of naphthenic acids to the NPRI while beneficial for the environment will also hold companies operating within the oil sands region processing bituminous sand much more accountable. This therefore promotes further investigation into novel and effective approaches for treatment of oil sands process water.

The distribution of the sizes of NAs appears to be a factor in the toxicity of OSPW. Holowenko et al. (2002) noted that a decrease in toxicity was apparent with an increase in the proportion of the "c22+ cluster", this suggests that toxicity may be associated with these lower molecular weight/lower carbon NAs.

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Toxicity associated with NAs in OSPW located within tailings ponds tends to decrease through time. Numerous studies have attributed this reduction to the biodegradation of NAs reducing their concentration within OSPW. Holowenko et al. (2002) noted a significant reduction on toxicity of aged OSPW compared to that of newer OSPW located within tailings ponds. This corresponded to a reduction in concentration of lower molecular weight NAs.

2.2.4.3   Abundance
There several factors associated with the abundance of NAs located within OSPW. The factors include the properties of the extracted bituminous sand, the extraction process, the age of the OSPW, and whether any treatment was performed on the OSPW. This results in a wide variety of concentrations of NAs being reported at a variety of affected sites. Anderson et al. (2012) reported the concentrations of naphthenic acids using Fourier Transform Infrared Spectroscopy (FTIR) from a variety of sites. They reported concentrations ranging from 13 to 72 mg/L. Grewer et al. (2010) investigated NAs and other acid-extractables in oil sands process affected water using both FTIR and gas chromatography – mass spectroscopy (GC-MS). They reported NA concentrations of 14 to 130 mg/L through the FTIR method from the tested sites, while NA concentrations using the GC-MS method were determined to be 5.9 to 47mg/L. Holowenko et al. (2002) reported concentrations of 24 to 68 mg/L by implementing the GC-MS method from numerous locations containing OSPW. Holowenko et al. (2000) reported concentrations of NAs in the range of 61 to 88 mg/L in samples taken from the Mildred Lake Settling Basin operated by Syncrude Canada Ltd.

As has been shown a wide range of concentrations of NAs have been reported in numerous OSPW samples. Even with this wide variety of concentrations, it should be noted that all

reported concentrations still have potential for significant negative consequences for terrestrial organisms.

2.3 Treatment Options

There has been a significant amount of investigations on methods that may be implemented to reduce the concentrations of naphthenic acids contained within OSPW.

2.3.1 Ozonation

The oxidation of NAs is one approach that may be implemented for the reduction of toxicity of OSPW. Several researchers have investigated the ability and mechanisms behind the oxidation of NAs. One approach that has been investigated for the oxidation of NAs within OSPW is the application of ozone.
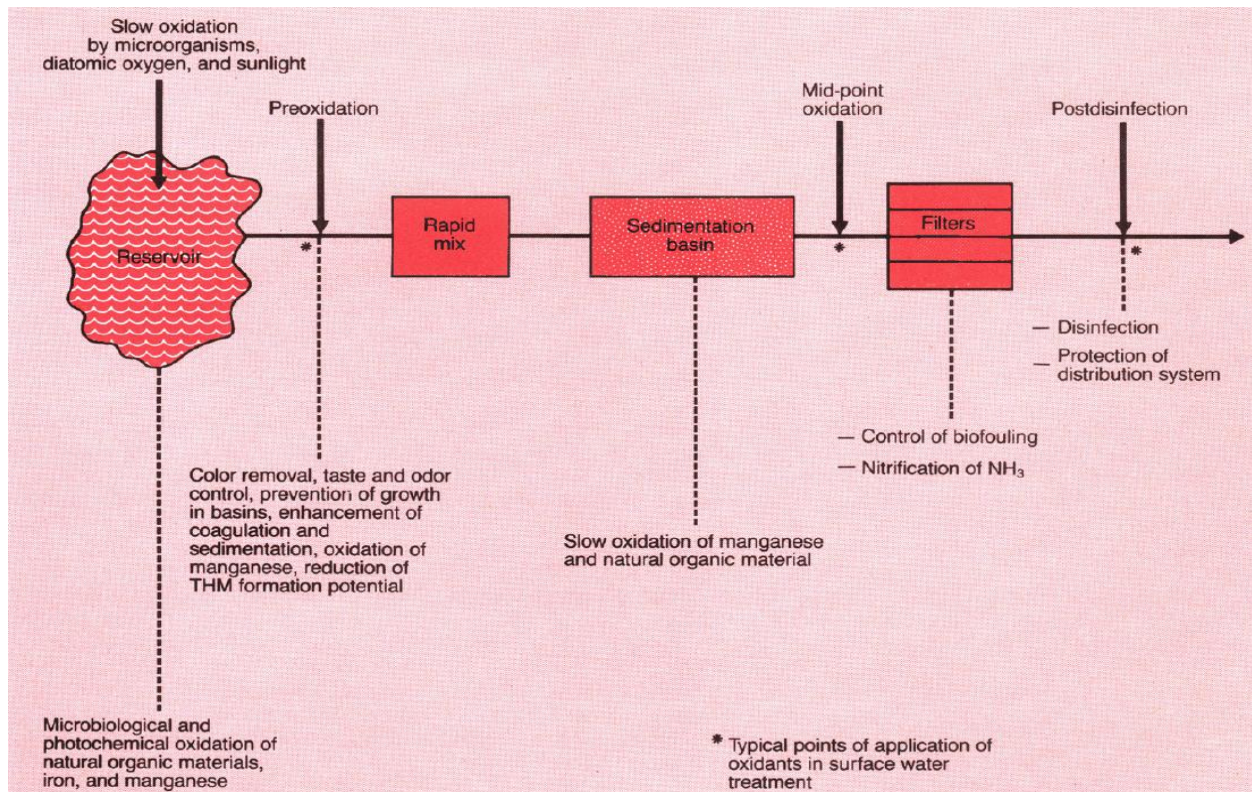
Figure 2-2: Chemical oxidants and points of application in wastewater treatment (Glaze, 1987).

The pathway to the destruction of biological species from ozone may be either from ozone itself or from hydroxyl radicals formed from the ozone in solution (Glaze, 1987). Figure 2-3 shows the decomposition ozone in of pure water.
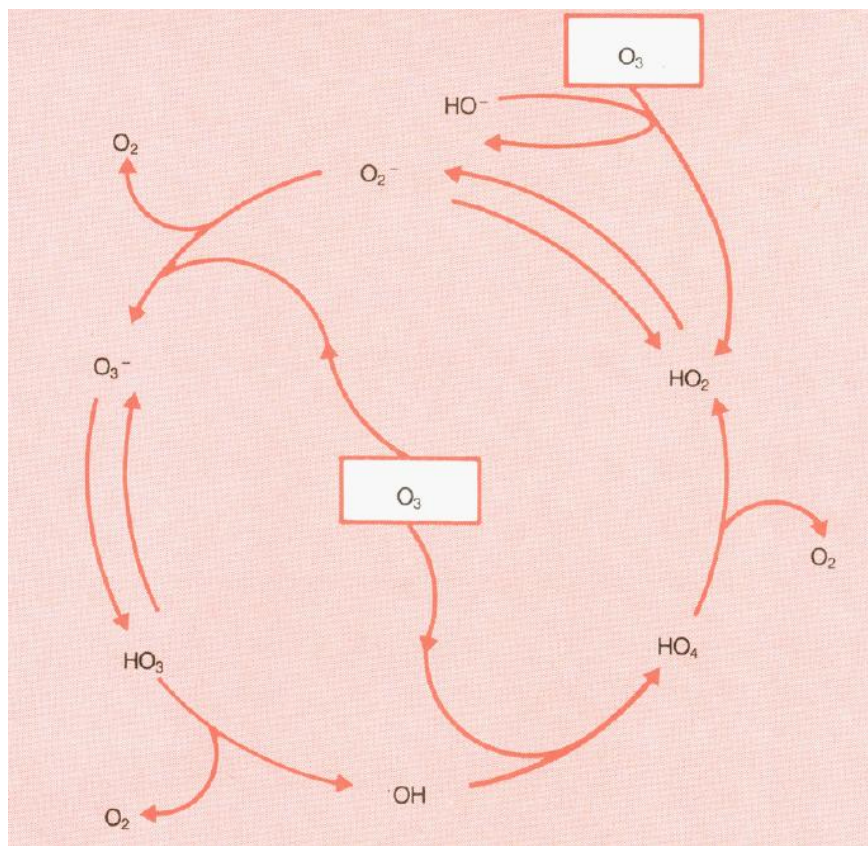
Figure 2-3: Cyclic chain mechanism of ozone decomposition in pure water (Glaze, 1987).

Perez-Estrada et al. (2011) reported positive results reducing the concentrations of NAs both in OSPW and synthetic solutions of NAs with treatment of ozone. It was noted that the ability of NAs to oxidize was increased with increasing n value, that is an increase in the number of carbon atoms, with the exception of the smallest NA in each Z-series. This increase in reactivity with increasing carbon was expected due to the overall increase in the number of hydrogen atoms available for hydroxyl radical abstraction. They also noted that reactivity increased with a decrease in z values, that is an increase in the number of rings.

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Anderson et al. (2012) investigated the ability of ozonation to reduce the toxicity of OSPW to *Chironomus dilutus*. They reported significant reduction of toxicity towards these organisms when exposed to OSPW that was ozonated at 30 and 80 mg/L; displaying improved survival, pupation, and emergence compared to that of the untreated water. He et al. (2012) also reported a reduction in toxicity when OSPW was treated with ozone. Attenuation of some of the effects of OSPW on fathead minnows was reported when OSPW was treated with ozone.

Scott et al. (2008) removed sediment from OSPW by membrane filtration and then treated the samples with ozone at dissolved concentration of approximately 35mg/L over 130 minutes. A significant improvement in the water quality parameter COD was noted as a result of the applied treatment, as well as a sharp decrease in NA concentration. A slight increase in BOD was observed during the experiment, they noted that this commonly occurs during the treatment of wastewaters with ozone. TOC did not significantly change over the course of the experiment suggesting that the NAs were not completely mineralized to carbon dioxide but were oxidized to other organic compounds that remain in solution. These results may be seen in Figure 2-4. Similarly to Perez-Estrada et al.'s (2011) results, Scott et al. (2008) noted ozone treatments reduced ability to oxidize NAs with low *n* values.
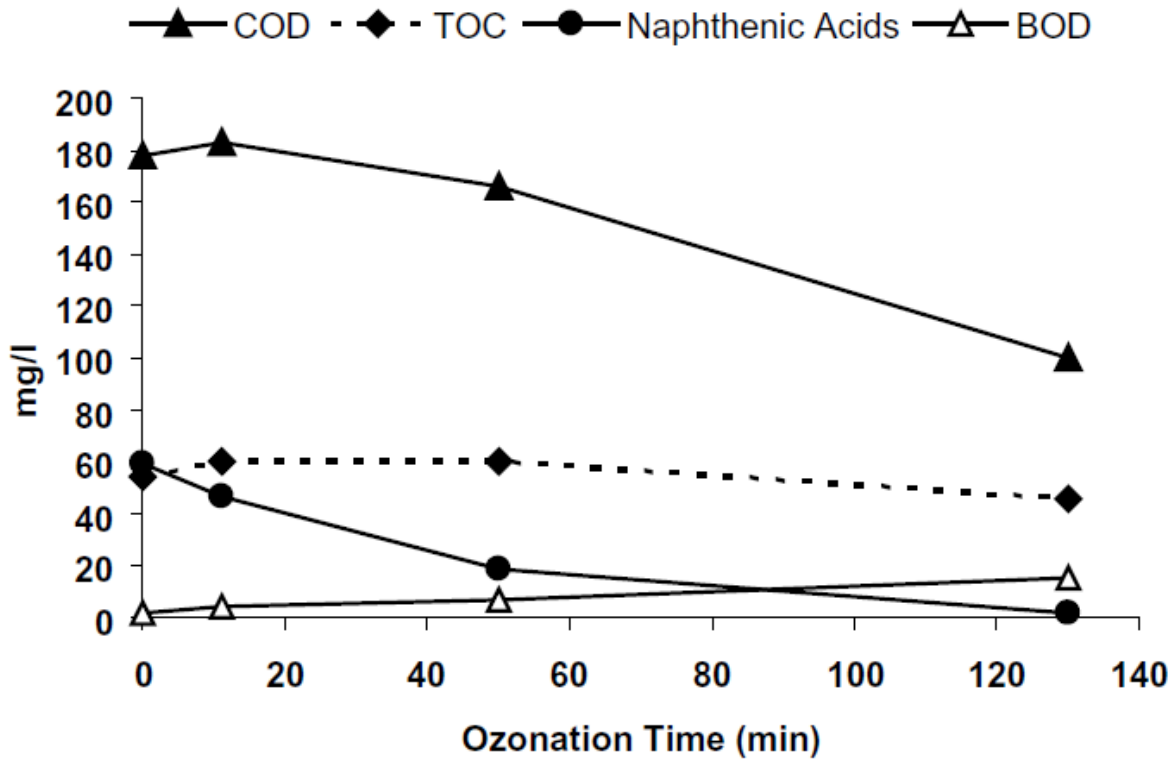
Figure 2-4: Changes in charactersistics of sediment free OSPW ozonated for up to 130min (Scott et al. 2008)

2.3.2 Bioremediation

There has been considerable research done on the effectiveness and mechanisms behind

bioremediation of oil sands tailings ponds (Fought et al. 1985, Herman et al., 1994, Holowenko

et al., 2000, Holowenko et al., 2002). Bioremediation involves the implementation of

microorganisms to remove pollutants through biodegradation, in this case, naphthenic acids. It

has been shown that biodegradation of the caustic hot water process undesirable products in

OSPW stored in tailings ponds occurs from indigenous microorganisms (Fought et al. 1985).

Significant volumes of methane and carbon dioxide have been noted being produced from

tailings storing OSPWs. Holowenko et al. (2000) estimated that the Mildred Lake Settling Basin

operated by Syncrude Canada Ltd. produced a daily flux of $12g\ CH_4/d$. This suggests that

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significant biodegradation of organic materials within the tailings is occurring. Both aerobic and anaerobic degradation of NAs may occur in situ.

2.3.2.1 Aerobic degradation

Herman et al. (1994), investigated organisms that are indigenous to oil sands tailings and their effectiveness in the degradation of naphthenic acids, both synthetic NAs and OSPW extracted NAs. In their findings, they found that the most prominent species responsible for the degradation naphthenic acids where *Pseudomonas stutzeri* and *Alcaligenes denitrificans*. During a laboratory analysis over a 25 day period, Herman et al. (1994) discovered that the bacteria were able to convert up to 50% and 20% of the organic carbon into carbon dioxide in the synthetic and extracted NAs, respectively. This resulted in a decrease in toxicity of approximately 50% for the extracted NAs and a loss of acute toxicity for the synthetic NAs using the Microtox EC50 method.

Another experimental study by Misiti et al. (2013) reported similar results for the aerobic degradation of a synthetic NAs mixture. Over a seven day period a marked reduction of NAs concentration was reported, from 250 to less than 50 mg/L. Approximately 44% of the NA-carbon was utilized biomass growth, 28.5% was mineralized to CO_2, and 27.5 were likely partially oxidized to biotrasformation intermediates as shown in Figure 2-5. Misiti et al. (2013) states that 15-26% of NAs were persistent under all conditions tested and that this may be due to a certain fraction of the NAs mixture being either recalcitrant or not bioavailable.
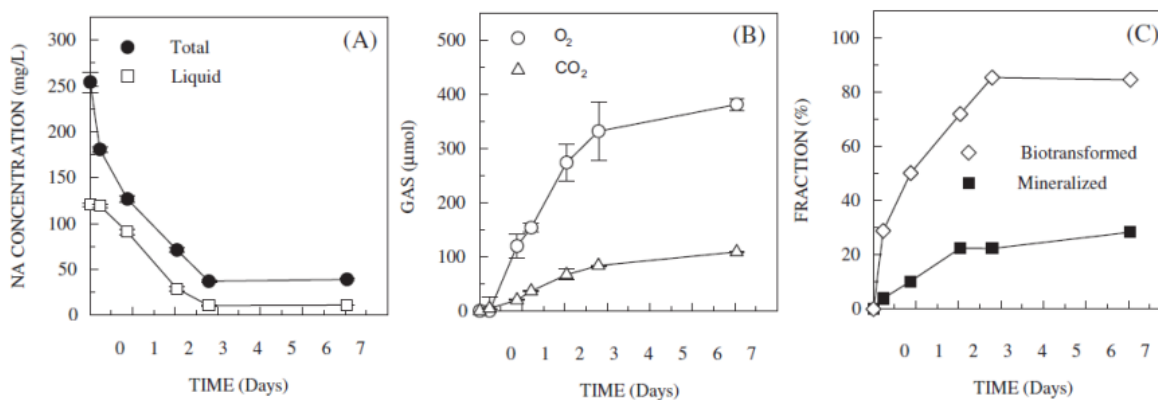
Figure 2-5: Aerobic degradation of NAs using a NA-enriched culture over 7 days: NA concentration (A), Seed-correction carbon dioxide production (B), fraction of NA biotransformed and mineralized (C) (Misiti et al., 2013)

2.3.2.2 Anaerobic degradation

There is contradictory evidence on the ability of NAs to be biodegraded under conditions

depleted of oxygen. This process involves the reduction of carbon to its most reduced state, -4, in

methane form (Rittman and McCarty, 2001). Holowenko et al. (2000), investigated methane

production on fine tailing samples containing a concentration of NAs of between 61 and 88

mg/L. The samples where monitored over a period of 250 days for production of methane. Their

experimental results may be seen in Figure 2-6. Higher concentrations of naphthenic acids

resulted in a much longer lag time, but with all concentrations of naphthenic acids, excluding the

highest, the same methane production as the control sample was ultimately achieved. Holowenko

et al. (2001), hypothesized that the lag time may be attributed to a change in the composition of

the consortium of microorganisms, with a small population of more resistant species becoming

more dominant. Alternatively, a new genotype may have arisen as a result of transfer of genetic

information from one species to another. Lastly, some members of the consortium may have

altered the naphthenic acids to products that were less inhibitory to the methanogens

(Holowenko et al., 2001).
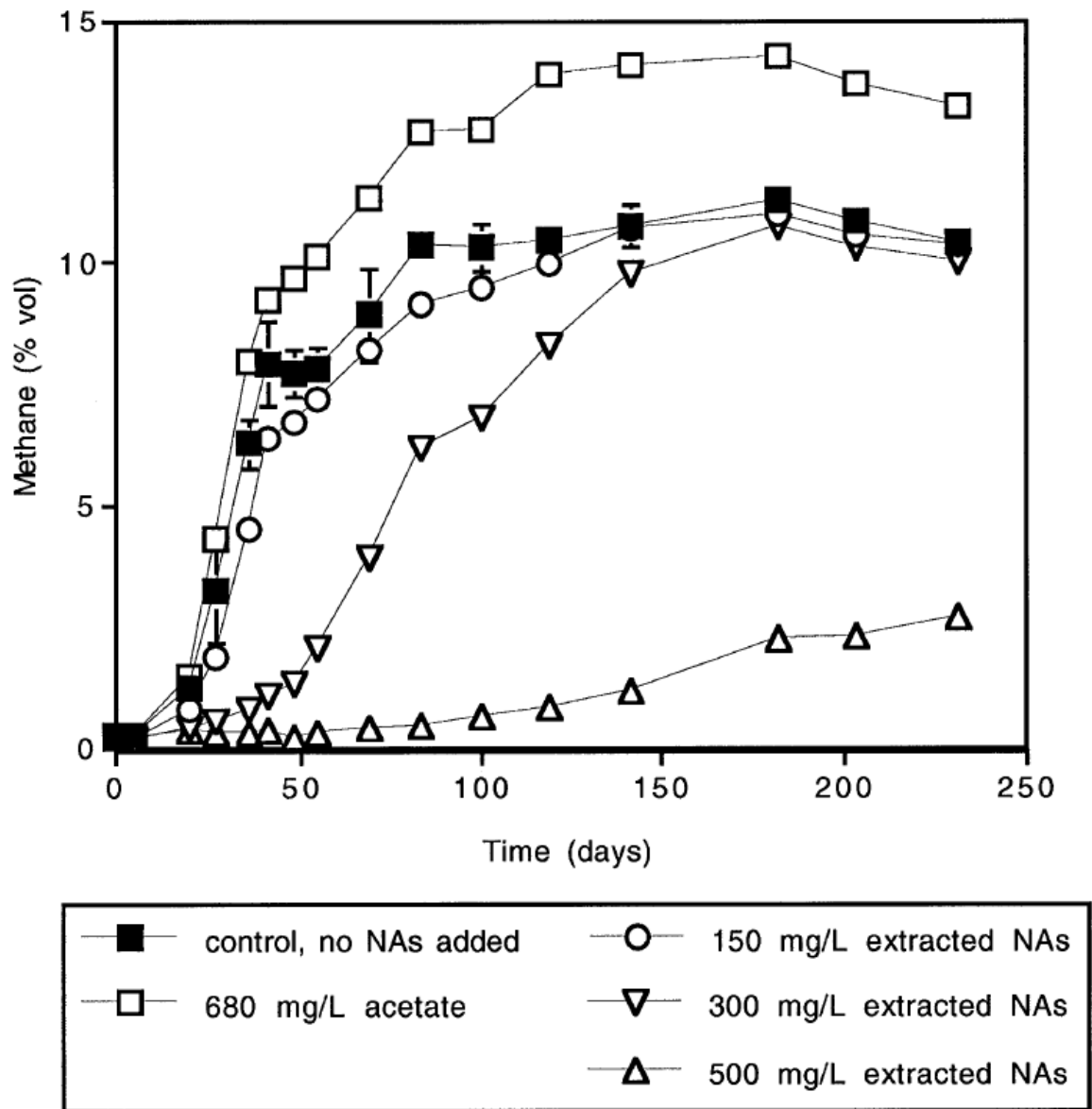
Figure 2-6. Methane production as a function of time for variety of concentrations of naphthenic acids (Holowenko et al., 2001)

Oiffer et al. (2009) investigated the fate of an anaerobic plume of OSPW. The location of experiment was a shallow sand aquifer adjacent to an oil sands tailings impoundment. They reported that NAs were not significantly biodegraded during transport in the plume over a 20 year period. Hasegawa et al. (2013) further suggests the inability of NAs to be degraded under

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anoxic conditions. Their investigation involved attempts to explain the souring of crude oil by microorganisms under anaerobic conditions. In their experiment microorganism cultures were obtained from oil field water and subsequently added to a water oil mixture. This was then incubated over a 90 day period at 28°C. Significant degradation of alkanes and aromatics to volatile fatty acids was reported while no degradation of NAs occurred.

There is clearly mixed evidence on the viability of the anaerobic biodegradation of NAs, some authors suggesting a great reduction in NAs while others reporting limited to none. It is evident that greater investigation into the anaerobic biodegradation is required.

2.3.3 Adsorption

Another potential approach for the treatment of NAs contained within OSPW is adsorption. Adsorption is the accumulation of a substance or material at an interface between a solid surface and a solution. Both physical and chemical forces are involved in adsorption; including van der Waals forces, electrostatic outer-sphere interactions, ligand exchange mechanism, covalent bonding, and hydrogen bonding (Sparks, 1995). Gaikar and Maiti (1996) investigated the NAs adsorption capacity by various adsorbents shown in Table 2-3.

Adsorption capacities and Langmuir equilibrium constants at 28°C

Adsorbent	Loading capacity (moles/kg)	Equilibrium constant $(10^{-3}\ cm^3/mole)$
Na–X	0.155	105.5
Polyvinylpyridine	0.60	44.7
Bentonite	0.442	54.74
Indion FFIP	0.401	63.92
Tulsion A-2X MP	0.92	56.19
Indion 850	0.884	61.71
Tulsion A-2X MP [a]	0.89	55.1
Tulsion A-2X MP [b]	0.89	52.39

Solvent: n-heptane.
[a] In presence of 5.1% toluene.
[b] In presence of 10.3% toluene.

Ion exchange resins were packed into a glass column and a solution containing NAs was pumped vertically into the packed column. They explained that the major adsorption mechanism for the ion exchange resins was the acid-base interaction between the tertiary amine groups on the ion exchange resins and the NAs.

Azad et al. (2013) examined the adsorption of NAs by both activated carbon and nickel based alumina. Although rapid adsorption of synthetic NAs occurred in both activate carbon and nickel based alumina only an ultimate reduction of TOC of 50% and 40% was achieved, respectively. The nickel based alumina adsorption of NAs over time is seen in Figure 2-7.
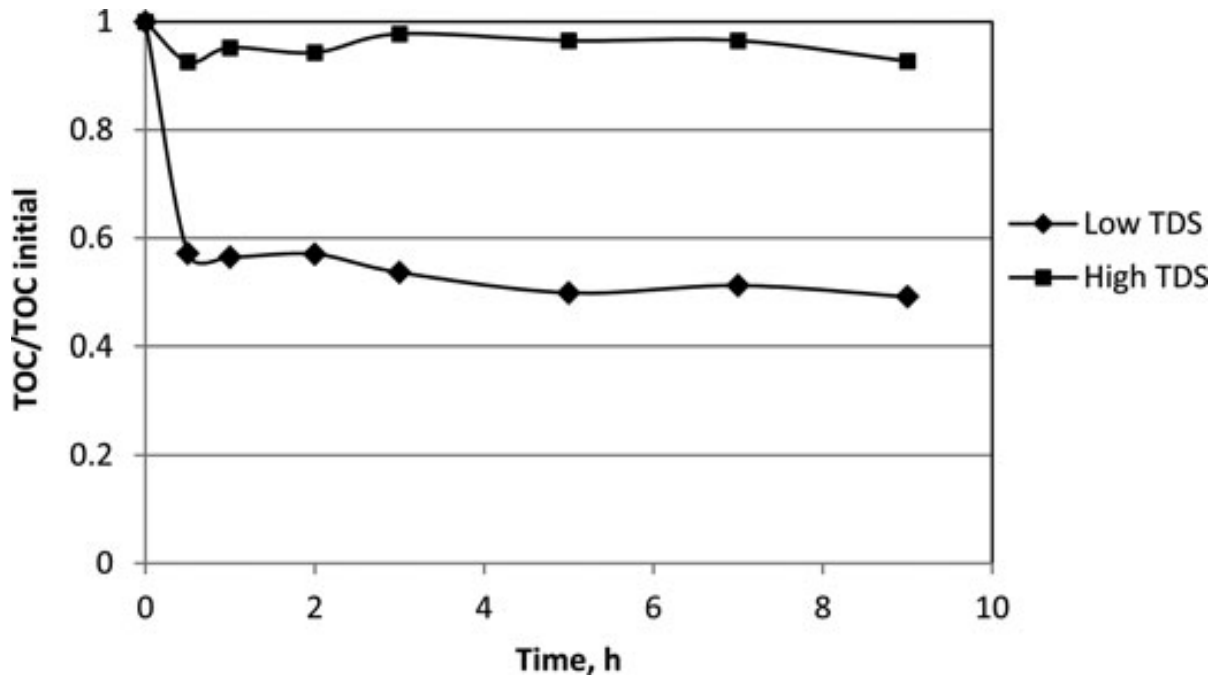
Figure 2-7: Adsorption of NAs by nickel based alumina as measured by TOC (Azad et al. 2013).

Sodium chloride was added to solution to examine the influence of high TDS on adsorption of NAs. As may be seen at high TDS levels the effectiveness of adsorption of NAs is highly reduced. Gamal El-Din et al. (2011) was able to achieve a high removal rate of NAs during the treatment of OSPW using petroleum coke as an adsorbent. Fresh OSPW was obtained from a active settling basin and then subsequently treated with 22% by weight of hot petroleum coke. Removal 91% of total acid-extractable organics and 84% of NAs was achieved.

The ability of adsorbents to effectively treat NAs in OSPW seems scattered, with some adsorbents achieving favourable results while not with others. As well, adsorbents are only able to uptake a specific amount of mass before they are either treated themselves or disposed of.

2.3.4   Membrane Filtration

Membranes are one potential approach for the treatment of NAs within OSPW. Membrane filtration is a form of physical treatment that involves a porous membrane and pressure

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differential. Undesirable molecules are unable to diffuse through the membrane and thus a

concentration gradient is formed. There is very limited knowledge on the application of

membranes for treatment of NAs in OSPW. Peng et al. (2003) applied nanofiltration for the

treatment of OSPW with considerable success. Pretreated OSPW from several sources in the oil

sands region were treated using three different membranes shown in Figure 2-8. Total organic

carbon and NAs concentrations were reduced by greater than 95%.
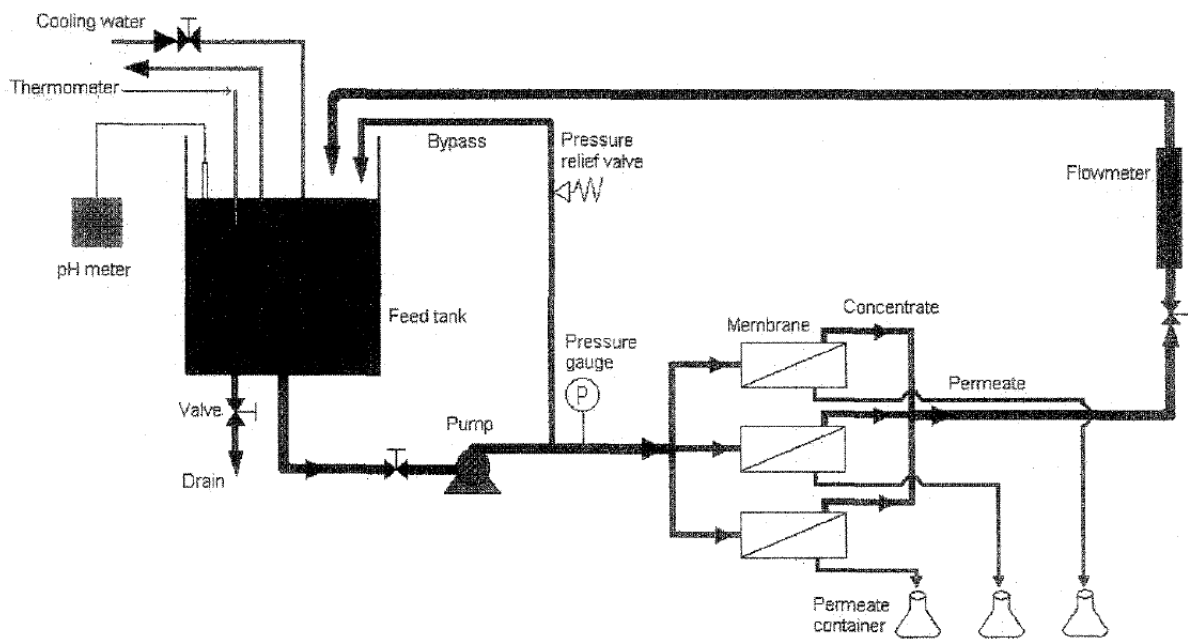
Figure 2-8: Experimental setup of Peng et al. (2003) treatment of OSPW using nanofiltration.

There has been some investigation into the treatment of wastewater polluted with organic

pollutants by filtration such as: oily effluent from a refinery process (Zhong et al., 2003) and

plastic additives (Agenson et al., 2003). Pre-treatment of wastewater is commonly required

before the implementation of membrane filtration as was the case in Zhong et al.'s (2003)

investigation by implementing a flocculation process. This is to prevent a larger solutes and

particulate matter that could be removed by other means from fouling the membrane material

and causing a sharp decrease in flux. Agenson et al. (2003) noted that retention of molecules during nanofiltration was largely associated with molecular width, molecular length, and the logarithm of octonol-water partition coefficient of the target solutes.

It is clearly evident that the development of the petroleum reserves within Canada's oil sands region is have a traumatic impact on the environment. Particularly a result of the high volumes of OSPW effluent being produced which has been reported to be highly toxic to a variety of organisms. As stated, this toxicity is primarily associated with NAs within the OSPW. Current literature into treatment options includes: ozonation, biodegradation, membrane filtration, and adsorption. These previously discussed methods show mixed levels of effectiveness. Therefore, it is apparent that investigation into alternative potential treatment options is required.

2.4   Freeze Concentration for Water and Wastewater Treatment

Freeze concentration is a method that may be applied to create a concentration differential of a substrate in solution. Freeze concentration has been extensively investigated and used in the food industry to provide an effective means for concentrating liquid food products (Sanchez et al., 2009). Recently, there has been considerable interest in examining the potential for freeze concentration for use in wastewater treatment. Specifically for treating effluents or toxic water from pulp mill effluent, nylon manufacturing effluent, piggery wastewater, oil sands tailings water and a variety of hazardous waste streams, for example (Ruemekorf et al., 2000, Gao et al., 1999, Rodriguez et al., 2000, Loraine et al., 2001). Freeze concentration takes advantage of the mechanisms and phenomena associated with the solute interaction during phase change of liquid to solid water. This can be performed by cooling the solution adequately to result in the formation of ice crystals. During this freezing process the ice crystals are formed from pure water, leaving impurities in the remaining liquid (Halde, 1980). This results in a concentration

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gradient between that of the solid and liquid phase. There have been numerous experimental studies into the mechanisms and modeling of this phenomena (Korber et al., 1983, Grange et al., 1975, Halde, 1980). There are two main methods that may be implemented to effectively perform freeze concentration. These methods are suspension crystallization and progressive concentration. These methods will be discussed further in the following sections.

2.4.1 Freezing of Water

The act of freezing is an important phenomenon that occurs widely in the natural world. Freezing may be defined as the phase transition of a substance from a liquid to solid form. This event is observable for many materials, although occurring at differing conditions depending on the material. During the freezing process of water, ice crystals are formed as a result of this thermodynamic change. This process is known as nucleation. There are two types for nucleation that classically occur, homogenous and heterogeneous. Homogenous nucleation involves the formation of ice crystals in the absence of particulate matter or other ice crystals, while heterogeneous nucleation is the formation of ice crystals influenced by foreign particles or existing ice crystals (deMan, 1999). After these nucleation steps crystal growth then occurs. This is the enlargement of the existing crystals through the addition of water molecules adjacent to the particular crystal.

The actual temperature upon which nucleation and subsequent crystal growth occurs can vary greatly from the 0°C freezing point of water. This variability of freezing temperatures is coined and depends on the properties of the solution to be frozen, as well as the corresponding atmospheric properties. Smaller volumes of water can be supercooled to a greater degree, for example: 1mL of ultrapure water may be supercooled to -32°C, droplets of 0.1mm diameter to -35°C, and droplets of 1μm to -41°C (deMan, 1999). The presence of particulate matter promotes

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heterogeneous nucleation, Heneghan et al. (2002) was able to decrease the level of supercooling by 7.65K during the freezing of pure water through the addition of insoluble silver iodide. Similarly, Gao et al. (1999) investigated heterogeneous ice nucleation in a variety of industrial wastewater. They discovered that freezing temperature was largely influenced by the pH, amount of impurities present, and droplet volume.

2.4.2 Freeze Concentration

As previously stated, freeze concentration is a phenomena that may be applied to form a concentration differential within a solution. There have been significant experimental investigations into the mechanisms, properties, factors, and practicality of freeze concentration. Liu et al. (1997) indicated that freeze-concentration could be a viable option for wastewater treatment processes when combined with a low temperature energy recovery system. In fact, two commercial plants implementing a freeze concentration method for treatment of waste water currently exist; one located in Singapore for the pre-concentration of a chemical plant effluent, and one located in the Netherlands for a styrene monomer/ propylene oxide liquid effluent (Holt, 1999).

2.4.3 Advantages of Freeze Concentration

There are numerous advantages of freeze concentration as a wastewater treatment method over traditional means of wastewater treatment. One advantage is the flexibility of feed water composition of freeze concentration, biological treatment is fairly sensitive to changes in feed composition (Ruemekorf et al., 2000). Biological treatment can also be hindered by heavy metals or toxic compounds but may be effectively treated by freeze concentration (Partyka, 1986, Ruemekorf, 1994). Wakisaka et al. (2001) also states that the high purity ice crystals formed

during treatment may be used for cold heat storage for implementation of air condition systems, particularly in warmer climates.

2.4.4 Concentration Polarization

Crystal growth during the solidification phenomenon of water occurs through the agglomeration of water molecules (deMan, 1999). This results in the rejection of impurities, both solute and particulate matter from the corresponding ice crystals. During the growth of the ice crystals and rejection of solutes and particulates from the ice, results in a concentration differential between that of the solid and liquid phases. This build up of solute at the solid-liquid interface is known as concentration polarization. This associated phenomenon has been experimentally investigated and validated by a variety of researchers. Grange et al. (1975) experimentally and analytically investigated the salt redistribution phenomena occurring during one dimensional freezing of concentrated salt solutions. They reported that the salt concentration at the solid-liquid interface is not constant but increases with time due to the increased solute rejection from the advancing ice front. Korber et al. (1983) analyzed the solute polarization occurrence during the freezing of aqueous salt solutions. Similarly solute rejection occurred during the freezing event at varying rates influenced by both time and ice front growth velocity.

A schematic of the occurrence of concentration polarization may be seen in Figure 2-9. Where C_i is the concentration of solute in the liquid phase at the solid liquid interface, C_L is the concentration of solute in the bulk solution, C_s is the concentration of solute in the solid phase, u is the speed of ice front progression, x is the distance from the origin. As is shown, a sharp increase in solute concentration occurs at the boundary layer of the solid-liquid interface as a result of the rejection of solutes from the advancing ice front. Miyawaki et al. (1998) supported this model experimentally through the progressive freeze concentration of glucose solutions.

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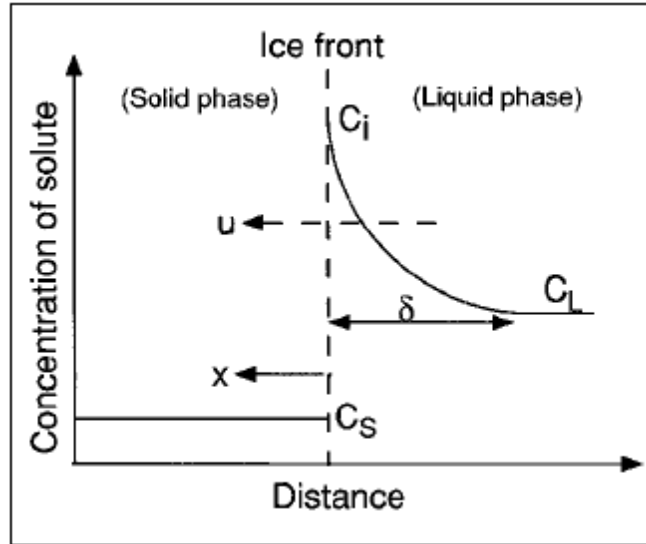
Figure 2-9: Concentration polarization at the ice front in progressive freeze-concentration (Miyawaki et al, 1998).

2.4.5   Factors that Influence Freeze Concentration

There are several factors that influence freeze concentration. The velocity of ice growth

influences the concentration at the boundary layer, with a higher velocity resulting in a higher

concentration and the potential for entrapment of solute (Korber et al. 1983). Halde (1980) also

supports this. In addition, he suggests chemical interactions and particles size and shape

influence the interaction at the solid-liquid interface during freeze concentration.

2.4.6   Methods of Freeze Concentration

As previously discussed there are two forms of freeze concentration that may be implemented;

progressive freeze concentration and suspension freeze concentration. Suspension crystallization

involves the formation, growth, and subsequent separation of various ice crystals (Sanchez et al.,

2009). These high purity ice crystals formed during the process result in a high degree of

concentration differential. Conversely, the progressive freeze concentration involves the

formation, growth, and separation of a single ice crystal. A diagram overview these two

processes may be seen in Figure 2-10.
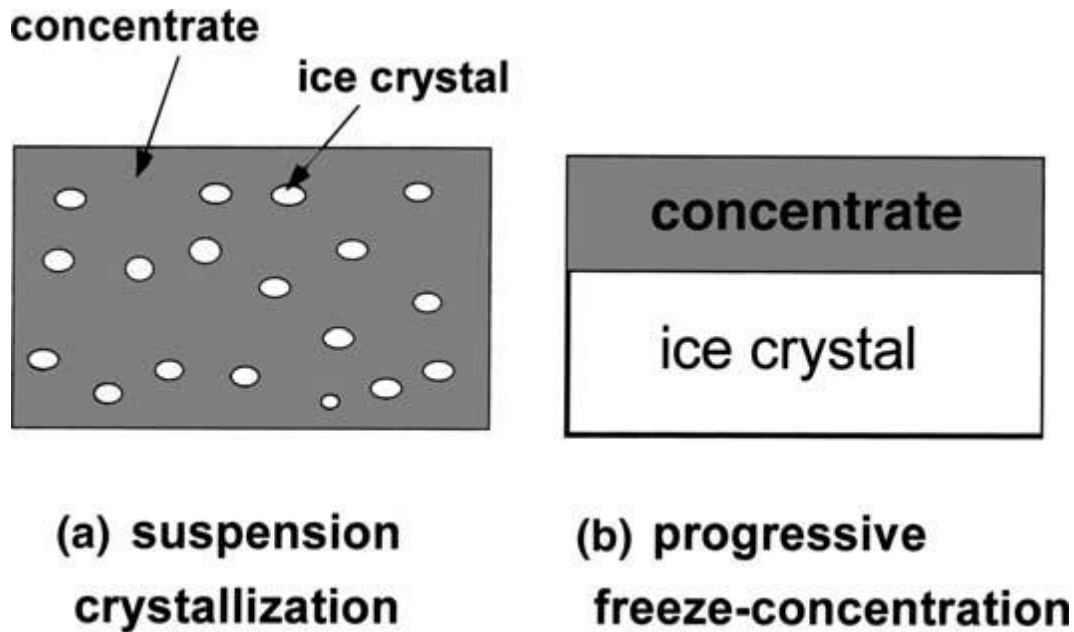
Figure 2-10: Two approaches for applying freeze concentration (Miyawaki et al., 2005)

2.4.6.1 *Suspension Crystallization*

Suspension crystallization has been extensively researched in the food industry (Sanchez et al.

2009). As stated, it is the formation and growth of numerous ice crystals. In the food industry

this results in desirable high quality concentrated food stuffs for the unfrozen concentrated

portion as the frozen portion is largely free from solutes and particulate matter. This is

particularly desirable for wastewater treatment. Suzuki et al. (2002) were able to effectively

remove phosphate, magnesium, and calcium from swine wastewater through suspension

crystallization enhanced by aeration in a pilot scale study. Reduction of 65% of phosphate, 51%

of magnesium, and 34% of calcium was obtained.

One caveat of suspension crystallization is due to the resulting presence of large quantities of

individual ice crystals. Separation of these ice crystals from the unfrozen concentrated solution

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can prove difficult and requires a complex system with a high initial investment (Gu et al, 2005). Progressive freeze concentration is not hindered by this problem.

2.4.7 Progressive Freeze Concentration

The technique that is used to apply progressive freeze concentration (PFC) allows for ease in the separation of the concentrate solution from the formed solid as only a single crystal is formed. In a laboratory setting progressive freeze concentration may be implemented using a cooling bath and simply lowering a vessel into the chilled bath the desired ice front propagation speed. This method has been used extensively for a variety of different solutes by numerous researchers (Liu et al., 1997, Miyawaki et al., 2012, Miyawaki et al., 1998, Gu et al., 2005, Halde, 1980, Ramos et al, 2005). Figure 2-11 displays a typical setup for progressive freeze concentration in a laboratory scale experiment designated.
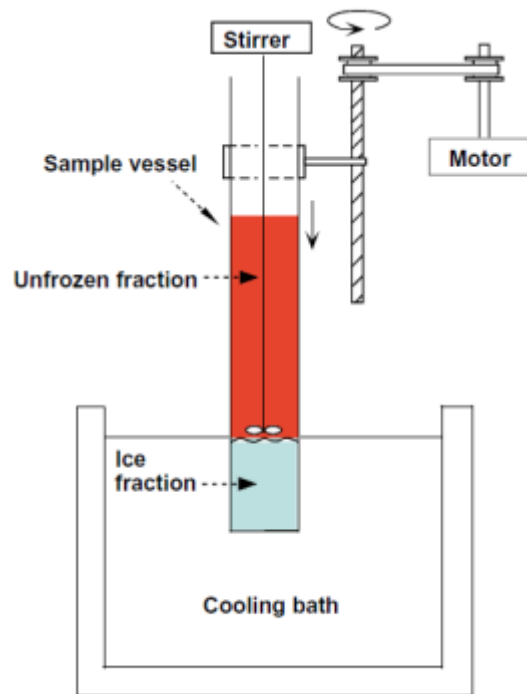
Figure 2-11: Apparatus for vertical progressive freeze-concentration (Miyawaki et al., 2012).

As is shown, the vessel is lowered at a constant rate into the cooling bath through a motor. The crystal growth thus occurs at a constant rate based on the rate of decent of the motor. As the crystal grows, the concentration differential between the liquid phase, that is the unfrozen fraction, to that of the solid phase, that is the frozen fraction increases as a function of distance from origin and time. There is also a mechanical stirrer situated just above the ice front. The significance of this will be discussed in proceeding sections.

There has also been considerable investigation into the scale up of progressive freeze-concentration for use in industrial or municipal applications. Wakisaka et al. (2001) reported substantial success in pilot-scale progressive freeze concentration system for treatment of wastewater. Jusoh et al. (2009) also achieved considerable success in the scale up and implementation of a novel progressive freeze concentration apparatus. The general concept behind the scale up of a progressive freeze concentration device may be seen in Figure 2-12. As is shown, the crystal growth occurs normal to the flow of the solution. As solution flows through the device it becomes increasingly concentrated with the growth of the crystals situated on the sides of the tube. The length of the tube may depend on the required concentration of the final solution.
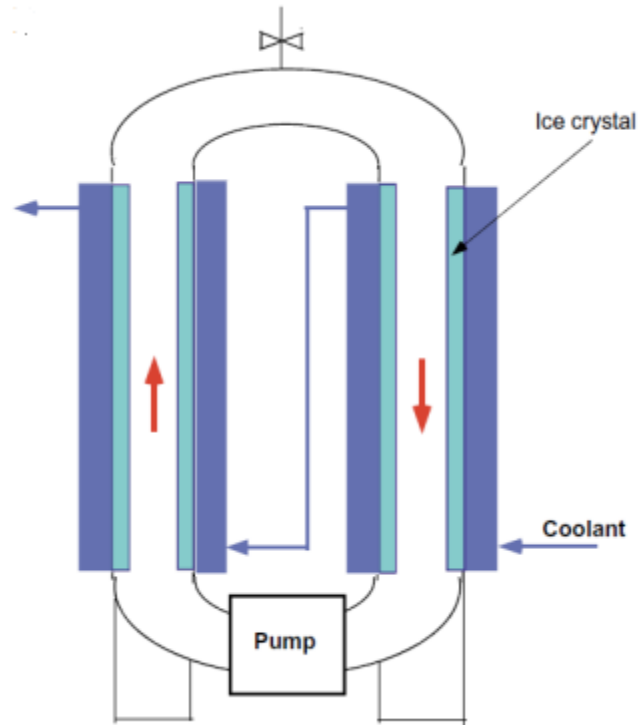
Rodriguez et al. (2000) examined progressive freeze concentration as a treatment option for the removal of valeric acids from wastewaters. At feed water concentrations of 25g/L and flow rate of 30,000kg/h they were able to achieve removal rates of 78%. This was in comparison to valeric acid removal rates of 90% using reverse osmosis. They also noted that freeze concentration used as much as five times the energy compared to reverse osmosis but was compensated by the higher capital costs and replacements of membranes for reverse osmosis. Gao & Shao (2009) implemented freeze concentration for the removal of pharmaceutically active compounds in water. They noted removal rates of 84-92% for feed water in the range of ng/L to mg/L of pharmaceutically active compounds with single stage freezing; double stage freezing increased the removal rates to 99%. Progressive freeze concentration has also shown to be effective for the desalination of water (Fujioka, 2013). At a range of 1.75%wt to 3.5% wt sodium chloride

concentration they achieved high separation efficiency between the ice and liquid portions

reporting very concentrations of sodium chloride in the solid phase.

2.4.7.1 *Effective Partition Constant*

Miyawaki et al. (1998) provided an in depth analysis of progressive freeze-concentration,

including theoretical breakdown and experimental operating conditions on effectiveness of

freeze-concentration. They outlined the effectiveness of the progressive freeze-concentration

process may be represented as the effective partition constant. That is, the concentration of solute

in liquid phase over the concentration of solute in solid phase as outlined in Equation 1 below:

Equation 1: Effective partition constant (Miyawaki et al., 1998)

$$K = C_S/C_L$$

Where K is the effective freeze-concentration partition constant, C_S is the concentration of solute

in solid phase, C_L is the concentration of solute in liquid phase. Thus, an increasingly smaller

value of K correlates with a greater effectiveness of freeze-concentration. A mass balance may

be performed on the solute by assuming complete mixing in the liquid phase and no mixing in

the solid phase resulting in Equation 2.

Equation 2: Solute mass balance(Liu et al., 1997):

$$C_L V_L = -C_S dV_L + (C_L + dC_L)(V_L + dV_L)$$

Where V_L is the solution volume. Using Equation 1 and integrating results in the

Equation 3: Experimental calculation of effective partition constant (Liu et al., 1997).

$$(1 - K)\log(V_L/V_O) = \log(C_O/C_L)$$

Where C_O is the initial concentration of the solute before freeze-concentration and V_O is the initial volume of the solution to be concentrated. This equation may be then implemented to experimentally determine the effective partition constant of varying experimental trials. These trials may test the influence of the previously stated factors; agitation level, rate of ice front growth, impurity size, impurity type, and impurity concentration.

2.4.7.2   *Factors Influencing Progressive Freeze Concentration*
There are many factors that affect the effectiveness of the ability to create a concentration gradient during progressive freezing and will be discussed in the preceding sections. These factors include; rate of ice front progression, agitation level, impurity size, and impurity concentration.

2.4.7.2.1 Freezing Rate
The rate of ice front growth during freeze concentration is a critical factor for effective treatment. This can be attributed to the previously discussed concentration polarization and the corresponding means of mass transfer of the solute during the growth the crystal at the solid/liquid interface. As stated, at the solid/liquid interface the primary means of mass transfer of the solute within solution is diffusion due to the velocity of liquid approaching zero at the interface. Therefore if crystallization does not proceed slowly, solute atoms are rejected by the advancing solid at a greater rate than they can diffuse into the bulk of the solution. An increasing concentration gradient thus develops just ahead of the advancing crystal (Burton et al., 1953). With this higher concentration adjacent to the solid liquid interface compared to that of the bulk liquid the solute has an increased chance of incorporation into the advancing solid front. Grange et al. (1975) reported little solute rejection associated with rapid ice front advancement, this was attributed to the entrapment of the solute by the ice crystals of the advancing solid. They state that bulk entrapment at the interface accounts for the majority of solute in the solid. Conversely,

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Korber et al. (1983) reported little solute entrapment with reduced ice front advancement due to the solute being able to diffuse away almost as fast as the interface advances.

This relationship was also shown during Miyawaki et al. (1998) investigation into progressive freeze-concentration using glucose as a solute, which may be seen in Figure 2-13.
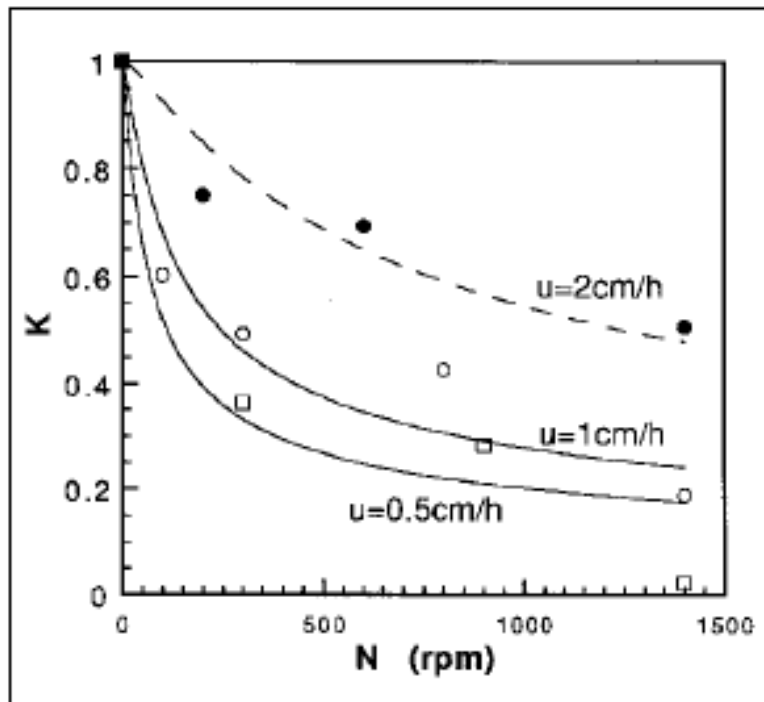
Figure 2-13: Results of progressive freeze-concentration displaying the effects of stirring rate (N) and rate of advance of ice front (u) on effective partition constant (k) (Miyawaki et al., 1998).

As may be seen, with an increased rate of ice front growth corresponds with an increase in the value of K, with a higher value of K associating with a decrease in concentration gradient being produced. Conversely, a lower rate of ice front propagation corresponds with a decrease in K showing an increase in the concentration gradient being produced. Fujioka et al. (2013) also reported similar results associated with ice growth rate during the progressive freezing of water

containing sodium chloride with a higher level of contamination of the solid phase being associated with a faster freezing rate.

2.4.7.2.2 Agitation Level

Another critical factor during the progressive freeze concentration process is the level of agitation within the liquid phase. Its importance can be related concentration polarization occurring at the boundary layer of the solid/liquid interface. Agitation within the liquid phase promotes homogenization of the liquid through convective mass transfer. This reduces the influence of concentration polarization of the sample by reducing the buildup of solute located adjacent to the boundary region thus optimizing the rate of diffusion from the boundary region. Similarly the influence of agitation was reported during the previously stated study of Miyawaki et al. (1998). In Figure 2-13, it is shown that with an increase in rpm of the mechanical agitation corresponds to a decrease in the value of k, evidence of an increase in concentration gradient. Conversely they reported an increase in the value of k with a decrease in rpm of the mechanical agitation within the liquid, which corresponds to a reduction in the formed concentration gradient. Other investigations into the factors influencing the effectiveness of freeze concentration noted similar relationships between k values and rpm of mechanical agitation (Halde, 1980, Gu et al., 2005, Liu et al., 1997, Fujioka et al., 2013).Liu et al. (1997) stated that no freeze-concentration occurred when no stirring was performed, K = 1, while K decreased drastically with increasing rates of stirring.

There have been some investigations into other sources of the required agitation during progressive freeze concentration. Matsuda & Kawasaki (1997) reported a correlation with increase in concentration gradient formed with the application of supersonic radiation as a means of agitation at the solid/liquid interface.

2.4.7.2.3 Supercooling

Supercooling can occurring during progressive freeze concentration and can significantly influence the process. As previously noted the level of supercooling depends on the composition of the solution being frozen. During their investigation into freeze concentration as a treatment option for a variety of wastewater streams (synthetic wastewater, urban wastewater, and oil cutting wastewater) Lorain et al. (2001) noted the inability of their samples to spontaneously crystallize at freezing temperatures of -10°C. To solve this concern pure water was frozen at the bottom of their freezing vessel thus providing a seed ice crystal for crystal growth to occur. This procedure is common during progressive freeze concentration (Liu et al., 1999, Gu et al., 2005).

2.4.7.2.4 Impurity Size and Type

The size of impurities contained within the sample to be treated plays a critical role with regards to the effectiveness of the progressive freeze concentration process. During an investigation into progressive freeze concentration, Halde (1980) reported significant differences in the effectiveness of forming a concentration gradient for a variety of different sizes of impurities. It was reported that coarser particles where much more effectively removed than finer particles, calcium carbonate particles where much more effectively removed than fine clay particles. It was also reported that dissolved impurities had differing levels of effectiveness for removal. Sodium chloride had much higher levels of impurities contained within ice when compared to that of glucose (Matsuda et al., 1999)

Sato and Ishibashi (1977), reported that solid particles with smaller density, diameter, and with rough surfaces were less likely to incorporated into the solid phase during progressive freeze concentration. Lui et al. (1999) reported significantly different values for partition constants between salts and that of tomato solids, with higher k values being report for salts. This suggests

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that salts are incorporated into the ice phase at a higher rate during progressive freeze-concentration than that of solid constituents.

Lorain et al. (2001) investigated the potential of freeze concentration as a treatment option for soluble pollutants. They a wide range of effectiveness of treatment at an efficiency of 83% to 98% for urban, vinaigrette, mayonnaise, and cutting oil streams of wastewater at concentrations of 65mg/L to 3000mg/L.

2.4.7.2.5 Impurity Concentration

The concentration of impurities contained within the solution to be concentrated through progressive freezing plays an important role. Matsuda et al. (1999) examined the treatment efficiency ultrasonic radiation progressive freeze concentration of three solutions types: sodium chloride, L-phenyl alanin, and saccharose at concentrations of $0.5kg/m^3$ and $5.0kg/m^3$. They reported that solutions with lower mass concentrations where more easily concentrated with higher contaminate levels being reported in the ice phase at higher concentrations. This is a significant issue during progressive freeze concentration, as the liquid portion of the sample becomes increasingly concentrated due to the rejection of solutes and particles from the solid portion. This relationship was also noted by Rodriguez et al. (2000) for the treatment of valeric acid in a wastewater stream at a concentration of 0.5 to 25g/L with higher levels of ice contamination by valeric acid at higher feed water concentrations. This is shown below in Figure 2-14.
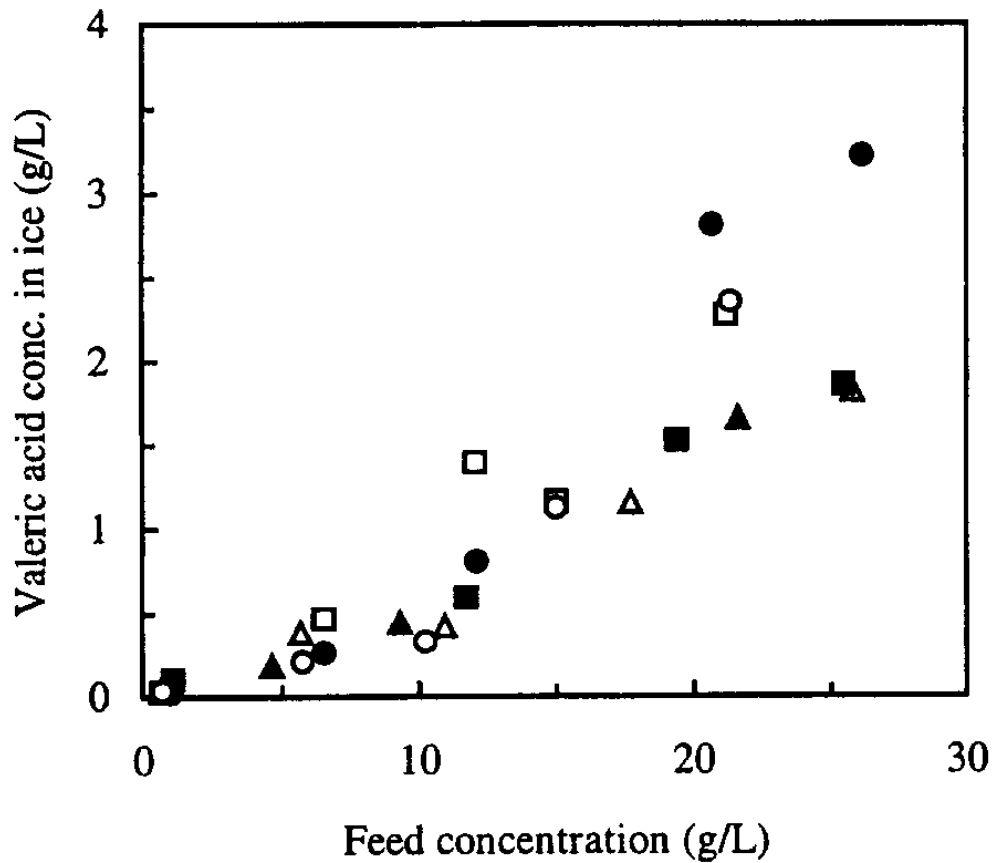
Figure 2-14: Freeze concentration for the removal of valeric acid from industrial wastewater (Rodriguez et al., 2000).

2.5   Power Ultrasonic Freezing

Acoustic waves exceeding the human audible range are termed ultrasound, typically spanning
the range of 15KHz to 10 MHz (Suslick, 1990). Acoustic waves may be generated from an
ultrasonic device which contains a piezoelectric plate that vibrates at specific frequencies
propagating a sound wave perpendicular to the plate. Ultrasonic waves may propagate through
all states of substance; gas, liquid, or solid. When a sound wave travels through a medium the
particles are agitated and will oscillate about their original point transferring the energy to
adjacent particles. Sound wave propagation occurring in liquids and gases produces longitudinal

waves. In solids, sound wave propagation also occurs in transverse waves, this is attributed to solids possessing shear elasticity and thus supporting tangential stresses (Mason & Lorimer, 2002). Ultrasonic waves, when traveling through a medium have many influences on the properties and interactions of that medium and any constituents contained within the medium. Specifically, within a liquid, ultrasound can result in intensive agitation and mixing caused by rapid formation, expansion, and violent collapse of bubbles, as well as through acoustic streaming. In some instances ultrasound irradiation can increase chemical reactivities by nearly a millionfold (Suslick, 1990). Ultrasound also has an influence on heat transfer coefficients, enhancing the rate of heat transfer within a medium. Another potential effect of ultrasound upon a material is heat transferred from the acoustic wave into the medium resulting in a temperature increase. A typical power ultrasound setup is shown in Figure 2-15.

Due to these properties, ultrasound has numerous industrial and research applications. Sivakumar et al. (2007) applied ultrasound to aid in the recovery of chrome from leather tannery effluent. Sonication provided enhanced dispersion and particle size reduction for magnesium oxide used for precipitation of chrome. As more magnesium oxide was available for reaction and reaction rate was enhanced a threefold increase in recovery was obtained. Ultrasound has also shown promise in pharmaceutical applications. Ambrus (2012) applied power ultrasound to significantly enhance the dissolution of poorly soluble gemfibrozil. The specific surface area of the drug was increased as a result of particle size reduction. There is also considerable

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investigation into a hybrid system of cavitation induced through ultrasound and fenton chemistry for the treatment of organic wastewater (Bagal & Gogate, 2014).

2.5.1 Acoustic Cavitation

The process of the formation, growth and implosive collapse of bubbles within a liquid medium is known as acoustic cavitation (suslick, 1990). As an ultrasonic wave propogates through a medium the effected particles are displaced from their point of origin, oscillating about this origin. Also occurring during this displacement of particle is a significant pressure fluctuation. Similarly to oscillation of the particle the pressure will fluctuate positively and negatively about the present medium pressure. This pressure oscillation may be attributed to the displacement of the particles. During periods when the particles are displaced they will come within close proximity to surrounding particles, this compression will result in a localized pressure increase. Conversely, when the particles are displaced at the greatest distance from surrounding particles will result in a localized pressure drop (Mason & Lorimer, 2002). During ultrasonic application to a liquid medium, if the pressure change is significantly large during the pressure oscillation voids within the liquid may be formed. This occurs during the negative pressure phase as a result of the distance between the molecules exceeding the critical molecular distance necessary to hold the liquid intact, thus the liquid breaks down and voids or cavities are formed. Two different scenarios may occur to these formed cavities; transient cavitation and stable cavitation. During stable cavitation, the formed bubbles oscillate during the pressure changes and eventually disappear. Transient cavitation results in rapid growth of the cavity with eventual violent collapse. Transient cavitation can occur both during high-intensity ultrasound and at lower intensities. During high acoustic intensity, if the rate of expansion of the cavity is sufficiently rapid, it will not have time to recompress during the positive pressure period of the acoustic

cycle (Suslick, 1990). At lower acoustic intensities cavity growth occurs as a result of rectified

diffusion, the cavity's surface area in slightly greater during expansion than during compression;

therefore, growth process are slightly faster than shrinking process (Suslick, 1990). Both

preceding points thus cause the growth of cavity present during ultrasonic acoustic application. A

diagrammatic representation of both transient and stable cavitation may be seen in Figure 2-16.
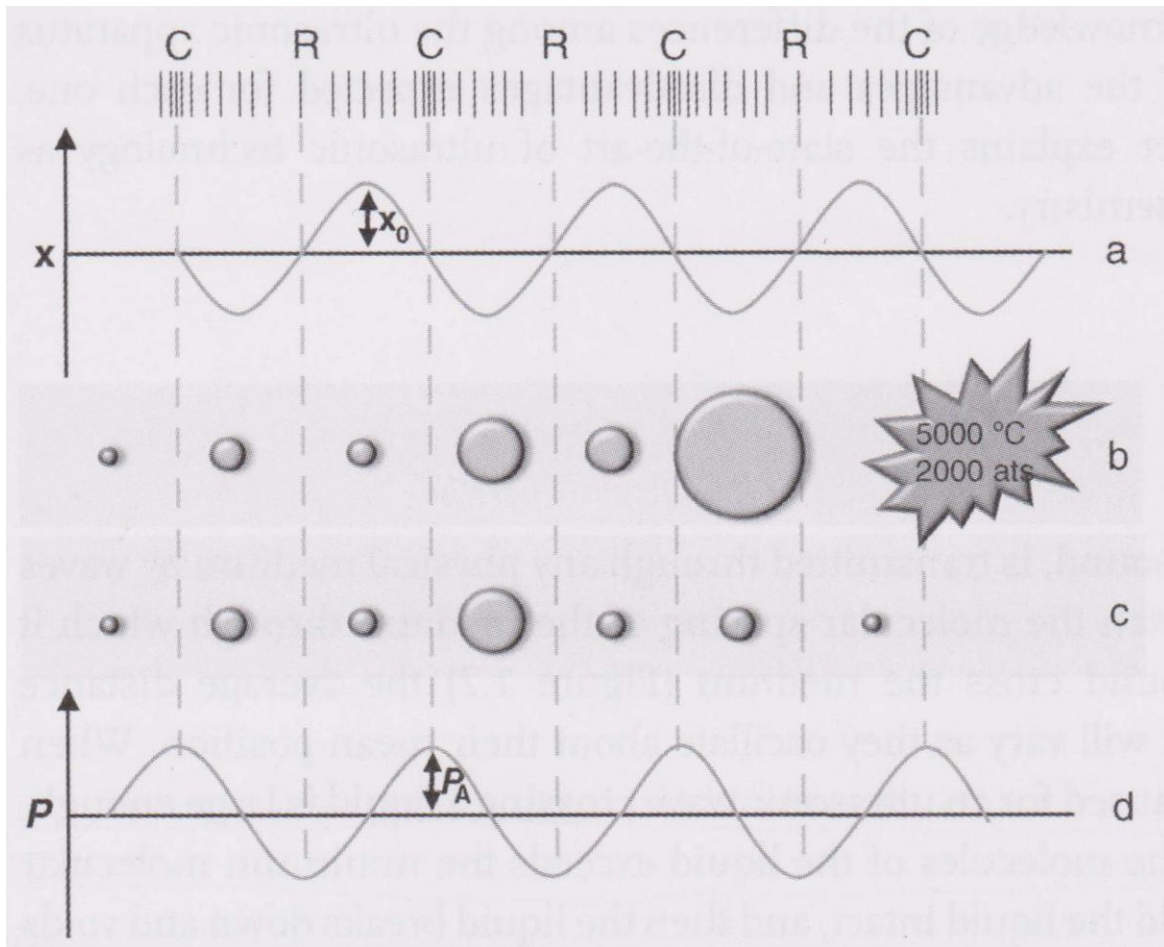
Figure 2-16: Formation and collapse of cavitation bubbles, where; (a) is displacement, (b) is transient cavitation, (c) is stable cavitation, (d) is pressure (Santos et al., 2009).

During transient cavitation the cavitation bubbles will continue to grow with further pressure

oscillations until a critical bubble size is reached. This is known as the resonant bubble size, the

point at which rapid expansion occurs in a single expansion cycle. Once the cavity has

overgrown, it can no longer efficiently absorb energy from the sound field and can no longer sustain itself and thus the surrounding liquid rushes in and the cavity implodes (Suslick, 1990). The critical bubble size is determined by the frequency of the ultrasound, Suslick (1990) reports that at 20 kHz the critical size is approximately 170 μm in diameter.

2.5.1.1 *Factors Influencing Acoustic Cavitation*

There are several factors that affect the effectiveness of ultrasonic waves to influence acoustic cavitation.

2.5.1.1.1 Ultrasound Intensity and Frequency

For transient cavitation to occur requires a minimum period of negative pressure to allow for bubble growth. At increasing frequency, oscillation period is much shorter and thus the negative pressure period is reduced. If this value is below the threshold of cavitation, no transient cavitation will occur. This may be overcome by increasing the value of applied ultrasonic intensity. Greater intensity ensures that the cohesive forces of the liquid may be overcome and acousitic cavitation may occur at higher frequencies (Mason & Lorimer, 2002).

2.5.1.1.2 Temperature

An increase in temperature results in a decrease in cavitation threshold. This may be attributed to the decrease in viscosity and surface tension of the liquid or an increase in the vapour pressure (Mason & Lorimer, 2002).

2.5.1.1.3 Viscosity

The viscosity of the liquid upon which acoustic cavitation is occurring influences the threshold of cavitaiton. Mason and Lorimer (2002) state that an increase in liquid viscosity results in a greater negative pressure required to instigate acoustic cavitation. This is attributed to the negative pressure being required to trump the natural cohesive forces acting in a liquid, being greater with increased viscosity.

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2.5.1.1.4 Gas, Particulate Matter and Solutes

The presence of gas and particulate matter enhance the process of acoustic cavitation. This is due to the process being nucleation driven, as it occurs at pre-existing weak points within the liquid, such as gas-filled crevices in suspended particulate matter or transient microbubbles remaining from previous cavitation events (Luque-Garcia & Luque de Castro, 2003). Conversely, the presence of solutes may also have a negative influence on bubble growth. Ashokkumar (2011), reported reduced bubble growth with the presence of a solute relative to that of pure water and postulated that this may be a result of the reduction of coalescence between bubbles.

2.5.1.2 *Acoustic Cavitation Effects*

This rapid formation, growth, and subsequent violent collapse of cavities within a liquid exposed to ultrasonic waves have numerous influences on the medium.

Acoustic cavitation can significantly enhance mass transfer within a liquid medium. The implosion of microbubbles formed through acoustic cavitation may be in two different variety, asymmetric collapse and symmetric collapse. During symmetric collapse, shockwaves are propagated to the surrounding solids causing microscopic turbulence. During asymmetric collapse the bubble is in the vicinity of a solid material, and is unable to collapse symmetrically, and will send out microjets (Hagenson & Doraiswamy, 1998). These two collapses thus will significantly enhance the mass transfer and heat transfer within the liquid medium as a result of increased convective heat and mass transfer. This would aid in the progressive freeze concentration process, providing both mixing in the bulk solution as well as mixing at the solid-liquid interface.

 During cavitation collapse at a solid liquid interface a deformation of the cavity occurs, sending out a fast-moving stream of liquid through the cavity at the surface with velocities greater than

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100m/s (Suslick, 1990). While this localized mixing has great potential for mixing at a solid liquid interface, it also may damage the solid structure upon which the acoustic cavitation is occurring. Luque-Garcia & Luque de Castro (2003) outline that the formed liquid jets during the collapse of acoustically formed cavitation bubbles at a solid liquid interface can impact the solid surface intensely and can result in serious damage to the impact zone.

Acoustic cavitation can also significantly influence chemical reactions. During the violent formation, growth, and subsequent collapse of acoustically formed bubbles extreme levels of temperature and pressure occur. Suslick (1990) states that temperatures of 5000°C and pressures of 500atm. Energy is critical during chemical reactions and thus this high temperature, pressure change, and vibrations can significantly aid in chemical reactions. This phenomenon is known as sonochemistry (Suslick, 1990).

The formation of free radicals during the application of ultrasound on an aqueous solution can significantly influence the properties of a solution. Several authors have provided evidence of the formation of free radicals during acoustic cavitation such as hydroxyl and hydrogen peroxide (Makino et al., 1982, Makino et al., 1983, Riesz & Kondo, 1992). Makino et al. (1982) provided evidence of the formation of hydroxyl and hydrogen atoms during sonication by a process of spin trapping. A diamagnetic nitroso or nitrone compound was used to convert the short lived radicals in to relatively longer lived nitroxyl radicals which were viewable by electron spin resonance spectroscopy. This formation of free radicals could potential aid in the treatment of NAs during ultrasonic progressive freeze concentration.

2.5.2 Acoustic Streaming

As ultrasonic waves propagate through a medium, they influence the mediums composed particles to oscillate about a point of origin. This acoustic wave will also cause a pressure fluctuation about the current standard pressure. This propagating pressure wave will cause mixing within a liquid medium. Vichare et al. (2001) states that propagating pressure waves in an unbound liquid will cause bulk movement of a liquid due to the periodic pressure field created by an ultrasonic device. During the forward stroke of the device the adjacent liquid is pushed away from the device, while during the backwards stroke fluid rushes from the sides of the device to fill the space occupied by the preceding forward movement. This process is known as acoustic streaming (Vichare et al., 2001). A diagrammatic representation of this process may be seen in Figure 2-17.

First forward stroke   Backward stroke   Second Forward stroke

a

Rushing liquid

2nd fluid packet

1st fluid packet

Fluid packet being pushed away in the forward stroke

Stationary first fluid packet

* entrainment
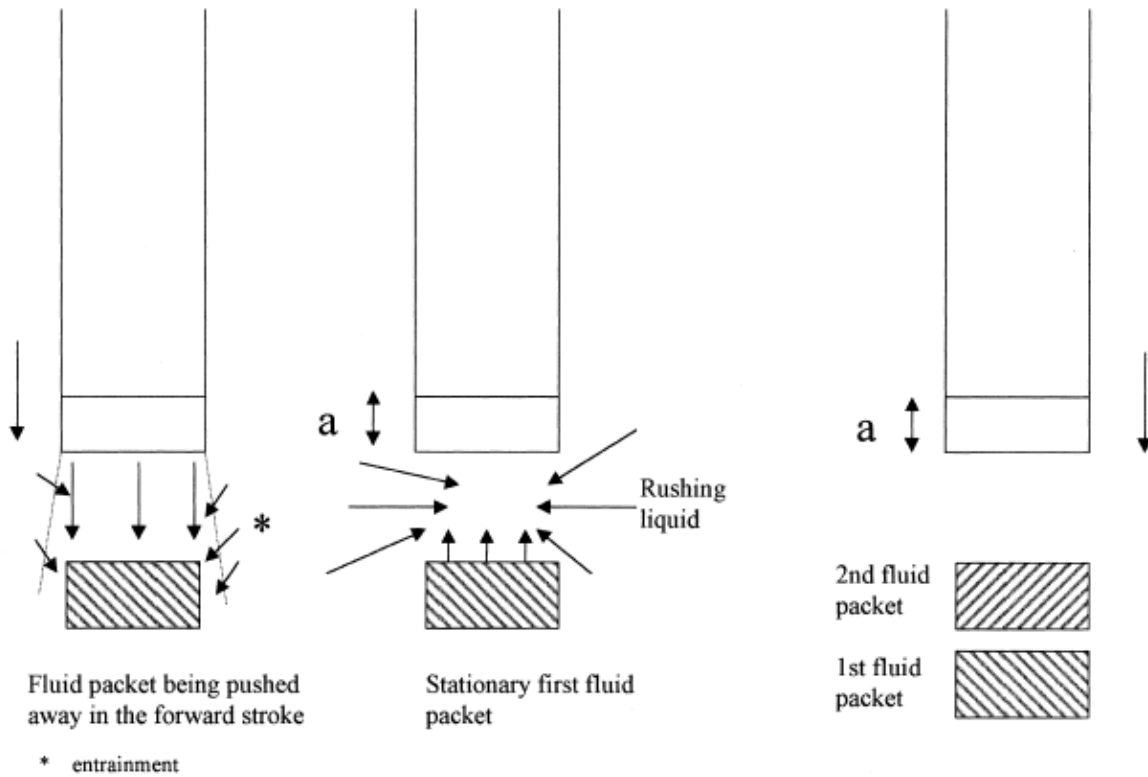
Figure 2-17: Generation of net displacement of the fluid due to the vibrations of the horn (Vichare et al., 2001).

If ultrasonic vibrations are applied to liquid medium contained within a vessel, the bulk fluid flow can cause mixing flow within the liquid. This ultrasonic induced liquid motion can generate both micromixing and macromixing (Monnier et al., 1999).

Figure 2-18 illustrated the ultrasound induced mixing process.

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2.5.2.1 *Factors Influencing Acoustic Streaming*

There are several factors that will influence the effectiveness of acoustic streaming caused by the

application of ultrasonic waves. These factors include frequency, amplitude and the location of

the applied ultrasound. These points will be discussed in the preceding section.

2.5.2.1.1 Frequency

Suri et al. (2002) obtained results displaying that applied frequency of ultrasonic waves on a

liquid medium has little influence on acoustic streaming.

2.5.2.1.2 Amplitude

The amplitude of the applied ultrasonic waves has an influence on the effectiveness of mixing

within a liquid media. Higher applied amplitude results in a greater differential of the pressure

gradient, with larger positive and negative swings. The increase in the level of pressure

oscillations leads to increase in bulk flow movement. Suri et al. (2002) reported enhanced mixing

rate with increasing levels of applied amplitude for ultrasonic waves. Similarly, Monnier et al. (1999) reported an increase in mixing effectiveness on a micro scale corresponding with increased amplitude up to an intensity level of $10Wcm^{-2}$.

2.5.2.1.3 Location of Source

Vichare et al. (2001) reported optimum mixing by acoustic streaming when placement of ultrasound source was on the surface of liquid medium. A reduction in mixing efficiency was reported as the source is lowered into the medium, with reduction increasing with increasing displacement from liquid surface.

2.5.3   Heat Transfer Coefficient and Freezing Rate

Ultrasound has been reported to enhance the heat transfer coefficient of a variety of media. Li and Sun (2002) investigated the effect of applying power ultrasound during immersion freezing of potatoes. They discovered that power ultrasound had a positive effect on heat transfer. This was attributed to the agitation of the liquid, with an increase in power resulted in greater agitation and thus greater increase in heat transfer coefficient. They also reported that when ultrasonic waves where applied during a phase change, from liquid to solid, the freezing rate was significantly increased. This was attributed to the violent sonic agitation increasing the rate of removal of latent heat. Delgado et al. (2009) also reported an enhancement of freezing rate during the immersion freezing of apples with applied ultrasonic waves.

The application of ultrasound also has the ability to enhance rate of heat transfer within metals. Fairbanks (1979) reported a significant increase in the heat transfer coefficient during the application of ultrasound to steel using a frequency of 20khz and a power of 75 watts. During the application to steel an increase in thermal conductivity of 2.25 to 3.55 was observed. This increase in heat transfer coefficient for metals is beneficial for enhancing the heat transfer

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between the stainless steel vessels used in the experiment and the solution to be progressively frozen as well as, between the stainless steel vessel and the cooling bath. This increase in heat transfer will thus aid in increasing the rate of freezing during the progressive freeze process.

2.5.4 Effect of Power Ultrasound on Ice Nucleation and Supercooling

As discussed, crystal growth is desired over nucleation the progressive freezing process. At a high degree of supercooling, nucleation is more dominant, while at a lower degree of supercooling crystal growth is favoured (Zeng & Sun, 2006). Thus, a low level of supercooling is desired during the progressive freezing process. The application of ultrasound has been reported to influence ice nucleation as well as supercooling levels during the freezing process. Delgado et al. (2009) reported an increase in nucleation temperature during the application of ultrasound when compared to that of no applied ultrasound.

Hozumi et al. (2002) reported that high intensity ultrasound had a significant influence on the freezing of super cooled water. At applied ultrasonic waves of 45 kHz with an intensity 0.28 Wcm^{-2} freezing temperature of supercooled water was increased. They attributed this to the formed bubbles in the water sample inducing cavitations thus freezing the supercooled water at the bubble locations. Chow et al. (2003) also noted a reduction in supercooling corresponding to an increase in sonication intensity at 20 kHz. This relationship is shown in Figure 2-19.

2.5.5 Heat Generation in Liquid during Acoustic Wave Propagation

As the molecules of a medium vibrate under the action of a sound wave, they experience viscous interactions which degrade the acoustic energy into heat (Mason & Lorimer, 2002). This generated heat can cause bulk heating during the application of ultrasonic waves increasing the temperature of the traveled medium. If acoustic cavitation is present, the heat transferred into the medium is potentially even greater. Suslick (1990) states that during the compression of cavities in an irradiated liquid the collapse is more rapid than thermal transport and therefore short lived, localized hot spots occur. These localized hot spots will thus increase the heat within the liquid medium, potentially influencing the liquids temperature. Hickling (1965) investigated the formation ice crystals during bubble cavity collapse. He concluded that the heat generated from

the compressed gas during cavitation does not seriously interfere with the formation of ice crystals.

Li and Sun (2002) applied ultrasonic waves intermittently in order to avoid too much heat generation during the immersion freezing of potatoes with ultrasound. This process is known as pulsed ultrasound. Pulsed ultrasound maintains the ability to agitate a liquid medium to promote mixing, albeit at a lower rate, but also significantly reduces the heat transferred to the liquid medium from ultrasonic waves.

2.5.6 Effect of Pulsed Ultrasound

To reduce the effects of heat transfer from applied ultrasonic waves to the medium while maintaining effective mixing, pulsed ultrasound may be used. Pulsed ultrasound is the cycling, on and off, of ultrasonic waves when applied to a medium. Delgado et al. (2009) implemented a pulse ultrasound method during the ultrasonic immersion freezing of apples to reduce the effects of heat generation during ultrasonic application. This was performed by applying the ultrasound intermittently at 30 second intervals. Vetri & Nagarajan (2008) investigated the properties of pulsed ultrasonic mixing. They concluded that mixing efficiency appeared to have an essentially linear dependence on the on/off cycle ratio, that is the ratio of ultrasonic waves on to ultrasonic waves off. Understandable as ultrasound application is reduced then mixing efficiency is reduced. They also reported that as the on/off ratio increases the temperature within the liquid medium rises due to ultrasonic energy also increases. An optimum level of ultrasonic application is thus required for the most favourable conditions to reduce the influence of generated heat while reaching an efficient level of acoustic agitation.

2.5.7 Ultrasound as a Method of Wastewater Treatment

Ultrasound has shown promise as a method for the treatment of wastewater effluent. There are several reasons for the viability of this application and they include; the previously discussed formation of free radicals of hydroxide and hydrogen peroxide, and the high temperature and pressure occurring during acoustic cavitation. Both hydroxide and hydrogen peroxide are powerful oxidizing agents and can aid in the degradation of cellular material. As well, the high temperature and pressure created during acoustic cavitation. Ward et al. (1999) stated the primary means of cell death during the sonication of cells suspended within an aqueous medium was due shear stresses applied to the cell membranes.

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Chapter 3   Materials and Methods

3.1   Naphthenic Acids Selected

Three different individual NAs where chosen to be investigated, as well, a synthetic solution of NAs containing numerous different NAs. These NAs were chosen for two reasons, their presence within OSPW (Holowenko et al., 2002), and that they have been extensively investigated by other researchers. The three chosen NAs are cyclohexanecarboxylic acid, *trans*-4-pentylcyclohexanecarboxylic acid, and cyclohexanepentanoic acid. NAs comprise of a wide range of compounds that are chemically and physically similar and are thus extremely difficult to analyse independently. They are a weak acid and have a pKa value of approximately 5 (Brient, 1995) and are therefore soluble in alkaline solutions. For this reason the chosen NAs were dissolved in solutions of dilute sodium hydroxide.

3.1.1   Concentration

A wide range of concentrations of NAs within OSPW has been reported by investigators, concentration values as low as 6mg/L, to as high as 130mg/L have been reported within OSPW (Grewer et al., 2010, Holowenko et al., 2002, Anderson et al., 2012). Therefore, four different concentrations were chosen to be investigated to cover the wide range of NAs observed within the OSPW. The four concentrations chosen were 20, 60, 90, and 120mg/L.

3.1.2   Cyclohexanecarboxylic Acid

Cyclohexanecarboxylic acid has the chemical formula of $C_7H_{12}O_2$ with a molecular weight of 128.17g/mol. Cyclohexanecarboxylic acid has a white crystalline appearance at room temperature and a melting point of 29-31°C, boiling point of 232-233°C, flash point of 110°C, and a density of 1.033g/cm^3 at 25°C (Sigma Aldrich, 2013a). The chemical structure of

cyclohexanecarboxylic acid may be seen in Figure 3-1. The cyclohexanecarboxylic acid used was supplied by Sigma Aldrich (St. Louis, Missouri). It has a reported purity of 98.0%.

The biodegradability of cyclohexanecarboxylic acid was investigated by Herman et al. (1994). They reported a biodegradation of 50% of cyclohexanecarboxylic acid in samples by microbial populations indigenous to oil sands tailings ponds over a 24 day period. The reported acute toxicity of cyclohexanecarboxylic acid is reported as an LD50 Oral – rat at 3 265 mg/kg (Sigma Aldrich, 2013)
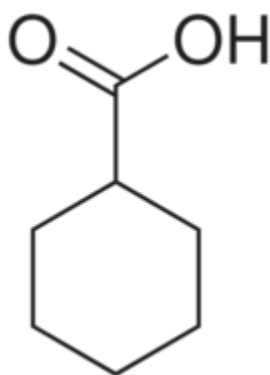
Figure 3-1: Cyclohexanecarboxylic Acid Chemical Structure (Sigma Aldrich, 2013a)

3.1.3   *Trans*-4-Pentylcyclohexanecarboxylic Acid

Trans-4-Pentylcyclohexanecarboxyilc acid has the chemical formula of $C_{12}H_{22}O_2$ with a molecular weight of 198.3 g/mol. It is in solid form at room temperature has a melting point of 51-53⁰C, and a flash point of 113⁰C (Sigma Aldrich, 2013b). Herman et al. (1994) reported the biodegradation of *trans*-4-pentylcyclohexanecarboxylic acid at values of up to 24% over a 24 day period by microbes indigenous to the oil sands region.

The *trans*-4-pentylcyclohexanecarboxylic acid used during the experiments was supplied by Sigma Aldrich (St. Louis, Missouri). It has a purity of 97%. The chemical structure of trans-4-Pentylcyclohexanecarboxylic acid may be seen in Figure 3-2.
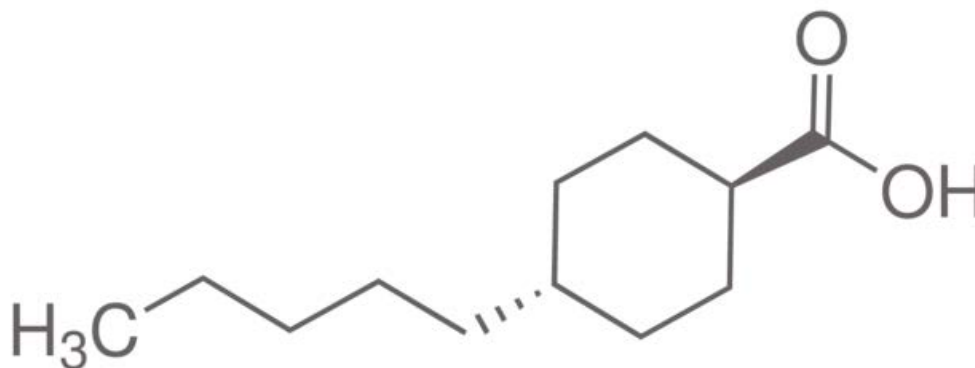
Figure 3-2: trans-4-Pentylcyclohexanecarboxylic acid Chemical Structure (Sigma Aldrich, 2013b)

3.1.4 Cyclohexanepentanoic Acid

Cyclohexanepentanoic acid has the chemical formula of $C_{11}H_{20}O_2$ with a molecular weight of 184.28g/mol. It is in liquid form at room temperature with a melting point of 16-17°C, a boiling point of 126-127°C, flash point of 113°C and a density of 0.96g/cm^3 at 20°C (Sigma Aldrich, 2013c). Cyclohexanepentanoic acid has been investigated for its biodegradability; Herman et al. (1994) reported biodegradation of up to 58% of cyclohexanepentanoic acid in samples by microbial population indigenous to oil sands tailings water over a 24 day period.

Cyclohexanepentanoic acid used for this experiment was purchased from Sigma Aldrich (St. Louis, Missouri) and the reported purity of the chemical was 98%. Its chemical structure may be seen in Figure 3-3.
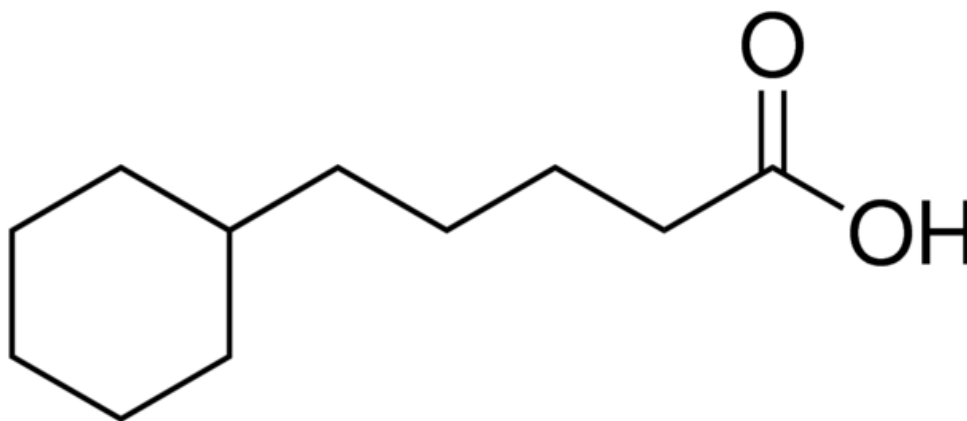
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3.1.5 Synthetic Naphthenic Acid

The synthetic mixture of NAs contains a mixture of alkylated cyclopentane carboxic acids derived from petroleum. This material was obtained from Sigma Aldrich (St. Louis, Missouri). The exact composition of the supplied synthetic NAs mixture is unknown as no detailed analysis was provided by the supplier. This mixture is in a viscous liquid form with a boiling point of 106.4 – 333.6°C at 1,013hPa, flash point of 101°C, density of 0.92 g/cm^3 at 20°C, water solubility of 0.05g/L at 20°C, and a viscosity of 22 mm^2/s at 20°C.

Herman et al. (1994) reported the biodegradation of a synthetic mixture of NAs supplied by Kodak Chemicals (New York, USA) by microbial populations indigenous to the oil sands tailings ponds over a 24 day period. A reduction of approximately 50% of initial organic carbon present was reported, as well as a reduction of toxicity after the biodegradation of NAs was also reported.

3.1.6   Feed Water Preparation

The feed water to be treated was made by spiking various concentrations of NAs into dilute

sodium hydroxide solutions. The amount of sodium hydroxide required increased with greater

mass of NAs being dissolved. This was performed by adding approximately 200mg of sodium

hydroxide pellets (purity 97.0%) supplied by Fisher Scientific (Hampton, New Hampshire) to a

1L volumetric flask. This sodium hydroxide solution was then used at volumes of 100, 150, 200,

or 250mL depending on the desired NAs concentration, corresponding to 20, 60, 90, and

120mg/L, respectively. This selected volume of dilute sodium hydroxide solution was then added

to a 1L volumetric flask with the corresponding measured mass of the chosen NAs. The

remaining volume in the volumetric flask was then filled with highly purified water.

For experimental runs requiring chloride and sulfate, sodium chloride of purity 99.0% supplied

by EM Science (Hatfield, Pennsylvania) and sodium sulfate of purity 99.0% supplied by Caledon

Laboratories (Georgetown, Ontario) was used. Solutions of approximately 5g/L of each of

chloride and sulfate was then mixed and subsequently added to the NAs solutions at appropriate

volumes.

3.1.6.1   Preparation of Synthetic Naphthenic Acid Solution

Since the exact composition of the supplied synthetic NAs material was unknown, therefore, to

achieve solutions similar in nature to that of the samples containing the three known NAs used in

this experiment the water quality parameter COD was used as a benchmark. COD values

obtained from feed water containing the three chosen NAs at total concentrations of

approximately 20, 60, 90, and 120mg/L were then used as reference values. The synthetic NAs

were added to 250mL of dilute sodium hydroxide solution (200mg/L) and 750mL of pure water

and then subsequently diluted to achieve COD values similar to that of the individual NAs.

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3.1.7 Pure Water

In attempts to minimize contamination within the produced samples, and potential effects, highly refined water was used. This water was supplied from the device Barnstead Easypure II manufactured by Thermo Scientific (Massachusetts, USA) and provides water with very low counts of particles and bacteria by means of a 0.2μm filter. The water quality parameters outlined by the manufacturer and tested in lab may be seen below in Table 3-1.

Table 3-1: Water Quality Parameters of Output Water from Barnstead Easypure II.

	Resistivity (MΩ-cm at 25°C)	Total Organic Carbon (ppb)	Bacteria (CFU/mL)	Pyrogens (EU/mL)	Measured pH	Measured Conductivity (μS/cm)
Value	18.2	5-10	<1	NA	≈6.5	0.0

3.1.8 Feed Water Characteristics

Two types of synthetic wastewater were used in this study: one with only NAs and the other with NAs and inorganic contaminates (chloride and sulfate).Prior to progressive freeze concentration tests the feed water quality parameters pH, conductivity, TS, and COD were measured. Table 3-2 lists the characteristics of the feedwater tested that contained no inorganic contaminates and Table 3-3 lists the characteristics of the feedwater containing inorganic contaminates.

Table 3-2: Characteristics of feed water samples containing no inorganic contaminates.

NA Present	Initial Total NA Concentration (mg/L)	pH	Conductivity (μs/com)	Total Solids (mg/L)	COD (mg/L)
Cyclohexanecarboxylic acid	20.43	10.35	73.50	33.10	50.07
Cyclohexanecarboxylic acid	61.13	10.20	79.20	79.98	149.14
Cyclohexanecarboxylic acid	91.41	8.76	82.70	124.70	217.35
Cyclohexanecarboxylic acid	119.97	10.25	116.80	162.63	290.60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	20.72	10.54	77.70	65.90	49.60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	59.61	10.41	85.95	85.73	154.26
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	88.70	10.55	105.60	115.90	223.60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	120.50	10.62	136.83	152.13	309.98
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	21.17	10.53	75.90	47.20	53.70
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	60.57	10.38	85.06	86.51	160.31
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	90.39	10.57	114.00	128.60	222.20
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120.48	10.54	131.53	154.05	304.84
Synthetic NA Mixture	60.00	10.61	89.85	66.90	147.40
Synthetic NA Mixture	120.00	11.00	197.35	145.03	293.02

Table 3-3: Characteristics of feed water samples containing inorganic contaminants (chloride and sulfate).

NA Present	Initial NA Concentration (mg/L)	Chloride Concentration(mg/L)	Sulfide Concentration (mg/L)	pH	Conductivity (µs/com)	TS (mg/L)	COD (mg/L)
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120.21	39.67	0.00	10.44	179.10	189.83	301.31
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120.73	503.49	0.00	10.34	1104.00	654.53	302.53
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120.31	39.67	40.68	10.47	288.00	2849.15	300.10
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120.25	503.49	508.49	10.32	OR	1386.60	302.53

3.2 Experimental Apparatus

A device was implemented to control progressive freeze concentration. It was constructed from an array of different components to provide the requirements for the implementation of progressive freeze concentration. The setup consists of a linear rail affixed to a wooden support horizontally. A linear carriage is then able to slide with ease along the y-axis of the rail. Two sets of stainless steel arms are then attached to the linear carriage which holds two stainless steel vessels for the solutions to be treated. The carriage is then connected to a planetary gearbox. This gearbox provides a constant rate of decent for the carriage and thus the stainless steel vessels. Below the vessels sits a freezing bath upon which the vessels are lowered into. The planetary gearbox is powered by a variable power supply, thus allowing for changes in the rate of decent. An ultrasound transducer and a mechanical mixer are affixed above each vessel. A detailed description of each component follows.

3.2.1 Planetary Gearbox

A planetary gearbox is a gear system that provides an extremely high gear ratio in a relatively small and simple design. It is typically composed several gears revolving around an inner gear, hence the designation planetary gearbox. A planetary gearbox set manufactured by Tamiya (Shizuoka, Japan), model number 72001, was chosen as shown in Figure 3-4.
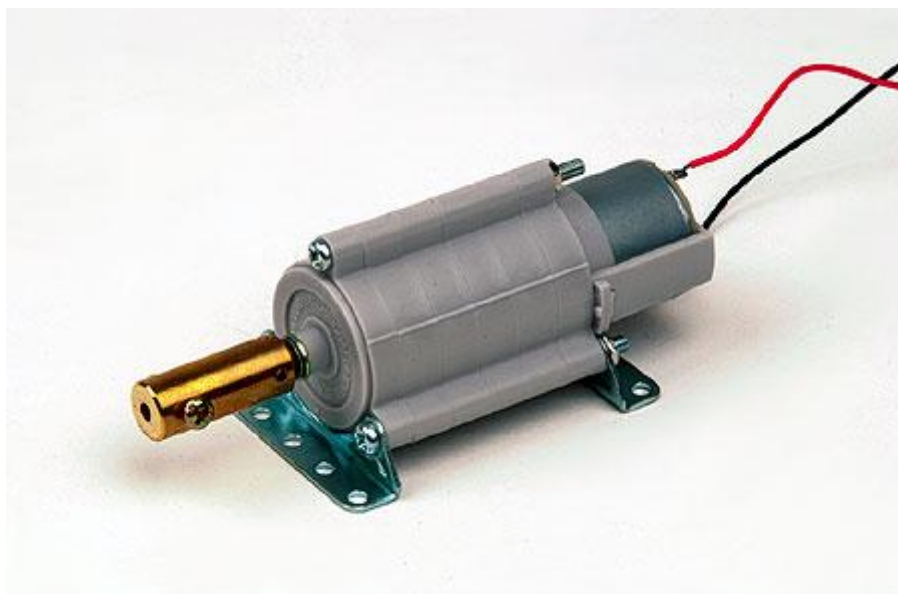
Figure 3-4: Tamiya Planetary Gearbox

Each of the kits supply two of each gear ratio stages of 4:1 and 5:2. Two kits were combined to provide a gear ratio of 160000:1. The corresponding gearbox was then powered by a supplied motor (RC-260, Mabuchi Motor, Matsudo, Japan).

3.2.2   Power Supply

The power of the RC-260 motor was provided by a variable power supply (E3611A, Hewlett Packard, California, USA) shown in Figure 3-5. This allowed for fine adjustment of the supplied voltage to the motor, thus allowing for accurate setting of the rate of lowering of the vessels into the cooling bath.

3.2.3 Freezing Bath

A Thomas Programmable Ultra-Low Refrigerating/Heating Circulator model 9712G11C manufactured by Thomas Scientific (New Jersey, USA) was implemented to provide adequate temperatures during the freezing process. This device has a temperature range of 200^0 C to -45 ^{0} C with a control stability of $\pm0.01°$C. The bath was filled with Motomaster Long-life Premixed Antifreeze with a freezing point of -33.6°C.

Figure 3-6: Thomas Programmable Ultra-Low Refigerating/Heating Circulator model 9712G11C

3.2.4 Ultrasonic Processor

During the progressive freeze concentration of the samples one means of agitation was in the form of applied ultrasonic energy. This sonication of the samples was provided using Sonics Vibra-Cell High Intensity Ultrasonic Processor model VC750 manufactured by Sonics and Materials Inc (Connecticut, USA) shown in Figure 3-7. The processor operates at a frequency of 20kHz with a maximum power output of 750W and an adjustable amplitude. A probe tip of diameter 25 mm was used.

Figure 3-7: Sonics Vibra-Cell Ultrasonic Process VC750

3.2.5 Mechanical Mixer

The other means of providing agitation during progressive freeze concentration of the samples was mechanical mixing. This was applied by means of stainless steel stirring blades within the solution powered by an electric motor. The device that supplied this purpose was a 5-Speed Rival Hand Mixer model number HM-708 manufactured by Jarden Corporation (New York, USA) shown in Figure 3-8.

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Figure 3-8: Rival 5-Speed Hand Mixer HM-708

The mixer was supplied power by a variable power supply. This was required to allow for fine adjustment of the rotational speed of the stainless steel blades that provide the mechanical mixing for the samples. A Variac Autotransformer, model number W5MT, manufactured by General Radio (Massachusetts, USA) was chosen.

The mixer and variable power supply was subsequently calibrated to provide mechanical mixing at the required levels of mixing at 100, 200, and 300 RPM corresponding to dial values on the power supply of 27.5, 33.5, and 39.5, respectively.

3.2.6 Overall Design

A diagram of the experimental setup may be seen below in Figure 3-9

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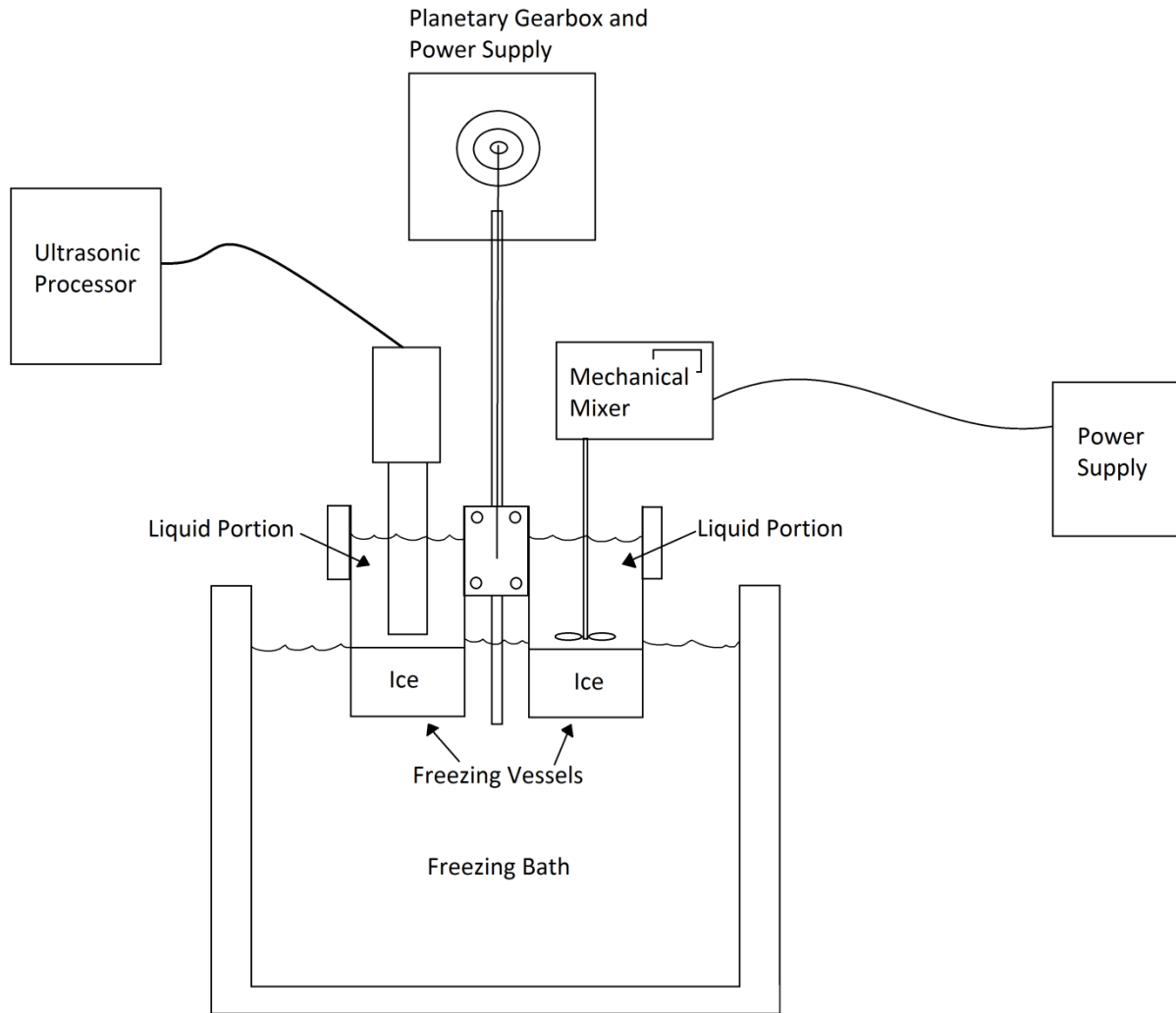
Figure 3-9: Overall Setup of Progressive Freeze Concentration Apparatus.

3.3 Experimental Design

3.3.1 Part 1: Investigation of the effects of Initial Feedwater NAs concentration, chemical nature of NAs, freezing method on the freeze separation efficiency of NAs, and partition coefficients of NAs

The ability of progressive freeze concentration to effectively separate NAs of different composition and concentration is critical for determining its potential for treatment of OSPW.

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Therefore a variety of concentrations and NAs compositions were tested which are outlined below in Table 3-4.

The partition coefficient (K) is a good gauge of the effectiveness of progressive freeze concentration as it examines the behaviour of impurities ability to incorporate or reject during the formation of ice crystals. In order to determine the partition coefficient of the selected NAs under different experimental conditions, partial freezing of the samples at 20, 40, 60, and 80% of the initial (total) sample volume were performed. This was tested for single NAs, two NAs, and three NAs solution at concentrations of both 60 and 120mg/L as outlined in Table 3-4. All of these listed conditions were tested for both mechanical and ultrasonic progressive freeze concentration. The follow conditions were set constant for the duration of part 1:

- Freezing Bath Temperature: -15°C

- Mechanical RPM: 300

- Ultrasound Cycle Time: 1s on / 10s off

- Ultrasound Amplitude: 20%

Table 3-4: Summary of experimental conditions tested for Part 1.

NAs Present	Approximate Total Initial Concentration	Level of Freezing (% of initial sample)
Cyclohexanecarboxylic acid	20	80
Cyclohexanecarboxylic acid	60	80
Cyclohexanecarboxylic acid	90	80
Cyclohexanecarboxylic acid	120	80
Cyclohexanecarboxylic acid	60	20
Cyclohexanecarboxylic acid	60	40
Cyclohexanecarboxylic acid	60	60
Cyclohexanecarboxylic acid	120	20
Cyclohexanecarboxylic acid	120	40
Cyclohexanecarboxylic acid	120	60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	20	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	60	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	90	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	120	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	60	20
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	60	40
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	60	60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	120	20
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	120	40
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	120	60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	20	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	60	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	90	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic	120	80

acid, Cyclohexanepentanoic acid		
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	60	20
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	60	40
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	60	60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120	20
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120	40
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120	60

3.3.2   Part 2: Investigation of the Effects of Initial Feedwater NAs Concentration, Freezing Method, Freezing Temperature, and Mixing Intensity

The influence of four factors on the effectiveness of progressive freeze concentration was investigated for this section. These factors include initial feedwater NAs concentration, freezing method, mixing intensity, and freezing temperature. The following levels of each of the factors was tested; two levels for initial feedwater NAs concentration (60 and 120mg/L), two levels for freezing method (mechanical and ultrasound), two levels for freezing temperature (-15, and -25°C), three levels for mechanical mixing intensity (100, 200, and 300 RPM), three levels ultrasound mixing cycle time (1s/10s, 1s/20s, and 1s/30s cycle time), and two levels for ultrasound mixing amplitude (20% and 30% amplitude). These factorials were experimentally tested in a full factorial design for a total of 24 treatment conditions because the methods mechanical and ultrasound may be run concurrently. An experimental design matrix for the method of ultrasonic progressive freeze concentration may be seen below in Table 3-5, while the design matrix for the mechanical method may be seen in Table 3-6. Each experimental condition was run in duplicate for a total of 48 runs. All experimental runs were performed on a mixture of

three NAs (Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid,

Cyclohexanepentanoic acid) and were frozen to a level of 80% of the initial volume.

Table 3-5: Full factorial design matrix for ultrasonic progressive freeze concentration.

Initial Concentration (mg/L)	Freezing Temperature (°C)	Ultrasound Off Cycle Time (s)	Ultrasound Amplitude (%)
120	-15	10	30
120	-15	10	20
120	-15	20	30
120	-15	20	20
120	-15	30	30
120	-15	30	20
120	-25	10	30
120	-25	10	20
120	-25	20	30
120	-25	20	20
120	-25	30	30
120	-25	30	20
60	-15	10	30
60	-15	10	20
60	-15	20	30
60	-15	20	20
60	-15	30	30
60	-15	30	20
60	-25	10	30
60	-25	10	20
60	-25	20	30
60	-25	20	20
60	-25	30	30
60	-25	30	20

Table 3-6: Full factorial design matrix for mechanical progressive freeze concentration.

Initial Concentration (mg/L)	Freezing Temperature (°C)	Mechanical Mixing Intensity (RPM)
120	-15	100
120	-15	200
120	-15	300
120	-25	100
120	-25	200
120	-25	300
60	-15	100
60	-15	200
60	-15	300
60	-25	100
60	-25	200
60	-25	300

3.3.3 Part 3: Investigation of the Effects of Inorganic Contaminants on Freeze Concentration of NAs and Comparison of the Removal of Synthetic NAs and 3 NAs Mixture

3.3.3.1 Effect of Synthetic NAs Solution

The exact composition of the synthetic NAs material was unknown and therefore to obtain the desired concentrations of 60 and 120mg/L a relationship between COD and dilution level with synthetic NAs solution was developed. 0.2mL of liquid synthetic NAs was dissolved in dilute sodium hydroxide solution. This solution was then further diluted to ratios of 1:2, 1:4, and 1:8, for synthetic NAs solution to water, respectively. These dilute solutions were then tested for COD which may be seen below in Figure 3-10.
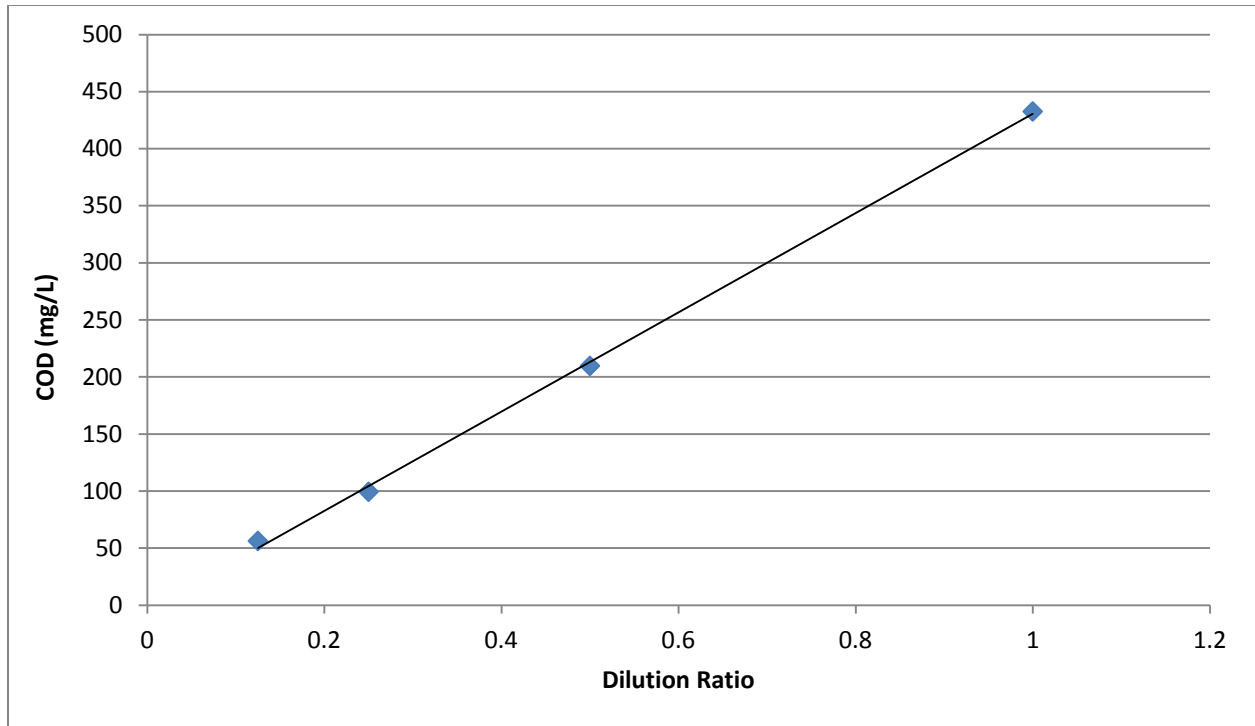
Figure 3-10: Relationship between COD and dilution of 0.2mL synthetic NAs in 1L of dilute sodium hydroxide solution.

COD values obtained at 60mg/L and 120mg/L for the previously tested NAs solutions of Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, and Cyclohexanepentanoic acid were approximately 150mg/L and 300mg/L, respectively. These COD values were used as a benchmark to get an approximate synthetic NA solution at those concentrations. The experimental factors tested in this section may be seen below in

Table 3-7. Duplicates were performed upon each experimental run.

Table 3-7: Summary of varied experimental factors for effect synthetic NAs solution

Approximate Synthetic NA Concentration (mg/L)	US Off Cycle Time (s)
60	10
60	20
120	10
120	20

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The follow factors remained constant throughout this section and were set at the follow values:

- Freezing Bath Temperature: -15°C

- Mechanical RPM: 100

- Ultrasound Amplitude: 20%

- Freezing Level: 80% of initial volume

3.3.4 Effect of Inorganic Contaminates

The influence of the inorganic contaminants chlorine and sulfate were also examined in this study. Feed water containing a three NAs mixture with two levels chloride concentration (40 and 500mg/L), as well as, feed water containing a three NAs mixture with two levels of both chloride and sulfate (40mg/L of chloride + 40mg/L of sulfate and 500mg/L of chloride and 500mg/L of sulfate) were tested. These concentrations were chosen as they represent both the high and low concentrations of these inorganic contaminates commonly found in OSPW as outlined by Allen (2008) Duplicates were performed upon each experiment. Table 3-8 outlines the factors varied during this experimental section.

Table 3-8: Summary of varied experimental factors for effect inorganic contaminates

Chloride Concentration (mg/L)	Sulfate Concentration (mg/L)	Total Inorganic Impurities Added in the Feedwater (mg/L)
40	0	40

500	0	500
40	40	80
500	500	1000

The following factors remained constant throughout this section and were set at the following values:

- NAs: Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid

- Approximate Total NAs Concentration: 120mg/L (40mg/L of each NAs)

- Freezing Bath Temperature: -15°C

- Mechanical RPM: 100

- Ultrasound Amplitude: 20%

- Freezing Level: 80% of initial volume

3.4 Progressive Freeze Concentration Tests

Two volumes of 400mL of the prepared solutions at room temperature that contained varying concentrations and identities of NAs were accurately measured in a volumetric flask and placed in the two stainless steel beakers. These beakers were then affixed to the linear rail and then at a constant rate lowered into cooling bath to be progressively frozen. The ultrasonic probe was then situated into one of the beakers and provided varying levels of ultrasonic agitation. The mechanical mixer was situated in the other beaker and provided varying levels of mechanical agitation. The required freezing time of the samples depended on the desired level of freezing with 20, 40, 60, and 80% required approximately 1.15, 2.25, 3.25, and 4.5 hours, respectively. This freezing level was approximated with markings placed on the stainless steel beakers

corresponding to 20, 40, 60, and 80% freezing level. When the freezing bath solution is in contact with those markings the test may be stopped. Upon completion, the unfrozen portion was then separated from the frozen portion. The samples were then allowed to reach room temperature and their volumes measured in a graduated cylinder for determination of exact freezing level. The ice samples were not washed with pure water after they were collected.

3.5 Sample Analysis

Samples collected from each experiment includes: the feed water sample (control), the frozen (ice) portion, and the unfrozen (liquid) portion. Four parameters were tested on each of the collected samples: chemical oxygen demand (COD), total solids (TS), conductivity, and pH. For each of the tested parameters and Standard Methods for the Examination of Water and Wastewater (AHPA, 2005) were followed.

3.5.1 COD

The closed reflux colourimetric method (2510B, AHPA, 2005) was used to determine COD during experimentation. 2 ml of sample was added to pre-made COD reagent vials supplied by CHEMetrics (Virginia, USA). Vials containing mercury (model K-7365) were implemented when chloride or sulphide was added to feed water to avoid interference while all other vials used to determine COD were mercury free (model K-7366). The vials were then heated to 150 °C in a digester block (Model COD125, Thermo Fisher Scientific Inc., Massachusetts, USA) for 2 hours. After given ample time for the vials to cool they were measured using a spectrophotometer (Model DR2800, Hach Company, Colorado, USA).

3.5.2   TS

The total solids dried 103-105°C method (2540B, AHPA, 2005) was used to determine TS during experiments. 25mL of sample were dried in an oven (Model 51221142, Precision Scientific Inc., Illinois, USA) at 103°C for 12 hours.

3.5.3   Conductivity

The conductivity was determined following procedure 2510B outlined in Standard Methods (AHPA, 2005). The conductivity meter ECTestr 11 Plus (Oakton, Illinois, USA) was used.

3.5.4   pH

The electrometric method (4500H+, AHPA, 2005) was implemented to determine the pH during the experiments. The pHTestr 30 (Oakton, Illinois, USA) was used to determine the pH of the samples.

3.6   Data Analysis

The obtained experimental results were normalized by dividing by the control values (C/Co), where C is the impurity concentration of the treated samples and Co is the impurity concentration of the feed water (control).   Analysis of variance (ANOVA) was then performed using the statistical analysis software R (R Development Core Team, 2008). Upon detection of a statistical significance the *post hoc* Tukey's HSD was implemented. A confidence interval of 95% ($\alpha = 0.05$) was applied for all statistical analysis investigations.

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Chapter 4 - Investigation of the effects of initial NAs concentration, chemical nature of NAs and freezing method on freeze concentration efficiency

This section investigates the influence of several factors upon the effectiveness of using progressive freeze concentration for the treatment of NAs in solution. The factors investigated include the type of NA present, the feed concentration of NAs, the final percent frozen of the sample, and the freezing method. Progressive freeze concentration was able to effectively concentrate/ separate NAs obtaining up to a 5 fold increase in concentration in the liquid unfrozen portion and removal rates of up to 99% in the solid frozen potion. Both the progressive freeze concentration methods ultrasound and mechanical were equally effective during experimentation.

4.1 Introduction

Canada's oil sands reserves provide a vast amount economic growth and benefit to the nation. This is not without significant undesirable environmental and health consequences (Allen, 2008). With the evidence that the development of Canada's oil sands is negatively affecting the ecosystem continuing to stack up, research into mitigation methods is ever more critical. The toxicity of oil sands process-affected water (OSPW) has been primarily attributed to the presence of Naphthenic Acids (NAs) by numerous reports (Clemente & Fedorak, 2005). NAs compose of a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids that occur naturally in crude oil (Seifert, W.K., 1975) and are solubilised into OSPW due to the caustic agents typically used in the extraction process (Clemente & Fedorak, 2005). Methods that have been previously investigated for the reduction of toxicity of NAs from OSPW include

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bioremediation (Misiti et al., 2013, Herman et al., 1994, Holowenko et al., 2000) and chemical oxidation (Perez-Estrada et al., 2011, Anderson et al., 2012, Scott et al., 2008). These methods have been proven partially successful. Oxidation has been shown to be able to reduce toxicity of OSPW, but it is selective on its ability to oxidize NA's favouring larger molecules (Perez-Estrada et al., 2011). Bioremediation has also shown to be successful as a treatment option but is burdened by its particularly slow and selective biodegradation of NA's (Clemente et al., 2004). Investigation into alternative approaches for the treatment of NAs contained with OSPW is clearly required.

Freeze concentration has shown great ability for treatment of industrial wastewater treatment such pulp mill effluent, nylon manufacturing effluent, piggery wastewater, oil sands tailings water and a variety of hazardous waste streams (Ruemekorf et al., 2000, Gao et al., 1999, Rodriguez et al., 2000, Loraine et al., 2001). Freeze concentration works through the interactions of solute and ice during the phase change of water from a liquid to solid. During freezing ice crystals are formed from pure water molecules ejecting solutes from this solid phase (Halde, 1979). Freeze concentration has been extensively researched in the food industry to result in highly concentrated and high quality food stuffs from the liquid phase (Sanchez et al., 2009). Conversely the resulting solid phase containing very low levels of solutes is one of the reasons freeze concentration is very effective for the treatment of wastewater. Gao & Shao (2009) performed freeze concentration on pharmaceutically active compounds and achieved removal rates of 84-92% for single stage unidirectional downward freezing and approximately 99% for two stage unidirectional downward freezing.

Freeze concentration is typically performed through the nucleation and growth of numerous small ice crystals. While effective the process of separating the ice crystals is particularly

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difficult and costly (Liu et al., 1998). Progressive freeze concentration eliminates this step through the growth of a single ice crystal and thus separation of concentrated liquid solution from ice is easily performed. The partition coefficient (K) is a good means to examine solute-ice interaction. As well, it is a good measure of the effectiveness of progressive freeze concentration. The partition coefficient is calculated experimentally using Equation 4 (Liu et al., 1997). Were V_L is the volume of the liquid portion, V_O is the volume of the feed water sample, C_O is the feed water concentration, and C_L is the concentration of the liquid portion.

Equation 4: Experimental calculation of effective partition constant (Liu et al., 1997).

$$(1 - K)\log \left({V_L}/{V_O} \right) = \log \left({C_O}/{C_L} \right)$$

The objectives of this study were to investigate the effectiveness of progressive freeze concentration to remove NAs in a solution/synthetic wastewater. Two different means of implementing progressive freeze concentration were tested and compared; power ultrasonic progressive freeze concentration and mechanical progressive freeze concentration. The effect of the chemical nature of NAs (single NAs, two NAs, and three NAs solutions) and concentration of NAs (20, 60, 90, and 120 mg/L) on progressive freeze concentration efficiency was examined. The partition coefficient was also experimentally determined for each of the three different NAs solutions by partial freezing at 20, 40, 60, and 80% of the initial (total) sample volume.

4.2 Materials and Methods

4.2.1 Naphthenic Acids

Three difference NAs were chosen to be investigated: cyclohexanecarboxylic acid, *Trans*-4-Pentylcyclohexanecarboxyilc, and Cyclohexanepentanoic acid. There chemical nature and characteristics are discussed below.

4.2.1.1 Cyclohexanecarboxylic Acid

The chemical formula for Cyclohexanecarboxylic acid is $C_7H_{12}O_2$. It has molecular weight of 128.17g/mol and has a white crystalline appearance at room temperature and a melting point of 29-31°C, boiling point of 232-233°C, flash point of 110°C, and a density of 1.033g/cm^3 at 25°C (Sigma Aldrich, 2013a). The cyclohexanecarboxylic acid used was supplied by Sigma Aldrich (St. Louis, Missouri). It has a reported purity of 98.0% and an acute toxicity of LD50 Oral – rat at 3 265 mg/kg (Sigma Aldrich, 2013)

4.2.1.2 Trans-4-Pentylcyclohexanecarboxylic Acid

The chemical formula of *Trans*-4-Pentylcyclohexanecarboxyilc acid is $C_{12}H_{22}O_2$. It has a molecular weight of 198.3 g/mol and is in solid form at room temperature. It has a melting point of 51-53°C and a flash point of 113°C (Sigma Aldrich, 2013b). The *trans*-4-pentylcyclohexanecarboxylic acid used during the experiments was supplied by Sigma Aldrich (St. Louis, Missouri) with a reported purity of 97%.

4.2.1.3 Cyclohexanepentanoic Acid

The chemical formula of Cyclohexanepentanoic acid is $C_{11}H_{20}O_2$. It has a molecular weight of 184.28g/mol and is in liquid form at room temperature with a melting point of 16-17°C, a boiling point of 126-127°C, flash point of 113°C and a density of 0.96g/cm^3 at 20°C (Sigma Aldrich,

2013c). Cyclohexanepentanoic acid used for this experiment was purchased from Sigma Aldrich (St. Louis, Missouri). Its purity was reported to be 98%.

4.2.2   Experimental Apparatus

The experimental apparatus designed and built to perform progressive freeze concentration consists of a linear rail attached to a wooden support system which is situated above a freezing bath. A linear carriage with two sets of arms for holding two stainless steel beakers then slides along the linear rail lowering the beakers into the cooling bath (Thomas Programmable Ultra-Low Refrigerating/Heating Circulator model 9712G11C manufactured by Thomas Scientific New Jersey, USA). The lowering rate is controlled by a planetary gearbox set manufactured by Tamiya (Shizuoka, Japan), model number 72001 which is driven by a supplied motor (RC-260, Mabuchi Motor, Matsudo, Japan). The gearbox motor is powered by a variable power supply (E3611A, Hewlett Packard, California, USA). The agitation for mechanical freeze concentration was supplied by a 5-Speed Rival Hand Mixer model number HM-708 manufactured by Jarden Corporation (New York, USA), while the agitation for the ultrasonic freeze concentration was supplied by Sonics Vibra-Cell High Intensity Ultrasonic Processor model VC750 manufactured by Sonics and Materials Inc (Connecticut, USA). The overall design may be seen below in Figure 4-1.
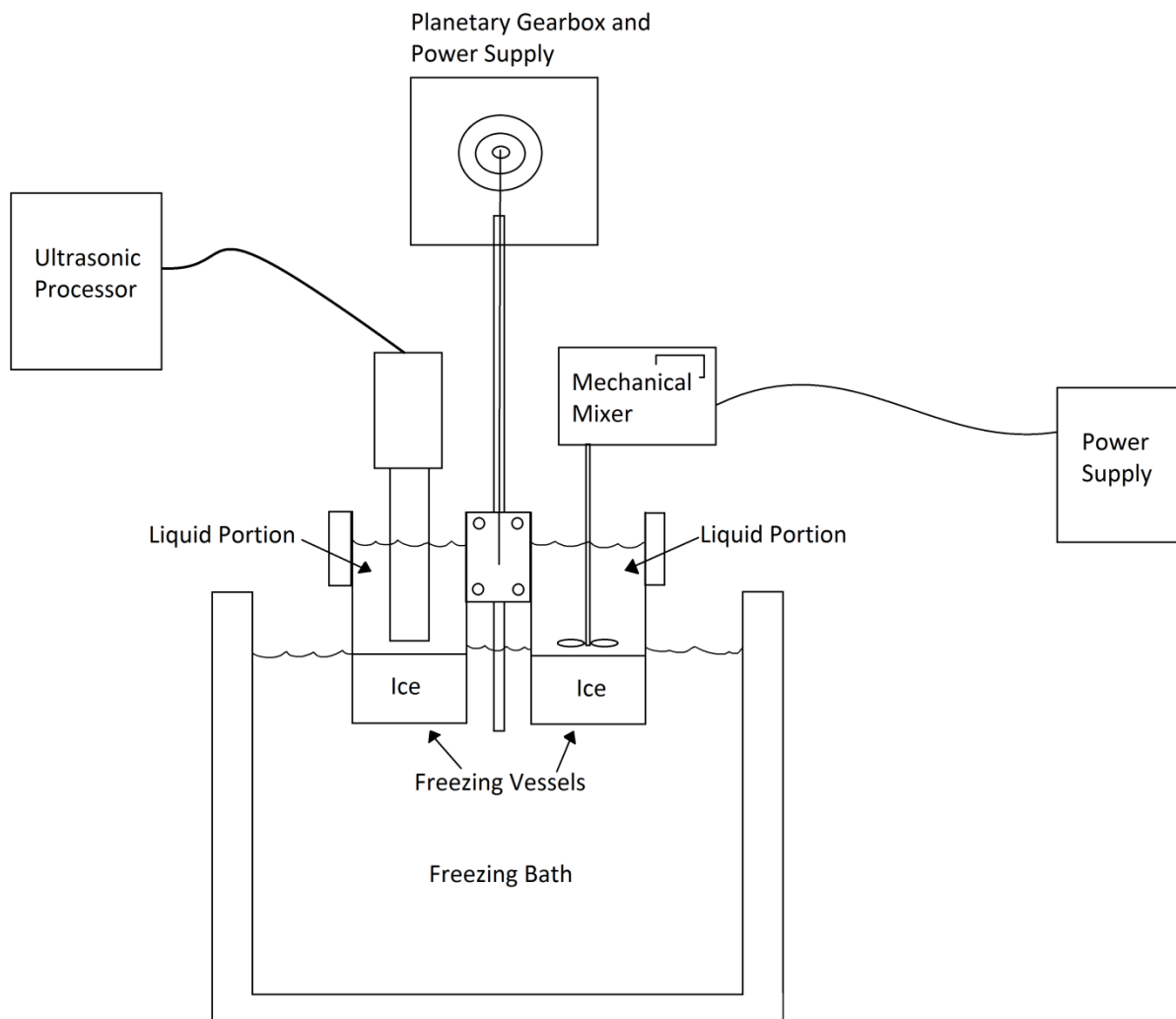
Figure 4-1: Overall Setup of Progressive Freeze Concentration Apparatus.

4.2.3 Experimental Design

Concurrent treatment of both mechanical and ultrasonic progressive freeze concentration was

performed to allow the comparison of these treatment methods. To examine the influence of the

chemical nature of NAs and progressive freeze concentration efficiency three different types of

solutions were tested. The three different mixtures were single NAs containing

cyclohexanecarboxylic acid, a two NAs mixture containing both cyclohexanecarboxylic acid and

trans-4-Pentylcyclohexanecarboxylic acid, and the three NAs solutions containing the previously

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listed NAs and cyclohexanepentanoic acid. The affect of NAs concentration on progressive freeze concentration efficiency was examined by testing each of the three listed NAs mixtures at concentrations of 20, 60, 90, and 120 mg/L.

For determination of the partition coefficient and to examine the effect of the degree of freezing on the separation efficiency of NAs feedwaters with three different NAs (single NAs, two NAs, and Three NAs solutions) and initial concentrations of 60mg/L and 120mg/L was frozen at 20, 40, 60, and 80% of the initial (total) sample volume. The following experimental parameters were kept constant throughout the experiment:

- Freezing Temperature: -15°C

- Mechanical RPM: 300

- Ultrasound Cycle Time: 1s on / 10s off

- Ultrasound Amplitude: 20%

Table 4-1 summarizes the experimental conditions tested.

Table 4-1: Summary of experimental conditions tested.

NAs Present	Approximate Total Initial Concentration	Level of Freezing (% of initial sample)
Cyclohexanecarboxylic acid	20	80
Cyclohexanecarboxylic acid	60	80
Cyclohexanecarboxylic acid	90	80
Cyclohexanecarboxylic acid	120	80
Cyclohexanecarboxylic acid	60	20
Cyclohexanecarboxylic acid	60	40
Cyclohexanecarboxylic acid	60	60
Cyclohexanecarboxylic acid	120	20
Cyclohexanecarboxylic acid	120	40
Cyclohexanecarboxylic acid	120	60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	20	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	60	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	90	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	120	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	60	20
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	60	40
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	60	60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	120	20
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	120	40
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	120	60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	20	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	60	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	90	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120	80
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	60	20
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	60	40
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	60	60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120	20
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120	40
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120	60

4.2.4   Water Sample Preparation

The samples containing NAs to be treated using progressive freeze concentration were produced

using pure water from Barnstead Easypure II manufactured by Thermo Scientific

(Massachusetts, USA). The water quality of this water may be seen below in Table 4-2.

Table 4-2: Water quality parameters of output water from barnstead easypure II.

	Resistivity (MΩ-cm at 25°C)	Total Organic Carbon (ppb)	Bacteria (CFU/mL)	Pyrogens (EU/mL)	Measured pH	Measured Conductivity (µS/cm)
Value	18.2	5-10	<1	NA	≈6.5	0.0

Sodium hydroxide was then added to make dilute sodium hydroxide solution of pH ≈ 10. This

was performed due to NAs relationship between solubility and pH, with higher values of pH

corresponding to increased solubility (Headley & McMartin, 2004). 200mg of sodium hydroxide

pellets (purity 97.0%) supplied by Fisher Scientific (Hampton, New Hampshire) was added to a

1L volumetric flask containing pure water. This sodium hydroxide solution was then used at

volumes of 100, 150, 200, or 250mL depending on the desired NAs concentration, corresponding

to 20, 60, 90, and 120mg/L, respectively. The average water quality parameters for each of the

different concentrations and present NAs used in the feed solutions may be seen below in Table

4-3.

NA Present	Initial Total NA Concentration (mg/L)	pH	Conductivity (μs/com)	TS (mg/L)	COD (mg/L)
Cyclohexanecarboxylic acid	20.43	10.35	73.50	33.10	50.07
Cyclohexanecarboxylic acid	61.13	10.20	79.20	79.98	149.14
Cyclohexanecarboxylic acid	91.41	8.76	82.70	124.70	217.35
Cyclohexanecarboxylic acid	119.97	10.25	116.80	162.63	290.60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	20.72	10.54	77.70	65.90	49.60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	59.61	10.41	85.95	85.73	154.26
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	88.70	10.55	105.60	115.90	223.60
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid	120.50	10.62	136.83	152.13	309.98
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	21.17	10.53	75.90	47.20	53.70
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	60.57	10.38	85.06	86.51	160.31
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	90.39	10.57	114.00	128.60	222.20
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120.48	10.54	131.53	154.05	304.84

4.2.5   Feed Water Characteristics

In order to determine the effectiveness of progressive freeze concentration it was important to examine the relationship between the tested water quality parameters, pH, conductivity, TS, COD and the concentration of NAs present in the sample. This relationship was examined by evaluating these water quality parameters on the sample feed water, which contains a known concentration of NAs.

4.2.5.1   Conductivity

The relationship between the concentration of NAs within solution and conductivity showed a linear correlation with a coefficient of determination values, or R^2, of 0.735. As the concentration of NAs increased, the conductivity similarly increased relatively proportionally. This relationship may be seen in Figure 4-2. This lowered R^2 value may be attributed to NAs being a weak acid (Brient, 1995). Higher concentrations of sodium hydroxide were used with increasing concentration of NAs. Therefore this difference in sodium hydroxide concentrations would also influence the conductivity.

4.2.5.2   pH

The relationship between the concentration of NAs within solution and pH showed a poor correlation. The pH of remained relatively constant with an increase in NAs concentration. This constant value of pH may be attributed to the increase quantity of sodium hydroxide added with an increase NAs concentration, thus negating any change in pH. The coefficient of determination value was very low at 4E-5. This relationship is shown in Figure 4-2.

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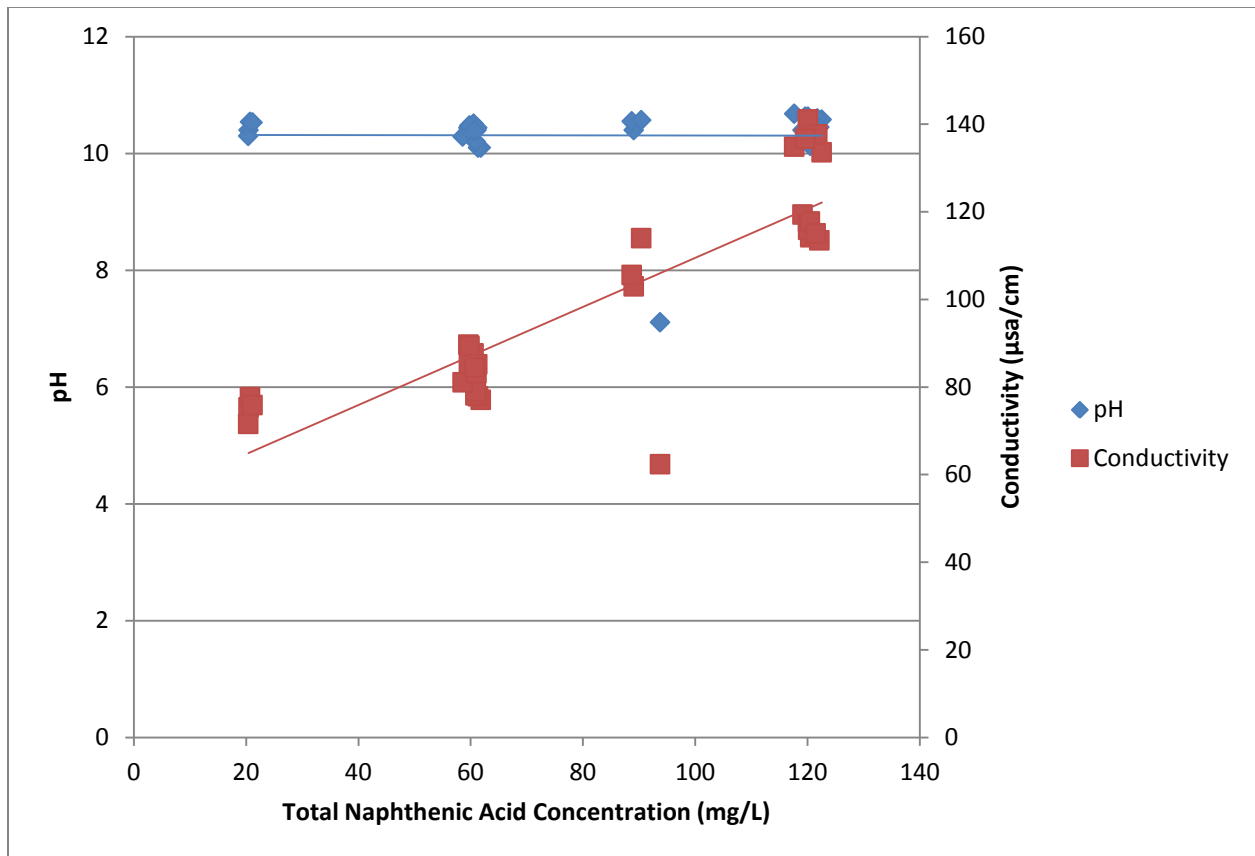
Figure 4-2: Relationship between concentration of NAs in solution and the water quality parameters pH and conductivity.

4.2.5.3   COD

As shown in Figure 4-3, the relationship between COD and the concentration of NAs within solution displayed a strong relationship. An increase in NAs concentration corresponded with an increase in COD with a R^2 of 0.9935. The strong linear correlation between COD and the concentration of NAs suggest that COD, a routine water quality monitoring parameter could be used to represent the concentration of NAs in oil sands tailings water.

4.2.5.4   TS

The relationship between TS and the concentration of NAs within solution showed a good relationship. An increase in NAs concentration related to an increase in TS. This decent

correlation was shown with a coefficient of determination value of 0.9145. This relationship may be seen in Figure 4-3.

4.2.5.5 Comparison of Water Quality Parameters

The water quality parameters COD, TS, and conductivity displayed a decreasing relationship between total NAs concentration with R^2 values of 0.9935, 0.9145, and 0.735, respectively. This reduction in correlation TS and conductivity may be attributed to the addition of sodium hydroxide in the feed water at increasing quantities with an increase in total NAs concentration. Since COD is a measure of the chemically oxidizable organic material it is not influenced by the concentration of sodium hydroxide and thus gives a more accurate representation of the NAs within solution compared to the other parameters.

4.2.6   Experimental Design

In order to determine the influence of concentration on the effectiveness of progressive freeze concentration, four different concentrations of NAs were chosen to be tested. These chosen concentrations correspond to values that have been reported within OSPW (Allen, 2008). 120mg/L was chosen due to it being at the high end of reported values, while 20mg/L was chosen due to it being at the low end of reported NAs concentration, while two intermediate values were chosen at 60mg/L and 90 mg/L.

Three different individual NAs were chosen to investigate the ability of progressive freeze concentration to treat and the effect of individual NAs. The three chosen NAs include cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic acid, and cyclohexanepentanoic acid. Three different solutions were used, one containing cyclohexanecarboxylic acid, another containing both cyclohexanecarboxylic acid and tran-4penylcyclohexanecarboxylic acid, and the third containing all three of the chosen NAs.

The influence of the percentage of freezing of the samples was also investigated. This is an important factor because as the sample begins to progressively freeze the unfrozen portion becomes increasingly concentrated with NAs. An increase in concentration of contaminants increases that chance for solute incorporation into the frozen portion (Pradistsuwana et al., 2003). This can lead to decreased effectiveness of the process. There frozen levels of 20%, 40%, 60% and 80% were tested.

4.2.7   Freezing Experiments

Feed water samples were treated using a device that performs progressive freeze concentration in a batch process. Two volumes of 400ml at room temperature were placed within separate 600ml

stainless steel beakers. The beakers were then lowered, at a constant rate, into a cooling bath set at a temperature -15°C. The solutions were concurrently agitated by two methods, pulsed ultrasound and mechanical mixing. The pulsed ultrasound was set at an interval of 1 second applied sonication and 10 seconds off sonication, while the mechanical agitation was applied at 300 RPM. After treatment, the unfrozen portion was separated from the ice portion. The ice portion was allowed to thaw and then both portions were measured volumetrically to determine the percentage of the sample that was frozen during trial. The ice surface was not washed with pure water after the ice samples were collected.

4.2.8 Chemical Analysis

Feed water (control) samples, ice samples and unfrozen liquid samples were collected from each experiment. The water quality parameters such as pH, conductivity, total solids (TS), and chemical oxygen demand (COD) were measured following the procedures outlined in the Standard Methods for Examination of Water and Wastewater (APHA, 2005).

4.2.9 Data Analysis

The obtained data of the water quality parameters for each sample run were normalized by dividing by the control values, the feed stream. Values obtained that were below detectable limits of the test methods used where set at zero. This was to allow for testing of statistical significance between the tested factors. Statistical significance between tested factors was calculated using the statistical program R (R Development Core Team, 2013). Statistical significance was detected using analysis of variance (ANOVA). Upon the detection of a significant difference the

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post hoc analysis Tukey's HSD test was performed to determine which level of factor was significantly different. A confidence interval of 95% was chosen for statistical analysis.

4.3 Results and Discussion

The ability of progressive freeze concentration to treat different NAs in solution at various levels of concentrations common to OSPW as well as at varying levels of freezing was determined by measuring pH, conductivity, TS, and COD of the contaminated feed water for the unfrozen and frozen portions. The freezing methods ultrasound and mechanical were also investigated. The experimental results and discussed below.

4.3.1 Effect of the Degree of Freezing on the Separation Efficiency of NAs

The effect of the degree of freezing, that is, the portion (%) of the total volume of the feed water turned into ice during a freezing test on NAs separation efficiency was examined.

4.3.1.1 The Impurity Concentrations in the Unfrozen Liquid vs. the Degree of Freezing

The capacity of freeze concentration of NAs in the unfrozen liquid is noted by a marked increase in COD concentration in the liquid samples. As illustrated in Figure 4-4, when freezing of the feed water proceeded from 20%, 40%, 60%, and to 80% of the initial volume, the COD concentration in the unfrozen liquid increased from 1.26, 1.60, 2.35, and 4.60 times of that in the feed water, respectively. This difference in the COD concentration between the unfrozen liquid and the control (feed water) were statistically significant after 20%, 40%, 60%, and 80% (p = 3.90E-7, 0.00E-7, 0.00E-7, and 0.00E-7 respectively). The fact that the unfrozen liquid contained 4.6 times the NAs than that in the feed water after freezing at approximately 80% of the feed water clearly demonstrates the capability of the freeze concentration process. These obvious increases in COD concentration in the unfrozen liquid when the degree of freezing increased

from 20% to 40%, 40% to 60%, and 60% to 80% were also statistically significant (p = 1.93E-8, 0.00E-7, 0.00E-7, and 0.00E-7 respectively).

The concentration of TS in the unfrozen liquid displayed similar trends as that of COD. The unfrozen liquid had 1.28, 1.59, 2.42, and 4.70 times of solids than that in the control samples when it was frozen at 20%, 40%, 60%, and 80%, respectively. This increase in the concentration of solids over the feed water was deemed statistically significant in all degrees of freezing (p = 2.54E-2, 0.00E-7, 0.00E-7, and 0.0E-7 for 20%, 40%, 60% and 80%, respectively). The increase in solids between the degree of freezing 20% and 40% was deemed insignificant (p = 0.0865), but the increase between 40% and 60%, 60% and 80% was deemed significant (p = 0.00E-7, 0.00E-7, respectively).

Conductivity showed a similar pattern as TS and COD, with an increase in conductivity ratios corresponding to an increase in the degree of freezing, with increases of 1.03, 1.25, 1.86, and 3.50 corresponding to 20%, 40%, 60%, and 80%, respectively. As apparent, the increase of conductivity ratios over the control at 20% was not significant (p = 0.992) but the remaining increases were calculated to be significant (p = 1.22E-3, 0.00E-7, and 0.00E-7 for 40%, 60%, and 80%, respectively). Similar to TS, the increase in conductivity ratio between 20% and 40% was not significant (p = 0.0596). As well, the increase from 40% to 60% and 60% to 80% was significant (p = 0.00E-7 and 0.00E-7, respectively).

The water parameter pH deviated from this pattern shown in COD, TS, and conductivity and decreased compared to that of the feed water. The pH ratios decreased with increasing levels of freezing at 0.957, 0.938, 0.923, and 0.927 for freezing levels of 20%, 40%, 60%, and 80% respectively. This reduction in pH values over the control were deemed statistically significant (p

= 4.77E-3, 5.30E-6, 0.00E-7, and 0.00E-7 for 20%, 40%, 60%, and 80%, respectively) but the decrease of pH ratios between the freezing levels was not significant (p >0.05 Table 0-28)

This reduction in pH values may be attributed to the diffusion of CO_2 into solution over the course of the experiment resulting in a reduction of pH through the formation of carbonates (Olutoye & Mohammed, 2006). Greater degrees of freezing levels also resulted in lower levels of pH ratios; this can be explained as higher levels of freezing required more time, thus allowing more time for diffusion of CO_2 into solution. These results may be seen below in Figure 4-4. Workman & Reynolds (1950) in contrast, noted in increase in pH in an unfrozen sample (7.0) compared to the frozen sample (6.2) and original pH (6.3) during the partial freezing of sodium chloride solutions. They attributed this change to the partial incorporation of chloride ions into the ice and the rejection of sodium ions resulting in the formation of sodium hydroxide, thus increasing the pH. Although, this experiment was performed in a atmosphere controlled setting using helium to avoid the interactions of carbon dioxide.
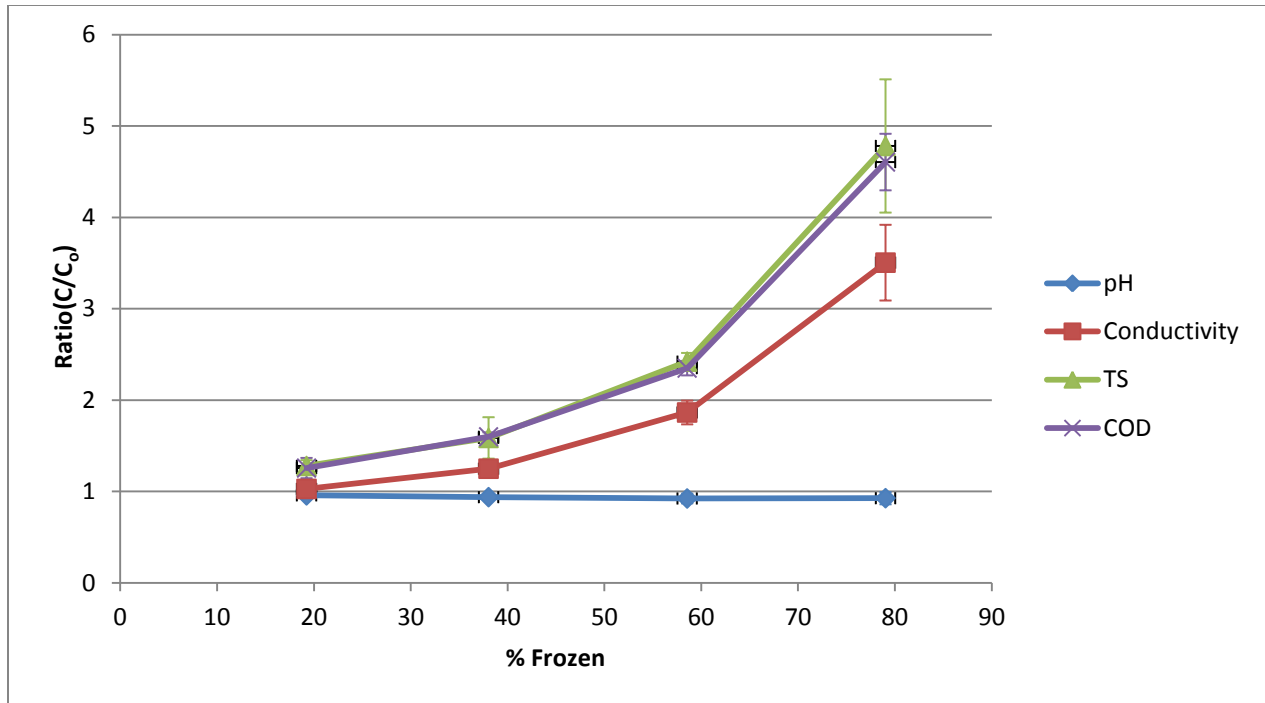
Figure 4-4: Effect of percent frozen on the water quality parameters pH, TS, conductivity, and COD for the liquid portion of progressive freeze concentration of NA solutions (Three different feed water solutions containing cyclohexanecarboxylic acid at 61.13mg/L and 119.97mg/L, cyclohexanecarboxylic acid and trans-4-pentylcyclohexanecarboxylic at 59.61mg/L and 120.50mg/L, and cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.57mg/L and 120.48mg/L).

This increase in ratios for the water quality parameters COD, TS, and conductivity with an increase in percent frozen values show that the NAs in solutions are effectively being concentrated in the liquid phase and thus being rejected in the solid phase. This pattern is similar to published values; Liu et al. (1999) observed an increase in concentration as high as 4.37 compared to the feed water when progressively freezing solutions of tomato juice.

4.3.1.2 *Impurity Concentration in Ice Samples*

Samples frozen at 20%, 40%, 60%, and 80% all reported very low values of NAs within the solid portion of samples. This was shown in the COD ratios of the frozen portion at levels of 0.0343, 0.0184, 0.0194, and 0.0204 at frozen levels of 20%, 40%, 60%, and 80%, respectively. This reduced COD ratios determined % removal rates of NAs in the ice samples of 96.6%, 98.2%, 98.1%, and 98.0%. The decrease of impurity concentration in ice samples compared to the feed

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water was statistically significant (p = 0.00E-7 for 20%, 40%, 60%, and 80%). Although 20% displayed a slightly higher concentration in the frozen portion compared to those with higher degree of freezing, this difference was determined to be statistically insignificant (Table 0-43).

TS concentration data also pointed to low levels of NAs within the solid portion of the samples. TS ratios were 0.0232, 0.0223, 0.0225, and 0.0760 for frozen levels (removal rates of 97.7%, 97.8%, 97.7%, and 92.4%) at 20%, 40%, 60%, and 80%, respectively. All of these reductions were statistically significant compared to that of the feed water (Table 0-46). As shown, there is a significant reduction in the removal of NAs at a freezing level of 80% compared to lower levels of freezing: 60%, 40%, and 20% (p = 3.59E-3, 3.86E-3, and 4.35E-3). The reported increase of TS within the frozen portion at 80% compared to lower freezing levels suggest that there is an increase in contaminates being incorporated within the frozen portion. When the freezing reached 80% of the initial feedwater volume more impurities were rejected and concentrated in the unfrozen liquid. Rejection of impurities from the advancing ice front becomes less effective with higher concentrations of contaminates (Matsuda et al., 1999).

Conductivity similarly reported lower levels of NAs in the solid portion at ratios of 0.0172, 0.0102, 0.0120, and 0.0233 (removal rates of 98.2%, 99.0%, 98.8%, and 97.7%) for frozen levels at 20%, 40%, 60%, and 80%, respectively. When comparing to the feed water, these reductions were determined to be significant (P values as indicated in Table 0-49 of Appendix). There was no reported significant differences for contaminate level in the solid port amongst the varying freezing levels (P values as indicated in Table 0-49 of Appendix).

The pH values of the solid portion were reduced compared to that of the feed water obtaining values close to neutral pH at ratios of 0.633, 0.611, 0.616, and 0.636 for frozen levels of 20%,

40%, 60%, and 80%, respectively with the reported change being statistically significant ($p =$ 0.00E-7, 0.00E-7, 0.00E-7, and 0.00E-7, respectively). The reduction in pH of the solid portion during all freezing levels to approximately neutral compared to the alkaline feed water further suggests that contaminates are largely being eliminated from the treated water. These results may be seen in Table 4-4.

Table 4-4: Effect of degree of freezing on the reduction of impurity content in the ice samples.

	% Frozen			
Water Quality Parameter	19.25	38.05	58.56	79.05
pH/pH_o	0.633+/−0.0143	0.611+/−0.0172	0.616+/−0.0156	0.636+/−0.0810
Conductivity/Conductivity$_o$ (% Removal)	0.0172+/−0.00535 (98.2%)	0.0102+/−0.00175 (99.0%)	0.0120+/−0.00693 (98.8%)	0.0233+/−0.0429 (97.7%)
TS/TS$_o$ (% Removal)	0.0232+/−0.0378 (97.7%)	0.0223+/−0.0391 (97.8%)	0.0225+/−0.0338 (97.7%)	0.0760+/−0.0652 (92.4%)
COD/COD$_o$ (% Removal)	0.0343+/−0.0157 (96.6%)	0.0184+/−0.0145 (98.2%)	0.0194+/−0.0140 (98.1%)	0.0204+/−0.0258 (98.0%)

4.3.2 Influence of Freezing Methods on Removal of NAs

Two methods of providing agitation within the liquid were implemented during progressive freeze concentration, ultrasonic and mechanical. The preceding section will investigate the influence of the freezing method.

4.3.2.1 Concentration of Impurities in Unfrozen Liquid
Both methods of applying agitation during the freezing process were effective in concentrating the NAs into the liquid portion. The experimental results revealed that, both ultrasound and mechanical agitation resulted in a large increase in concentration of COD over the control at ratios of 2.97 and 3.06, respectively. This approximate 3 fold increase in both cases was significantly different when comparing them to the feed water ($p =$ 0.00E-7, 0.00E-7). As well, the concentration ratios obtained from freezing with mechanical mixing and power ultrasonic

freezing indicated there was no noticeable different between the two freezing methods in terms of their freeze concentration (p = 0.990).

There was also a large significant increase in solids concentration for freezing methods ultrasound and mechanical over the control at 3.11 and 3.15, respectively (p = 0.00E-7, 0.00E-7). There was no detectable significant difference among the two tested methods in terms of the concentration of solids (0.986).

Similarly, conductivity reported an increase in concentration over the feed water at 2.39 and 2.30 for freezing methods ultrasound and mechanical, respectively. This increase in concentration over the feed water was significant (p = 0.00E-7, 0.00E-7). Similarly to COD and TS there was no detectable difference between the efficacy of the freezing methods (p = 0.908).

The water parameter pH for both ultrasound and mechanical freezing was reduced compared to that of the feed water at ratios of 0.954 and 0.913, respectively. The reported pH reduction was deemed statistically significant compared to the control (p = 1.00E-8, 0.00E-7 for ultrasound and mechanical, respectively). As well, the greater reduction of pH ratios for mechanical freezing compared to ultrasound freezing was deemed significant (p = 2.34E-5). The reason for this difference in pH change may be a result of the previously stated diffusion of CO_2 into solution (Olutoye & Mohammed, 2006). The mechanical method of freezing provides enhancement of convective mass transfer as the solution is being stirred continuously in contrast to the ultrasonic method which is being provided intermittent agitation. These preceding results are shown below in Figure 4-5.
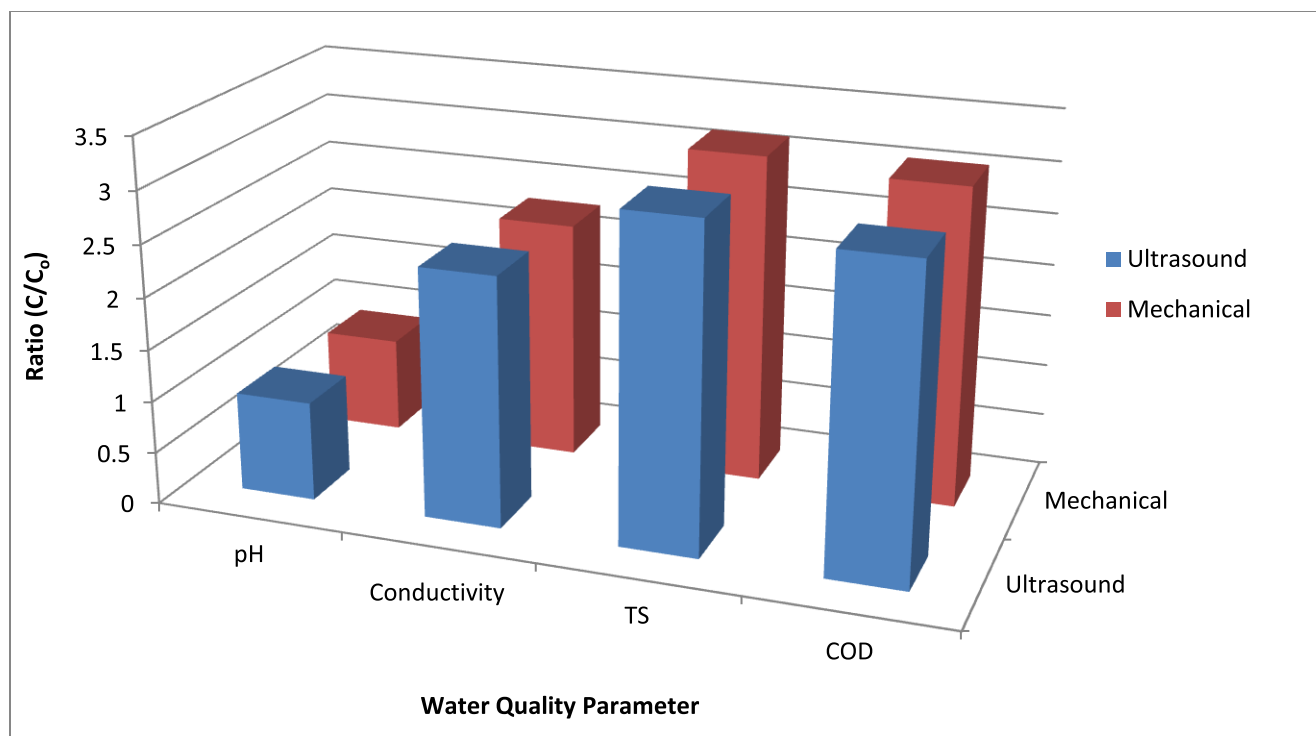
Figure 4-5: Effect of freezing method on the water quality parameters TS, conductivity, and COD for the liquid portion of progressive freeze concentration of NA solutions (for three different feed water solutions containing cyclohexanecarboxylic acid at 20.43mg/L, 61.13mg/L, 91.41mg/L, and 119.97mg/L, cyclohexanecarboxylic acid and trans-4-pentylcyclohexanecarboxylic at 20.72mg/L, 59.61mg/L, 88.70mg/L, and 120.50mg/L, and cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 21.17mg/L, 60.57mg/L, 90.39mg/L, 120.48mg/L).

4.3.2.2   *Impurity Concentration in Ice Samples*

The tested progressive freeze concentration methods, ultrasound and mechanical, provided a high degree of NAs removal from that of the solid phase. Both methods achieved similar markedly lower values of conductivity in the frozen portion. TS also reported a similar reduction compared to that of the control at ratios of 0.0475 and 0.0463 for ultrasound and mechanical, respectively. The COD of the solid portion, as well, was reduced to ratios of 0.0232 for ultrasound and 0.216 for mechanical. The pH was lowered to values of 0.6270 and 0.6278 for methods ultrasound and mechanical, respectively. All of these markedly reduced values of water the quality parameters in the frozen portion compared to that of the feed water were statistically significant (Table 0-42, Table 0-45, Table 0-48, Table 0-51). These results are shown in Table 4-5.

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Table 4-5: Effect of freezing methods on impurity removal in ice samples.

Water Quality Parameter	Method	
	Ultrasound	Mechanical
pH/pH_o	0.627+/−0.0544	0.628+/−0.0589
Conductivity/Conductivity$_o$ (% Removal)	0.0138+/−0.0135 (98.6%)	0.0217+/−0.0393 (97.8%)
TS/Ts$_o$ (% Removal)	0.0475+/−0.0580 (95.3%)	0.0463+/−0.0579 (95.4%)
COD/COD$_o$ (%Removal)	0.0232+/−0.0190 (97.7%)	0.0216+/−0.0230 (97.8%)

As summarized in Table 4-5, the average impurity removal efficiency in the ice samples

produced using ultrasonic methods was between 95% to 99% and the mechanical freezing

method achieved very similar level of impurity removal in the ice samples (95%-98%). As

shown there was no detectable difference in the efficiency of these methods (Table 0-42, Table

0-45, Table 0-48, Table 0-51).

4.3.3 Effect of Chemical Nature of Naphthenic Acids on Freeze Concentration Efficiency

4.3.3.1 Unfrozen Liquid Samples

Feed water with a single NA or a mixture of NAs was examined to see if the chemical nature of

the NAs affects the freeze concentration efficiency. The feed waters used in the freeze

concentration tests are: a single NA solution containing cyclohexanecarboxylic acid, the two

NAs mixture solution containing cyclohexanecarboxylic acid and trans-4-

pentylcyclohexanecarboxylic acid, and the three NAs mixture containing

cyclohexanecaroboxylic acid, trans-4-pentylcyclohexanecarboxylic acid, and

cyclohexanepentanoic acid. As shown in Figure 4-6, the concentration ratio of all chemical

parameters examined were are at approximately the same level, not matter if the feed water was

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spiked with single, double, or three acid mixture. This was shown statistically with no difference among the tested solutions ability to concentrate NAs being reported (Table 0-7, Table 0-10, Table 0-13, and Table 0-16 in Appendix) except for pH between the single and three NAs mixtures (p = 0.0121).

The progressive freeze concentration process was able to effectively increase the concentration of all three types of tested NAs solutions within the liquid portion. COD concentration in the liquid portion were increased by 4.53, 4.69, and 4.64 times compared to that of the control samples for solutions single, two, and three NAs solutions, respectively. This approximately 4.5 fold increase is significant over the feed water (p = 0.00E-7, 0.00E-7, and 0.00E-7).

TS concentration in the unfrozen liquid with different NAs displayed comparable results with a ratio of 4.99, 4.60, and 4.60 for the single, two, and three NAs solutions, respectively. Again, this increase in solids concentration over the control was deemed significant (p = 0.00E-7, 0.00E-7, and 0.00E-7).

Conductivity levels obtained displayed similar results with ratios of 3.61, 3.45, and 3.37 for single, two, and three NAs solutions, respectively. These values were statistically significant compared to that of the feed water (0.00E-7, 0.00E-7, and 0.00E-7).

pH values of the liquid samples were all lower than that of the feed water with pH ratios 0.907, 0.920, and 0.967 for single, two, and three NAs solutions, respectively. This noteworthy decrease in pH values was only significant for single and two NAs solutions but not for the three NAs solution (p = 4.00E-7, 2.75E-4, and 0.287). This phenomenon associated with a decrease in pH was noted and explained previously. The reason for lack of significant reduction of pH in the three NAs is unknown but perhaps may be due to the addition of cyclohexanepentanoic acid and

its interactions during the progressive freeze concentration process. These aforementioned results may be seen below in Figure 4-6.
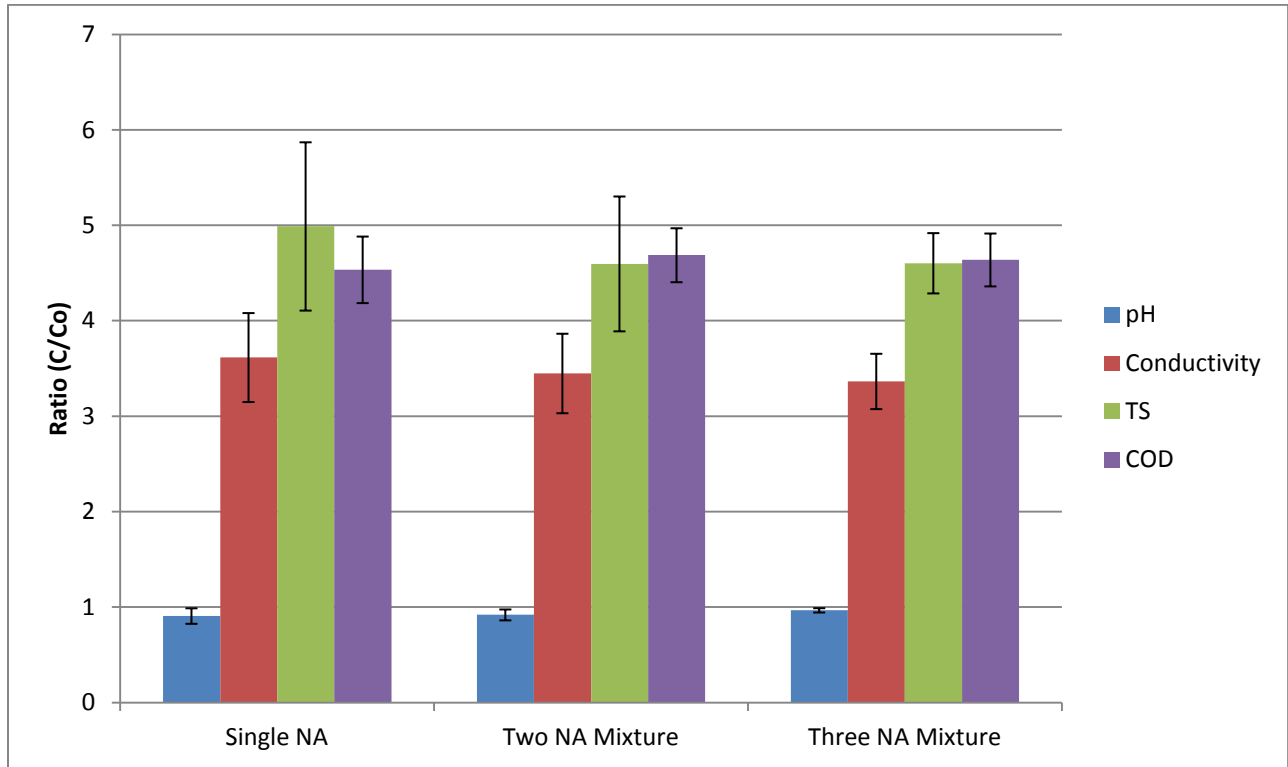
Figure 4-6: Effect of type of NAs present in feed solution on the water quality parameters pH, TS, conductivity, COD for the liquid portion of the progressive freeze concentration of NA solutions (Single NA mixture = cyclohexanecarboxylic acid at 20.43mg/L, 61.13mg/L, 91.41mg/L, and 119.97mg/L, Two NA Mixture = cyclohexanecarboxylic acid and trans-4-pentylcyclohexanecarboxylic at 20.72mg/L, 59.61mg/L, 88.70mg/L, and 120.50mg/L, Three NA Mixture = cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 21.17mg/L, 60.57mg/L, 90.39mg/L, 120.48mg/L).

4.3.3.2   Solid Portion

Progressive freeze concentration was able to effectively reduce the concentration of NAs in the ice for feedwater containing the previously listed combinations of NAs. For COD concentration a 98.9% reduction (or $C/C_o = 0.0108$) for the single NAs (cyclohexanecarboxylic acid), 96.9% reduction ($C/C_o = 0.0315$) for the two NAs mixture (cyclohexanecarboxylic acid and trans-4-pentylcyclohexane), and a 97.2% reduction ($C/C_o = 0.0279$) for the three NAs mixture (cyclohexanecarboxylic acid, trans-4-pentylcyclohexane, and cyclohexanepentanoic acid) was obtained. These high removal rates were significantly different compared to that of the control

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(Table 0-31 in Appendix). As well, there was no noticeable influence on the removal rates from the three different feedwaters tested (p = 0.0898, 0.0984, and 0.198, for single NAs to two NAs, two NAs to three NAs, and single NAs to three NAs, respectively). This suggests that the chemical nature of NAs was not a factor that influenced the freeze separation/ concentration of NAs.

A significant reduction in solids (TS) concentration over the feed water was observed in all ice samples, regardless if there was only one acid, or mixtures of two or three acids (p = 0.00E-7, 0.00E-7, 0.00E-7). The concentration ratios were 0.0963, 0.0468, and 0.0837 for single, two NAs, and three NAs mixtures, respectively, which corresponded to a 90.4%, 95.3%, and 91.6% reduction of TS concentration in the ice samples. This increase in removal rates for the two NAs mixture compared to the single and three NAs mixtures is noteworthy at a significance level between two NAs mixture and three NAs mixture (p = 0.0352). It was not significant between the single NA and three NAs mixture, perhaps due to the single NA high standard deviation (p = 0.133). This difference in TS reduction may be attributed progressive freeze concentrations ability to concentrate different molecules. Matsuda et al. (1999) reported differing levels of effectiveness of concentrating impurities based on the present molecules, with molecules of larger molecule weight being more easily removed from the solid phase. This was also suggested in Halde (1980), who points out that smaller particles are more likely to be entrapped in an advancing ice front.

Conductivity also reported reduced levels of NAs within the solid portion at ratios of 0.0427 (removal rate of 95.7%), 0.00839 (99.2%), and 0.00809 (99.2%) for single, two, and three NAs mixtures. These reductions were significant over the feed water (p = 0.00E-7, 0.00E-7, and 0.00E-7, respectively). This obvious reduction between the single NA solution and the two and

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three NAs mixtures was significant (p = 0.0431 and 0.0401). This further suggests that the chemical nature of cyclohexanecarboxylic acid is having an influence on the efficacy of progressive freeze concentration. This may perhaps be a result of the smaller molecular size as pointed out by Halde (1980) and Matsuda et al. (1999). These results may be seen below in Figure 4-7.
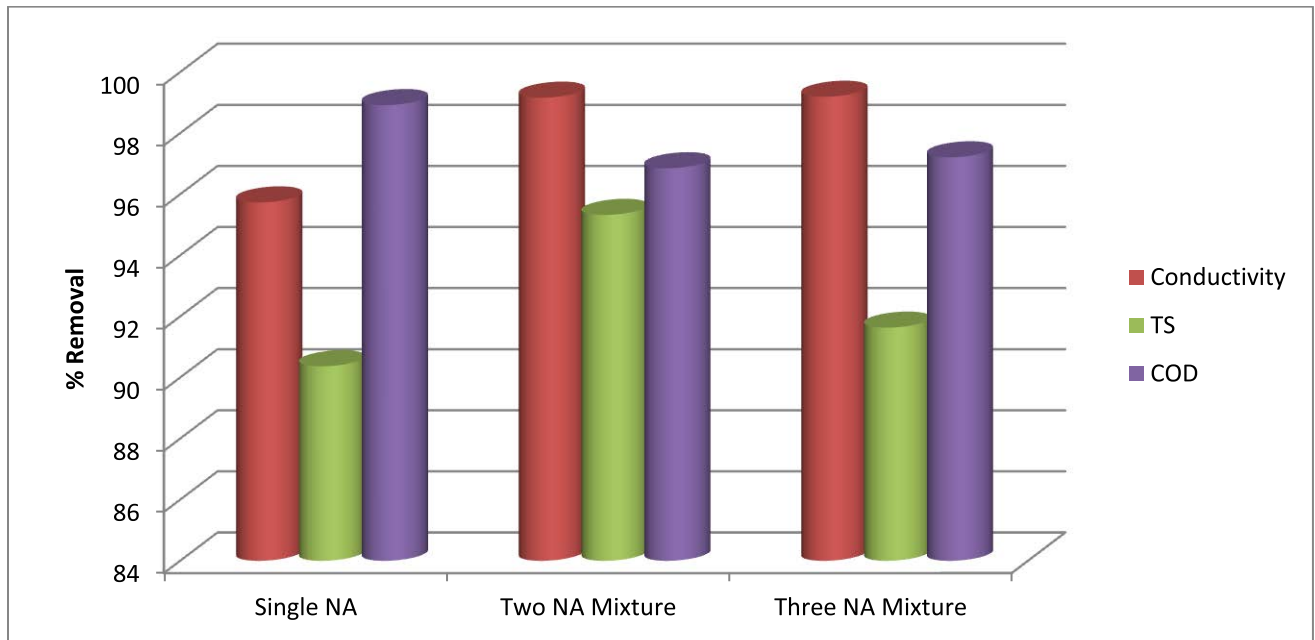
Figure 4-7: Effect of type of NAs present in the feed solution on the removal rate calculated from water quality parameters TS, conductivity, and COD for the solid portion of the progressive freeze concentration of NA solutions (Single NA mixture = cyclohexanecarboxylic acid at 20.43mg/L, 61.13mg/L, 91.41mg/L, and 119.97mg/L, Two NA Mixture = cyclohexanecarboxylic acid and trans-4-pentylcyclohexanecarboxylic at 20.72mg/L, 59.61mg/L, 88.70mg/L, and 120.50mg/L, Three NA Mixture = cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 21.17mg/L, 60.57mg/L, 90.39mg/L, 120.48mg/L).

The water quality parameter pH detected a notable reduction from the feed water after treatment (p = 0.00E-7, 0.00E-7, 0.00E-7) for the single, two, and three NAs mixtures at ratios of 0.682, 0.594, and 0.608, respectively. The greater decrease of pH values for two and three NAs mixtures is noteworthy (p = 6.61E-4 and 4.69E-3, respectively). This further suggests that the chemical nature of NAs does have an influence on the efficiency of rejection of solutes during treatment.

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4.3.4   Effect of the Initial Naphthenic Acid Concentration in Feed Water

4.3.4.1   Liquid Portion

The experimental results for the liquid portion indicated that the initial NAs concentration in the feed water did no influence the capacity of freeze concentration to remove NAs. For example, COD concentrations in the unfrozen liquid resulted in ratios of 4.80, 4.49, 4.60, and 4.54 when feed water was spiked with 20, 60, 90, and 120 mg/L of NAs, respectively. These concentration ratios were not statistically different amongst each other but were reported different when compared to that of the control (Appendix, Table 0-6).

TS exhibited similar pattern of high concentration of NAs in the liquid portion. Ratios of 5.09, 4.60, 4.58, and 4.87 for concentrations of 20, 60, 90, and 120 mg/L were reported, respectively. Similarly to COD, an increase in concentration did not reduce the ability to freeze concentrate NAs and result in approximately 4.5 to 5 fold increase in solids over the control (Appendix, Table 0-9).

In contrast, conductivity reported an increase in conductivity ratios with an increase in concentration of NAs in the feed water. Values of 3.13, 3.40, 3.81, and 3.74 corresponded to NAs feed concentration values of 20, 60, 90, and 120 mg/L, respectively. This difference was reported to be significant between the concentrations of 20 and 90, 20 and 120 mg/L, and 60 and 90mg/L (p = 4.00E-6, 1.05E-4, and 5.02E-3). This increase in conductivity corresponding to an increase in initial NAs concentration may be due a non linear relationship between ion concentration and conductivity. McNeil & Cox (2000) report that conductivity does not give a precise representation of total dissolved ions. Although it must be noted that the greater than 3 fold increase in conductivity for all concentrations was reported to be significant in comparison to the feed water (Appendix, Table 0-12).

The water quality parameter pH decreased as a result of progressive freeze concentration resulting in ratios of 0.962, 0.879, 0.929, and 0.939 corresponding to NAs feed concentration of 20, 60, 90, and 120mg/L. This reduction in pH from the feed water values is significant except at NAs feed water concentration of 20mg/L (Appendix, Table 0-15). As well, the difference in reduction of pH between NAs feed concentration of 20mg/L and 60mg/L was significant (p = 0.00528). These results may be seen graphically below in Figure 4-8.
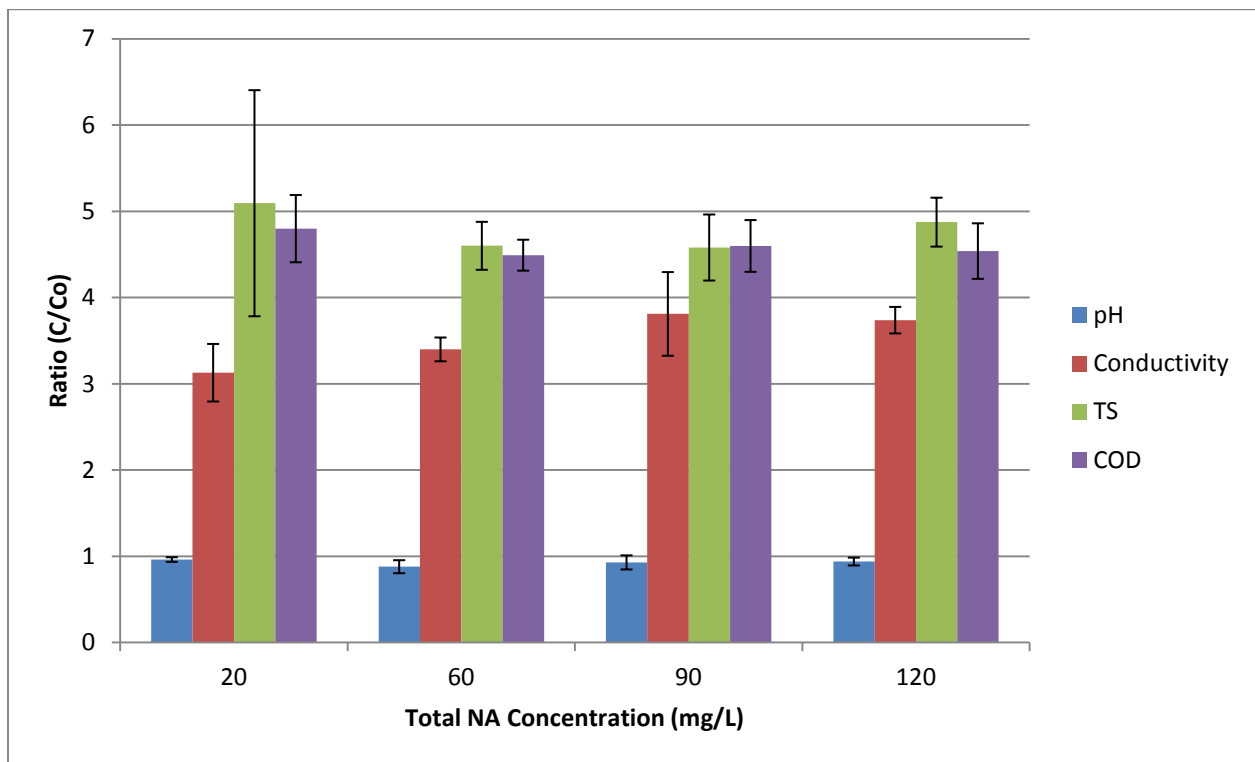
Figure 4-8: Effect of NA concentration on the water quality parameters pH, TS, conductivity, COD for the liquid portion of the progressive freeze concentration of NA solutions (for solutions of single NA mixture = cyclohexanecarboxylic, two NA Mixture = cyclohexanecarboxylic acid and trans-4-pentylcyclohexanecarboxylic, and three NA Mixture = cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at concentrations of 20.69mg/L, 60.72mg/L, 90.48mg/L, and 118.78mg/L).

4.3.4.2 Solid Portion

Progressive freeze concentration was able to significantly reduce the concentration of all tested NA concentrations within the solid portion of the samples tested (Appendix, Table 0-30, Table 0-33, Table 0-36, Table 0-39). Although, the water quality parameters COD, TS, and

conductivity showed higher levels of contaminates in the solid portion at concentrations of

20mg/L compared to that of higher concentrations of 60, 90, and 120 mg/L. This difference was

determined to be not significant for the pH, conductivity, and TS values (Appendix, Table 0-34,

Table 0-37, Table 0-40). It was significant in the instance of COD (Appendix, Table 0-30). This

may be attributed to the high standard deviation between the samples at NAs concentrations of

20mg/L. The normalization of the values may also have an influence. As the feed water COD

concentration increases but resulting COD concentration in the solid phase remains the same the

resulting ratio will be smaller. These results may be seen below in Table 4-6.

Table 4-6: Effect of NA concentration on the water quality parameters pH, TS, conductivity, COD for the frozen portion of the progressive freeze concentration of NA solutions.

Water Quality Parameter	Average Initial NAs Concentration (mg/L)			
	20.7	60.7	90.5	118.8
pH/pH$_o$	0.632	0.614	0.688	0.603
Conductivity/Conductivity$_o$ (% Removal)	0.0364+/−0.0738 (96.4%)	0.0198+/−0.0267 (98.0%)	0.0241+/−0.0330 (97.6%)	0.00928+/−0.00395 (99.1%)
TS/Ts$_o$ (% Removal)	0.115+/−0.0768 (88.5%)	0.0821+/−0.0811 (91.8%)	0.0439+/−0.0345 (95.6%)	0.0587+/−0.0323 (94.1%)
COD/COD$_o$ (% Removal)	0.0341+/−0.0408 (96.6%)	0.0191+/−0.020 (98.1%)	0.0165+/−0.0161 (98.4%)	0.00910+/−0.0107 (99.1%)

4.3.5   Combined Effect (Interactions) of NA Concentration and Chemical Identity

4.3.5.1   Results of the Unfrozen Liquid

According to water quality parameter COD there was a significant combined effect of NA

concentration and the chemical identity of the NAs in solution on the effectiveness of

progressive freeze concentration (p = 0.00236). TS detected a significant combined effect of NA

concentration and chemical identity of NA present (p = 1.24E-13). This is apparent in below in

Table 4-7 with single NA at 20mg/L having a much higher concentration ratio than that of the

other concentrations and NA solutions. Conductivity detected no significant influence of the combined effects of NA concentration and NA identity on the effectiveness of progressive freeze concentration (p = 0.0659). Similar to COD and TS, a significant influence of combined effects of total NA and identity of NA was detected by pH (p = 0.000499).

Table 4-7: Combined effect of NA concentration and type of NAs on the concentration ratios of COD, TS, conductivity, and pH (Single NA mixture = cyclohexanecarboxylic acid, Two NA Mixture = cyclohexanecarboxylic acid and trans-4-pentylcyclohexanecarboxylic, Three NA Mixture = cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid).

COD				
	Approximate NA Concentration (mg/L)			
Type of Solution	20	60	90	120
Single NA	4.8021	4.4938	4.5658	4.1510
Two NA Mixture	5.0137	4.5646	4.4007	4.7696
Three NA Mixture	4.5795	4.4131	4.8624	4.6960
TS				
	Approximate NA Concentration (mg/L)			
Type of Solution	20	60	90	120
Single NA	6.2056	4.6692	4.2931	4.5862
Two NA Mixture	3.5410	4.7459	4.9160	5.1828
Three NA Mixture	4.4237	4.3159	4.8188	4.8544
Conductivity				
	Approximate NA Concentration (mg/L)			
Type of Solution	20	60	90	120
Single NA	3.2767	3.3950	4.0897	3.7856
Two NA Mixture	2.9292	3.4892	3.5180	3.8584
Three NA Mixture	3.0303	3.3166	3.5439	3.5699
pH				
	Approximate NA Concentration (mg/L)			
Type of Solution	20	60	90	120
Single NA	0.9610	0.8177	0.9473	0.9005
Two NA Mixture	0.9507	0.9258	0.8555	0.9462
Three NA Mixture	0.9763	0.9561	0.9655	0.7902

4.3.5.2 Frozen Portion

Similar to the liquid phase, no significant influence was detected for combined effects in of NAs concentration and chemical identity in conductivity levels (p = 0.114). A significant influence on the combined effects of NA concentration and NA identity was detected in the frozen portion of progressive freeze concentration for water quality parameters COD, TS, and pH (p = 1.20E-7, 0.0237, and 0.0308, respectively). This may be attributed to the fact that the COD ratio was below detectable limits for both 20mg/L for single NA solution, and 60mg/L for two NAs mixture as well, for the TS ratio for two NAs mixture at 60mg/L as shown in Table 4-8. Therefore, this may have led to a false detected difference as the concentration of NAs in solution may not actually be zero.

COD				
	Approximate NA Concentration (mg/L)			
Type of Solution	20	60	90	120
Single NA	0.0000	0.0080	0.0168	0.0208
Two NA Mixture	0.0539	0.0000	0.0368	0.0729
Three NA Mixture	0.1314	0.0743	0.0599	0.0846
TS				
	Approximate NA Concentration (mg/L)			
Type of Solution	20	60	90	120
Single NA	0.1371	0.1271	0.0394	0.0187
Two NA Mixture	0.0539	0.0000	0.0368	0.0729
Three NA Mixture	0.1314	0.0743	0.0599	0.0846
Conductivity				
	Approximate NA Concentration (mg/L)			
Type of Solution	20	60	90	120
Single NA	0.0647	0.0298	0.0396	0.0138
Two NA Mixture	0.0071	0.0103	0.0090	0.0082
Three NA Mixture	0.0092	0.0095	0.0083	0.0059
pH				
	Approximate NA Concentration (mg/L)			
Type of Solution	20	60	90	120
Single NA	0.6589	0.6275	0.7736	0.6178
Two NA Mixture	0.5968	0.5833	0.6005	0.5941
Three NA Mixture	0.6130	0.6159	0.6055	0.5983

4.3.6 Partition Coefficient

As previously stated, a good means to evaluate the effectiveness of progressive freeze

concentrations ability to concentrate a particular substance in the liquid phase is the partition

coefficient (K). This method is outlined by Liu et al. (1997). The partition coefficient of each of

the three different NAs solutions at concentrations of 60 and 120mg/L was calculated for the

water quality parameters COD, TS, and conductivity. The results are discussed below.

4.3.6.1 COD

The partition coefficient of COD causing materials was determined for initial NAs concentration

of 60mg/L and 120mg/L. The partition coefficients of the NAs examined were obtained by

plotting the relative concentration (C_o/C_L) vs. the volume ratio of the liquid phase (V_L/V_o). The

resulting graph may be seen below in Figure 4-9. As is shown, a linear relationships exists with a

decrease in volume of the liquid phase corresponds with an increase in concentration of NAs in

the liquid phase. This is similar to results obtain by Liu et al. (1997).
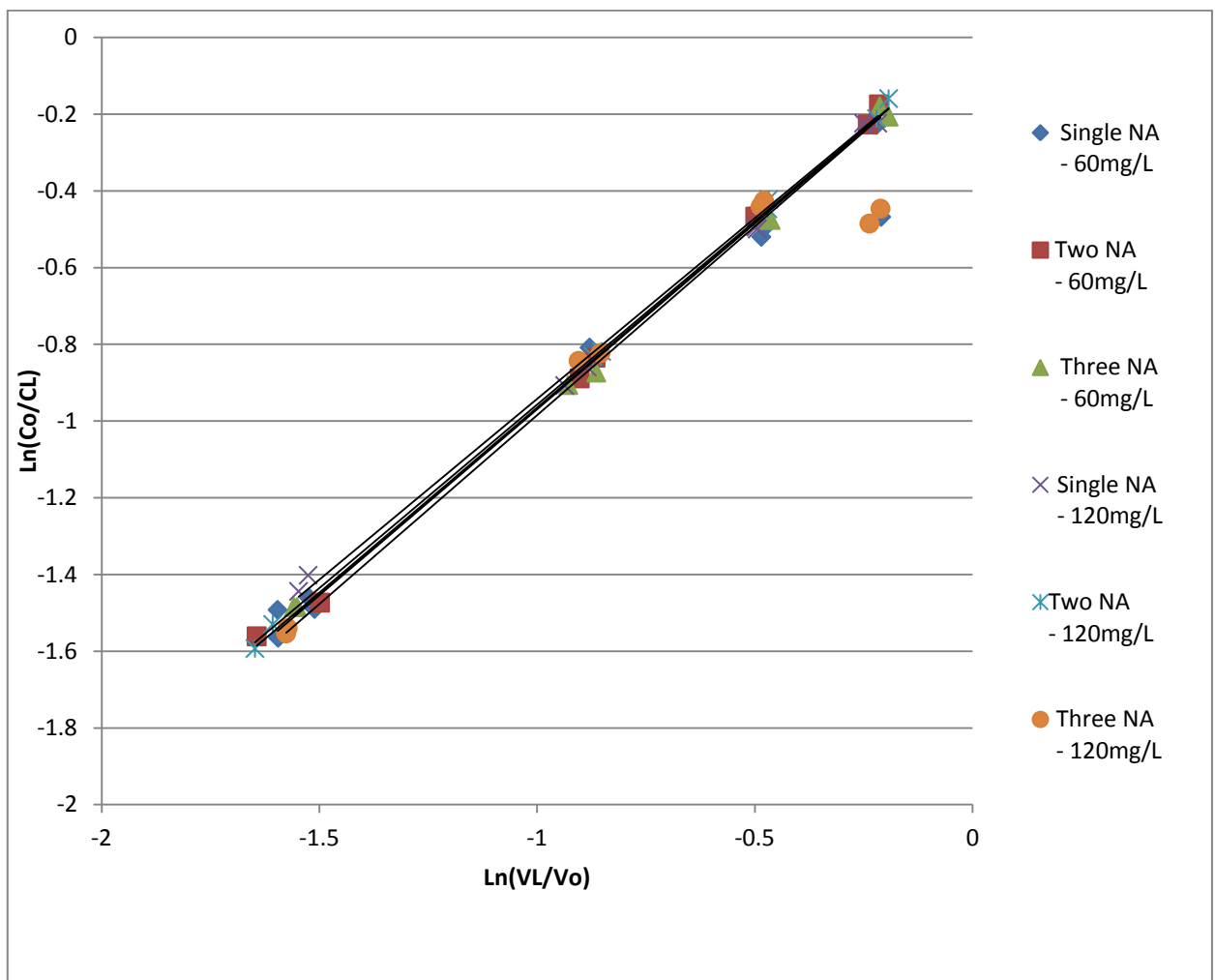
Figure 4-9: Determination of the partition coefficient for feed water containing different combinations of NAs using water quality parameter COD (Single NA = cyclohexanecarboxylic acid, Two NA Mixture = cyclohexanecarboxylic acid and trans-4-pentylcyclohexanecarboxylic, Three NA Mixture = cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid, V_L = volume of the liquid phase, V_o = volume of feed water, C_L = concentration NAs in liquid phase, C_o = concentration of NAs in feed water).

The resulting calculated partition coefficient values may be seen below in Table 4-9. Low values of K were obtained across all types and concentrations of NAs solutions tested suggesting effective concentration of contaminants in the liquid phase and thus reduced levels in the solid phase. For concentrations of 60 mg/L the partition coefficient was lower for the single NA solutions compared to that of the two and three NAs mixtures. Conversely, at 120mg/L the K values are larger but decrease with the subsequent solutions at values of 0.0578, 0.0432, 0.0153 for the single, two, and three NAs mixtures, respectively. This increase in K values corresponding to an increase in feed concentration and thus reduction of separation efficiency was also noted by Ruiz & Caicedo (2009). The notable reduced value of K for three NAs mixture at 120mg/L compared to the other K values correlates to a reduction an R^2 value at 0.9213 suggesting a reduction in the correlation and therefore less precision for the reported K value. Liu et al. (1999) reported similar results for the progressive freeze concentration of tomato juice. The obtained K values approaching zero thus suggesting excellent concentration/ separation performance.

Table 4-9: Partition coefficient determined by water quality parameter COD of progressive freeze concentration of NA solutions.

Water Quality Parameter	Total Naphthenic Acid Concentration (mg/L)	Type of NA Solution	Partition Coefficient (K)	R^2
COD	60	Single NA	0.0309	0.9666
COD	60	Two NA Mixture	0.0353	0.9985
COD	60	Three NA Mixture	0.0331	0.9978
COD	120	Single NA	0.0578	0.9969
COD	120	Two NA Mixture	0.0432	0.9992
COD	120	Three NA Mixture	0.0153	0.9213

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4.3.6.2 TS

The same method was used to derive the partition coefficients of TS at initial NAs concentrations of 60mg/L and 120mg/L. The relationship between the relative concentration (Co/CL) and the volume ratio of the unfrozen liquid phase (VL/Vo) may be seen below in Figure 4-10. Similarly to COD, a linear relationship exists between the volume of the liquid phase and the concentration of NAs in the liquid phase.
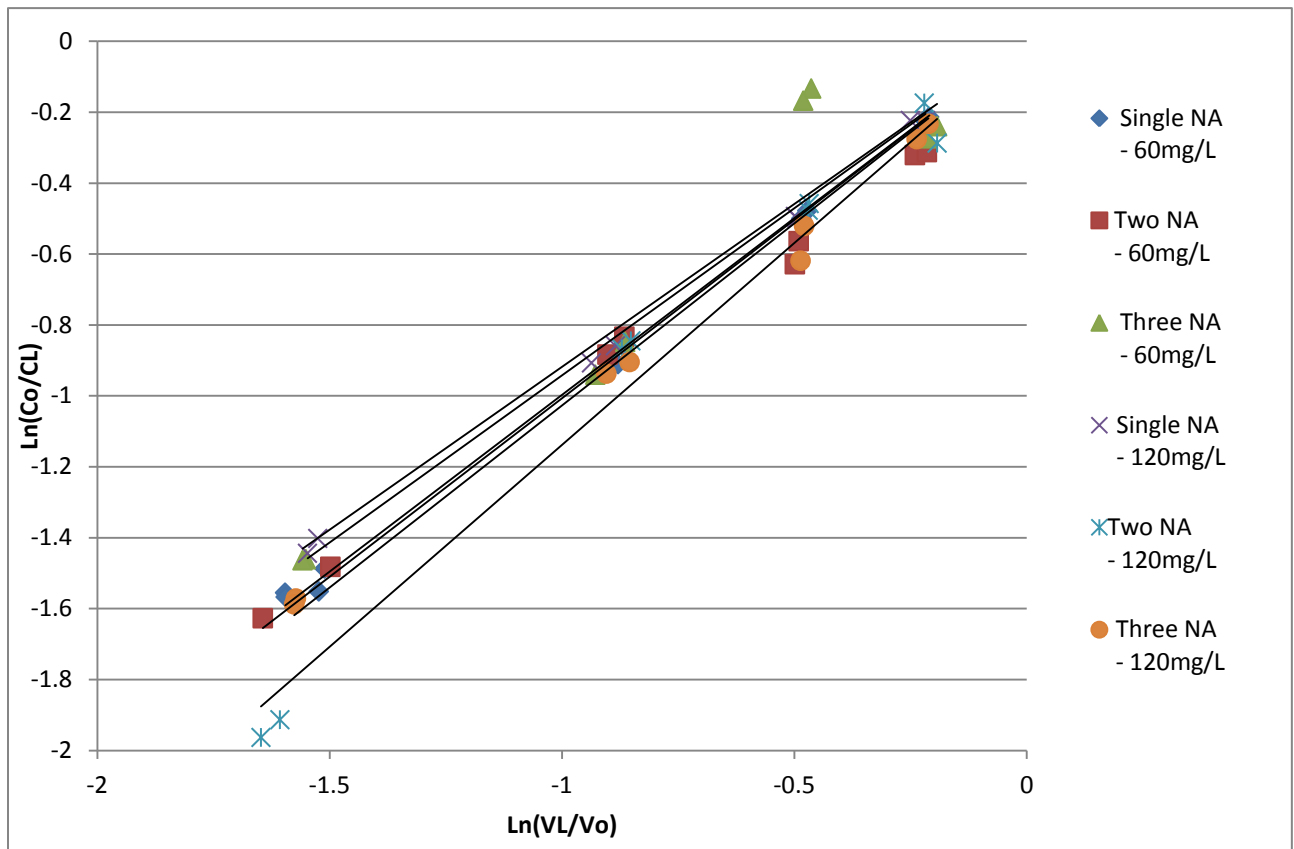
Figure 4-10: Determination of the partition coefficient for feed water containing different combinations of NAs using water quality parameter TS (Single NA = cyclohexanecarboxylic acid, Two NA Mixture = cyclohexanecarboxylic acid and trans-4-pentylcyclohexanecarboxylic, Three NA Mixture = cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid, V_L = volume of the liquid phase, V_o = volume of feed water, C_L = concentration NAs in liquid phase, C_o = concentration of NAs in feed water).

The resulting partition coefficient values may be seen below in Table 4-10. As shown, very low

levels of K were obtained, suggesting high efficiency in concentrating NAs in the liquid phase

and thus reduced concentrations in the solid phase. In some instances, 60mg/L for two NAs

mixture and 120mg/L for two and three NAs mixture, obtained negative K values. This suggests

greater than 100% separation efficiency and may be explained through experimental error. It can

be noted that similarly Liu et al. (1997) presented K values at or slightly below zero.

Table 4-10: Partition coefficient determined by water quality parameter TS of progressive freeze concentration of NA solutions.

Water Quality Parameter	Total Naphthenic Acid Concentration (mg/L)	Type of NA Solution	Partition Coefficient (K)	R^2
TS	60	Single NA	0.0034	0.9981
TS	60	Two NA Mixture	-0.0064	0.9765
TS	60	Three NA Mixture	0.082	0.918
TS	120	Single NA	0.0578	0.9969
TS	120	Two NA Mixture	-0.1383	0.9811
TS	120	Three NA Mixture	-0.0266	0.9897

4.3.6.3 Conductivity

The water quality parameter conductivity of the liquid portion of the samples was used to

determine the partition coefficient of the tested NAs at concentrations of 60mg/L and 120mg/L.

This was performed graphically using the relative concentration (Co/CL) and the volume ratio of

the liquid phase (VL/Vo). This relationship may be seen below in Figure 4-11.

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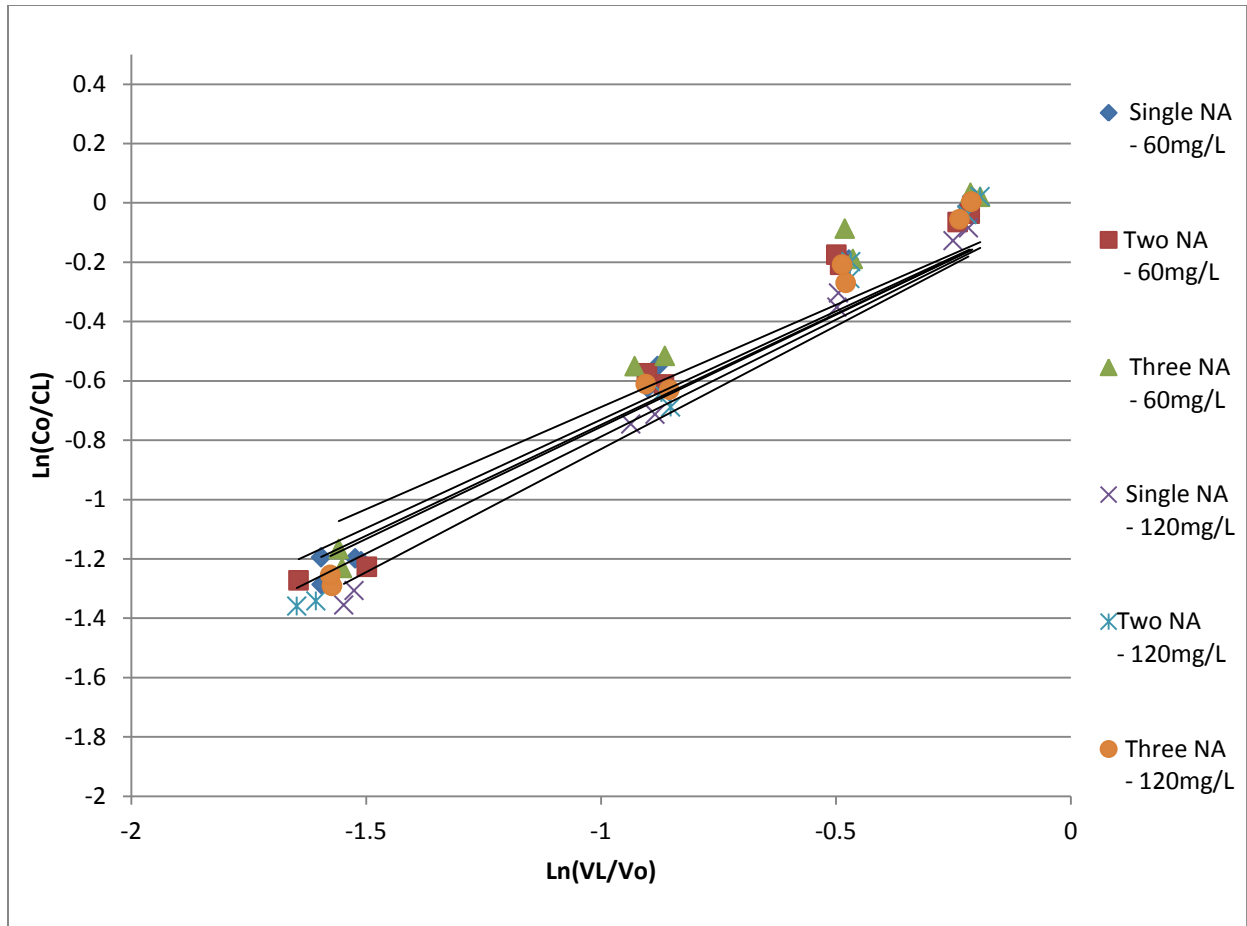
Figure 4-11: Determination of the partition coefficient for feed water containing different combinations of NAs using water quality parameter conductivity (Single NA = cyclohexanecarboxylic acid, Two NA Mixture = cyclohexanecarboxylic acid and trans-4-pentylcyclohexanecarboxylic, Three NA Mixture = cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid, V_L = volume of the liquid phase, V_o = volume of feed water, C_L = concentration NAs in liquid phase, C_o = concentration of NAs in feed water).

The corresponding K values calculated from Figure 4-11 may be seen below in The corresponding K values calculated from Figure 4-11 may be seen below in Table 4-11. These reported K values are significantly larger than those calculated for both COD and TS. Lower K values were reported compared that of NA concentrations of 60 and 120mg/L. An increase in K values was shown for more complex mixtures of NAs for both 60 and 120 mg/L.

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Table 4-11: Partition coefficient determined by water quality parameter conductivity of progressive freeze concentration of NA solutions.

Water Quality Parameter	Total Naphthenic Acid Concentration (mg/L)	Type of NA Solution	Partition Coefficient	R^2
Conductivity	60	Single NA	0.2523	0.9473
Conductivity	60	Two NA Mixture	0.2694	0.9334
Conductivity	60	Three NA Mixture	0.3114	0.8982
Conductivity	120	Single NA	0.1704	0.9775
Conductivity	120	Two NA Mixture	0.2124	0.9513
Conductivity	120	Three NA Mixture	0.2451	0.9466

4.3.7 Zero Values

During the investigation into the effectiveness of progressive freeze concentrations, extremely low concentrations of NAs in the solid portion were obtained during many experimental conditions. These very low concentrations, in some instances, were below the detectable limit of the water quality parameter tests COD and TS. In these cases, zero values were reported for the water quality parameter, although there may have been minute levels of NAs present in the solid portion. This allows for the statistical analysis of the data to be able to be performed.

4.3.7.1 COD

As previously stated, COD was determined by using the closed reflux colouremtric method. Therefore the detectable limit of the COD in the tested samples is related to the ability of the applied spectrophotometers to detect a change in the transmittance of the tested samples. The stated photometric accuracy of applied spectrophotometer (DR 2800, Hach Company, Colorado, USA) is 5 mAbs at 0.0 – 0.5 Abs and 1% at 0.50 – 2.0 Abs. The experimental conditions upon which concentrations of NAs were below the detectable limit for COD may be seen below in Table 4-12.

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Table 4-12: Experimental conditions were water quality parameter COD was below detectable limit in the solid portion of progressive freeze concentration of NA solutions.

Freezing Method	Percent Frozen (%)	Type of Solution	Total NA Concentration (mg/L)
Ultrasound	80	Single NA	20
Mechanical	80	Single NA	20
Ultrasound	80	Single NA	60
Ultrasound	80	Single NA	20
Mechanical	80	Single NA	20
Ultrasound	80	Single NA	60
Mechanical	80	Single NA	60
Ultrasound	80	Single NA	90
Mechanical	80	Single NA	90
Ultrasound	40	Single NA	60
Mechanical	60	Single NA	60
Mechanical	80	Two NA Mixture	90
Ultrasound	80	Two NA Mixture	120
Mechanical	80	Two NA Mixture	120
Mechanical	80	Three NA Mixture	120

4.3.7.2 TS

The detectable limit of the water quality parameter TS depends on the accuracy of the analytical balance implemented to measure the change of mass of dried crucibles. The chosen analytical balance was model number XS205 manufactured by Mettler Toledo (Ohio, USA). Its standard deviation for the fine range is listed as 0.04 mg. The experimental conditions upon which NA concentration were below detectable limit for TS may be seen below in Table 4-13.

Table 4-13: Experimental conditions were water quality parameter TS was below detectable limit in the solid portion of progressive freeze concentration of NA solutions.

Freezing Method	Percent Frozen (%)	Type of Solution	Total NA Concentration (mg/L)
US	80	Single NA	20
M	80	Single NA	60
US	80	Single NA	90
US	40	Single NA	60
M	40	Single NA	60
US	20	Single NA	60
US	60	Single NA	60
M	60	Single NA	60
US	80	Two NA Mixture	60
M	80	Two NA Mixture	60
US	20	Two NA Mixture	60
M	20	Two NA Mixture	60
US	40	Two NA Mixture	60
M	40	Two NA Mixture	60
US	60	Two NA Mixture	60
US	20	Three NA Mixture	60
M	20	Three NA Mixture	60
M	40	Three NA Mixture	60
US	20	Three NA Mixture	120
M	20	Three NA Mixture	120
US	40	Three NA Mixture	120
M	40	Three NA Mixture	120
US	60	Three NA Mixture	120
M	60	Three NA Mixture	120
US	60	Three NA Mixture	60
M	60	Three NA Mixture	60

4.4   Conclusion

This experimental investigation showed that progressive freeze concentration is an effective means for the removal of NAs from solution. The following conclusions were drawn based on the experimental results:

- Both ultrasonic and mechanical methods of progressive freeze concentration were equally effective at the treatment of NAs in solution.
    - The liquid unfrozen portion obtained approximately a 3 fold increase of both COD and TS over the feed water for ultrasonic and mechanical freeze concentrations. As well, both methods reported a 2.5 fold increase in conductivity was reported. A difference amongst the methods was reported for pH.
    - The methods were equally effective at the rejection of NAs from the solid portion for the tested parameters COD, TS, conductivity, and pH achieving removal rates of 95.3% to 98.6%.
- NAs of concentration between 20mg/L and 120mg/L were effectively separated/ concentrated. Initial feedwater NAs concentration was not a factor that influenced the removal efficiency of NAs
    - In the liquid portion COD and TS reported ratios over the feed water of between 4.5 and 5.1. No influence of the increase in concentration for these parameters was detected. Conductivity reported a significant increase in values associated with an increase in concentrations of NAs at ratios of 3.1 to

3.7 for 20mg/L and 120mg/L, respectively. A slight decrease in pH was noted but was only significant at 60mg/L and 120mg/L.

- In the ice samples collected both TS and conductivity reported very low levels of contaminates with removal rates of 88.5% and 99.1% with no influence caused by initial NAs feed water concentration. COD similarly reported high removal rates 96.6% and 99.1%. Concentrations of 20mg/L reported decreased effectiveness in removal. A reduction in pH was reported for all NAs feed water concentrations, a notable difference between concentrations of 90mg/L and 120mg/L was reported.

- Progressive freeze concentration successfully concentrated solutions containing different forms of NAs.

  - The chemical nature of NAs did not influence the ability to concentrate contaminates in the liquid portion; achieving concentration ratios (C/C_o) of 3.4 to 5.0 for COD, TS, and conductivity. pH ratios were significantly reduced in the case of single and two NAs solution but not for three NAs solution compared to the control.

  - Low levels of NAs were reported for the three tested solutions in the frozen portion of the treated samples. COD, TS, and conductivity reported removal rates of between 90.4% to 99.2%. pH values were also reduced to ratios of between 0.59 and 0.68. A difference in effectiveness was reported for TS between solutions with 3 NAs mixture and 2 NAs mixture. A significant influence was also acknowledged between 1 NAs solution and both 2 and 3

NAs mixtures for the water quality conductivity and pH, with higher removal

rates being reported for 1 NAs solutions.

- Partition coefficients (K) were calculated to be between 0.31 and -0.014 depending on

water quality parameter. This suggests high levels of separation/concentration

effectiveness and is in support of present literature.

4.5 References

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Chapter 5 - Investigation of the Effects of NAs Concentration, Freezing Method, Freezing Temperature, and Mixing Intensity

This chapter examines the influence of several factors on the effectiveness of progressive freeze concentration. They include: the intensity of agitation, freezing temperature, initial (feed water) NAs concentration, and freezing methods (freeze concentration with power ultrasonic freezing and mechanical mixing). Both methods provided a high degree of both NAs concentration in the liquid fraction and a high removal rate of NAs from the solid fraction. Agitation level appeared to influence NAs contamination in the solid phase; a decrease in applied mechanical RPM and a decrease in ultrasound amplitude resulted in increased contamination of the solid phase. Freezing temperature also influenced the efficacy of treatment, with lower temperatures reporting reduced solute separation effectiveness.

5.1 Introduction

It was shown in Chapter 4 that progressive freeze concentration is an effective means for the removal of NAs in solution. A high degree of freeze concentration was obtained in the unfrozen liquid fraction while a high removal rate occurred in the frozen fraction/ice. This chapter provides further examination into the effectiveness, as well as optimizing the progressive freeze concentration to remove NAs from feedwater. Certain factors in literature have been associated to influence freeze concentration. These factors include: freezing temperature, agitation/mixing intensity and initial solute concentration. The agitation intensity during progressive freeze concentration has been reported to be critical due to concentration polarization. During the freezing process solutes rejected from the ice structure become increasingly concentrated at the solid-liquid interface, thus an increase in mass transfer in the solution provided by either mechanical mixing or ultrasonic irradiation reduces this affect. Kawasaki et al. (2006) reported

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an increase in separation efficiency corresponding to an increase in ultrasound intensity during the freeze concentration of sodium chloride, L-phenyl alanine, and saccharose solutions. Similarly, Liu et al. (1997) reported a higher freeze concentration ratio with a higher rate of mechanical mixing during the progressive freeze concentration of glucose solutions. Furthermore, initial concentration is also very important as with increased initial concentrations a higher degree of concentration polarization occurs. This results in an increased chance for solute entrapment in the ice phase. This was noted by Liu et al. (1999) with the progressive freeze concentration of tomato juice, dilute juice was able to achieve a purity of almost 0% solids content in the ice phase, while this was unattainable at higher solids concentrations. A lower temperature results in an increase rate of ice development, Jusoh et al. (2008) reported a reduction in removal efficiency associated with a decrease in temperature. These stated factors will be therefore examined in this chapter.

5.2   Materials and Methods

5.2.1   Experimental Apparatus

The experimental apparatus is outlined and explained in Chapter 4.

5.2.2   Experimental Design

A full factorial design was implemented to examine the factors: freezing temperature, agitation level/intensity for mechanical and ultrasound freezing, initial NAs concentration in the feed water, and the progressive freeze concentration method. Freezing temperature was applied at two levels: -15℃ and -25℃. Initial feed water concentration was applied two levels: 60mg/L and 120mg/L. Ultrasound intensity was applied two ways: at cycle times of: 1s on/ 10s off, 1s on/ 20s off, and 1s on/ 30s off, as well, through ultrasound amplitudes of 20% and 30%. Mechanical

agitation was implemented at 3 levels: 100RPM, 200RPM, and 300RPM. This results in

2*2*3*2*2 or a total of 48. A design matrix of the experimental conditions is shown in Table 5-1

and Table 5-2.

Table 5-1: Full factorial design matrix for ultrasonic progressive freeze concentration.

Initial Concentration (mg/L)	Freezing Temperature (^{o}C)	Ultrasound Off Cycle Time (s)	Ultrasound Amplitude (%)
120	-15	10	30
120	-15	10	20
120	-15	20	30
120	-15	20	20
120	-15	30	30
120	-15	30	20
120	-25	10	30
120	-25	10	20
120	-25	20	30
120	-25	20	20
120	-25	30	30
120	-25	30	20
60	-15	10	30
60	-15	10	20
60	-15	20	30
60	-15	20	20
60	-15	30	30
60	-15	30	20
60	-25	10	30
60	-25	10	20
60	-25	20	30
60	-25	20	20
60	-25	30	30
60	-25	30	20

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Table 5-2: Full factorial design matrix for mechanical progressive freeze concentration.

Initial Concentration (mg/L)	Freezing Temperature (°C)	Mechanical Mixing Intensity (RPM)
120	-15	100
120	-15	200
120	-15	300
120	-25	100
120	-25	200
120	-25	300
60	-15	100
60	-15	200
60	-15	300
60	-25	100
60	-25	200
60	-25	300

5.2.3   Water Sample Preparation

The feed water was prepared following the procedure outlined in Chapter 4. The feed water characteristics are shown below in Table 5-3.

Table 5-3: Characteristics of feed water samples for freeze concentration tests.

NAs Present	Total NA Concentration (mg/L)	pH	Conductivity (µs/com)	Total Solids (mg/L)	COD (mg/L)
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	60.5	10.4	85.0	87.0	162.2
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120.4	10.5	133.4	155.3	308.0

5.2.4 Experiments

The experimental procedure that was performed was mirrored from Chapter 4.

5.2.5 Data Analysis

Results were normalized by dividing by the control values (C/C_o), where C is the impurity concentration in the treated sample and C_o is the impurity concentration in the feed water (control). Analysis of variance (ANOVA) was then used to analyze the resulting data through the statistical analysis software R (R Development Core Team, 2008). Tukey's HSD was applied when required. A confidence interval of 95% was implemented during all analysis. The experimental runs were duplicated and the data is reported as averages of the duplicates.

5.3 Results and Discussion

5.3.1 Influence of Freezing Temperature on the Efficiency of Progressive Freeze Concentration

5.3.1.1 *Effect of Temperature on Naphthenic Acid Concentration in the Unfrozen Liquid*

Freezing at $-15^{\circ}C$ or $-25^{\circ}C$ did not affect freeze concentration of COD causing materials in the unfrozen liquid. The COD concentration ratios in the unfrozen liquid was 4.60 ($-15^{\circ}C$) and 4.55 ($-25^{\circ}C$) with no statistical difference (p = 0.506). Similarly, conductivity reported no significant difference in concentration ratios, at values of 3.54 and 3.46 for $-15^{\circ}C$ and $-25^{\circ}C$, respectively (p = 0.302). pH was also not significantly influenced by a reduction in freezing temperature (p = 0.719). These results match that of Hung et al. (1996), who investigated of the unidirectional freezing of waste-activated sludges reporting no influence on experimental results on freezing temperature.

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Conversely, freezing temperature did affect concentration of TS in the unfrozen liquid. Concentration ratios of 4.57 was obtained for -15°C and 4.78 for -25°C (p = 0.00286). These results are shown below in Figure 5-1.
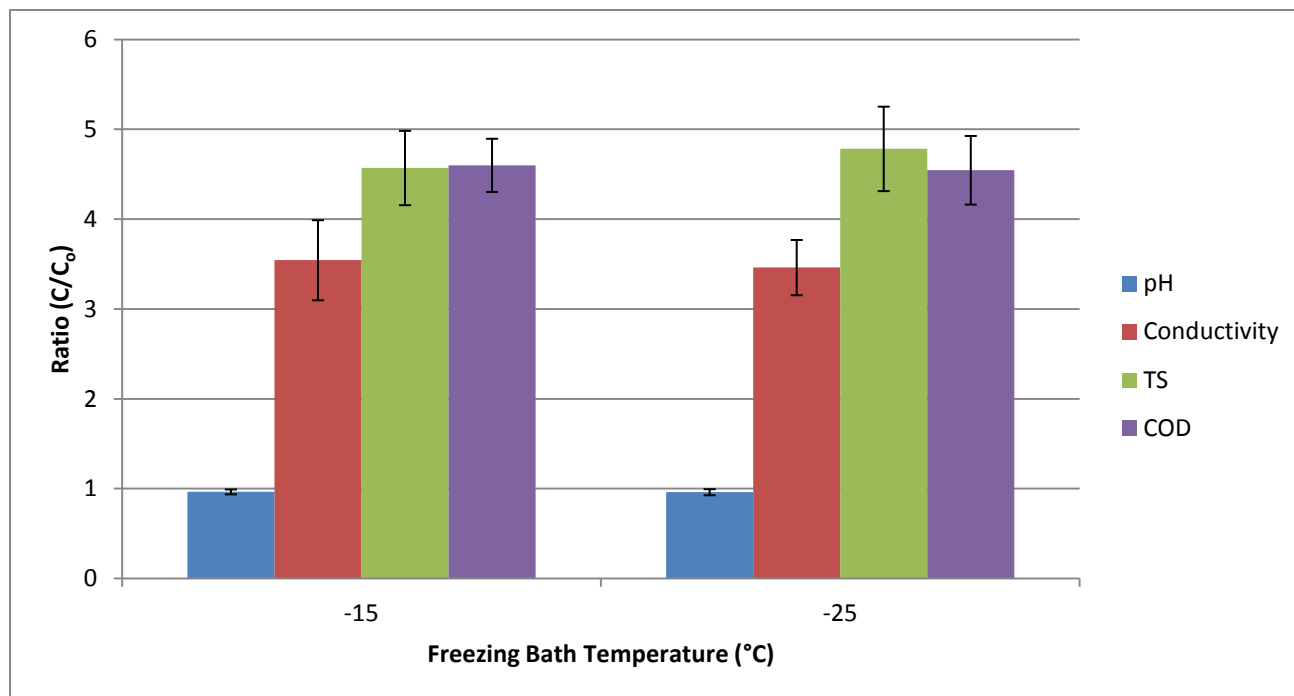
Figure 5-1: Influence of freezing temperature on the impurity concentrations in the unfrozen portion of progressive freeze concentration of NAs solutions (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

5.3.1.2 *Effect of Freezing Temperature on Removal of Naphthenic Acid Concentration in the Ice Samples*

A decrease in freezing temperature from -15°C to -25°C resulted in a significant increase in COD concentration (p = 0.0112) in the ice samples.COD removal efficiency dropped form 97.5% to 95.9% when freezing temperature decreased from -15°C to -25°C. Similarly, a reduction in solids removal was noted in the ice samples collected at -25°C (94.2%) as compared with those obtained at -15°C (95.6%). However, this difference was not substantial (p = 0.198). Obvious reduction in ionic species removal (conductivity, p = 0.0367) was also observed when the ice was formed at a colder temperature as shown in Figure 5-2.This reduction in efficiency

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with lower freezing temperature was also noted by Jusoh et al. (2008). They reported an increase in K values, which corresponds to a decrease in separation efficiency, with a decrease in freezing temperature (-6°C, -8°C, and -10°C) during the progressive freeze concentration of simulated wastewater. The pH values for both freezing temperatures were reduced approximately equally to ratios of 0.603 and 0.602 (p = 0.938). This fall in pH is comparable to the results obtained in Chapter 4. The three NAs mixture from Chapter 4 (the solution used in this experiment) obtained a reduction in pH ratio to a value 0.608.

The reduction in contaminate removal efficiency with a decrease in freezing temperature is attributed to the increase in ice growth rate at lower temperatures causing an increased entrapment of contaminates in the solid portion. Weeks & Lofgren (1966) also reported this during the freezing of sodium chloride solutions with an increase solute in the solid phase corresponding to a decrease in freezing temperature. Gao et al. (2003) similarly experienced a decrease in COD removal efficiency during the spray freezing of oil sands tailings water with a decrease in temperature. At a freezing temperature of -10°C, 67% of the resulting meltwater has >80% removal, while freezing at -24°C no meltwater achieved > 80% COD removal. At warmer freezing temperatures this effect appears not so obvious. Mahmutoglu & Esin (1996) did not experience a change in the distribution coefficient between the ice and liquid phase at freezing temperatures of between -6.5°C and -14.2°C during the freeze concentration of carrot juice.
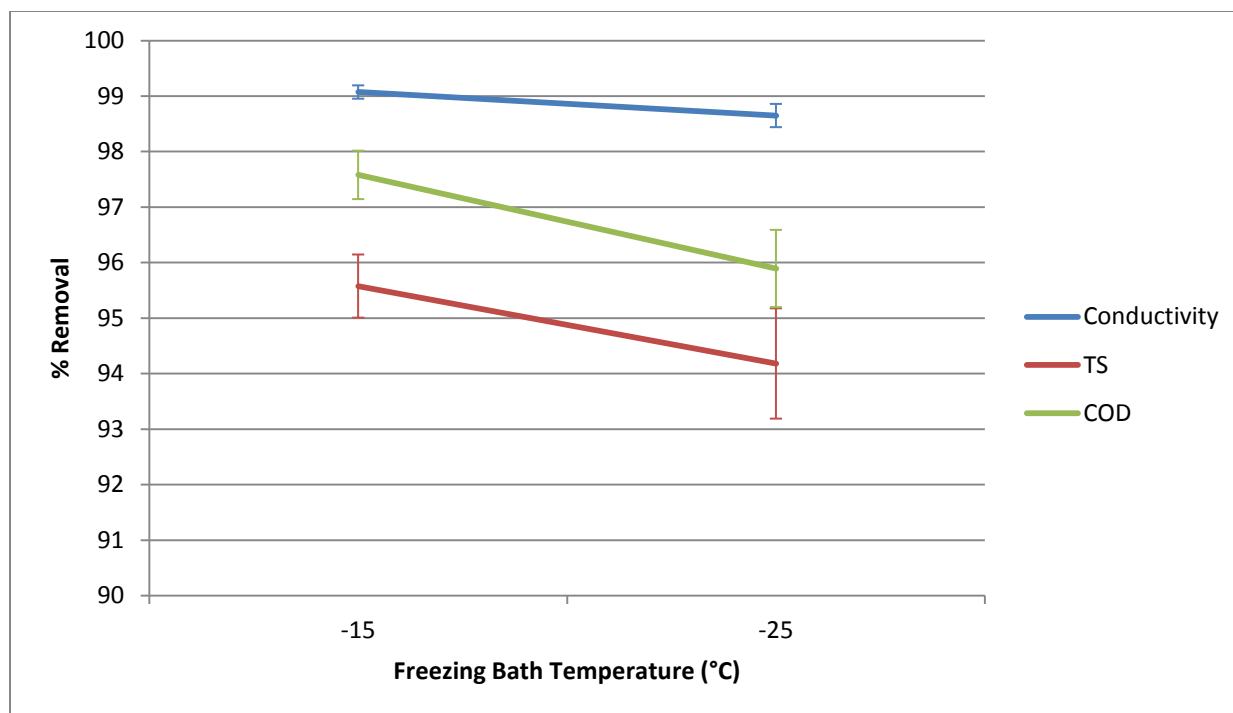
Figure 5-2: Influence of freezing temperature on impurity removal efficiency in the ice samples (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

5.3.2 Examination of the Influence of Ultrasound Agitation Intensity on Effectiveness of Progressive Freeze Concentration of Naphthenic Acids

The level of ultrasonic agitation as administered through cycle times and ultrasound amplitude is examined in this section. Cycle times of 1s on/10s off, 1s on/20s off, and 1s on/ 30s off were examined, as well as amplitudes of 20% and 30%. All three levels of ultrasonic irradiation cycle times and the two levels of amplitude provided a statistically significant higher degree of contaminate concentration in the liquid phase over the control. As well, all ice samples had significant low concentrations of contaminates as compared to that in the control.

5.3.2.1 Influence of Ultrasound Cycle Time

5.3.2.1.1 Contaminate Levels in the Liquid Portion
All levels of cycle time reported an increase in COD concentration in the liquid portion of approximately 4.5 fold. They cycling time did not affect the freeze concentration of COD

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causing materials (p = 0.790, 0.932, and 0.427 between cycles times of 1s/10s and 1s/20s, 1s/10s and 1s/30s, and 1s/20s and 1s/30s, respectively). A high increase in TS concentration was also noted with ratios at 4.82, 4.58, and 4.68, for off cycle times of 30s, 20s, and 10s. No significant difference in terms of TS concentrations in the liquid portion was noted (Table 0-111). Conductivity reported a 3.5 increase over the control with no difference among the cycle times (Table 0-114). The pH of the unfrozen samples decreased slightly more during the cycle time of 1s/10s at a ratio of 0.589 compared to longer off pulse times (20s and 30s) at ratios of approximately 0.608. This reduction in pH levels was determined to be insignificant (Table 0-117). These results are shown graphically below in Figure 5-3.
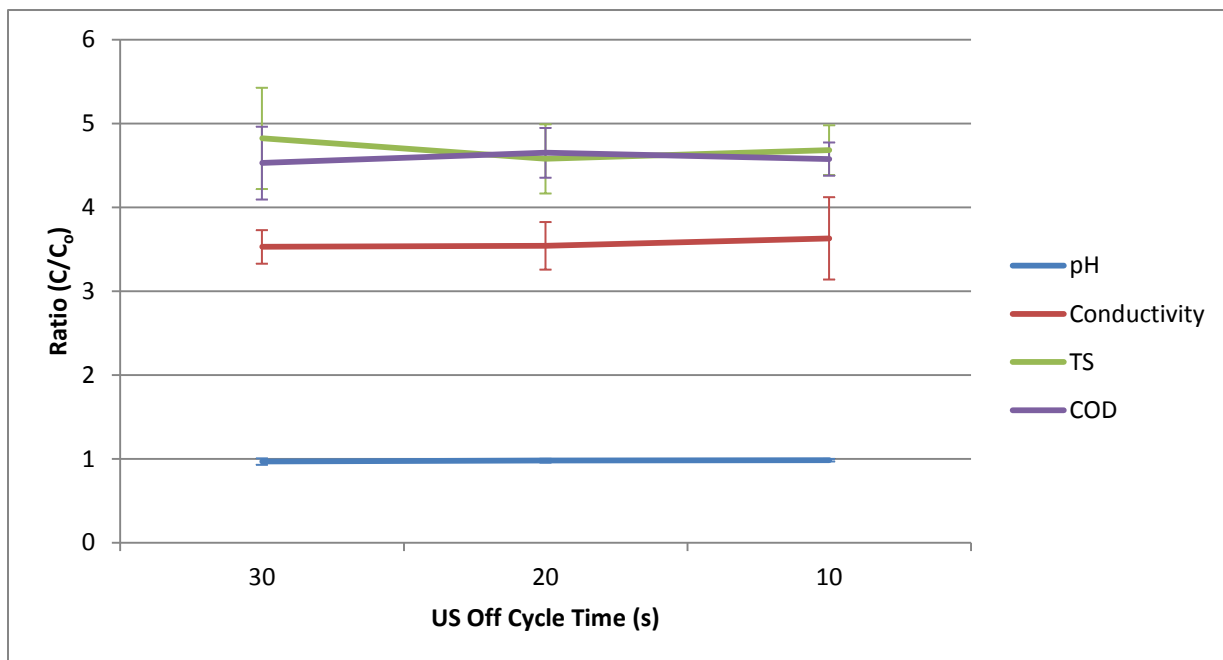
Figure 5-3: Influence of ultrasound off cycle time on impurity concentration in the unfrozen liquid of progressively frozen NAs solutions (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

5.3.2.1.2 Contaminate Levels in the Solid Portion

Ultrasonic freeze concentration achieved an average of 97% reduction of COD concentration in the ice samples collected. No significant difference was noted between the cycle times for the rejection of NAs from the solid portion as evaluated by COD concentration (the statistical analysis results are summarized in Appendix, Table 0-120). TS also suggested a high rate of rejection of NAs from the solid portion at removal rates of 93.6%, 96.4%, and 94.8% for cycle times of 1s/30s, 1s/20s, and 1s/10s with no significant difference amongst the cycle times (Table 0-123). Conductivity reported very low levels of NAs in the solid portion with removal rates of approximately 99% for all ultrasound cycle times (Table 0-126). A notable reduction of pH values was reported at levels of 0.607, 0.608, and 0.589 for cycle times of 1s/30s, 1s/20s, and 1s/10s, respectively. The greater reduction of pH in cycle time of 1s/10s was significant compared to the cycle times of 1s/20s and 1s/30s ($p = 0.00850$ and 0.0152). This may perhaps be due to the enhancement of mass transfer rate by higher levels of ultrasonic irradiation. This promotes a higher diffusion rate of carbon dioxide into solution thus lowering the pH values as discussed previously.
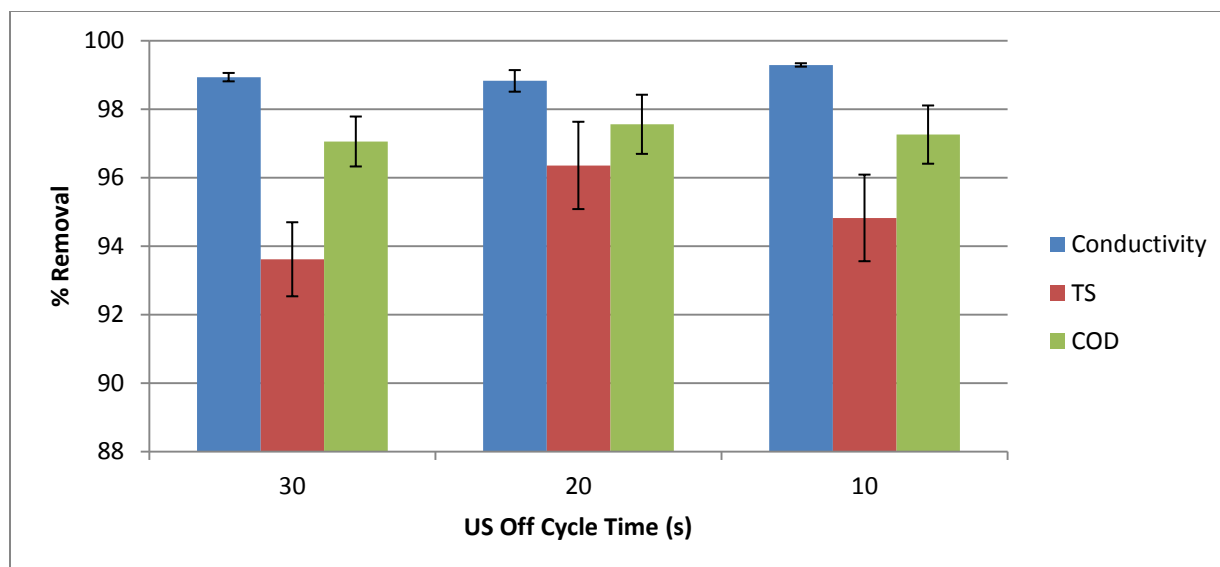
Figure 5-4: Influence of ultrasound off cycle time on removal efficiency of impurities in the ice samples (Initial cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic total acid concentration in the control is at 60.52mg/L and 120.37mg/L, respectively).

Very high efficiency of removal of impurities from the solid phase for all the cycle times suggest that the cycle time 1s/30s would be the most appropriate for the treatment of NAs in OSPW. At this cycle level the lowest energy could be used while not compromising removal or concentration efficiency. Although this removal efficiency may be reduced when higher levels of contaminates are present. Liu et al. (1997) reported a correlation in the separation efficiency of progressive freeze concentration (of blue dextrose and glucose) and the applied intensity of mechanical agitation. At lower levels of RPM there was an increase in K values, conversely, at a higher RPM they reported a decrease in K values. Therefore in a further study, it would be recommended to examine lower levels of ultrasound irradiation cycle times.

5.3.2.2   *Influence of Ultrasound Amplitude*

5.3.2.2.1 Contaminate Levels in the Liquid Portion

When the amplitude of ultrasound energy was increased from 20% to 30%, the concentration ratios of COD and conductivity in the unfrozen liquid dropped significantly ($p = 0.0242$ and $p = 0.0177$, respectively) suggesting that higher ultrasound intensity caused poor rejection of both

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organic and inorganic impurities during freezing. The COD concentration was reported at ratios of 4.67 for 20% amplitude and 4.50 for 30%. The conductivity was reduced from 3.66 for 20% amplitude to 3.47 for 30% amplitude. However for TS, there was an insignificant ($p = 0.742$) reduction in TS between 20% and 30% amplitude at solids ratios of 4.73 to 4.66, respectively. The pH was slightly reduced at both amplitudes to an approximate ratio of 0.975 as is shown in Figure 5-5.
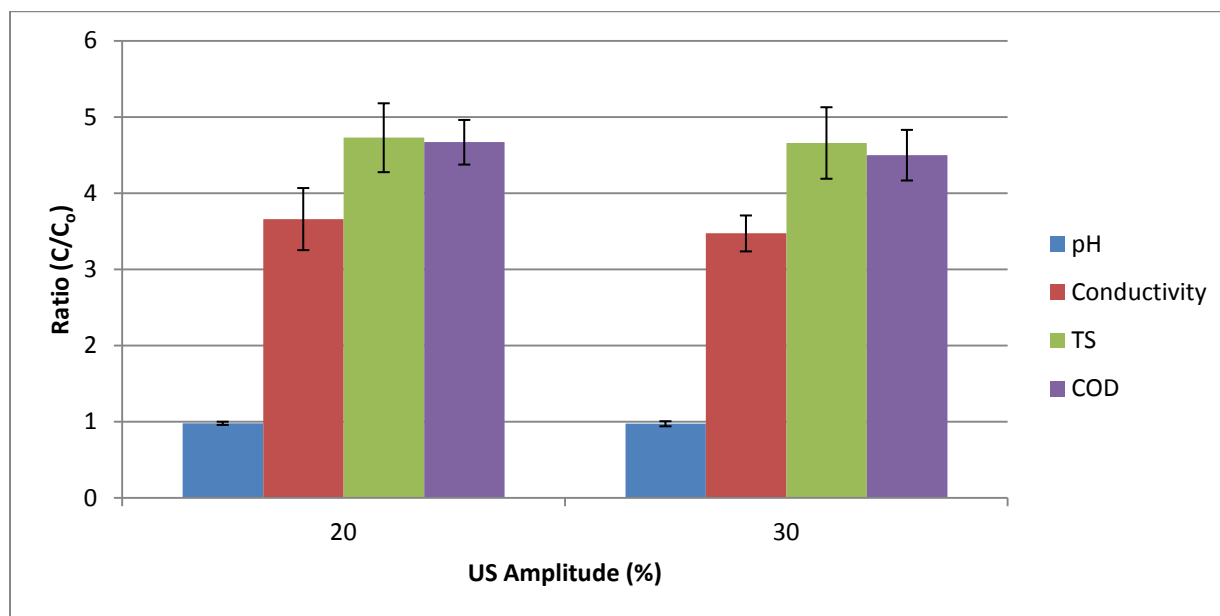
Figure 5-5: Influence of ultrasound amplitude on contaminate levels in the liquid portion of progressively frozen NAs solutions based on pH, conductivity, TS, and COD (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

From these above results, it suggests that less NAs are being concentrated in the liquid portion with an increase in ultrasound amplitude. Examination of the results for the frozen portion suggests otherwise and this phenomenon is discussed below.

5.3.2.2.2   Contaminate Levels in the Solid Portion

In the solid portion impurity removal efficiency was insignificantly increased in terms of COD concentration ($p = 0.0666$) when applying a higher level of ultrasonic amplitude with removal rates of 96.6% for 20% amplitude and 98.0% for 30% amplitude. Likewise, TS reported an

insignificant increase ($p = 0.170$) in removal efficiency at a 94.0% to 95.8% for 20% and 30%, respectively. Increase in removal efficiency was significant ($p = 0.0339$) for conductivity when ultrasound energy increased from 20% (98.8% removal) to 30% (99.2% removal). Figure 5-6 illustrates the change in impurity removal efficiency vs. amplitude of ultrasound energy. The pH values of the ice samples was reduced significantly ($p = 0.0259$) with an increase in amplitude at ratios of 0.608 for 20% amplitude and 0.595 for 30% amplitude.
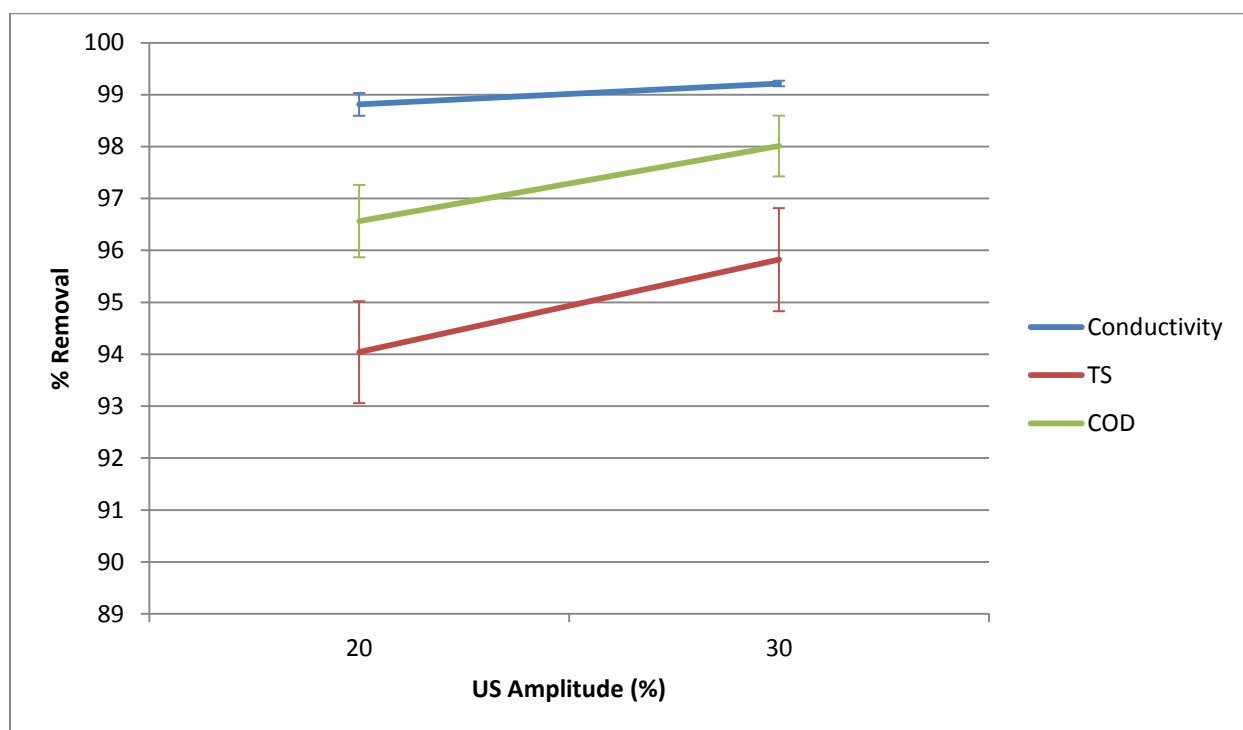
Figure 5-6: Influence of ultrasound amplitude on contaminate levels in the solid portion of progressively frozen NAs solutions based on pH, conductivity, TS, and COD (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

Kawasaki et al. (2006) correspondingly also achieved an increase in separation efficiency of solute between the solid and liquid phases with an increase in ultrasound intensity during the progressive freeze concentration of solutions containing molecules such as sodium chloride at concentrations of 0.015mol/L. When ultrasound intensity was increased from 30W to 54W sodium chloride in the liquid phase increased and decreased in the solid phase.

The increase in removal efficiency of NAs with an increase in ultrasound amplitude reported in the frozen fraction does not correspond with a higher level of contaminates in the liquid phase. Surprisingly, a lower level of concentration of NAs was reported. Other phenomena may be responsible. An increase in amplitude of the applied ultrasound would result in an increase in the occurrence of acoustic cavitation (Mason & Lorimer, 2002). Acoustic cavitation has been reported to result in the formation of free radicals such as hydroxyl and hydrogen peroxide (Makino et al., 1983 & Riesz & Kondo, 1992).Therefore these free radicals are potentially oxidizing the NAs contained within the solution during ultrasonic progressive freeze concentration and thus reducing their concentrations in both the solid and liquid phases.

5.3.3   Analysis of the Effect of the Mechanical Agitation Level of Progressive Freeze Concentration of Naphthenic Acids

Mechanically agitated progressive freeze concentration was able to effectively separate NAs in the unfrozen liquid fraction while leaving the frozen solid fraction relatively free of contamination of NAs. All agitation levels of (100, 200, 300RPM) provided a statistically significant reduction of of NAs in the solid phase over the control.

5.3.3.1   Naphthenic Acid Levels in the Unfrozen Segment

There was an insignificant increase in the concentration of NAs with an increase in the RPM of mechanical mixing (Table 0-92). The COD concentration ratios of the unfrozen liquid samples obtained with mixing at 100, 200, and 300 RPM were 4.44, 4.59, and 4.65, respectively. Total solids concentration remained relatively unchanged with an increase in RPM (Table 0-94) at ratios of 4.75, 4.51, and 4.71, respectively. Increase in mixing intensity from 100RPM to 300 RPM did not make any profound changes in concentration of conductivity. The unfrozen liquid

samples contained about 3.5 times of ionic species as compared to the controls (Table 0-96) for

RPM values of 100, 200, and 300. The pH was reduced over the control at values of 0.955,

0.954, and 0.944 for RPM of 100, 200, and 300, respectively. This reduction of pH with

increased agitation level was deemed insignificant (Table 0-98). This increase in concentration

of NAs is displayed in Figure 5-7.
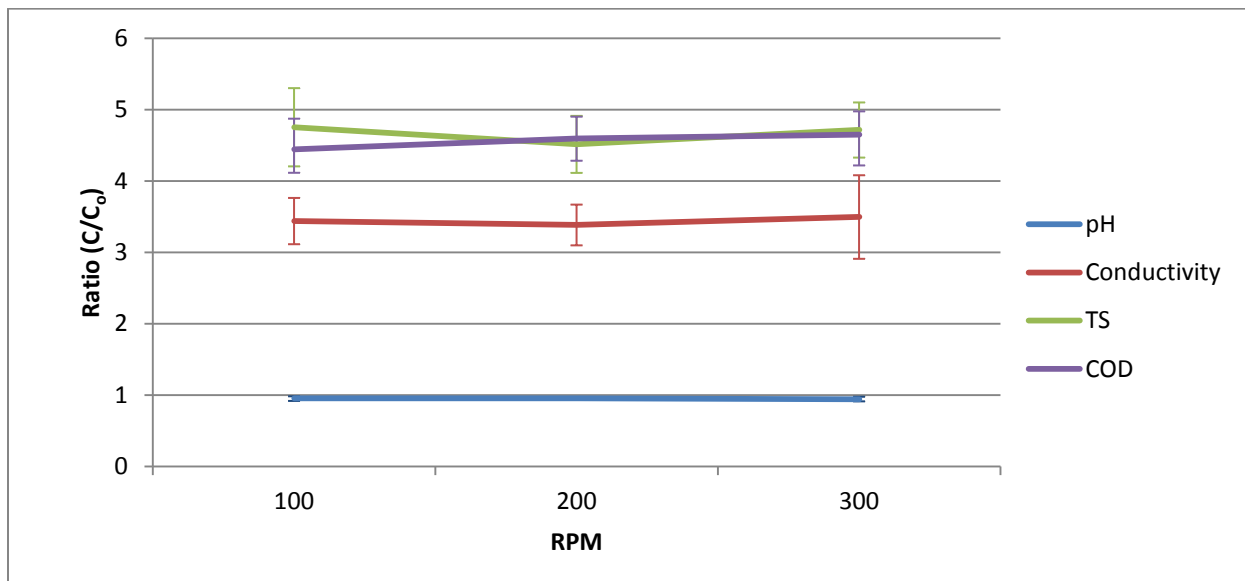
Figure 5-7: Effect of mechanical agitation level (RPM) on efficacy of progressive freeze concentration to concentrate NAs in the unfrozen portion, measured by pH, conductivity, TS, and COD (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

The high level of concentration of NAs reported by the water quality parameters COD, TS, and

conductivity show that mechanical progressive freeze concentration is effective at all levels of

agitation (RPM).

5.3.3.2 Naphthenic Acid Levels in the Frozen Segment

COD levels in the frozen fraction decreased with an increase RPM resulting in ratios of 0.0508

(94.9% removal), 0.0333 (96.7% removal), and 0.0289 (97.1% removal) for agitation levels of

100, 200, and 300 RPM, respectively. This increase in efficiency with increase in agitation level

was determined to be statistically insignificant (Table 0-100). Conductivity ratios followed the

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same trend as COD with a ratio of 0.0193 (98.1% removal) for 100 RPM, 0.0100 (99.0 %

removal) for 200 RPM, and 0.00941(99.1% removal) for 300 RPM. This increase in removal

efficiency was significant between RPM levels of 100 and 300 ($p = 0.0339$), but not between 100

and 200RPM or 200 and 300RPM ($p = 0.0533$ and 0.998). The percentage removal of solids in

the frozen phase reached 93.7% for 100 RPM, 96.1% for 200 RPM, and 94.7% for 300 RPM.

The difference in TS removal was not statistically significant for the three agitation levels. The

results for the statistical analysis are listed in Table 0-102 of the appendix. The pH was reduced

at greater levels increasing RPM levels. The ratios of pH were 0.615, 0.604, and 0.591 for 100,

200, and 300 RPM, respectively. This reduction was again significant between 100 and 300

RPM ($p = 0.000159$) levels but not between 100 and 200RPM or 200 and 300RPM ($p = 0.202$

and 0.0777, respectively). This further suggests the enhancement of mass transfer of carbon

dioxide into solution and thus reducing pH at higher levels of mixing as discussed previously.

Alternatively, this increase in pH values in the solid phase associated with decreased mechanical

agitation may suggest contamination of the solid phase by sodium hydroxide, thus increasing the

pH. These results are shown below in Figure 5-8.
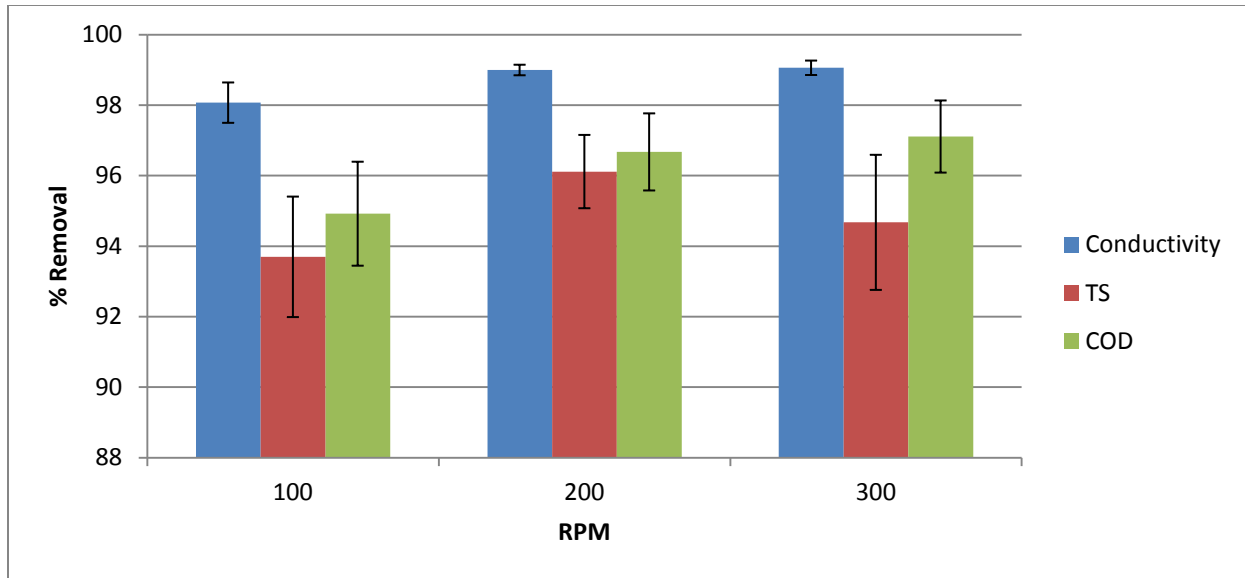
Figure 5-8: Effect of mechanical agitation level (RPM) on efficacy of progressive freeze concentration to remove NAs in the ice samples, measured by conductivity, TS, and COD (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

It is apparent that there are negligible differences with an influence of effectiveness on progressive freeze concentration with an increase level of mixing. This is in contrast to the relationship that has been noted by several authors with an increase in agitation level reported reduced ice contamination (Liu et al., 1997, Liu et al. 1999, and Miyawaki et al. 1998, Ramos et al, 2005).

5.3.4 Further Analysis into the Effect of the Initial Naphthenic Acid Concentration in Feed Water

5.3.4.1 *Liquid Portion*

An increase of NAs concentration from 60 mg/L to 120mg/L in the feed water did not influence ($p = 0.931$) COD concentrations in the unfrozen liquid samples collected with both ratios at approximately 4.6. This was also true for conductivity with ratios of approximately 3.5 ($p = 0.366$). In contrast, solid concentrations were significantly higher ($p = 0.00662$) when the feed water contained more NAs (120mg/L) the concentration for 120mg/L of NAs was 4.58 compared

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to 4.78 for initial feed water with 60mg/L. In both concentrations, pH was slightly reduced to an approximate ratio of 0.96 (p = 0.339). See Figure 5-9 below.
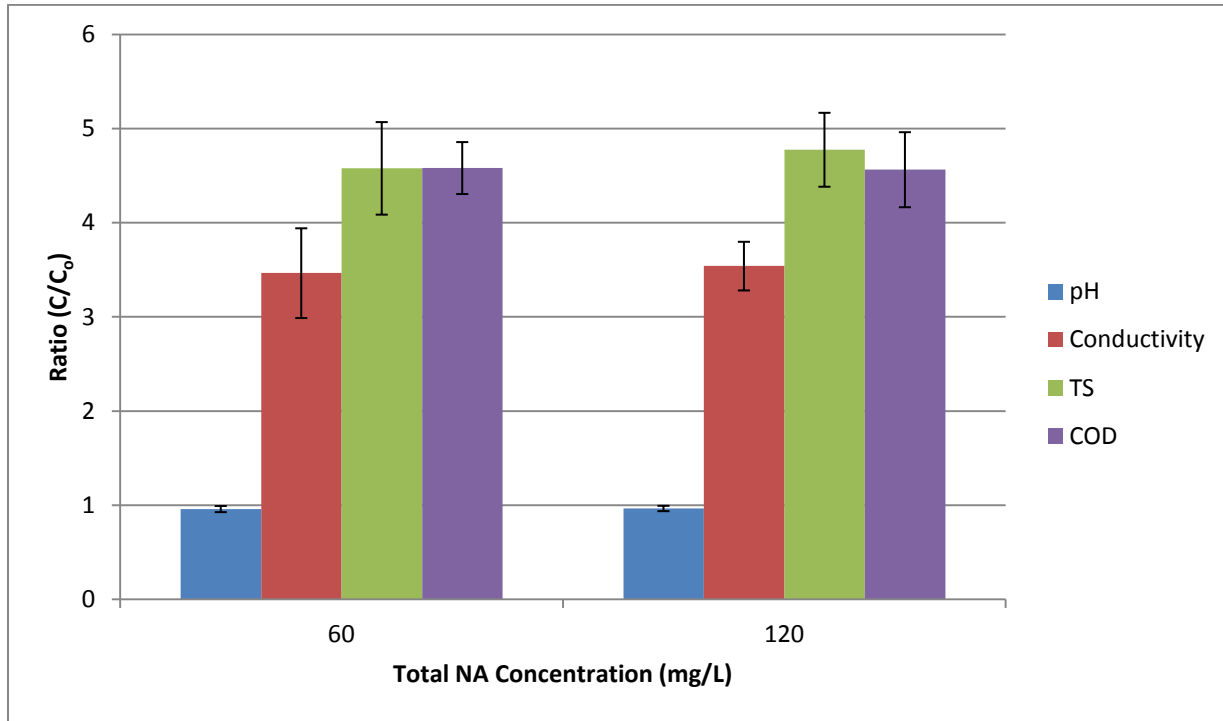
Figure 5-9: Effect of feed water NAs concentration on water quality parameters pH, TS, conductivity, and COD for the liquid portion of progressive freeze concentration of NAs solutions (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

5.3.4.2 Solid Portion

Negligible differences in removal rates were observed for COD, conductivity and pH (p = 0.425, 0.960, and 0.794). These ratios may be seen in Table 5-4. Higher values of concentration ratios obtained in the frozen portion for solids concentration at an initial NAs feed water concentration of 60mg/L when compared to 120mg/L with removal rates of 93.3% vs. 96.4%, respectively (p = 0.000364). In contrast several authors have noted a reduction in separation efficiency in solid phases when feed water solute concentration is increased during the progressive freeze concentration (Miyawaki et al., 2012 & Miyawaki et al., 2005). This difference may be attributed

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to the lower concentrations of NAs being tested. Perhaps at higher concentrations a notable

reduction in efficacy would be noted.

Table 5-4: Affect of feed water NAs concentration on water quality parameters pH, TS, conductivity, and COD for the solid portion of progressive concentration of NAs solutions (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

	Total NA Concentration (mg/L)	
Water Quality Parameter	60.52	120.37
pH/pH_o	0.601±0.00337	0.604±0.00381
$Conductivity/Conductivity_o$ (% Removal)	0.0111±0.00183 (98.9%)	0.0116±0.00164 (98.8%)
TS/Ts_o (% Removal)	0.0665±0.00981 (93.3%)	0.0359±0.00520 (96.4%)
COD/COD_o (% Removal)	0.0363±0.00687 (96.4%)	0.0289±0.00477 (97.1%)

5.3.5 Further Testing of Freezing Methods Ultrasound and Mechanical on Removal of NAs

Both mechanical and ultrasound progressive freeze concentration methods provided a high level

of removal from the feed water.

5.3.5.1 Concentration of Impurities in the Unfrozen Portion

High COD levels were obtained for both mechanical and ultrasound progressive freeze

concentration in the unfrozen segment. The ratios obtained were 4.56 and 4.58 for mechanical

and ultrasound. These values were not significantly different ($p = 0.895$). TS similarly reported

no significant difference ($p = 0.869$) amongst progressive freeze concentration methods at values

of 4.66 and 4.69. Conductivity was reported to be slightly less for mechanical mixing compared

to ultrasound at 3.44 vs. 3.57 for mechanical and ultrasound, respectively. This difference was

determined to be insignificant ($p = 0.0577$). pH value was slightly less for mechanical mixing

opposed to ultrasound with ratios of 0.951 and 0.976 for mechanical and ultrasound,

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respectively. Although this difference in pH values was significant (p = 0.00E-7). This reduction

in pH value for mechanical over ultrasound progressive freeze concentration was also observed

in chapter 4 and is discussed there. Table 5-5 displayed results of the unfrozen fraction for both

ultrasound and mechanical progressive freeze concentration methods.

Table 5-5: Ability of progressive freeze concentration methods ultrasound and mechanical to concentrate NAs (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

	Freezing Method	
Water Quality Parameter	Ultrasound	Mechanical
pH/pHo	0.976±0.00400	0.951±0.00406
Conductivity/Conductivityo	3.57±0.0494	3.44±0.0597
TS/Tso	4.69±0.0660	4.66±0.0655
COD/CODo	4.58±0.0464	4.56±0.0523

5.3.5.2 Concentration of Impurities in the Frozen Portion

Very high removal rates of NAs were obtained for both progressive freezing methods ultrasound

and mechanical. Removal rates of 94.8% to 99.0% were obtained with no significant difference

observed between these methods (Table 0-76, Table 0-80, and Table 0-84) as shown in Figure

5-10. Unlike the unfrozen fraction, a significant difference in pH was not reported between

ultrasound and mechanical methods (p = 0.841) at ratios of 0.601 and 0.603 for ultrasound and

mechanical, respectively.
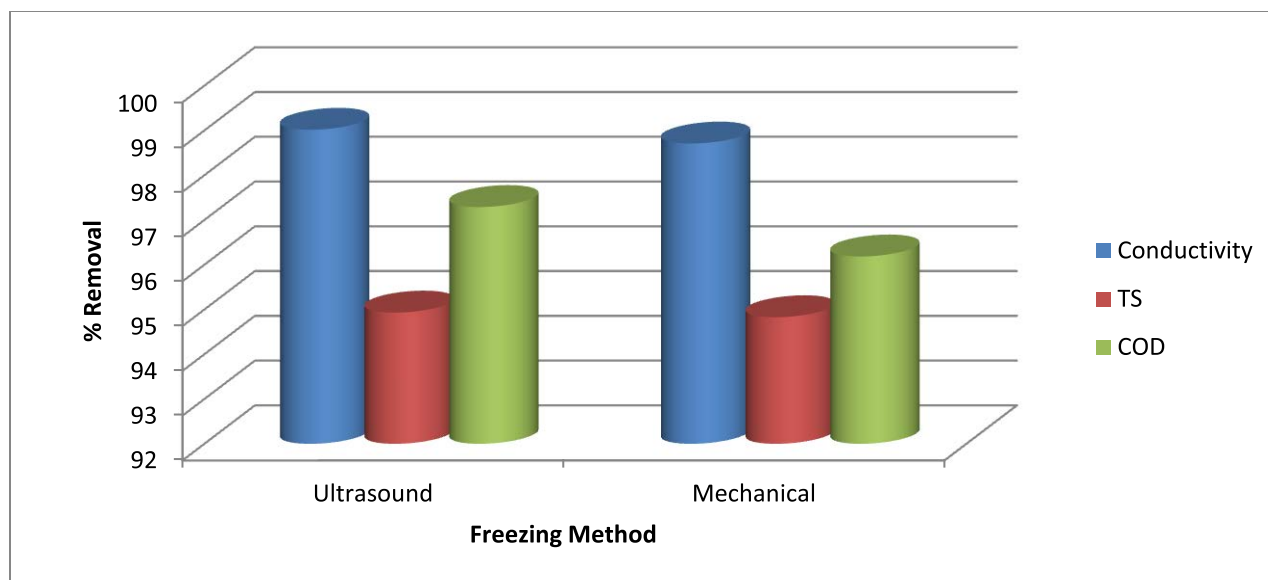
Figure 5-10: Ability of progressive freeze concentration methods ultrasound and mechanical to remove NAs from wastewater (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

There is a particularly large differential in the pH value of the ice samples compared to the pH values of the unfrozen liquid. In the case of the unfrozen portion the majority of the original species in solution are present and thus the pH should be fairly close to the control. It is slightly reduced due to the interactions atmospheric CO_2 over the course of the experiment. As for the ice samples the majority of the contaminates are rejected from this phase and thus the pH is vastly reduced.

5.3.6 Combined Effect of Freezing Temperature and Total Naphthenic Acids Concentration on the Efficacy of Progressive Freeze Concentration

COD concentrations within the liquid unfrozen portion of progressively frozen NAs solutions were not affected by the combined effect of freezing temperature and initial total NAs concentration (p = 0.378). On the other hand a combined effect was noted for conductivity (p = 0.00261). At a freezing temperature of -15⁰C the conductivity ratio was higher with a feed water concentration of 60mg/L total NAs at 3.59 compared to 120mg/L at 3.50. Conversely, at -25⁰C

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feed water containing 120mg/L total NAs the conductivity ratio was higher than that of 60mg/L

at 3.58 and 3.34, respectively. These results are shown below in Table 5-6.

Table 5-6: Combined influence of freezing temperature and feed water total NAs concentration on efficacy of progressive freeze concentration of NAs for water quality parameters COD and conductivity in the unfrozen fraction (cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid at 60.52mg/L and 120.37mg/L).

COD		
	Approximate Total NA Concentration (mg/L)	
Freezing Temperature (°C)	60	120
-15	4.59±0.235	4.61±0.351
-25	4.58±0.317	4.51±0.443
Conductivity		
	Approximate Total NA Concentration (mg/L)	
Freezing Temperature (°C)	60	120
-15	3.59±0.584	3.50±0.247
-25	3.34±0.303	3.58±0.269

A combined effect of total NAs concentration of the feed water and freezing temperature was

noted for both solid concentration and pH values of the unfrozen portion (p = 0.00186 and

0.000154). As is seen below in Table 5-7, total solids concentration ratios in the liquid phase at -

15°C was slightly lower at total NAs feed water concentration of 60mg/L (4.38) compared to

120mg/L (4.76). While at a freezing temperature of -25°C there was little difference in total

solids concentration ratios at approximately 4.78 for both total NAs feed water concentrations.

pH ratios at -15°C freezing temperature were slightly higher at an initial total NAs concentration

of 120mg/L (0.965) compared to 60mg/L (0.954) in the liquid fraction. This relationship

swapped at a freezing temperature of -25°C as the pH ratios of 120mg/L feed water total NAs

concentration was 0.957 compared to 60mg/L feed water total NAs concentration was 0.975.

TS		
	Approximate Total NA Concentration (mg/L)	
Freezing Temperature (°C)	60	120
-15	4.38±0.385	4.77±0.351
-25	4.78±0.510	4.79±0.437
pH		
	Approximate Total NA Concentration (mg/L)	
Freezing Temperature (°C)	60	120
-15	0.955±0.0313	0.975±0.0170
-25	0.966±0.0333	0.957±0.0344

In terms of the frozen fraction it was determined that there is a combined effect of freezing temperature and initial total NAs feed water concentration on the solid frozen portion. This was noted in sample TS removal and pH values (p = 0.00979 and 0.0154). Removal efficiency of total solids at freezing temperature of -15°C was slightly higher at initial total NAs concentration 60mg/L (96.6%) than 120mg/L (96.5%). While at a freezing temperature of -25°C removal efficiency of total solids was greater at an initial total NAs feed water concentration of 120mg/L at 98.9% compared to 60mg/L at 93.7%. In terms of pH, ratios were similarly higher at a freezing temperature of -15°C and a total NAs concentration of the control at 60mg/L compared to 120mg/L (0.606 and 0.600, respectively). This was reversed at a freezing temperature of -25°C with pH ratios of 0.597 and 0.608 for an initial total NAs concentration of 60mg/L and 120mg/L, respectively. No combined effect was seen for water quality parameters COD and conductivity (p = 0.965 and 0.328) as shown in Table 5-8.

COD		
	Approximate Total NA Concentration (mg/L)	
Freezing Temperature (°C)	60	120
-15	0.0265±0.00694	0.0201±0.00574
-25	0.0413±0.0126	0.0365±0.00760
TS		
	Approximate Total NA Concentration (mg/L)	
Freezing Temperature (°C)	60	120
-15	0.0338±0.0139	0.0354±0.00884
-25	0.0633±0.0235	0.0169±0.0113
Conductivity		
	Approximate Total NA Concentration (mg/L)	
Freezing Temperature (°C)	60	120
-15	0.00822±0.000309	0.0103±0.00239
-25	0.0141±0.00359	0.0129±0.00225
pH		
	Approximate Total NA Concentration (mg/L)	
Freezing Temperature (°C)	60	120
-15	0.606±0.00378	0.600±0.00565
-25	0.597±0.00547	0.608±0.005101

5.4 Conclusion

The following statements were concluded upon completion of this experimental analysis:

- Both freezing temperatures tested were able to obtain a high degree of separation efficiency of NAs. Although, at the colder freezing temperature (-25°C) a significantly increased level of NAs were reported in the solid portion over a warmer freezing

temperature (-15°C) and this corresponded to a reduced ability to concentrate impurities in the liquid phase. This was noted through lower solids concentration in the liquid fraction for -25°C and increased COD concentration and conductivity levels in the solid portion compared to -15°C.

- All durations of ultra sonic cycle times (1s on/10s off, 1s on/20s off, 1s on/30s off) implemented during treatment provided a high degree of concentration of NAs in the liquid fraction and the effective elimination of NAs from the solid fraction. There was no significant difference amongst these cycle times ability to perform treatment. This suggests that the cycle time of 1s on/ 30s off would be most appropriate for treatment as this level of ultrasonic irradiation would consume the least amount of energy. Perhaps in a future study even lower levels of cycle time should be examined.

- Ultrasound at higher levels of amplitude (30% vs. 20%), surprisingly, reported reduced concentrations of NAs in the liquid phase compared to lower applied amplitude as noted by significantly reduced concentration of COD and conductivity levels in the liquid portion. Conversely the higher amplitude reported greater removal rates as noted by conductivity levels. This was theorized to perhaps be due to the deterioration of NAs by the increased rate of acoustic cavitation with the increase intensity of ultrasound.

- All levels of mechanical agitation provided a high degree of concentration of NAs in the liquid portion and a high degree of removal of NAs from the solid portion. Conductivity reported a significant reduction in removal efficiency with reduced RPM levels. It was also noted that a significant reduction in pH occurred with increased level of agitation. This was hypothesized to be a result of an increase in mass transfer rate of carbon dioxide into solution thus lowering the pH.

- Both mechanical and ultrasound progressive freeze concentration methods provided a high level of NAs partitioning between the liquid and solid portions resulting in high concentration of NAs in the liquid phase and very low concentrations of NAs in the solid phase. A significant difference amongst pH values was noted between ultrasound and mechanical, with a higher reduction being noted in the liquid portion of the mechanical method. This was assumed to be due to the previously mentioned increased diffusion rate of carbon dioxide.

- A reduction in removal and concentration efficiency of NAs was noted in TS concentration in both the liquid and solid fractions with a corresponding decrease in NAs concentration. This was in contrast to the other water quality parameters which noted no significant difference with a change of NAs concentration in the feed water. This discrepancy may be a result of experimental error and limitations of the analysis equipment.

- There was a notable two factor interaction between the initial feed water concentration and the freezing temperature. This was detected in TS, conductivity, and pH in the unfrozen portion, and in TS and pH in the frozen portion.

5.5 References

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Chapter 6 - Chapter: Progressive Freeze Concentration of Synthetic Naphthenic Acids and Influence of Inorganic Compounds on Removal of Naphthenic Acids

The ability of progressive freeze concentration to separate a synthetic NAs mixture is examined in this chapter. Its efficacy is compared to that of the progressive freeze concentration of a solution containing a three NAs mixture. As well, the influence of added inorganic contaminates, chloride and sulfate, at low and high concentrations on removal efficiency of NAs was also examined. Progressive freeze concentration was slightly more effective in the separation of synthetic NAs compared to the three NAs mixture. Inorganic impurities added to the feed water at the low range of concentrations (40mg/L) did not influence the efficacy of progressive freeze concentration of NAs. A significant reduction in NAs freeze concentration efficiency in the liquid fraction and a much higher contamination of NAs in the solid phase was observed when inorganic impurity concentration increased to 500mg/L.

6.1 Introduction

OSPW contain a wide assortment individual NAs ranging in molecular size, carbon number, and ring numbers (Clemente & Fedorak, 2005). It has been reported that the molecular size of NAs is related to toxicity (Microtox^{TM}), NAs with smaller molecular size seem more toxic (Holowenko et al., 2002). Currently investigated treatment methods of NAs show selectivity during treatment resulting in reduced effectiveness of for certain fractions of NAs. Ozonation appears to favour NAs of larger molecular size (Scott et al., 2008, Perez-Estrada et al., 2011) while biodegradation appears to favour smaller molecular size (Holowenko et al., 2002). Therefore it is critical to test the ability of progressive freeze concentration to treat a wide range of NAs. The OSPW also

contain a wide range of inorganic contaminates as outlined in Chapter 2. Particularly prevalent contaminates in OSPW include chloride and sulfate at concentrations of 40 to greater than 500mg/L (Allen, 2008). This is particularly critical for investigation as it has been noted that a correlation between separation efficacy and solute feed water concentration exists, with a reduction in separation efficacy corresponding to an increase in solute concentration (Gunathilake et al., 2013, Matsuda et al., 1999, Miyawaki et al., 2013, Miyawaki et al., 2005).

6.2   Materials and Methods

6.2.1   Experimental Apparatus

The experimental apparatus is detailed in Chapter 4.

6.2.2   Experimental Design

6.2.2.1   *Freeze Concentration of Synthetic Naphthenic Acids Solution*

There was no documentation provided on the composition of the synthetic NAs supplied by Sigma Aldrich (St. Louis, Missouri). The synthetic NAs were in a viscous liquid form with a boiling point of 106.4°C – 333.6°C at 1,013hPa and a flash point of 101.0°C. Its density was 0.92 g/cm^3 at 20°C and a solubility of 0.05g/L. A benchmark using the three NAs solution was therefore applied to achieve the desired concentrations of 60mg/L and 120mg/L. This was done by diluting 0.2mL of synthetic NAs in 250mL of dilute sodium hydroxide solution (200mg/L) and 750ml of pure water and then further diluted to ratios of 1:2, 1:4, and 1:8 parts, synthetic NAs solution to water. The COD of each of these resulting solutions was then determined and the following graph was generated in Figure 6-1.
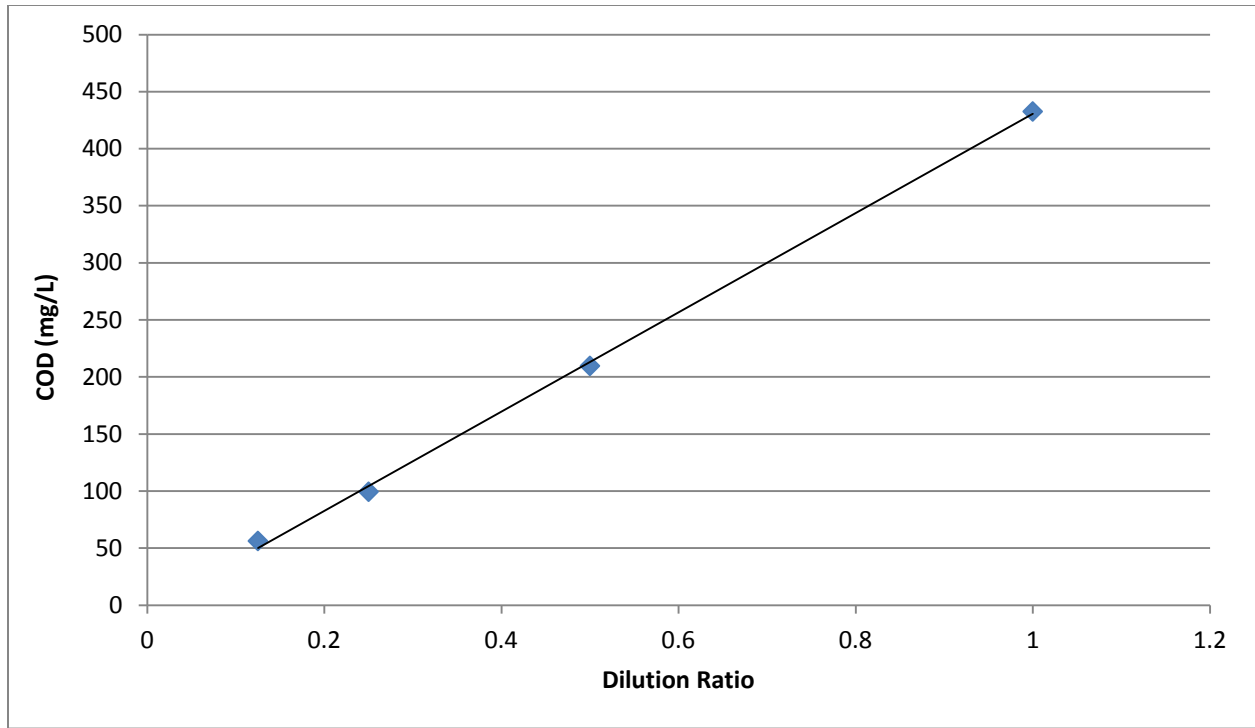
COD values for the three NAs solution feed water were listed to be approximately 150mg/L and 300mg/L for total NAs at 60mg/L and 120mg/L, respectively. The dilution levels of synthetic NAs that result in these COD concentration were thus used. The concentrations and ultrasound cycle times tested for this chapter for synthetic NAs are shown below in Table 6-1. Duplicates of each experimental run were performed.

Table 6-1: Summary of varied experimental factors for effect synthetic NAs solution.

Approximate Synthetic NA Concentration (mg/L)	US Off Cycle Time (s)
60	10
60	20
120	10
120	20

The follow parameters remained constant through the synthetic NAs experimentation:

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- Freezing Bath Temperature: -15°C

- Mechanical RPM: 100

- Ultrasound Amplitude: 20%

- Freezing Level: 80% of initial volume

6.2.2.2 *Investigation of the Effect of Inorganic Contaminants on Removal of NAs*

Chloride and sulfate were both added to a mixture of three NAs feed water to examine the effects of these added inorganic materials on the effectiveness of progressive freeze concentration. Chloride and sulfate were selected as they are the main inorganic contaminant in OSPW. Concentrations of 40 and 500mg/L were selected as this covers the concentrations range of both contaminates found in OSPW (Allen, 2008). Table 6-2 details the experimental conditions tested. Duplicates runs were performed.

Table 6-2: Summary of varied experimental factors for effect inorganic contaminates

Chloride Concentration (mg/L)	Sulfate Concentration (mg/L)
40	0
500	0
40	40
500	500

The following conditions remained constant throughout this section:

- NAs: Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid

- Approximate Total NAs Concentration: 120mg/L

- Freezing Bath Temperature: -15°C

- Mechanical RPM: 100

- Ultrasound Cycle Time: 1s on/ 10s off

- Ultrasound Amplitude: 20%

- Freezing Level: 80% of initial volume

6.2.3   Water Sample Preparation

The feed water was prepared following the procedure outline in Chapter 4. It was modified by adding the dilutions of synthetic NAs discussed above. Chloride and sulfate were added to the three NAs feed water by first weighing an appropriate mass of sodium chloride and sodium sulfate. These were then dissolved individually in highly refined water in 1L volumetric flasks and diluted to provide the required concentrations of 40mg/L or 500mg/L. The water quality of these described feed waters is shown in Table 6-3 and Table 6-4.

Table 6-3: Characteristics of feed water samples containing inorganic contaminates (OR = conductivity exceeds maximum measurable value of implemented device: range 0µs/cm - 2000µs/cm)

NA Present	Initial NA Concentration (mg/L)	Chloride Concentration(mg/L)	Sulfide Concentration (mg/L)	pH	Conductivity (µs/cm)	TS (mg/L)	COD (mg/L)
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120.21	39.67	0	10.44	179.1	189.83	301.31
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120.73	503.49	0	10.34	1104	654.53	302.53
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120.31	39.67	40.68	10.47	288	2849.15	300.1
Cyclohexanecarboxylic acid, trans-4-Pentylcyclohexanecarboxylic acid, Cyclohexanepentanoic acid	120.25	503.49	508.49	10.32	OR	1386.6	302.53

Table 6-4: Characteristics of feed water samples containing synthetic NAs solution.

NA Present	Initial Total NA Concentration (mg/L)	pH	Conductivity (µs/cm)	TS (mg/L)	COD (mg/L)
Synthetic NAs	60	10.61	89.85	66.9	147.4
Synthetic NAs	120	11	197.35	145.03	293.02

6.2.4 Experiments

Chapter 4 outlines the experimental procedure performed.

6.2.5 Data Analysis

The data analysis was mirrored from Chapter 4 and Chapter 5.

6.3 Results and Discussion

6.3.1 Comparison of Progressive Freeze Concentration of Synthetic Naphthenic Acids Solution and Three Naphthenic Acids Mixture

Progressive freeze concentration was able to effectively reduce concentrations of a synthetic NAs solution from the feed water. It was slightly more effective at reducing concentration of synthetic NAs compared to the three NAs mixtures. This will be discussed below.

6.3.1.1 Comparison of Synthetic Naphthenic Acids and Three Naphthenic Acids in the Liquid Portion

The forms of the NAs did not affect the freeze concentration efficiency. Both synthetic NAs and three NAs mixture were highly concentrated in the unfrozen fraction during progressive freeze concentration. COD concentrations ratios were slightly higher (4.59) for three NAs solution compared to that of the synthetic NAs solution (4.50). This disparity was insignificant ($p = 0.504$). TS concentration in the unfrozen liquid samples were significantly different between the two solution types ($p = 0.000534$), with the synthetic NAs solution at a 5.0 fold increase in TS concentration compared to three NAs mixture at a 4.6 fold increase of solids in the unfrozen liquid. Conversely, conductivity levels were significantly higher ($p = 0.000183$) for the three NAs solution at a ratio of 3.65 compared to synthetic NAs solution at a ratio of 3.24. Interestingly, the pH value for the synthetic NAs solution was not decreased in the liquid portion following progressive freeze concentration, remaining unchanged from the feed water. This is in

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contrast from the three NAs mixture which was reduced to a ratio of 0.976. These results are shown below in Figure 6-2.
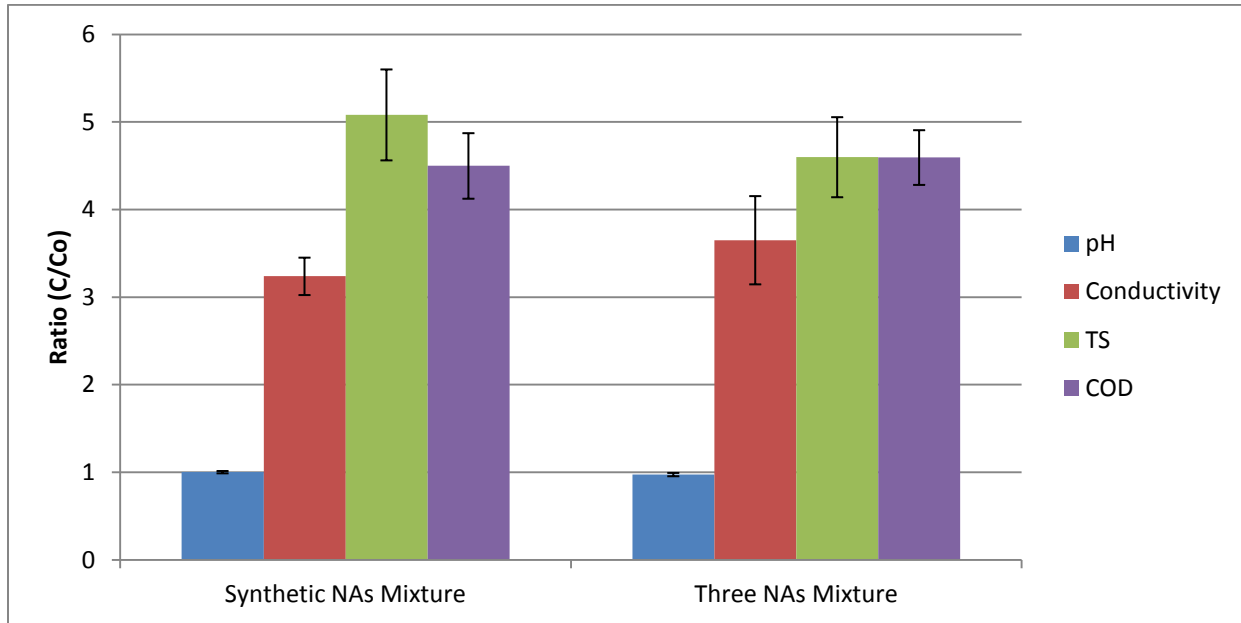
Figure 6-2: The ability of progressive freeze concentration process to concentrate synthetic NAs and a mixture of three NAs in the unfrozen portion (Three NAs mixture at 60.38mg/L and 120.24mg/L and synthetic NAs at 60mg/L and 120mg/L).

6.3.1.2   *Removal of Synthetic Naphthenic Acids and Three Naphthenic Acids in the Solid Portion*

TS concentration in the ice samples were significantly ($p = 0.0105$) less for the synthetic NAs compared to that of the three NAs mixture, with reported removal rates of 97.9% and 95.0%, respectively. Conductivity levels were prominently higher for the three NAs mixture in contrast to the synthetic NAs, suggesting reduced removal efficiency as visualized in Figure 6-3. Conversely, removal rates of COD causing material were slightly less in the synthetic NAs solution (96.2%) compared to that of the three NAs mixture (97.4%). Although, this difference in efficiency as noted by conductivity and COD was insignificant ($p = 0.287$ and 0.460, respectively). The pH ratio of the synthetic NAs was significantly ($p = 4.9E\text{-}5$) lower than the three NAs mixture with ratios of 0.583 and 0.608, respectively.

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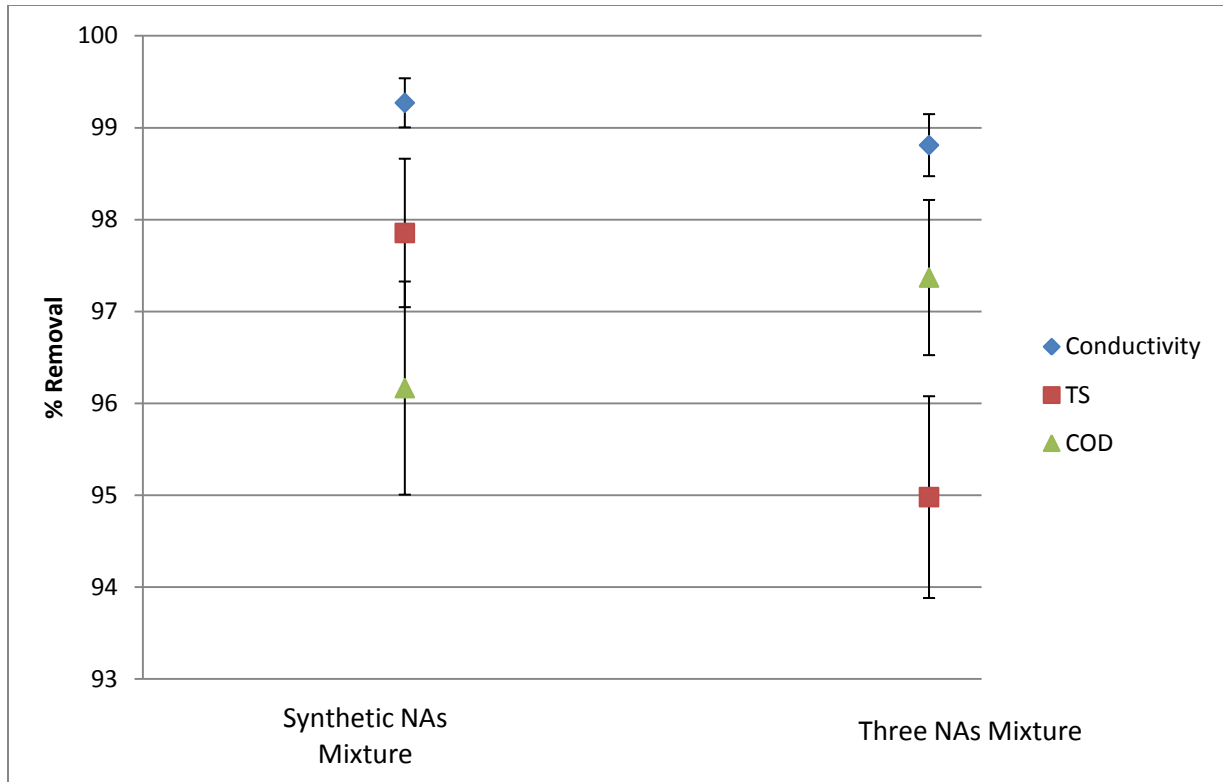
Figure 6-3: The ability of progressive freeze concentration to remove synthetic NAs and a mixture of three NAs in the frozen portion (Three NAs mixture at 60.38mg/L and 120.24mg/L and synthetic NAs at 60mg/L and 120mg/L).

As is shown above, there is a slight difference in the effectiveness between the progressive freeze concentration of the synthetic NAs and the three NAs mixture. The three NAs mixture reported both significantly reduced concentrations of TS in the unfrozen fraction and higher solids concentration levels in ice fraction. This suggests reduced separation efficiency of solids for treatment of three NAs solution vs. treatment of the synthetic NAs mixture. As previously stated, chemical nature and size played a role during the rejection of molecules from the ice phase during progressive freeze concentration (Halde, 1980, Matsuda et al., 1999). The characteristics of the NAs present in the synthetic NAs mixture was not provided by the manufacturer and thus identification of the composition of the mixture may provide proper insight.

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6.3.2 Influence of Freezing Methods on Removal of Synthetic NAs

6.3.2.1 Liquid Portion

Both ultrasound and mechanical progressive freeze concentration provided a high level of concentration of NAs within the unfrozen liquid portion. There was a significantly higher (p = 0.0311) COD ratio in ultrasound method at 4.66 compared to mechanical method at 4.34. It is shown below in Figure 6-4 no significant difference amongst TS concentrations, conductivity and pH levels was present (the statistical analysis results are summarized in Appendix, Table 0-185, Table 0-187, Table 0-189).
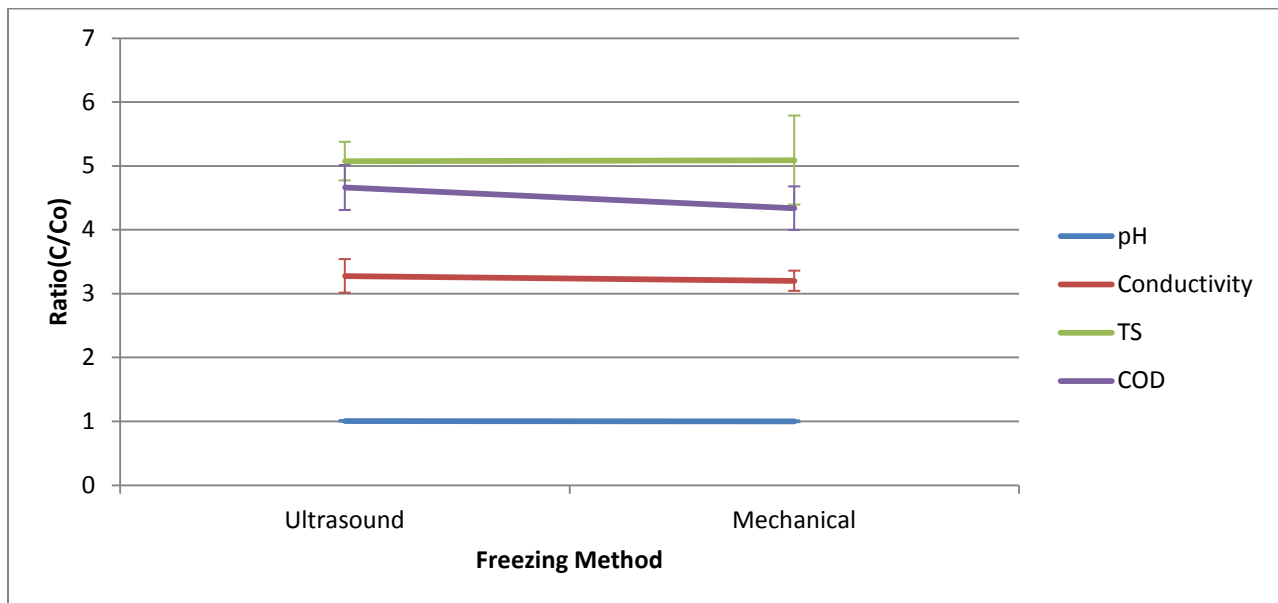
Figure 6-4: Freezing methods, ultrasound and mechanical, influence on the progressive freeze concentration of synthetic NAs in the liquid fraction (Synthetic NAs mixture at 60mg/L and 120mg/L).

6.3.2.2 Solid Portion

Although ultrasound reported higher removal COD causing material at 97.5% removal compared to mechanical at 94.8% this difference was insignificant (p = 0.227). Similarly there was an negligible (p = 0.227) increase in removal of ionic species from the frozen fraction with ultrasonic freezing method (99.6%) as compared to that of mechanical freezing method (99.0%).

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Conversely, TS concentration reduction were insignificantly less (p = 0.381) for ultrasound method at 97.9% compared to mechanical at 98.6%. This is shown below Figure 6-5. Both methods achieved a reduction in pH to ratios of approximately 0.6.
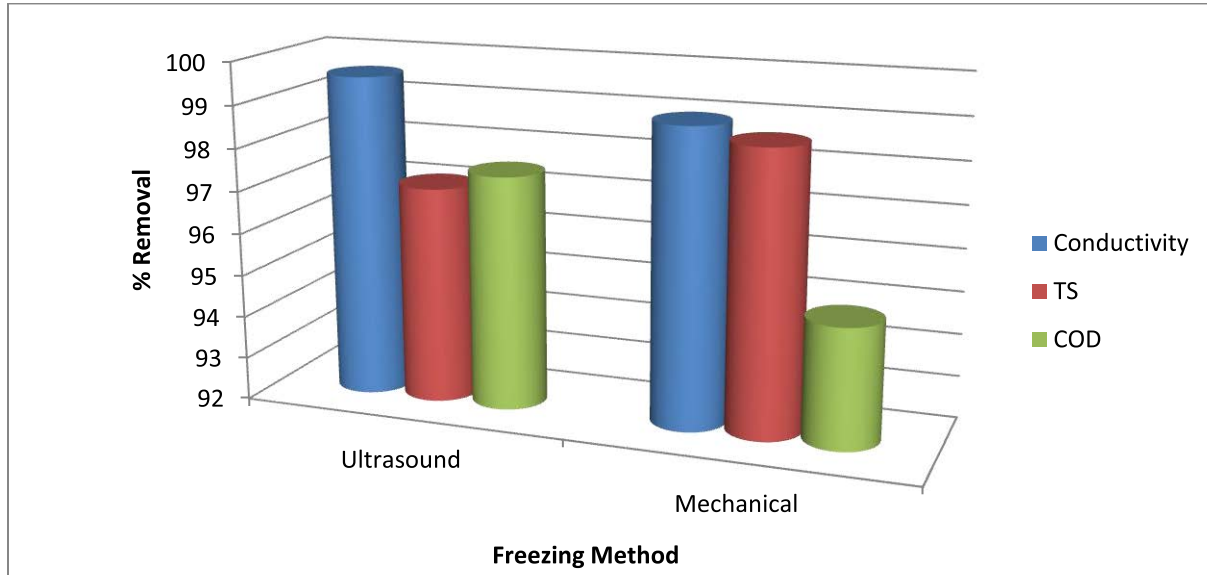
Figure 6-5: Freezing methods, ultrasound and mechanical, influence on the progressive freeze concentration of synthetic NAs in the solid fraction (Synthetic NAs mixture at 60mg/L and 120mg/L).

6.3.3 Effect of the Initial Feed Water Synthetic Naphthenic Acid Concentration on Separation Efficiency

6.3.3.1 Liquid Portion

Table 6-5 displays the comparison of two synthetic NAs acid concentrations at 60mg/L and 120mg/L. There was no detectable significant difference in the liquid portion with an increase in synthetic NAs in the feed water during progressive freeze concentration for the parameters pH, conductivity, TS, and COD (Table 0-168, Table 0-170, Table 0-172, Table 0-174).

Table 6-5: The influence of synthetic NAs concentration in the solid portion of progressive freeze concentration.

	Synthetic NAs Concentration	
Water Quality Parameter	60mg/L	120mg/L
pH/pH_o	1.001±0.00981	1.005±0.0166
$Conductivity/Conductivity_o$	3.219±0.138	3.258±0.279
TS/Ts_o	5.235±0.554	4.928±0.465
COD/COD_o	4.535±0.343	4.463±0.423

6.3.3.2   Solid Portion

Unlike the liquid portion, there was a difference detected with an increase in synthetic NAs feed water concentration in the solid portion. Significantly higher solids (TS) levels (p = 0.00882) was reported when a lower concentration of synthetic NAs was used in the feed water. TS concentration ratios of 0.00543 (99.4% removal) for feed water containing 120mg/L synthetic NAs was increased to 0.0375 (96.3% removal) for feed water at 60mg/L synthetic NAs. On the other hand, both COD concentrations and conductivity levels reported an insignificant higher removal rate (p = 0.370 and 0.448) with a decrease in synthetic NAs feed water concentration as revealed in Figure 6-6. At both synthetic NAs feed water concentrations pH was reduced to an approximate ratio of 0.6 (p = 0.396).
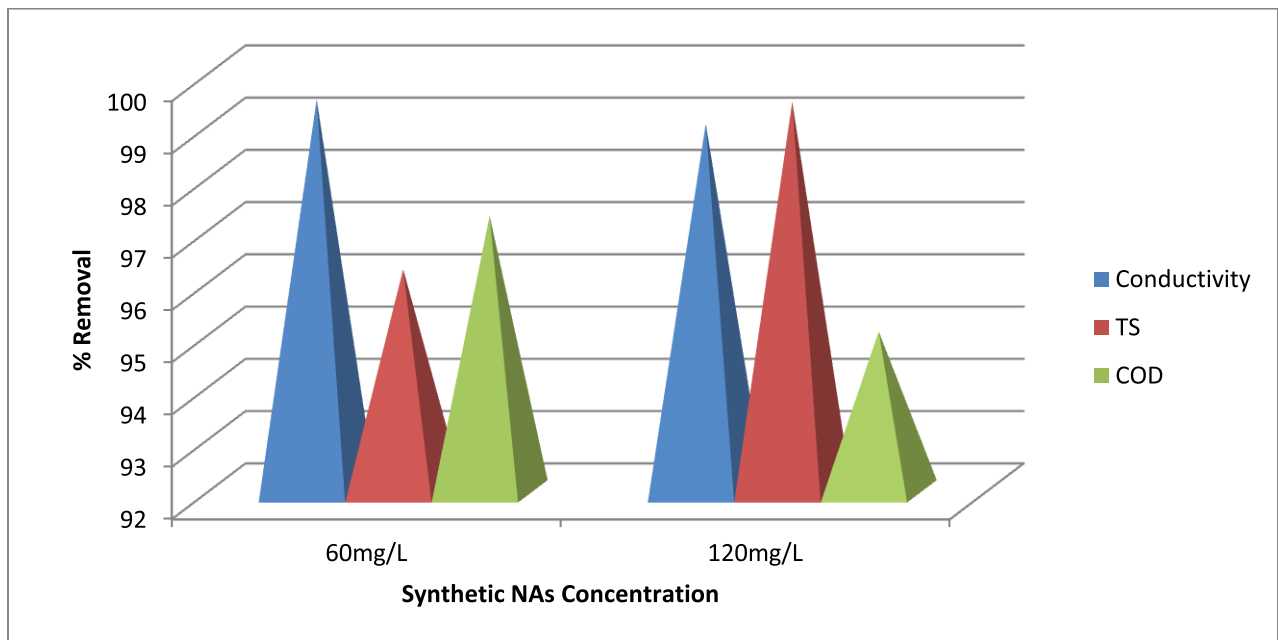
Figure 6-6: The effect of synthetic NAs concentration on progressive freeze concentrations ability for removal of NAs from the solid phase.

This reduction in efficacy of progressive freeze concentration with a decrease in feed water concentration was also prominent in Chapter 5 for TS concentrations and is discussed.

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6.3.4 Influence of Ultrasound Cycle Time on Progressive Freeze Concentration of Synthetic Naphthenic Acids Efficiency

Both tested levels of ultrasound intensity were able to effectively partition synthetic NAs between the solid and liquid segments.

6.3.4.1 *Effect of Cycling Time on Contaminate Levels in the Liquid Segment*

Total solids levels reported an approximate 5 fold increase in concentrations over the control (p = 0.278). COD levels were slightly reduced at a higher level of ultrasound intensity at ratios of 4.80 for cycle time of 1s/20s compared to 4.52 for cycle time of 1s/10s. Although this reduction was insignificant (p = 0.240). There was a significant reduction (p = 0.0407) in conductivity ratios with an increase in ultrasound intensity at ratios of 3.43 and 3.13 for 1s/20s and 1s/10s, respectively. At both levels of ultrasonic cycle times pH ratios remained at approximately 1 (p = 0.181).
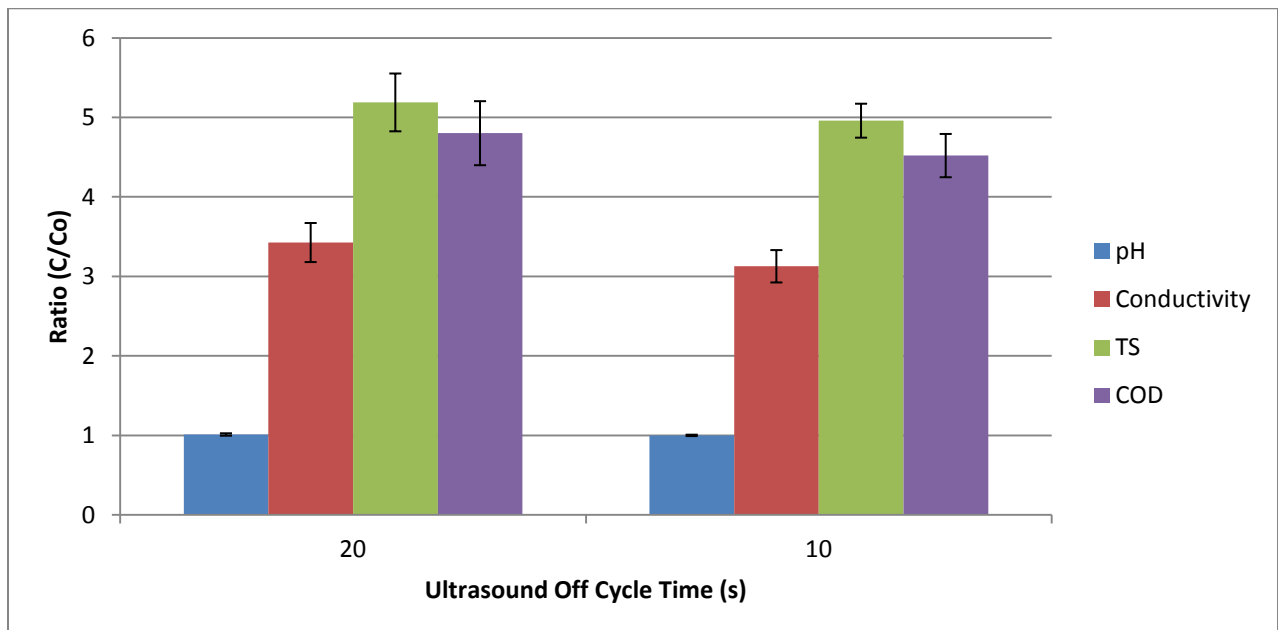
Figure 6-7: Ultrasound cycle time's effect on the concentration of synthetic NAs in the liquid portion of progressive freeze concentration.

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6.3.4.2   Cycling Time on Contaminate Levels in the Ice Samples

An increase in ultrasound agitation resulted in a notable (p = 0.00298) decrease in COD

concentration in the solid segment. The COD ratio for cycle time of 1s/20s was 0.0344 (96.6%

removal) compared to 0.0153 (98.5% removal) for 1s/10s. Removal efficiency was

insignificantly (p = 0.217) higher at a reduced agitation level resulting in removal rates of 98.9%

for 1s/20s cycle time and 95.3% for 1s/10s. Conductivity reported removal rates of 99.6% for

both cycle times (p = 0.603). At each cycle time the pH was reduced to a ratio of approximately

0.58 (p = 0.995). These removal rates and pH ratios are shown in Table 6-6.

Table 6-6: The effect of ultrasound cycle time on the concentration of synthetic NAs in the solid fraction of progressive freeze concentration.

	Ultrasound Off Cycle Time (s)	
Water Quality Parameter	20s	10s
pH/pH_o	0.579±0.0053	0.577±0.0049
$Conductivity/Conductivity_o$ (% Removal)	0.00443±0.0013 (99.6%)	0.00395±0.00072 (99.6%)
TS/Ts_o (% Removal)	0.0114±0.0228 (98.9%)	0.0467±0.0539 (95.3%)
COD/COD_o (% Removal)	0.0344±0.0067 (96.6%)	0.0153±0.0117 (98.5%)

These reported differences in conductivity for the liquid segment and COD for the solid segment

due to a change in cycle times for synthetic NAs was in contrast to Chapter 5, where no

detectable differences were determined for these parameters amongst the cycle times. This may

be a result of the smaller sample size tested in this experiment compared to Chapter 5. There is

also the possibility that a shorter cycle time could perhaps be oxidizing the NAs in solution at a

greater rate as the COD values were lower in both the liquid and solid segment. Higher

ultrasound intensity was reported in Chapter 5 to significantly reduce COD values in the frozen

portion.

6.3.5 Effect of Inorganic Contaminates on the Removal of Contaminates from Feed Water Containing NAs and Inorganic Contaminates Chloride and Sulfate

6.3.5.1 Liquid Portion

A statistically sharp decrease (p = 0.000488) in concentration of solids in the liquid portion of the progressive freeze concentration of NAs solution was reported with the addition of inorganics. With no inorganics, solids concentration ratio in the liquid portion was 4.76 compared to a TS concentration ratio of 3.94 for feed water containing inorganics. This decrease in effectiveness for the concentration of contaminates in the solid phase was also apparent with COD causing material in the liquid fraction. With no inorganic contaminates COD ratios were 4.73. This was reduced to a ratio of 3.58 with the addition of inorganic contaminates chloride and sulfate to the feed water stream. This reduction in efficiency was significant (p = 0.0000135).

Conversely, an increase in conductivity was reported with the addition of inorganics to the feed water. With no inorganics in the feed water conductivity ratios were 3.52 and this was increase to 4.02 with the addition of chloride and sulfate. The reasoning for this increase in conductivity ratio may be a result of the limitations of the conductivity probe; at higher concentration of ionic species the probe was unable to provide a reading. Therefore at inorganic concentrations greater than 40mg/L of both chloride and sulfate each were unable to return a result. This increase in conductivity ratios with an increase in inorganics concentration may also be influenced by the nonlinear relationship of total dissolved solids and electrical conductivity (Thirumalini & Joseph, 2009).

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With the addition of chloride and sulfate to the feed water a reduction in pH of the liquid phase was also noted. The pH ratio was reduced to 0.923 with inorganics compared to no inorganics at 0.969. This reduction was significant ($p = 0.0000344$). These results are shown below in Figure 6-8.
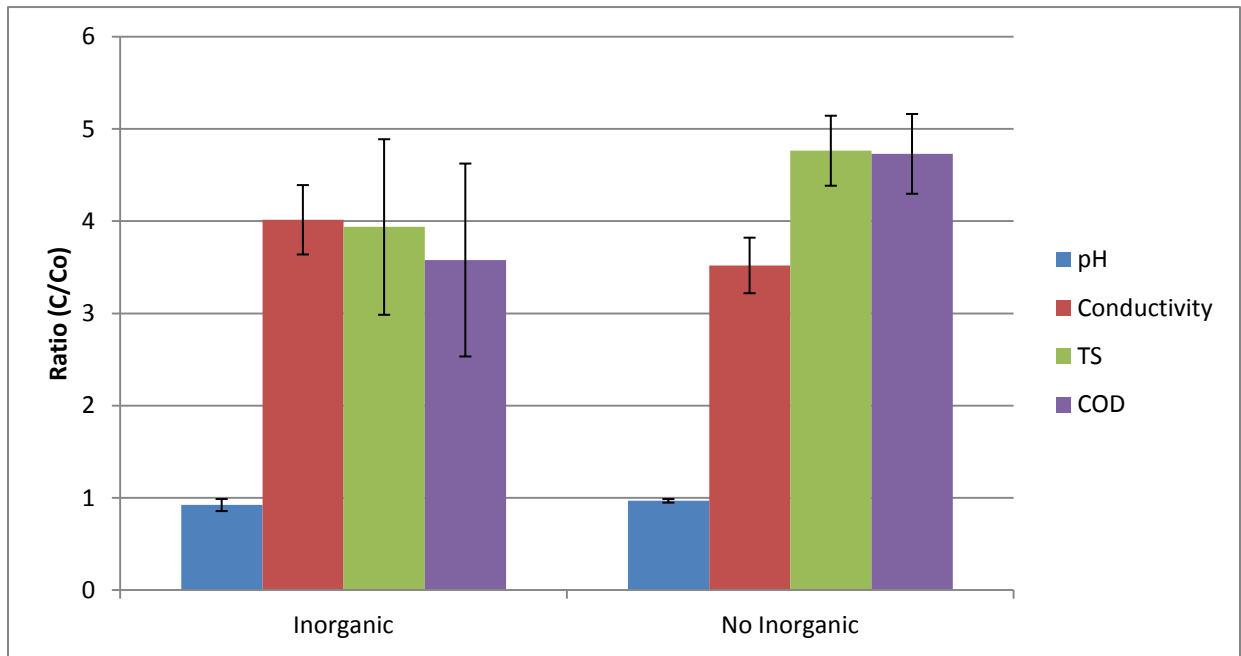
Figure 6-8: The influence of the presence of inorganic contaminates in the feed water on the concentration of contaminates in the liquid phase(total NAs at 120.37mg/L, chloride at 39.67mg/L and 503.49mg/L, and sulfate at 40.68mg/L and 508.49mg/L).

6.3.5.2 *Frozen Portion*

A significant decrease ($p = 0.0000344$) in the removal efficiency of COD causing material occurred with the addition of inorganics in the feedwater to a removal rate of 71.4% compared to that of 97.9% with no inorganics. This was also apparent in TS removal with a significant decrease ($p = 0.000779$) in removal efficiency with the addition of inorganics at 77.5% in contrast to 95.2% with no inorganics in the feedwater. There was also a notable reduction ($p = 0.000378$) in the removal of ionic species from the solid phase. No inorganics reported a removal

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efficiency of ionic species 98.8% this was reduced to 88.5% with the addition on inorganics

chloride and sulfate to the feedwater.

pH significantly increased ($p = 0.0000425$) to a ratio of 0.686 with the addition of chloride and

sulfate to the feedwater from a pH ratio of 0.608 with no inorganics.

Table 6-7: The influence of the presence of inorganic contaminates in the feed water on the removal contaminates from feed water (total NAs at 120.37mg/L, chloride at 39.67mg/L and 503.49mg/L, and sulfate at 40.68mg/L and 508.49mg/L).

Water Quality Parameter	Inorganic	No Inorganic
pH/pH_o	0.686±0.0777	0.608±0.0261
$Conductivity/Conductivity_o$ (% Removal)	0.115±0.128 (88.5%)	0.0115±0.0158 (98.8%)
TS/Ts_o (% Removal)	0.225±0.222 (77.5%)	0.0476±0.0416 (95.2%)
COD/COD_o (% Removal)	0.286±0.268 (71.4%)	0.0215±0.0321 (97.9%)

It is clearly apparent that the addition of inorganic contaminates chloride and sulfate in the

feedwater of NAs has a significant influence on the separation efficiency of contaminates in the

solid and liquid phase during progressive freeze concentration. This is evident from the reduction

in concentration of contaminates in the liquid phase as well as the increase in contamination of

the solid phase. This decrease in separation efficiency corresponding to an increase in

concentration of the feed water has been noted by numerous authors (Gunathilake et al., 2013,

Matsuda et al., 1999, Miyawaki et al., 2013, Miyawaki et al., 2005) and will be discussed further

below.

6.3.6 Influence of Freezing Methods on Removal of Contaminates from Feed Water Containing NAs, Chloride, and Sulfate

6.3.6.1 *Concentration of Impurities in the Unfrozen Liquid*

Both ultrasound and mechanical progressive freeze concentration provided a high concentration of contaminates in the liquid phase during the progressive freeze concentration of feed water containing NAs and the inorganic contaminates chloride and sulfate. It is shown in Figure 6-9 that there was no significant difference amongst the tested parameters (Table 0-200, Table 0-202, Table 0-204, and Table 0-206).
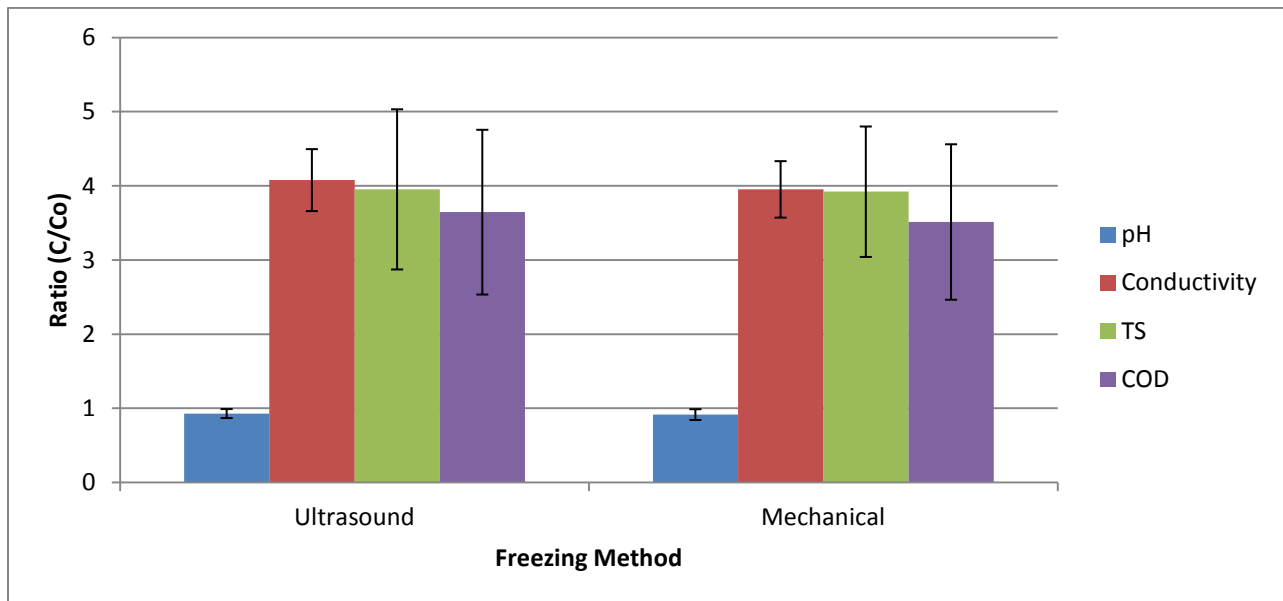
Figure 6-9: Freezing method's, ultrasound and mechanical, influence on the effectiveness of progressive freeze concentration of feed water containing NAs, chloride, and sulfate in the liquid fraction (total NAs at 120.37mg/L, chloride at 39.67mg/L and 503.49mg/L, and sulfate at 40.68mg/L and 508.49mg/L).

6.3.6.2 *Concentration of Impurities in the Unfrozen Liquid*

Progressive freeze concentration with implemented ultrasonic irradiation or mechanical agitation both provided statistically equal removal efficiency of contaminates during the progressive freeze concentration of water containing NAs and inorganic contaminates chloride and sulfate. These results are shown below in Table 6-8.

Table 6-8: Freezing method's, ultrasound and mechanical, influence on the effectiveness of progressive freeze concentration of feed water containing NAs, chloride, and sulfate in the frozen fraction (total NAs at 120.37mg/L, chloride at 39.67mg/L and 503.49mg/L, and sulfate at 40.68mg/L and 508.49mg/L).

Water Quality Parameter	Freezing Method	
	Ultrasound	Mechanical
pH/pHo	0.678±0.0863	0.695±0.0729
Conductivity/Conductivityo (% Removal)	0.101±0.142 (89.9%)	0.129±0.123 (87.1%)
TS/Tso (% Removal)	0.219±0.236 (78.1%)	0.232±0.222 (76.8%)
COD/CODo (% Removal)	0.266±0.275 (73.4%)	0.306±0.278 (69.4%)

6.3.7 Effect of the Concentration of Inorganic Contaminate Chloride and Sulfate on the Efficacy of Progressive Freeze Concentration

The addition of inorganic contaminates chloride and sulfate at increasing concentrations resulted in a substantial decrease in separation efficiency of progressive freeze concentration of NAs.

6.3.7.1 Unfrozen Fraction

COD concentration in the unfrozen fraction remained relatively unchanged, shown in Figure 6-10, after progressive freeze concentration treatment with the addition of contaminates chloride at 40mg/L and both chloride and sulfate at 40mg/L to feed water containing NAs (statistical results are summarized in Appendix Table 0-232). With the addition of 500mg/L of chloride to the feed water resulted in a marked decrease in concentration of COD at a ratio of 3.02 in the unfrozen fraction (p = 0.00E-7). Further increase in contaminates to 1000mg/L (sulfate and chloride at 500mg/L) resulted in a significantly lower reported COD ratio at 2.25 compared to chloride at 500mg/L (p = 0.000270).

This pattern of the decrease in concentration efficiency of contaminates in the liquid phase corresponding to an increase in contaminates in the feedwater was shadowed with total solids concentrations in the unfrozen fraction. No significant difference was detected among total solids

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ratios with NAs feed water containing no inorganics, chloride at 40mg/L, and chloride and sulfate at 40mg/L (statistical results are summarized in Appendix Table 0-234). Chloride at 500mg/L added to the NAs feed water significantly reduced the TS ratio in the unfrozen fraction to 3.50 (p = 8.90E-6). Both chloride and sulfate at 500mg/L (total inorganic concentration at 1000mg/L) added to the feed water further significantly decreased the TS in the unfrozen fraction to a ratio of 2.72 (p = 0.00277).

Conductivity ratios significantly increased (p = 0.000923) with the addition of chloride at 40mg/L to NAs feed water over the feed water containing no inorganics at values of 4.25 and 3.48, respectively. When both chloride and sulfate were added to the feed water at 40mg/L the conductivity of the unfrozen portion a ratio of 3.78 was observed. This value was not significantly different than the feed water containing no inorganics (p = 0.320). Higher concentration of inorganic contaminates resulted in conductivity values beyond the range of the conductivity probe (0μs/cm - 2000μs/cm) used and therefore the conductivity was unable to be determined due its limitations.

The values of pH ratios in the unfrozen fraction were decreased with an increase in inorganic contaminate concentration as seen in Figure 6-10. The decrease in pH with no inorganics and at chloride at 40mg/L was determined to be insignificant over the control while higher concentrations of Chloride and sulfate resulted in a significant reduction (The statistical results are summarized in Appendix, Table 0-236).
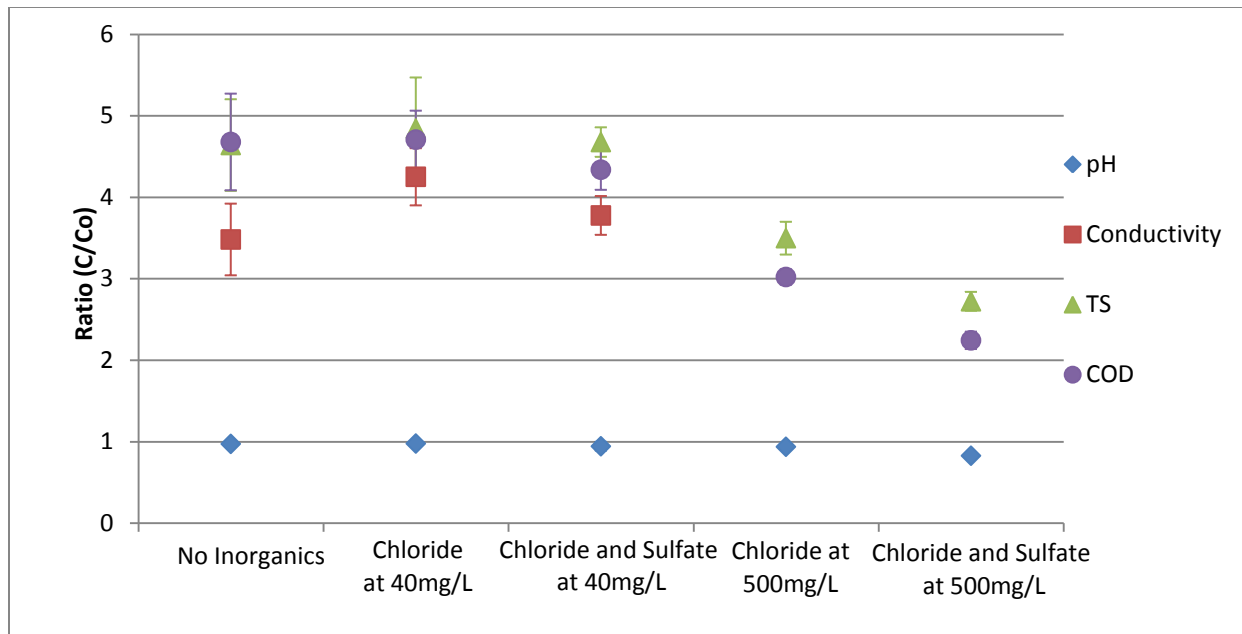
Figure 6-10: Inorganic contaminates and their effect on the efficiency of concentrating NAs in the liquid portion for progressive freeze concentration of NAs (total NAs at 120.37mg/L, chloride at 39.67mg/L and 503.49mg/L, and sulfate at 40.68mg/L and 508.49mg/L).

6.3.7.2   Frozen Fraction

Inorganic contaminates, chloride and sulfate, at 40mg/L added to a feed water stream containing NAs did not significantly (p = 0.809 and 0.306) influence the COD removal rates of contaminates in the frozen fraction of progressive freeze concentration compared to feed water containing only NAs. When concentrations of inorganics increased further a significant decrease in removal efficiency was noted. A chloride concentration of 500mg/L in the feed water reduced the removals rate of COD to 59.0% (p = 0.00E-7). A further decrease in removal rates to 35.4% occurred with a total inorganic concentration of 1000mg/L (chloride and sulfate at 500mg/L) in the feed water (p = 0.00E-7).

Total solids concentration exhibited similar results with no significant difference (p = 0.265 and 0.999) in solids concentration in the frozen fraction when chloride and sulfate were added to the feed water at 40mg/L. Removal rates of solids concentrations in the frozen fraction noticeably reduced with the addition of chloride at 500mg/L to 70.8% (p = 0.00E-7). A further reduction in

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removal efficiency (p = 0.00E-7) to 46.2% occurred with the addition of both chloride and sulfate at 500mg/L (1000mg/L total) to the feed water.

Similarly to COD and TS levels, there was no reported significant difference (p = 0.999 and 0.512) in conductivity levels in the frozen fraction with the addition of chloride at 40mg/L and both chloride and sulfate at 40mg/L. Although, a significant increase (p = 0.00E-7) in conductivity levels in the frozen fraction occurred with the addition of 500mg/L chloride into the feed water resulting in a reduced removal rate at 72.1%. This reduction in efficiency is shown below in Figure 6-11. The conductivity in the solid portion with the addition of 500mg/L chloride and 500mg/L sulfate to the feedwater was unable to be determined due to the value being out of the range of the device.

pH ratios remained relatively unchanged in the frozen fraction with the addition of chloride at 40mg/L and both chloride and sulfate at 40mg/L to the feed water compared to the feed water containing no inorganics at ratios of approximately 0.62 (p = 0.973 and 0.995). The pH ratios significantly increased (p = 0.00E-7 and 0.00E-7) to approximately 0.750 in the frozen fraction at inorganic feed water concentrations at 500mg/L of chloride and at 500mg/L for both chloride and sulfate compared to the feed water containing no inorganics.
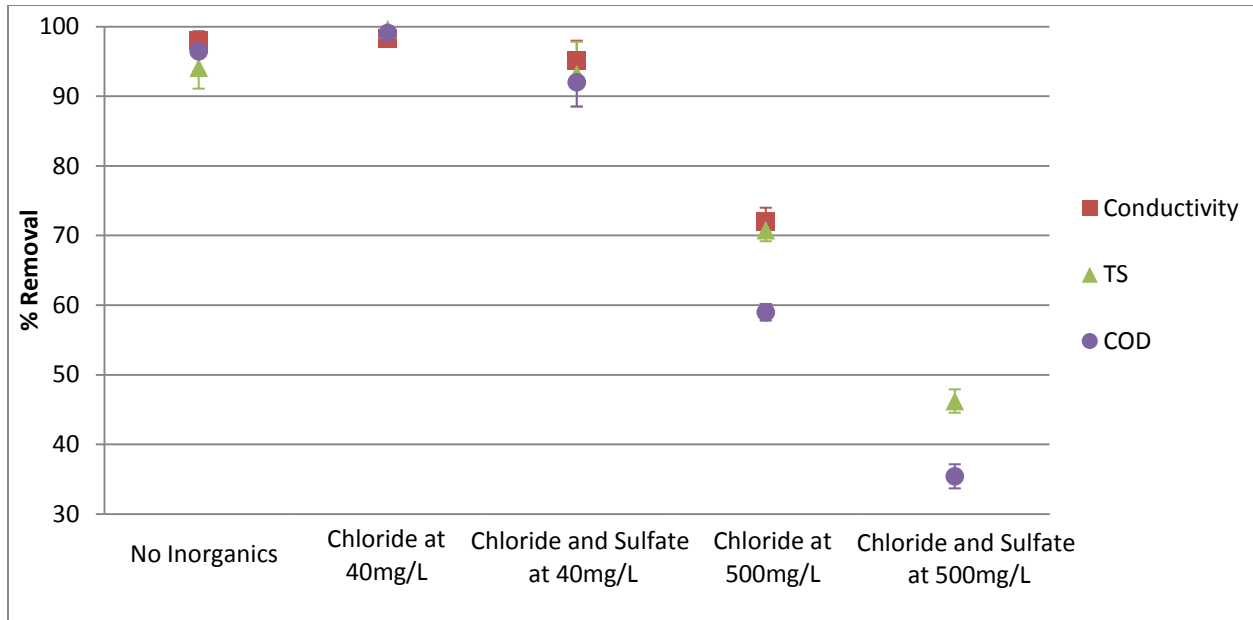
Figure 6-11: Inorganic contaminates and their effect on the efficiency of removal of NAs in the solid portion for progressive freeze concentration of NAs (total NAs at 120.37mg/L, chloride at 39.67mg/L and 503.49mg/L, and sulfate at 40.68mg/L and 508.49mg/L).

It is apparent from both the unfrozen and frozen fraction that at the high end of chloride and sulfate concentrations in the feed water corresponds to a reduction in separation efficiency of NAs. A notable reduction in concentration ability of contaminates in the unfrozen fraction as well as increased contaminate levels in the frozen portion was apparent in COD, TS, and conductivity levels. This decrease in effectiveness of progressive freeze concentration corresponding to an increase in concentration of solutes and particulate matter in the feed water has been noted by numerous authors (Gunathilake et al., 2013, Matsuda et al., 1999, Miyawaki et al., 2013, Miyawaki et al., 2005). An increase in agitation intensity has been shown to reduce this effect (Liu et al., 1997). COD and TS both displayed similar reduction in removal rates corresponding to an increase in inorganic concentrations. Although it appears that COD is reduced at a greater rate and this effect may be resulting from chloride interference. Chloride has the ability to interfere with COD resulting in falsely higher COD especially at higher concentrations of chloride (APHA, 2005).

6.4   Conclusion

The following conclusions were obtained as a result of this experimental analysis:

- Progressive freeze concentration provided high separation efficiency between the liquid and solid phase for feed water containing a synthetic NAs solution. There was a slightly greater removal rate of NAs from the solid phase in the synthetic NAs compared to the three NAs mixture.

- The two tested methods of progressive freeze concentration, ultrasound and mechanical, both provided a high efficacy for the separation of synthetic NAs in the solid and liquid fractions. TS were significantly higher in the liquid phase of synthetic NAs and significantly lower in the solid phase compared to the three NAs mixture suggesting a reduced removal efficiency for the three NAs mixture.

- Both ultrasound cycle times of 1s on/ 10s off and 1s on/ 20s off resulted in a high degree of concentration of synthetic NAs in the liquid portion and a high removal rate in the solid portion. NAs were removed slightly more efficiently from the solid fraction at a lower cycle time of ultrasound but there was also slightly less concentration of contaminates in the liquid phase. This suggests that perhaps the increase ultrasonic irradiation results in the decomposition of the synthetic NAs in solution through acoustic cavitation. Further investigation into this is required.

- Progressive freeze concentration concentrated synthetic NAs in the liquid phase at feed water concentrations of 60mg/L and 120mg/L. High removal rates for both feed water concentrations of the ice phase was also reported, but a reduced efficiency at 60mg/L was noted in TS concentrations. This shadowed the results obtained in

Chapter 5 and was suggested to be a results of experimental error and limitations in the analysis equipment.

- There was no reported significant difference between the ability of mechanical progressive freeze concentration and ultrasound progressive freeze concentration to treat a wastewater stream containing a three NAs mixture and inorganic contaminates chloride and sulfate.

- The addition of inorganics chloride and sulfate markedly reduced the removal efficiency of contaminates from the feedwater. Removal rates were reduced from greater than 98.8% to as low as 71.4% with the addition of inorganics.

- The concentration of inorganic contaminates in feed water containing the three NAs mixture influenced the efficacy in progressive freeze concentration. At concentrations of chloride at 40mg/L and both chloride and sulfate at 40mg/L no reduction in efficiency was noted. In contrast, with higher concentrations of inorganics, at 500mg/L and 1000mg/L, markedly reduced concentration ability in the liquid phase and a higher contaminate level in the solid phase was reported. This effect could potentially be countered by providing a higher level of mixing intensity by reducing the effects of concentration polarization.

6.5 References

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Chapter 7 - Conclusion

The investigation into progressive freeze concentration as a potential treatment option for NAs in OSPW was successful. Progressive freeze concentration was able to provide a high degree the concentration of contaminates in the unfrozen liquid portion while obtaining a high level of contaminate removal in the solid frozen portion. Both methods of implementation of progressive freeze concentration, ultrasound and mechanical, were equally effective at reducing TS, COD, and conductivity values in the frozen fraction of feed water containing single, two, and three NAs at concentrations of 20mg/L to 120mg/L. There was a difference in pH values in the unfrozen portion between mechanical and ultrasound and. this was assumed to be a result of mechanicals enhancement of the mass transfer of CO_2 into solution.

The partition coefficients (K) obtained for the three tested feedwater types (single, two, and three NAs mixtures) showed a high separation efficiency of NAs between the liquid and solid phase was obtained. These results were similar to previous investigations into partition coefficients.

Initial feedwater concentration of NAs did largely not influence the ability of progressive freeze concentration to concentrate/ remove NAs. High removal rates of contaminates from the solid phase was obtained between feed water concentrations of 20mg/L, 60mg/L, 90mg/L, and 120mg/L. A slight decrease in removal efficiency occurred for total solids removal with a decrease in NAs concentration. This was attributed to experimental error and limitations of the analysis equipment.

Progressive freeze concentration provided a high degree of separation between the solid and liquid phases for all NAs tested. Single, two, and three NAs mixtures, as well as the synthetic NAs were all concentrated in the liquid phase equally effectively. In the solid phase there was a

difference noted in removal efficiency of total solids concentrations between three NAs mixture and the two NAs mixture. There was also a slight decrease in efficiency of the three NAs mixture compared to the synthetic NAs.

The applied freezing temperature during progressive freeze concentration influenced the efficacy of progressive freeze concentration of NAs. A lower temperature (-25$^\mathbf{o}$C) markedly reduced the concentration of NAs in the liquid phase and increased contamination in the solid phase compared to a warmer freezing temperature (-15$^\mathbf{o}$C).

Ultrasound cycle time was not a factor in the effectiveness of progressive freeze concentration of NAs. All cycle times (1s on/10s off, 1s on/20s off, 1s on/30s off) provided a high degree of the separation of NAs between the solid and liquid phases. Ultrasound amplitude on the other hand did influence the progressive freeze concentration of NAs. A higher level of ultrasonic amplitude, at 30%, provided a higher removal efficiency of NAs from the solid phase compared to lower ultrasonic amplitude of 20%.

Mechanical agitation was not a significant influence on the progressive freeze concentration of NA. 100, 200, and 300 RPM level all provided a high level contaminate concentration in the liquid unfrozen portion and contaminate removal from the solid frozen portion. Conductivity values in the solid phase suggested a decrease in ion removal efficiency corresponding to a decrease in mechanical agitation. An increase in RPM corresponded to a decrease in pH values and this was assumed to be a result of enhanced CO_2 diffusion into solution thus lowering pH.

 The addition of inorganics, chloride and sulfate, significantly reduced the effectiveness of progressive freeze concentration. Although, this influence was only notable at higher concentrations of inorganics, as chloride and sulfate at 40mg/L provided no reduction in

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progressive freeze concentration efficacy but was reduced to as low as 35% with the addition of chloride and sulfate at higher concentrations.

7.1 Recommendations for Future Work

This experimental analysis provides evidence for progressive freeze concentration as a potential treatment option for NAs contained within OSPW. Additional investigation is recommended and required to provide further evidence for the viability of this solution. One method would be to perform progressive freeze concentration on OSPW obtained from tailings ponds. This would allow further investigation into the influence of agitation levels provided and the effect of concentration polarization during progressive freeze concentration. The high levels of contaminates and particulate matter present in OSPW provides significant complication as it was shown in this study that the addition of inorganics chloride and sulfate significantly reduced the contaminate removal during progressive freeze concentration. Implementing a scaled up continuous model of progressive freeze concentration could also provide further evidence for the viability as an actual treatment method.

It was reported in this experiment that higher ultrasound intensity influenced the NAs during the progressive freeze concentration, potentially being degraded through acoustic cavitation. Further investigation into this potential effect is warranted. This could be done by performing a wider range of ultrasound intensities and further analysis of the control and the resulting frozen and unfrozen portions through gas chromatography-mass spectrometry. This would allow for proper identification and fate of NAs during ultrasonic progressive freeze concentration.

Appendix

7.2 Experimental Results of Chapter 4

Table 0-1: Results of pH, conductivity, TS, and COD ratios for varying degrees of frozen percentages of progressive freeze concentration.

Frozen Percentage: Unfrozen Portion								
	20		40		60		80	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.9575	0.0177	0.9380	0.0301	0.9235	0.0536	0.9267	0.0673
Conductivity	1.0281	0.0521	1.2493	0.0850	1.8645	0.1298	3.5043	0.4142
TS	1.2795	0.0636	1.5862	0.2266	2.4214	0.0949	4.7814	0.7291
COD	1.2563	0.1110	1.5985	0.0482	2.3499	0.0794	4.6050	0.3094
Frozen Percentage: Frozen Portion								
	20		40		60		80	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.6328	0.0143	0.6109	0.0172	0.6164	0.0156	0.6363	0.0810
Conductivity	0.0172	0.0054	0.0102	0.0018	0.0119	0.0069	0.0233	0.0429
TS	0.0232	0.0378	0.0223	0.0391	0.0225	0.0338	0.0760	0.0652
COD	0.0343	0.0157	0.0184	0.0145	0.0194	0.0140	0.0204	0.0258

Table 0-2: Results of pH, conductivity, TS, and COD ratios for different concentrations of NAs of progressive freeze concentration.

Total NA Concentration: Frozen Portion								
	20		60		90		120	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.9623	0.0267	0.8793	0.0756	0.9289	0.0818	0.9395	0.0456
Conductivity	3.1282	0.3337	3.3989	0.1379	3.8103	0.4852	3.7380	0.1536
TS	5.0940	1.3108	4.6001	0.2781	4.5802	0.3830	4.8745	0.2837
COD	4.7990	0.3899	4.4913	0.1793	4.5987	0.3001	4.5389	0.3221
Total NA Concentration: Unfrozen Portion								
	20		60		90		120	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.6319	0.0758	0.6135	0.0395	0.6883	0.1229	0.6034	0.0133
Conductivity	0.0364	0.0738	0.0198	0.0267	0.0241	0.0330	0.0093	0.0040
TS	0.1149	0.0768	0.0821	0.0812	0.0439	0.0345	0.0587	0.0323
COD	0.0341	0.0408	0.0191	0.0200	0.0165	0.0161	0.0091	0.0107

Table 0-3: Results of pH, conductivity, TS, and COD ratios for different NA solutions of progressive freeze concentration (Single NA = cyclohexanecarboxylic acid, Two NA Mixture = cyclohexanecarboxylic acid and trans-4-pentylcyclohexanecarboxylic, Three NA Mixture = cyclohexanecarboxylic acid, trans-4-pentylcyclohexanecarboxylic and cyclohexanepentanoic acid).

NA Identity: Unfrozen Portion						
	Single NA		Two NA Mixture		Three NA Mixture	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.9075	0.0813	0.9195	0.0572	0.9674	0.0227
Conductivity	3.6155	0.4658	3.4487	0.4164	3.3651	0.2898
TS	4.9888	0.8813	4.5964	0.7063	4.6032	0.3158
COD	4.5344	0.3484	4.6872	0.2825	4.6378	0.2770
NA Identity: Frozen Portion						
	Single NA		Two NA Mixture		Three NA Mixture	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.6815	0.1086	0.5943	0.0082	0.6078	0.0089
Conductivity	0.0427	0.0611	0.0084	0.0013	0.0081	0.0017
TS	0.0963	0.0833	0.0468	0.0390	0.0837	0.0321
COD	0.0108	0.0156	0.0315	0.0392	0.0279	0.0263

Table 0-4: Results of pH, conductivity, TS, and COD ratios for freezing methods ultrasound and mechanical for progressive freeze concentration.

Freezing Method: Unfrozen Portion				
	Ultrasound		Mechanical	
	Mean	Std. Dev	Mean	Std. Dev
pH	0.9545	0.0425	0.9130	0.0559
Conductivity	2.3941	1.1658	2.2978	1.1171
TS	3.1143	1.6385	3.1550	1.6556
COD	2.9698	1.4900	3.0597	1.5184
Freezing Method: Frozen Portion				
	Ultraound		Mechanical	
	Mean	Std. Dev	Mean	Std. Dev
pH	0.6270	0.0544	0.6278	0.0589
Conductivity	0.0138	0.0135	0.0217	0.0393
TS	0.0475	0.0580	0.0463	0.0579
COD	0.0232	0.0190	0.0216	0.0230

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7.3 Statistical Analysis from Chapter 4

Table 0-5: ANOVA comparing the effect of total NA concentration and chemical nature of NAs on COD for the liquid portion of progressive freeze concentration.

COD Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Total NA	4	181	45.25	1412.603	2.00E-16
Identity of NA	2	0.16	0.08	2.464	0.09702
Total NA:Identity of NA	6	0.79	0.13	4.121	0.00236
Residuals	43	1.38	0.03		

Table 0-6: Tukey HSD test for factor total NA for Table 0-5.

Comparison for Factor: Total Naphthenic Acid Concentration					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20mg/L	120mg/L	0.246252	-0.102504	0.595008	0.2822974
60mg/L	120mg/L	-0.019927	-0.346158	0.306305	0.9997936
90mg/L	120mg/L	0.055771	-0.270461	0.382002	0.9885529
Control	120mg/L	-3.529836	-3.801585	-3.258087	0.0000000
60mg/L	20mg/L	-0.266179	-0.592411	0.060052	0.1593257
90mg/L	20mg/L	-0.190482	-0.516713	0.13575	0.4727099
Control	20mg/L	-3.776088	-4.047837	-3.50434	0.0000000
90mg/L	60mg/L	0.075697	-0.226334	0.377729	0.9535788
Control	60mg/L	-3.509909	-3.752073	-3.267745	0.0000000
Control	90mg/L	-3.585607	-3.827708	-3.343443	0.0000000

Table 0-7: Tukey HSD test for factor chemical nature of NAs for Table 0-5.

Comparison for Factor: Chemical Nature of Naphthenic Acids					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Two NAs Solution	Control	3.687167	3.4577585	3.916576	0.0000000
Single NAs Solution	Control	3.500022	3.3025788	3.697466	0.0000000
Three NAs Solution	Control	3.637758	3.4083498	3.867167	0.0000000
Single NAs Solution	Two NAs Solution	-0.187145	-0.448338	0.074048	0.2399439
Three NAs Solution	Two NA Solution	-0.049409	-0.335532	0.236714	0.9677003
Three NAs Solution	One NAs Solution	0.137736	-0.123457	0.398929	0.505317

Table 0-8: ANOVA comparing the effect of total NA concentration and chemical nature of NAs on TS for the liquid portion of progressive freeze concentration.

TS Unfrozen Portion

Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Total NA	4	187.21	46.8	1085.62	2.00E-16
Identity of NA	2	0.4	0.2	4.651	0.0148
Total NA:Identity of NA	6	7.53	1.26	29.121	1.24E-13
Residuals	43	1.85	0.04		

Table 0-9: HSD test for factor total NA for Table 0-8.

Comparison for Factor: Total Naphthenic Acid Concentration					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20mg/L	120mg/L	-0.087887	-0.803103	0.62733	0.9967688
60mg/L	120mg/L	-0.185481	-0.854506	0.483543	0.9341097
90mg/L	120mg/L	-0.205305	-0.874329	0.463719	0.9073214
Control	120mg/L	-3.785542	-4.342834	-3.228249	0.0000000
60mg/L	20mg/L	-0.097595	-0.766619	0.571429	0.9937378
90mg/L	20mg/L	-0.117419	-0.786443	0.551606	0.9873623
Control	20mg/L	-3.697655	-4.254948	-3.140363	0.0000000
90mg/L	60mg/L	-0.019824	-0.63922	0.599572	0.9999843
Control	60mg/L	-3.60006	-4.096682	-3.103439	0.0000000
Control	90mg/L	-3.580237	-4.076858	-3.083615	0.0000000

Table 0-10: HSD test for factor chemical nature of NAs for Table 0-8

Comparison for Factor: Chemical Nature of Naphthenic Acids					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Two NAs Solution	Control	3.529721	3.0712386	3.988204	0.0000000
Single NAs Solution	Control	3.773169	3.3785704	4.167769	0.0000000
Three NAs Solution	Control	3.603219	3.1447365	4.061702	0.0000000
Single NAs Solution	Two NAs Solution	0.243448	-0.278557	0.765454	0.6060174
Three NAs Solution	Two NA Solution	0.073498	-0.498331	0.645326	0.9861853
Three NAs Solution	One NAs Solution	-0.16995	-0.691956	0.352055	0.8232324

Table 0-11: ANOVA comparing the effect of total NA concentration and chemical nature of NAs on conductivity for the liquid portion of progressive freeze concentration.

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Total NA	4	91.47	22.867	610.251	2.00E-16
Identity of NA	2	0.46	0.232	6.204	0.004290
Total NA:Identity of NA	6	0.49	0.081	2.159	0.065910
Residuals	43	1.61	0.037		

Table 0-12: HSD test for factor total NA for Table 0-11.

Comparison for Factor: Total Naphthenic Acid Concentration					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20mg/L	120mg/L	-0.630761	-0.996649	-0.264873	0.0001046
60mg/L	120mg/L	-0.339026	-0.681283	0.003231	0.0533521
90mg/L	120mg/L	0.072363	-0.269894	0.41462	0.9747901
Control	120mg/L	-2.737956	-3.023054	-2.452859	0.0000000
60mg/L	20mg/L	0.291735	-0.050522	0.633992	0.129051
90mg/L	20mg/L	0.703124	0.3608666	1.045381	0.000004
Control	20mg/L	-2.107196	-2.392293	-1.822098	0.0000000
90mg/L	60mg/L	0.411389	0.0945205	0.728257	0.0050234
Control	60mg/L	-2.39893	-2.65299	-2.14487	0.0000000
Control	90mg/L	-2.810319	-3.064379	-2.556259	0.0000000

Table 0-13: HSD test for factor chemical nature of NAs Table 0-11.

Comparison for Factor: Chemical Nature of Naphthenic Acids					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Two NAs Solution	Control	2.448697	2.1500504	2.747344	0.0000000
Single NAs Solution	Control	2.686181	2.4291471	2.943215	0.0000000
Three NAs Solution	Control	2.365145	2.0664979	2.663791	0.0000000
Single NAs Solution	Two NAs Solution	0.237484	-0.10254	0.577508	0.2605567
Three NAs Solution	Two NA Solution	-0.083553	-0.45603	0.288925	0.9330325
Three NAs Solution	One NAs Solution	-0.321037	-0.661061	0.018988	0.0707296

Table 0-14: ANOVA comparing the effect of total NA concentration and chemical nature of NAs on pH for the liquid portion of progressive freeze concentration.

pH Unfrozen Portion

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Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Total NA	4	0.10632	0.02658	23.752	2.04E-10
Identity of NA	2	0.01737	0.008683	7.759	0.001327
Total NA:Identity of NA	6	0.03422	0.005703	5.097	0.000499
Residuals	43	0.04812	0.001119		

Table 0-15: HSD test for factor total NA for Table 0-14.

Comparison for Factor: Total Naphthenic Acid Concentration					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20mg/L	120mg/L	0.027698	-0.044488	0.099885	0.8133672
60mg/L	120mg/L	-0.059574	-0.127098	0.00795	0.1077995
90mg/L	120mg/L	-0.010607	-0.078131	0.056917	0.9916925
Control	120mg/L	0.060527	0.0042797	0.116774	0.0290703
60mg/L	20mg/L	-0.087272	-0.154796	-0.019748	0.0052753
90mg/L	20mg/L	-0.038305	-0.105829	0.029219	0.5017042
Control	20mg/L	0.032828	-0.023419	0.089075	0.4731239
90mg/L	60mg/L	0.048967	-0.013548	0.111482	0.1907568
Control	60mg/L	0.120101	0.0699771	0.170224	0.0000001
Control	90mg/L	0.071134	0.02101	0.121257	0.0017698

Table 0-16: HSD test for factor chemical nature of NAs Table 0-14.

Comparison for Factor: Chemical Nature of Naphthenic Acids					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Two NAs Solution	Control	-0.080485	-0.128663	-0.032307	0.0002746
Single NAs Solution	Control	-0.098779	-0.140244	-0.057314	0.0000004
Three NAs Solution	Control	-0.032597	-0.080775	0.015581	0.2869672
Single NAs Solution	Two NAs Solution	-0.018294	-0.073147	0.036559	0.8125329
Three NAs Solution	Two NA Solution	0.047888	-0.01221	0.107977	0.1618003
Three NAs Solution	One NAs Solution	0.066182	0.0113286	0.121035	0.0120932

Table 0-17: ANOVA comparing the effect of freezing method and % frozen on COD for the liquid portion of progressive freeze concentration.

COD Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value

Method	2	126.15	63.07	2667.55	2.00E-16
% Frozen	3	136.15	45.38	1919.341	2.00E-16
Method:% Frozen	3	0	0	0.065	0.978
Residuals	119	2.81	0.02		

Table 0-18: Tukey HSD test for the factor freezing method from Table 0-17.

Comparison for Factor: Freezing Method					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	2.003259	1.4617866	2.544731	0.0000000
Ultrasound	Control	1.967362	1.4258899	2.508835	0.0000000
Ultrasound	Mechanical	-0.035897	-0.661135	0.589342	0.9898288

Table 0-19: Tukey HSD test for the factor % frozen from Table 0-17.

Comparison for Factor: % Frozen					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
40%	20%	0.342338	0.1706184	0.514058	0.0000019
60%	20%	1.093795	0.9220751	1.265515	0.0000000
80%	20%	3.336551	3.191421	3.48168	0.0000000
Control	20%	-0.256295	-0.388614	-0.123976	0.0000039
60%	40%	0.751457	0.5797369	0.923176	0.0000000
80%	40%	2.994213	2.8490829	3.139342	0.0000000
Control	40%	-0.598633	-0.730952	-0.466314	0.0000000
80%	60%	2.242756	2.0976262	2.387886	0.0000000
Control	60%	-1.35009	-1.482409	-1.217771	0.0000000
Control	80%	-3.592846	-3.688152	-3.497539	0.0000000

Table 0-20: ANOVA comparing the effect of freezing method and % frozen on TS for the liquid portion of progressive freeze concentration.

TS Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	131.63	65.82	736.438	2.00E-16
% Frozen	3	140.17	46.72	522.819	2.00E-16
Method:% Frozen	3	0.01	0	0.042	0.988
Residuals	119	10.63	0.09		

Table 0-21: Tukey HSD test for the factor freezing method from Table 0-20.

Comparison for Factor: Freezing Method				
Comparison	Mean Diff	Lower Bound	Upper Bound	P Value

Mechanical	Control	2.05021	1.4861167	2.614303	0.0000000
Ultrasound	Control	2.005628	1.4415349	2.569721	0.0000000
Ultrasound	Mechanical	-0.044582	-0.69594	0.606777	0.9855764

Table 0-22: Tukey HSD test for the factor % frozen from Table 0-20.

Comparison for Factor: % Frozen		Mean Diff	Lower Bound	Upper Bound	P Value
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
40%	20%	0.306677	-0.026357	0.639712	0.0865286
60%	20%	1.141893	0.8088586	1.474928	0.0000000
80%	20%	3.375545	3.094079	3.65701	0.0000000
Control	20%	-0.279511	-0.536131	-0.022891	0.0254469
60%	40%	0.835216	0.5021813	1.16825	0.0000000
80%	40%	3.068867	2.7874018	3.350333	0.0000000
Control	40%	-0.586188	-0.842809	-0.329568	0.0000000
80%	60%	2.233652	1.9521859	2.515117	0.0000000
Control	60%	-1.421404	-1.678025	-1.164784	0.0000000
Control	80%	-3.655056	-3.839893	-3.470218	0.0000000

Table 0-23: ANOVA comparing the effect of freezing method and % frozen on conductivity for the liquid portion of progressive freeze concentration.

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	55.83	27.915	691.522	2.00E-16
% Frozen	3	77.04	25.68	636.14	2.00E-16
Method:% Frozen	3	0.03	0.012	0.289	0.833
Residuals	119	4.8	0.04		

Table 0-24: Tukey HSD test for the factor freezing method from Table 0-23.

Comparison for Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	1.277038	0.861409	1.692666	0.0000000
Ultrasound	Control	1.361976	0.9463474	1.777605	0.0000000
Ultrasound	Mechanical	0.084938	-0.394988	0.564865	0.9075132

Table 0-25: Tukey HSD test for the factor % frozen from Table 0-23.

Comparison for Factor: % Frozen		Mean Diff	Lower Bound	Upper Bound	P Value
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
40%	20%	0.22127	-0.005574	0.448114	0.0595947

60%	20%	0.836474	0.6096293	1.063318	0.0000000
80%	20%	2.498532	2.3068134	2.69025	0.0000000
Control	20%	-0.028072	-0.202867	0.146723	0.9918111
60%	40%	0.615203	0.3883592	0.842048	0.0000000
80%	40%	2.277262	2.0855433	2.46898	0.0000000
Control	40%	-0.249342	-0.424137	-0.074547	0.0012192
80%	60%	1.662058	1.4703399	1.853777	0.0000000
Control	60%	-0.864546	-1.039341	-0.68975	0.0000000
Control	80%	-2.526604	-2.652505	-2.400703	0.0000000

Table 0-26: ANOVA comparing the effect of freezing method and % frozen on pH for the liquid portion of progressive freeze concentration.

pH Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	0.1686	0.0843	70.563	2.00E-16
% Frozen	3	0.01046	0.00349	2.918	3.70E-02
Method:% Frozen	3	0.00329	0.0011	0.919	0.434
Residuals	119	0.14217	0.00119		

Table 0-27: Tukey HSD test for the factor freezing method from Table 0-26.

Comparison for Factor: Freezing Method					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.087078	-0.105215	-0.068941	0.0000000
Ultrasound	Control	-0.045912	-0.064049	-0.027774	1.00E-07
Ultrasound	Mechanical	0.041167	0.0202232	0.06211	2.34E-05

Table 0-28: Tukey HSD test for the factor % frozen from Table 0-26.

Comparison for Factor: % Frozen					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
40%	20%	-0.020411	-0.06275	0.021927	0.6701217
60%	20%	-0.034324	-0.076662	0.008014	0.1704973
80%	20%	-0.032731	-0.068513	0.003052	0.0901003
Control	20%	0.041912	0.0092881	0.074536	0.0047694
60%	40%	-0.013913	-0.056251	0.028426	0.8926650
80%	40%	-0.012319	-0.048102	0.023463	0.8752545
Control	40%	0.062324	0.0296996	0.094947	0.0000053
80%	60%	0.001593	-0.034189	0.037376	0.9999472
Control	60%	0.076236	0.0436122	0.10886	0.0000000
Control	80%	0.074643	0.0511448	0.098141	0.0000000

Table 0-29: ANOVA comparing the effect of total NA concentration and chemical nature of NAs on COD for the solid portion of progressive freeze concentration.

COD Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Total NA	4	13.399	3.35	31643.45	2.00E-16
Identity of NA	2	0.002	0.001	8.884	0.000059
Total NA:Identity of NA	6	0.007	0.001	11.52	1.20E-07
Residuals	43	0.005	0		

Table 0-30: Tukey HSD test for factor total NA for Table 0-29.

Comparison for Factor: Total Naphthenic Acid Concentration					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20mg/L	120mg/L	0.036433	0.0096258	0.053239	0.0029927
60mg/L	120mg/L	0.009972	-0.015104	0.035047	0.7928866
90mg/L	120mg/L	0.007387	-0.017688	0.032463	0.9190748
Control	120mg/L	0.990906	0.9700188	1.011794	0.0000000
60mg/L	20mg/L	-0.026461	-0.051536	-0.001385	0.0338361
90mg/L	20mg/L	-0.029045	-0.054121	-0.00397	0.0156073
Control	20mg/L	0.954474	0.9335862	0.975361	0.0000000
90mg/L	60mg/L	-0.002584	-0.0258	0.020631	0.9977998
Control	60mg/L	0.980935	0.9623211	0.999548	0.0000000
Control	90mg/L	0.983519	0.9649055	1.002133	0.0000000

Table 0-31: Tukey HSD test for factor chemical nature of NAs for Table 0-29.

Comparison for Factor: Chemical Nature of Naphthenic Acids					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Two NAs Solution	Control	-0.968964	-0.987734	-0.950194	0.0000000
Single NAs Solution	Control	-0.988281	-1.004436	-0.972126	0.0000000
Three NAs Solution	Control	-0.972103	-0.990873	-0.953333	0.0000000
Single NAs Solution	Two NAs Solution	-0.019317	-0.040688	0.002054	0.0898434
Three NAs Solution	Two NA Solution	-0.003139	-0.02655	0.020272	0.9843778
Three NAs Solution	One NAs Solution	0.016178	-0.005193	0.037549	0.1978289

Table 0-32: ANOVA comparing the effect of total NA concentration and chemical nature of NAs on TS for the solid portion of progressive freeze concentration.

TS Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value

	DF	Sum Sq	Mean Sq	F	p Value
Total NA	4	12.25	3.0625	2575.005	2.00E-16
Identity of NA	2	0.014	0.0068	5.719	0.00628
Total NA:Identity of NA	6	0.02	0.0033	2.75	2.37E-02
Residuals	43	0.051	0.0012		

Table 0-33: Tukey HSD test for factor total NA for Table 0-32.

Comparison for Factor: Total Naphthenic Acid Concentration					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20mg/L	120mg/L	0.042015	-0.024386	0.108417	0.3909044
60mg/L	120mg/L	0.035438	-0.026675	0.097551	0.4959792
90mg/L	120mg/L	-0.002836	-0.064949	0.059277	0.9999351
Control	120mg/L	0.953298	0.9015584	1.005038	0.0000000
60mg/L	20mg/L	-0.006577	-0.06869	0.055536	0.9981904
90mg/L	20mg/L	-0.044852	-0.106965	0.017262	0.2613154
Control	20mg/L	0.911283	0.8595432	0.963023	0.0000000
90mg/L	60mg/L	-0.038274	-0.09578	0.019231	0.3398808
Control	60mg/L	0.91786	0.8717532	0.963967	0.0000000
Control	90mg/L	0.956135	0.9100275	1.002241	0.0000000

Table 0-34: Tukey HSD test for factor chemical nature of NAs for Table 0-32.

Comparison for Factor: Chemical Nature of Naphthenic Acids					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Two NAs Solution	Control	-0.968106	-1.010421	-0.925792	0.0000000
Single NAs Solution	Control	-0.927896	-0.964315	-0.891478	0.0000000
Three NAs Solution	Control	-0.91248	-0.954795	-0.870166	0.0000000
Single NAs Solution	Two NAs Solution	0.04021	-0.007967	0.088387	0.1325817
Three NAs Solution	Two NA Solution	0.055626	0.0028506	0.108401	0.0351897
Three NAs Solution	One NAs Solution	0.015416	-0.032761	0.063593	0.8306048

Table 0-35: ANOVA comparing the effect of total NA concentration and chemical nature of NAs on conductivity for the solid portion of progressive freeze concentration.

Conductivity Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Total NA	4	13.34	3.335	4520.721	2.00E-16
Identity of NA	2	0.01	0.005	6.547	0.00329
Total NA:Identity of NA	6	0.008	0.001	1.841	1.14E-01
Residuals	43	0.032	0.001		

Table 0-36: Tukey HSD test for factor total NA for Table 0-35.

Comparison for Factor: Total Naphthenic Acid Concentration					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20mg/L	120mg/L	0.034178	-0.0167	0.085056	0.330689
60mg/L	120mg/L	0.010995	-0.036597	0.058587	0.9652469
90mg/L	120mg/L	0.014871	-0.032721	0.062463	0.9016523
Control	120mg/L	0.990725	0.9510809	1.030369	0.0000000
60mg/L	20mg/L	-0.023183	-0.070775	0.024409	0.6446104
90mg/L	20mg/L	-0.019307	-0.066899	0.028285	0.7807354
Control	20mg/L	0.956547	0.9169029	0.996191	0.0000000
90mg/L	60mg/L	0.003876	-0.040186	0.047938	0.9991261
Control	60mg/L	0.97973	0.9444018	1.015058	0.0000000
Control	90mg/L	0.975854	0.9405258	1.011182	0.0000000

Table 0-37: Tukey HSD test for factor chemical nature of NAs for Table 0-35.

Comparison for Factor: Chemical Nature of Naphthenic Acids					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Two NAs Solution	Control	-0.991377	-1.022387	-0.960367	0.0000000
Single NAs Solution	Control	-0.955259	-0.981949	-0.92857	0.0000000
Three NAs Solution	Control	-0.991771	-1.022781	-0.960761	0.0000000
Single NAs Solution	Two NAs Solution	0.036118	0.0008112	0.071424	0.0431401
Three NAs Solution	Two NA Solution	-0.000394	-0.03907	0.038283	0.9999928
Three NAs Solution	One NAs Solution	-0.036512	-0.071818	-0.001205	0.040118

Table 0-38: ANOVA comparing the effect of total NA concentration and chemical nature of NAs on pH for the solid portion of progressive freeze concentration.

pH Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Total NA	4	1.8582	0.4646	261.572	2.00E-16
Identity of NA	2	0.0503	0.0251	14.15	1.90E-05
Total NA:Identity of NA	6	0.0277	0.0046	2.599	0.0308
Residuals	43	0.0764	0.0018		

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Table 0-39: Tukey HSD test for factor total NA for Table 0-38.

Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Comparison for Factor: Total Naphthenic Acid Concentration
20mg/L	120mg/L	0.038118	-0.051689	0.127925	0.7512111
60mg/L	120mg/L	0.01057	-0.073437	0.094577	0.9964582
90mg/L	120mg/L	0.084882	0.0008753	0.168889	0.0465148
Control	120mg/L	0.396601	0.3266242	0.466578	0.0000000
60mg/L	20mg/L	-0.027548	-0.111554	0.056459	0.8849999
90mg/L	20mg/L	0.046764	-0.037243	0.130771	0.5204525
Control	20mg/L	0.358483	0.2885064	0.42846	0.0000000
90mg/L	60mg/L	0.074312	-0.003463	0.152087	0.0675741
Control	60mg/L	0.386031	0.3236723	0.44839	0.0000000
Control	90mg/L	0.311719	0.2493604	0.374078	0.0000000

Table 0-40: Tukey HSD test for factor chemical nature of NAs for Table 0-38.

Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Comparison for Factor: Chemical Nature of Naphthenic Acids
Two NAs Solution	Control	-0.406349	-0.459932	-0.352767	0.0000000
Single NAs Solution	Control	-0.3106	-0.356716	-0.264483	0.0000000
Three NAs Solution	Control	-0.391815	-0.445398	-0.338233	0.0000000
Single NAs Solution	Two NAs Solution	0.095749	0.0347432	0.156756	0.0006613
Three NAs Solution	Two NA Solution	0.014534	-0.052295	0.081363	0.9384701
Three NAs Solution	One NAs Solution	-0.081215	-0.142222	-0.020209	0.0046891

Table 0-41: ANOVA comparing the effect of freezing method and % frozen on COD for the solid portion of progressive freeze concentration.

Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
COD Frozen Portion
Method	2	30.545	15.273	71938.56	2.00E-16
% Frozen	3	0.002	0.001	3.072	3.05E-02
Method:% Frozen	3	0	0	0.417	0.7414
Residuals	119	0.025	0		

Table 0-42: Tukey HSD for the factor freezing method from Table 0-41.

Comparison	Mean Diff	Lower Bound	Upper Bound	P Value
Comparison for Factor: Freezing Method

Mechanical	Control	-0.977862	-0.985477	-0.970247	0.0000000
Ultrasound	Control	-0.976147	-0.983762	-0.968532	0.0000000
Ultrasound	Mechanical	0.001715	-0.007078	0.010508	0.8888433

Table 0-43: Tukey HSD test for the factor % frozen from Table 0-41.

Comparison for Factor: % Frozen					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
40%	20%	-0.015847	-0.032146	0.000451	0.0609212
60%	20%	-0.014867	-0.031166	0.001432	0.0916241
80%	20%	-0.012257	-0.026032	0.001519	0.1058722
Control	20%	0.965883	0.953324	0.978442	0.0000000
60%	40%	0.00098	-0.015319	0.017279	0.9998254
80%	40%	0.003591	-0.010184	0.017366	0.951128
Control	40%	0.981731	0.9691714	0.99429	0.0000000
80%	60%	0.002611	0.0111644	0.016386	0.9846908
Control	60%	0.98075	0.9681913	0.99331	0.0000000
Control	80%	0.97814	0.9690937	0.987186	0.0000000

Table 0-44: ANOVA comparing the effect of freezing method and % frozen on TS for the solid portion of progressive freeze concentration.

TS Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	29.418	14.709	12537.2	2.00E-16
% Frozen	3	0.028	0.009	8.026	6.46E-05
Method:% Frozen	3	0.001	0	0.246	0.864
Residuals	119	0.14	0.001		

Table 0-45: Tukey HSD for the factor freezing method from Table 0-44.

Comparison for Factor: Freezing Method					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.960872	-0.97974	-0.942004	0.0000000
Ultrasound	Control	-0.95673	-0.975597	-0.937862	0.0000000
Ultrasound	Mechanical	0.004142	-0.017644	0.025929	0.894054

Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
40%	20%	-0.000869	-0.039105	0.037368	0.9999964
60%	20%	-0.000665	-0.038901	0.037571	0.9999988
80%	20%	0.041837	0.0095211	0.074152	0.004352
Control	20%	0.976817	0.9473537	1.00628	0.0000000
60%	40%	0.000203	-0.038033	0.03844	1.0000000
80%	40%	0.042705	0.0103897	0.075021	0.003856
Control	40%	0.977685	0.9482224	1.007148	0.0000000
80%	60%	0.042502	0.0101863	0.074817	0.0035921
Control	60%	0.977482	0.9480189	1.006945	0.0000000
Control	80%	0.93498	0.9137587	0.956202	0.0000000

Comparison for Factor: % Frozen

Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	30.867	15.434	35081.07	2.00E-16
% Frozen	3	0.002	0.001	1.652	1.81E-01
Method:% Frozen	3	0.001	0	0.578	0.631
Residuals	119	0.052	0		

Conductivity Frozen Portion

Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.978226	-0.989028	-0.967425	0.0000000
Ultrasound	Control	-0.986029	-0.99683	-0.975228	0.0000000
Ultrasound	Mechanical	-0.007802	-0.020275	0.00467	0.3021135

Comparison for Factor: Freezing Method

Table 0-49: Tukey HSD test for the factor % frozen from Table 0-47.

Comparison for Factor: % Frozen					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
40%	20%	-0.006996	-0.030698	0.016707	0.9249162
60%	20%	-0.005256	-0.028959	0.018447	0.9726393
80%	20%	0.006791	0.0132419	0.026823	0.8813076
Control	20%	0.982801	0.9645371	1.001066	0.0000000
60%	40%	0.001739	-0.021963	0.025442	0.9996154
80%	40%	0.013786	-0.006246	0.033819	0.319994
Control	40%	0.989797	0.9715327	1.008061	0.0000000
80%	60%	0.012047	-0.007986	0.032079	0.459378
Control	60%	0.988058	0.9697933	1.006322	0.0000000
Control	80%	0.976011	0.9628554	0.989166	0.0000000

Table 0-50: ANOVA comparing the effect of freezing method and % frozen on pH for the solid portion of progressive freeze concentration.

pH Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	4.42	2.2101	1358.211	2.00E-16
% Frozen	3	0.009	0.0029	1.797	1.51E-01
Method:% Frozen	3	0.001	0.0003	0.178	0.911
Residuals	119	0.194	0.0016		

Table 0-51: Tukey HSD for the factor freezing method from Table 0-50.

Comparison for Factor: Freezing Method					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.371526	0.3922357	-0.350816	0.0000000
Ultrasound	Control	0.371802	-0.392512	-0.351093	0.0000000
Ultrasound	Mechanical	0.000276	-0.02419	0.023637	0.9995855

Table 0-52: Tukey HSD test for the factor % frozen from Table 0-50.

Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Comparison for Factor: % Frozen					
40%	20%	-0.022561	-0.06751	0.022388	0.6354338
60%	20%	-0.016613	-0.061562	0.028336	0.8441788
80%	20%	0.005614	-0.032374	0.043603	0.9940434
Control	20%	0.366775	0.33214	0.40141	0.0000000
60%	40%	0.005948	-0.039001	0.050897	0.9961102
80%	40%	0.028175	-0.009813	0.066164	0.2472126
Control	40%	0.389336	0.3547009	0.423971	0.0000000
80%	60%	0.022227	-0.015761	0.060216	0.4876167
Control	60%	0.383388	0.348753	0.418024	0.0000000
Control	80%	0.361161	0.3362142	0.386108	0.0000000

7.4 Experimental Results of Chapter 5

Table 0-53: Results of pH, conductivity, TS, and COD ratios for freezing temperatures -15⁰C and -25⁰C of progressive freeze concentration.

	-15		-25	
Freezing Temperature (°C): Unfrozen Portion				
	Mean	Std. Dev	Mean	Std. Dev
pH	0.965019	0.027048	0.96161	0.033758
Conductivity	3.543468	0.445687	3.461852	0.307431
TS	4.570284	0.413845	4.783378	0.469995
COD	4.599937	0.295897	4.54508	0.381986
Freezing Temperature(°C): Frozen Portion				
	-15		-25	
	Mean	Std. Dev	Mean	Std. Dev
pH	0.603246	0.023523	0.602025	0.026228
Conductivity	0.009264	0.008341	0.013499	0.014525
TS	0.044224	0.039422	0.058173	0.068825
COD	0.024196	0.030227	0.04106	0.048248

Total Naphthenic Acid Concentration (mg/L): Unfrozen Portion				
	60		120	
	Mean	Std. Dev	Mean	Std. Dev
pH	0.960229	0.032468	0.966401	0.028346
Conductivity	3.465254	0.476393	3.540067	0.258348
TS	4.578132	0.49141	4.77553	0.392388
COD	4.581387	0.275834	4.56363	0.398446
Total Naphthenic Acid Concentration (mg/L): Frozen Portion				
	60		120	
	Mean	Std. Dev	Mean	Std. Dev
pH	0.601475	0.023334	0.603796	0.026359
Conductivity	0.011147	0.012685	0.011616	0.011345
TS	0.066519	0.067928	0.035878	0.03601
COD	0.036316	0.047592	0.02894	0.033075

Freezing Method: Unfrozen Portion				
	Ultrasound		Mechanical	
	Mean	Std. Dev	Mean	Std. Dev
pH	0.975862	0.027681	0.950767	0.028095
Conductivity	3.565636	0.342898	3.439684	0.413368
TS	4.693372	0.457264	4.66029	0.453543
COD	4.583589	0.321474	4.561428	0.362503
Freezing Method: Frozen Portion				
	Ultrasound		Mechanical	
	Mean	Std. Dev	Mean	Std. Dev
pH	0.601629	0.025943	0.603642	0.02381
Conductivity	0.009845	0.007986	0.012918	0.01487
TS	0.050681	0.048691	0.051716	0.063396
COD	0.027109	0.03203	0.038147	0.047944

Ultrasound Off Cycle Time (s): Unfrozen Portion			
	30	20	10

	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.966592	0.038517	0.97736	0.022954	0.983634	0.015229
Conductivity	3.527184	0.200277	3.540291	0.283908	3.629432	0.491015
TS	4.821633	0.603819	4.577189	0.41275	4.681295	0.296795
COD	4.526821	0.434074	4.649169	0.296738	4.574777	0.198076
Ultrasound Off Cycle Time (s): Frozen Portion						
	30		20		10	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.60747	0.025113	0.60868	0.02651	0.588738	0.022554
Conductivity	0.010669	0.004914	0.011762	0.012613	0.007105	0.001986
TS	0.063837	0.043241	0.03644	0.050987	0.051766	0.050566
COD	0.029452	0.029173	0.024435	0.034534	0.027441	0.034019

Table 0-57: Results of pH, conductivity, TS, and COD ratios for ultrasound amplitude 20% and 30% of progressive freeze concentration.

Ultrasound Amplitude (%): Unfrozen Portion				
	20		30	
	Mean	Std. Dev	Mean	Std. Dev
pH	0.978728	0.021036	0.972996	0.033258
Conductivity	3.659775	0.407711	3.471497	0.235684
TS	4.72786	0.452043	4.658884	0.469516
COD	4.668404	0.293019	4.498773	0.332131
Ultrasound Amplitude: Frozen Portion				
	20		30	
	Mean	Std. Dev	Mean	Std. Dev
pH	0.608414	0.024875	0.594844	0.0257
Conductivity	0.011857	0.010731	0.007833	0.002594
TS	0.059591	0.048113	0.041771	0.048622
COD	0.034342	0.034145	0.019877	0.02866

Table 0-58: Results of pH, conductivity, TS, and COD ratios for mechanical agitation at 100RPM, 200RPM, and 300RPM of progressive freeze concentration.

Mechanical Agitation (RPM): Unfrozen Portion						
	100		200		300	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.966592	0.038517	0.97736	0.022954	0.983634	0.015229
Conductivity	3.527184	0.200277	3.540291	0.283908	3.629432	0.491015
TS	4.821633	0.603819	4.577189	0.41275	4.681295	0.296795
COD	4.526821	0.434074	4.649169	0.296738	4.574777	0.198076
Mechanical Agitation (RPM): Frozen Portion						

	100		200		300	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.60747	0.025113	0.60868	0.02651	0.588738	0.022554
Conductivity	0.010669	0.004914	0.011762	0.012613	0.007105	0.001986
TS	0.063837	0.043241	0.03644	0.050987	0.051766	0.050566
COD	0.029452	0.029173	0.024435	0.034534	0.027441	0.034019

7.5 Statistical Analysis from Chapter 5

Table 0-59: ANOVA comparing the effect of total NA concentration, freezing method, and freezing temperature on COD for the liquid portion of progressive freeze concentration.

COD Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	612.6	306.31	5404.22	2.00E-16
Total NA	1	0	0.01	0.134	0.7152
Freezing Temperature	1	0.1	0.07	1.274	0.2605
Method:Total NA	1	0	0.04	0.773	0.3806
Method:Freezing Temperature	1	0.2	0.22	0.3908	0.0496
Total NA:Freezing Temperature	1	0	0.04	0.78	0.3782
Method:Total NA:Freezing Temperature	1	0.3	0.27	4.788	0.0299
Residuals	183	10.4	0.06		

Table 0-60: Tukey HSD test for factor freezing method for Table 0-59.

Comparison of Factor: Freezing Method					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	3.5614280	3.4605284	3.6623276	0.0000000
Ultrasound	Control	3.5835888	3.4826892	3.6844884	0.0000000
Ultrasound	Mechanical	0.0221608	-0.0943480	0.1386696	0.8947605

Table 0-61: Tukey HSD test for factor total NAs for Table 0-59.

Comparison of Factor: Total NAs					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	0.0177566	-	0.1342877	0.9310980

			0.0987745		
Control	120mg/L	-3.5636301	-3.6645490	-3.4627112	0.0000000
Control	60mg/L	-3.5813867	-3.6823056	-3.8046780	0.0000000

Table 0-62: Tukey HSD test for factor freezing temperature for Table 0-59.

Comparison of Factor: Freezing Temperature					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
-15	Control	3.5999370	3.4993141	3.7005599	0.0000000
-25	Control	3.5450798	3.4444569	3.6457027	0.0000000
-25	-15	-0.0548572	-0.1710465	0.0613321	0.5058072

Table 0-63: ANOVA comparing the effect of total NA concentration, freezing method, and freezing temperature on TS for the liquid portion of progressive freeze concentration.

TS Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	648.9	324.5	3662.422	2.00E-16
Total NA	1	0.9	0.9	10.556	0.00138
Freezing Temperature	1	1.1	1.1	12.301	0.00057
Method:Total NA	1	0.1	0.1	0.941	0.3333
Method:Freezing Temperature	1	0.1	0.1	1.505	0.22147
Total NA:Freezing Temperature	1	0.9	0.9	9.972	0.00186
Method:Total NA:Freezing Temperature	1	0.2	0.2	1.774	0.18455
Residuals	183	16.2	0.1		

Table 0-64: Tukey HSD test for factor freezing method for Table 0-63.

Comparison of Factor: Freezing Method					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	3.6602898	3.5261685	3.7944111	0.0000000
Ultrasound	Control	3.6933724	3.5592511	3.8274937	0.0000000
Ultrasound	Mechanical	0.0330826	-0.1217874	0.1879525	0.8691704

Table 0-65: Tukey HSD test for factor total NAs for Table 0-63.

Comparison of Factor: Total NAs					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	-0.1973987	-0.3486153	-0.0461821	0.0066154
Control	120mg/L	-3.7755305	-3.9064879	-3.6445730	0.0000000
Control	60mg/L	-3.5781318	-3.7090892	-3.4471744	0.0000000

Table 0-66: Tukey HSD test for factor freezing temperature for Table 0-63.

Comparison of Factor: Freezing Temperature					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
-15	Control	3.5702841	3.4398725	3.7006956	0.0000000
-25	Control	3.7833782	3.6529666	3.9137897	0.0000000
-25	-15	0.2130941	0.0625078	0.3636804	0.0028606

Table 0-67: ANOVA comparing the effect of total NA concentration, freezing method, and freezing temperature on conductivity for the liquid portion of progressive freeze concentration.

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	301.02	150.51	2247.595	2.00E-16
Total NA	1	0.13	0.13	2.006	0.15838
Freezing Temperature	1	0.16	0.16	2.387	0.12405
Method:Total NA	1	0.09	0.09	1.314	0.25318
Method:Freezing Temperature	1	0.11	0.11	1.584	0.20974
Total NA:Freezing Temperature	1	0.62	0.62	9.314	0.00261
Method:Total NA:Freezing Temperature	1	0.19	0.19	2.848	0.09318
Residuals	183	12.25	0.07		

Table 0-68: Tukey HSD test for factor freezing method for Table 0-67.

Comparison of Factor: Freezing Method				
Comparison	Mean Diff	Lower	Upper	P Value

			Bound	Bound	
Mechanical	Control	2.4396845	2.3278387	2.5515303	0.0000000
Ultrasound	Control	2.5656359	2.4537901	2.6774817	0.0000000
Ultrasound	Mechanical	0.1259514	-0.0031970	0.2550998	0.0576837

Table 0-69: Tukey HSD test for factor total NAs for Table 0-67.

Comparison of Factor: Total NAs					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	-0.0748129	-0.2051297	-0.0555038	0.3661170
Control	120mg/L	-2.5400667	-2.6529243	-2.4272091	0.0000000
Control	60mg/L	-2.4652538	-2.5781114	-2.3523962	0.0000000

Table 0-70: Tukey HSD test for factor freezing temperature for Table 0-67.

Comparison of Factor: Freezing Temperature					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
-15	Control	2.5434681	2.4307150	2.6562213	0.0000000
-25	Control	2.4618523	2.3490990	2.5746055	0.0000000
-25	-15	-0.0816158	-0.2118120	0.0485803	0.3023982

Table 0-71: ANOVA comparing the effect of total NA concentration, freezing method, and freezing temperature on pH for the liquid portion of progressive freeze concentration.

pH Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	0.07971	0.03986	113.923	2.00E-16
Total NA	1	0.00091	0.00091	2.613	0.107704
Freezing Temperature	1	0.00028	0.00028	0.797	0.373089
Method:Total NA	1	0.00248	0.00248	7.078	0.008497
Method:Freezing Temperature	1	0.00000	0.00000	0.000	0.994362
Total NA:Freezing Temperature	1	0.00523	0.00523	14.946	0.000154
Method:Total NA:Freezing Temperature	1	0.00019	0.00019	0.535	0.465305

Residuals	183	0.06402	0.00035		

Comparison of Factor: Freezing Method					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.0492331	-0.0574464	-0.0410197	0.0000000
Ultrasound	Control	-0.0241377	-0.0323511	-0.0159244	0.0000000
Ultrasound	Mechanical	0.0250953	0.0156113	0.0345793	0.0000000

Comparison of Factor: Total NAs					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	-0.0061719	-0.0165361	0.0041922	0.3394421
Control	120mg/L	0.0335994	0.0246238	0.0425751	0.0000000
Control	60mg/L	0.0397714	0.0307957	0.0487470	0.0000000

Comparison of Factor: Freezing Temperature					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
-15	Control	-0.0349809	-0.0439891	-0.0259726	0.0000000
-25	Control	-0.0383899	-0.0473982	-0.0293817	0.0000000
-25	-15	-0.0034091	-0.0138109	0.0069927	0.7192921

COD Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	44.92	22.461	28865.15	2.00E-16

Total NA	1	0	0.001	1.678	0.1968
Freezing Temperature	1	0.01	0.007	8.772	0.00346
Method:Total NA	1	0	0.001	1.447	0.23057
Method:Freezing Temperature	1	0	0.001	1.361	0.24492
Total NA:Freezing Temperature	1	0	0	0.002	0.96507
Method:Total NA:Freezing Temperature	1	0	0.004	4.547	0.0343
Residuals	183	0.14	0.001		

Table 0-76: Tukey HSD test for factor freezing method for Table 0-75.

Comparison of Factor: Freezing Method					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.9618529	-0.9738603	-0.9498455	0.0000000
Ultrasound	Control	-0.9728908	-0.9848982	-0.9608834	0.0000000
Ultrasound	Mechanical	-0.0110379	-0.0249029	0.0028271	0.1471064

Table 0-77: HSD test for factor total NAs for Table 0-75.

Comparison of Factor: Total NAs					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	0.0073763	-0.0065603	0.0213129	0.4251884
Control	120mg/L	0.9710600	0.9589906	0.9831295	0.0000000
Control	60mg/L	0.9636837	0.9516142	0.9757532	0.0000000

Table 0-78: Tukey HSD test for factor freezing temperature for Table 0-75.

Comparison of Factor: Freezing Temperature					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
-15	Control	-0.9758042	-0.9876608	-0.9639476	0.0000000
-25	Control	-0.9589395	-0.9707961	-0.9470830	0.0000000
-25	-15	0.0168647	0.0031739	0.0305555	0.0112389

Table 0-79: ANOVA comparing the effect of total NA concentration, freezing method, and freezing temperature on TS for the frozen portion of progressive freeze concentration.

TS Frozen Portion

Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	43.21	21.605	15149.076	2.00E-16
Total NA	1	0.02	0.023	15.799	0.000101
Freezing Temperature	1	0	0.005	3.274	0.072012
Method:Total NA	1	0	0	0.006	0.938652
Method:Freezing Temperature	1	0	0.001	1.021	0.313575
Total NA:Freezing Temperature	1	0.01	0.01	6.814	0.009791
Method:Total NA:Freezing Temperature	1	0	0.001	0.662	0.417021
Residuals	183	0.26	0.001		

Table 0-80: Tukey HSD test for factor freezing method for Table 0-79.

Comparison of Factor: Freezing Method					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.9482839	-0.9649305	-0.9316371	0.0000000
Ultrasound	Control	-0.9493189	-0.9659655	-0.9326722	0.0000000
Ultrasound	Mechanical	-0.0010351	-0.0202570	0.0181868	0.9911189

Table 0-81: HSD test for factor total NAs for Table 0-79.

Comparison of Factor: Total NAs					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	0.0306409	0.0121533	0.0491285	0.0003639
Control	120mg/L	0.9641218	0.9481110	0.9801325	0.0000000
Control	60mg/L	0.9334809	0.9174701	0.9494916	0.0000000

Table 0-82: Tukey HSD test for factor freezing temperature for Table 0-79.

Comparison of Factor: Freezing Temperature					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
-15	Control	-0.9557759	-0.9722933	-0.9392584	0.0000000
-25	Control	-0.9418268	-0.9583443	-0.9253094	0.0000000
-25	-15	0.0139490	-0.0051237	0.0330218	0.1975441

Conductivity Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	46.91	23.457	0.00003554	2.00E-16
Total NA	1	0.00	0.000	0.08	0.77786
Freezing Temperature	1	0.00	0.000	6.524	0.01146
Method:Total NA	1	0.00	0.000	0.872	0.3515
Method:Freezing Temperature	1	0.00	0.000	0.556	0.45697
Total NA:Freezing Temperature	1	0.00	0.000	0.96	0.32836
Method:Total NA:Freezing Temperature	1	0.00	0.001	1.091	0.00115
Residuals	183	0.01	0.000		

Table 0-84: Tukey HSD test for factor freezing method for Table 0-83.

Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.9870823	-0.9905973	-0.9835673	0.0000000
Ultrasound	Control	-0.9901549	-0.9936699	-0.9866399	0.0000000
Ultrasound	Mechanical	-0.0030726	-0.0071313	0.0009862	0.1762501

Table 0-85: HSD test for factor total NAs for Table 0-83.

Comparison of Factor: Total NAs		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	-0.0004685	-0.0045606	0.0036237	0.9604904
Control	120mg/L	0.9883844	0.9848404	0.9919283	0.0000000
Control	60mg/L	0.9888528	0.9853089	0.9923968	0.0000000

Table 0-86: Tukey HSD test for factor freezing temperature for Table 0-83.

Comparison of Factor: Freezing Temperature		Mean Diff	Lower Bound	Upper Bound	P Value
-15	Control	-0.9907363	-0.9942244	-0.9872482	0.0000000
-25	Control	-0.9865009	-0.9899890	-0.9830128	0.0000000

-25	-15	0.0042354	0.0002077	0.0082631	0.0367407

Table 0-87: ANOVA comparing the effect of total NA concentration, freezing method, and freezing temperature on pH for the frozen portion of progressive freeze concentration.

pH Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Method	2	7.579	3.790	12534.96	2.00E-16
Total NA	1	0.000	0.000	0.428	0.5138
Freezing Temperature	1	0.000	0.000	0.118	0.7311
Method:Total NA	1	0.000	0.000	0.192	0.6616
Method:Freezing Temperature	1	0.000	0.000	0.004	0.9514
Total NA:Freezing Temperature	1	0.005	0.002	5.986	0.0154
Method:Total NA:Freezing Temperature	1	0.001	0.001	3.034	0.0832
Residuals	183	0.055	0.000		

Table 0-88: Tukey HSD test for factor freezing method for Table 0-87.

Comparison of Factor: Freezing Method					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.3963581	-0.4036911	-0.3890251	0.0000000
Ultrasound	Control	-0.3983709	-0.4057039	-0.3910379	0.0000000
Ultrasound	Mechanical	-0.0020128	-0.0104802	0.0064546	0.8406460

Table 0-89: HSD test for factor total NAs for Table 0-87.

Comparison of Factor: Total NAs					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	-0.0023217	-0.0107868	0.0061434	0.7937777
Control	120mg/L	0.3962037	0.3888727	0.4035346	0.0000000
Control	60mg/L	0.3985254	0.3911944	0.4058563	0.0000000

Table 0-90: Tukey HSD test for factor freezing temperature for Table 0-87.

Comparison of Factor: Freezing Temperature

Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
-15	Control	-0.3967538	-0.4040906	-0.3894169	0.0000000
-25	Control	-0.3979753	-0.4053121	-0.3906384	0.0000000
-25	-15	-0.0012215	-0.0096337	0.0072504	0.9380750

Table 0-91: ANOVA comparing the effect mechanical agitation (RPM) on COD for the unfrozen portion of progressive freeze concentration.

COD Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
RPM	3	304.77	101.59	1608	2.00E-16
Residuals	92	5.81	0.06		

Table 0-92: Tukey HSD for factor mechanical RPM for Table 0-91.

Comparison of Factor: RPM					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
100RPM	Control	3.44289338	3.25300440	3.6327824	0.0000000
200RPM	Control	3.59284829	3.40295931	3.7827373	0.0000000
300RPM	Control	3.64854230	3.45865332	3.8384313	0.0000000
200RPM	100RPM	0.14995491	-0.08261065	0.3825205	0.3363081
300RPM	100RPM	0.20564892	-0.02691664	0.4382145	0.1023295
300RPM	200RPM	0.05569401	-0.17687155	0.2882596	0.9232645

Table 0-93: ANOVA comparing the effect mechanical agitation (RPM) on TS for the unfrozen portion of progressive freeze concentration.

TS Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
RPM	3	322.1	107.4	1081	2.00E-16
Residuals	92	9.1	0.1		

Table 0-94: Tukey HSD for factor mechanical RPM for Table 0-93.

Comparison of Factor: RPM				
Comparison	Mean Diff	Lower Bound	Upper Bound	P Value

100RPM	Control	3.75328876	3.51525790	3.9913196	0.0000000
200RPM	Control	3.51310602	3.27507516	3.7511369	0.0000000
300RPM	Control	3.71447469	3.47644382	3.9525056	0.0000000
200RPM	100RPM	-0.24018274	-0.53170982	0.0513443	0.1435515
300RPM	100RPM	-0.03881408	-0.33034116	0.2527130	0.9853892
300RPM	200RPM	0.20136867	-0.09015841	0.4928958	0.2764879

Table 0-95: ANOVA comparing the effect mechanical agitation (RPM) on conductivity for the unfrozen portion of progressive freeze concentration.

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
RPM	3	142.95	47.65	552.7	2.00E-16
Residuals	92	7.93	0.09		

Table 0-96: Tukey HSD for factor mechanical RPM for Table 0-95.

Comparison of Factor: RPM					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
100RPM	Control	2.43910041	2.21730790	2.6608929	0.0000000
200RPM	Control	2.38435030	2.16255780	2.6061428	0.0000000
300RPM	Control	2.49560278	2.27381030	2.7173953	0.0000000
200RPM	100RPM	-0.05475011	-0.32638930	0.2168891	0.9522421
300RPM	100RPM	0.05650237	-0.21513690	0.3281416	0.9478650
300RPM	200RPM	0.11125249	-0.16038670	0.3828917	0.7075870

Table 0-97: ANOVA comparing the effect mechanical agitation (RPM) on pH for the unfrozen portion of progressive freeze concentration.

pH Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
RPM	3	0.05939	0.0198	50.76	2.00E-16
Residuals	92	0.03588	0.00039		

Table 0-98: Tukey HSD for factor mechanical RPM for Table 0-97

Comparison of Factor: RPM					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
100RPM	Control	-0.04498126	-0.05989873	-0.0300638	0.0000000
200RPM	Control	-0.04641819	-0.06133565	-0.0315007	0.0000000
300RPM	Control	-0.05629971	-0.07121718	-0.0413822	0.0000000
200RPM	100RPM	-0.00143693	-0.01970702	0.0168332	0.9968953
300RPM	100RPM	0.01131845	-0.02958855	0.0069516	0.3720008
300RPM	200RPM	-0.00988153	-0.02815162	0.0083886	0.4931769

Table 0-99: ANOVA comparing the effect mechanical agitation (RPM) on COD for the frozen portion of progressive freeze concentration.

COD Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
RPM	3	22.208	7.403	6541	2.00E-16
Residuals	92	0.104	0.001		

Table 0-100: Tukey HSD for factor mechanical RPM for Table 0-99.

Comparison of Factor: RPM					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
100RPM	Control	-0.94919373	-0.97460503	-0.9237824	0.0000000
200RPM	Control	-0.96672322	-0.99213453	-0.9413119	0.0000000
300RPM	Control	-0.96964178	-0.99505309	-0.9442305	0.0000000
200RPM	100RPM	-0.01752949	-0.04865186	0.0135929	0.4574041
300RPM	100RPM	-0.02044805	-0.05157042	0.0106743	0.3197189
300RPM	200RPM	-0.00291856	-0.03404093	0.0282038	0.9947732

TS Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
RPM	3	21.587	7.196	3595	2.00E-16
Residuals	92	0.184	0.002		

Table 0-102: Tukey HSD for factor mechanical RPM for Table 0-101.

Comparison of Factor: RPM					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
100RPM	Control	-0.93696040	-0.97075510	-0.9031657	0.0000000
200RPM	Control	-0.96114915	-0.99494385	-0.9273545	0.0000000
300RPM	Control	-0.94674182	-0.98053652	-0.9129471	0.0000000
200RPM	100RPM	-0.02418875	-0.06557863	0.0172011	0.4244189
300RPM	100RPM	-0.00978142	-0.05117130	0.0316085	0.9259721
300RPM	200RPM	0.01440733	-0.02698255	0.0557972	0.7991296

Conductivity Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
RPM	3	23.385	7.795	76207	2.00E-16
Residuals	92	0.009	0.000		

Table 0-104: Tukey HSD for factor mechanical RPM for Table 0-103.

Comparison of Factor: RPM					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
100RPM	Control	-	-	-	0.0000000

		0.98069571	0.98833511	0.9730563	
200RPM	Control	-0.98996057	-0.99759997	-0.9823212	0.0000000
300RPM	Control	-0.99059065	-0.99823006	-0.9829513	0.0000000
200RPM	100RPM	-0.00926486	-0.01862118	0.0000915	0.0532931
300RPM	100RPM	-0.00989495	-0.01925127	-0.0005386	0.0339368
300RPM	200RPM	-0.00063008	-0.00998640	0.0087262	0.9980425

Table 0-105: ANOVA comparing the effect mechanical agitation (RPM) on pH for the frozen portion of progressive freeze concentration.

pH Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
RPM	3	3.775	1.2584	5269	2.00E-16
Residuals	92	0.022	0.0002		

Table 0-106: Tukey HSD for factor mechanical RPM for Table 0-105.

Comparison of Factor: RPM					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
100RPM	Control	-0.38470651	-0.39637942	-0.3730336	0.0000000
200RPM	Control	-0.39553307	-0.40720598	-0.3838602	0.0000000
300RPM	Control	-0.40883474	-0.42050765	-0.3971618	0.0000000
200RPM	100RPM	-0.01082656	-0.02512290	0.0034698	0.2024538
300RPM	100RPM	-0.02412823	-0.03842457	-0.0098319	0.0001587
300RPM	200RPM	-0.01330167	-0.02759801	0.0009947	0.0777048

Table 0-107: ANOVA comparing the effect ultrasound off cycle time and ultrasound amplitude on COD for the unfrozen portion of progressive freeze concentration.

COD Unfrozen Portion

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Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Off Cycle Time	3	308.33	102.75	2105.326	2.00E-16
Amplitude	1	0.35	0.35	7.073	0.00928
Off Cycle Time:Amplitude	2	0.05	0.02	0.466	0.62883
Residuals	89	4.34	0.05		

Table 0-108: Tukey HSD for factor ultrasound off cycle time for Table 0-107.

Comparison of Factor: Off Cycle Time					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	0.07439184	-0.13549680	0.2842805	0.7902416
30s	10s	-0.04795640	-0.25784500	0.1619322	0.9324699
Control	10s	-3.57477698	-3.74615030	-3.4034036	0.0000000
30s	20s	-0.12234825	-0.33223690	0.0875404	0.4267135
Control	20s	-3.64916882	-3.82054220	-3.4777955	0.0000000
Control	30s	-3.52682058	-3.69819390	-3.3554472	0.0000000

Table 0-109: Tukey HSD for factor ultrasound amplitude for Table 0-107.

Comparison of Factor: Amplitude					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
30%	20%	-0.16963080	-0.32107650	-0.0181851	0.0242269
Control	20%	-3.66840420	-3.79956000	-3.5372484	0.0000000
Control	30%	-3.49877340	-3.62992920	-3.3676176	0.0000000

Table 0-110: ANOVA comparing the effect ultrasound off cycle time and ultrasound amplitude on TS for the unfrozen portion of progressive freeze concentration.

TS Unfrozen Portion

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Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Off Cycle Time	3	327.9	109.29	1063.869	2.00E-16
Amplitude	1	0.1	0.06	0.556	0.458
Off Cycle Time:Amplitude	2	0.1	0.07	0.71	0.49400
Residuals	89	9.1	0.1		

Table 0-111: Tukey HSD for factor ultrasound off cycle time for

Table 0-110.

Comparison of Factor: Off Cycle Time					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	-0.10410680	-0.39896072	0.1907472	0.7921527
30s	10s	0.14033760	-0.15451639	0.4351915	0.5997992
Control	10s	-0.36812955	-3.92204272	-3.4405482	0.0000000
30s	20s	0.24444430	-0.05040961	0.5392983	0.1395970
Control	20s	-3.57718870	-3.81793594	-3.3364415	0.0000000
Control	30s	-3.82163300	-4.06238028	-3.5808858	0.0000000

Table 0-112: Tukey HSD for factor ultrasound amplitude for

Table 0-110.

Comparison of Factor: Amplitude					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
30%	20%	-0.06897616	-0.29183300	0.1538806	0.7420673
Control	20%	-3.72786049	-3.92086000	-3.5348608	0.0000000
Control	30%	-3.65888433	-3.85188400	-3.4658847	0.0000000

Table 0-113: ANOVA comparing the effect ultrasound off cycle time and ultrasound amplitude on conductivity for the unfrozen portion of progressive freeze concentration.

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Off Cycle Time	3	158.08	52.69	969.901	2.00E-16
Amplitude	1	0.43	0.43	7.83	0.0063
Off Cycle Time:Amplitude	2	0.17	0.08	1.533	0.22150
Residuals	89	4.84	0.05		

Table 0-114: Tukey HSD for factor ultrasound off cycle time for Table 0-113.

Comparison of Factor: Off Cycle Time					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	-0.08914097	-0.31383270	0.1355507	0.7275866
30s	10s	-0.10224791	-0.32693960	0.1224438	0.6342398
Control	10s	-2.62943223	-2.81289220	-2.4459722	0.0000000
30s	20s	-0.01310693	-0.23779860	0.2115847	0.9987239
Control	20s	-2.54029125	-2.72375120	-2.3568313	0.0000000
Control	30s	-2.52718432	-2.71064430	-2.3437243	0.0000000

Table 0-115: Tukey HSD for factor ultrasound amplitude for Table 0-113.

Comparison of Factor: Amplitude					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
30%	20%	-0.18827790	-0.34930380	-0.0272520	0.0176644
Control	20%	-2.65977490	-2.79922740	-2.5203223	0.0000000
Control	30%	-2.47149700	-2.61094950	-2.3320445	0.0000000

Table 0-116: ANOVA comparing the effect ultrasound off cycle time and ultrasound amplitude on pH for the unfrozen portion of progressive freeze concentration.

pH Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Off Cycle Time	3	0.01636	0.005454	14.946	5.85E-08
Amplitude	1	0.00039	0.000394	1.081	0.301
Off Cycle Time:Amplitude	2	0.00077	0.000384	1.051	0.35400
Residuals	89	0.03247	0.000365		

Table 0-117: Tukey HSD for factor ultrasound off cycle time for Table 0-116.

Comparison of Factor: Off Cycle Time					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	-0.00627415	-0.02396286	0.0114146	0.7898699
30s	10s	-0.01704229	-0.03473100	0.0006464	0.0632711
Control	10s	0.01636559	0.00192282	0.0308084	0.0198075
30s	20s	-0.01076814	-0.02845685	0.0069206	0.3877235
Control	20s	0.02263974	0.00819697	0.0370825	0.0005063
Control	30s	0.03340788	0.01896511	0.0478506	0.0000002

Table 0-118: Tukey HSD for factor ultrasound amplitude for Table 0-116.

Comparison of Factor: Amplitude					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
30%	20%	-0.00573247	-0.01918829	0.0077233	0.5694923
Control	20%	0.02127150	0.00961842	0.0329246	0.0001035
Control	30%	0.02700397	0.01535089	0.0386571	0.0000009

Table 0-119: ANOVA comparing the effect ultrasound off cycle time and ultrasound amplitude on COD for the frozen portion of progressive freeze concentration.

COD Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value

Off Cycle Time	3	22.717	7.572	16212.301	2.00E-16
Amplitude	1	0.003	0.003	5.376	0.0227
Off Cycle Time:Amplitude	2	0.004	0.002	4.212	0.01790
Residuals	89	0.042	0.000		

Table 0-120: Tukey HSD for factor ultrasound off cycle time for Table 0-119.

Comparison of Factor: Off Cycle Time					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	-0.00300600	0.02414015	0.0181282	0.9823026
30s	10s	0.00201138	-0.01912277	0.0231455	0.9945403
Control	10s	0.97255927	0.95530330	0.9898152	0.0000000
30s	20s	0.00501738	-0.01611677	0.0261515	0.9250485
Control	20s	0.97556527	0.95830931	0.9928212	0.0000000
Control	30s	0.97054788	0.95329192	0.9878039	0.0000000

Table 0-121: Tukey HSD for factor ultrasound amplitude for Table 0-119.

Comparison of Factor: Amplitude					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
30%	20%	-0.01446496	-0.02970787	0.0007780	0.0666220
Control	20%	0.96565833	0.95245758	0.9788591	0.0000000
Control	30%	0.98012328	0.96692254	0.9933240	0.0000000

Table 0-122: ANOVA comparing the effect ultrasound off cycle time and ultrasound amplitude on TS for the frozen portion of progressive freeze concentration.

TS Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Off Cycle Time	3	21.635	7.212	6531.842	2.00E-16
Amplitude	1	0.004	0.004	3.452	0.0665
Off Cycle Time:Amplitude	2	0.003	0.002	1.504	0.22790
Residuals	89	0.098	0.001		

Comparison of Factor: Off Cycle Time					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	-0.01532678	-0.04663868	0.0159851	0.5774211
30s	10s	0.01207095	-0.01924095	0.0433829	0.7447318
Control	10s	0.94823359	0.92266753	0.9737996	0.0000000
30s	20s	0.02739773	-0.00391417	0.0587096	0.1079598
Control	20s	0.96356037	0.93799431	0.9891264	0.0000000
Control	30s	0.93616264	0.91059658	0.9617287	0.0000000

Table 0-124: Tukey HSD for factor ultrasound amplitude for Table 0-122.

Comparison of Factor: Amplitude					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
30%	20%	-0.01782061	-0.04120982	0.0055686	0.1703889
Control	20%	0.94040856	0.92015291	0.9606642	0.0000000
Control	30%	0.95822917	0.93797352	0.9784848	0.0000000

Table 0-125: ANOVA comparing the effect ultrasound off cycle time and ultrasound amplitude on conductivity for the frozen portion of progressive freeze concentration.

Conductivity Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Off Cycle Time	3	23.53	7.843	276900	2.00E-16
Amplitude	1	0.000	0.000	6.859	0.0104
Off Cycle Time:Amplitude	2	0.000	0.000	1.626	0.20260
Residuals	89	0.003	0.000		

Table 0-126: Tukey HSD for factor ultrasound off cycle time for Table 0-125.

Comparison of Factor: Off Cycle Time				
Comparison	Mean Diff	Lower Bound	Upper Bound	P Value

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20s	10s	0.00465700	-0.00045362	0.0097676	0.0872715
30s	10s	0.00356366	-0.00154695	0.0086743	0.2685048
Control	10s	0.99289510	0.98872231	0.9970679	0.0000000
30s	20s	-0.00109334	-0.00620395	0.0040173	0.9436429
Control	20s	0.98823811	0.98406531	0.9924109	0.0000000
Control	30s	0.98933144	0.98515865	0.9935042	0.0000000

Table 0-127: Tukey HSD for factor ultrasound amplitude for Table 0-125.

Comparison of Factor: Amplitude					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
30%	20%	-0.00402407	-0.00779889	-0.0002493	0.0338516
Control	20%	0.98814285	0.98487376	0.9914119	0.0000000
Control	30%	0.99216692	0.98889783	0.9954360	0.0000000

Table 0-128: ANOVA comparing the effect ultrasound off cycle time and ultrasound amplitude on pH for the frozen portion of progressive freeze concentration.

pH Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Off Cycle Time	3	3.813	1.2709	4610.885	2.00E-16
Amplitude	1	0.002	0.0022	8.017	0.00573
Off Cycle Time:Amplitude	2	0.001	0.0004	1.615	0.20466
Residuals	89	0.025	0.0003		

Table 0-129: Tukey HSD for factor ultrasound off cycle time for Table 0-128.

Comparison of Factor: Off Cycle Time					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	0.01994234	0.00390973	0.0359750	0.0084954
30s	10s	0.01873198	0.00269937	0.0347646	0.0152398
Control	10s	0.41126237	0.39817180	0.4243529	0.0000000
30s	20s	-0.00121036	-0.01724297	0.0148222	0.9972507
Control	20s	0.39132003	0.37822946	0.4044106	0.0000000

| Control | 30s | 0.39253039 | 0.37943982 | 0.4056210 | 0.0000000 |

Table 0-130: Tukey HSD for factor ultrasound amplitude for Table 0-128.

Comparison of Factor: Amplitude					
Comparison		Mean Diff	Lower Bound	Upper Bound	P Value
30%	20%	-0.01356975	-0.02579938	-0.0013401	0.0258806
Control	20%	0.39158605	0.38099488	0.4021772	0.0000000
Control	30%	0.40515580	0.39456463	0.4157470	0.0000000

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7.6   Experimental Results of Chapter 6

Table 0-131: Results of pH, conductivity, TS, and COD ratios of progressive freeze concentration of synthetic NAs.

Unfrozen Portion		
	Synthetic NAs	
	Mean	Std. Dev
pH	1.0031	0.01338
Conductivity	3.2384	0.21339
TS	5.08148	0.51912
COD	4.49884	0.37403
Frozen Portion		
	Synthetic NAs	
	Mean	Std. Dev
pH	0.58374	0.02195
Conductivity	0.00729	0.0107
TS	0.02145	0.03232
COD	0.03833	0.0464

Table 0-132: Results of pH, conductivity, TS, and COD ratios of progressive freeze concentration of synthetic NAs at 60mg/L

and 120mg/L.

Synthetic NAs Concentration: Unfrozen Portion				
	60mg/L		120mg/L	
	Mean	Std. Dev	Mean	Std. Dev
pH	1.00093	0.00981	1.00527	0.01662
Conductivity	3.21929	0.13808	3.25751	0.2787
TS	5.23544	0.55449	4.92752	0.46457
COD	4.53464	0.34283	4.46305	0.42348
Synthetic NAs Concentration: Frozen Portion				
	60mg/L		120mg/L	
	Mean	Std. Dev	Mean	Std. Dev
pH	0.57869	0.00423	0.5888	0.03092

Conductivity	0.00499	0.0009	0.00959	0.01525
TS	0.03747	0.03762	0.00543	0.01537
COD	0.02726	0.01599	0.04941	0.06385

Table 0-133: Results of pH, conductivity, TS, and COD ratios of progressive freeze concentration of synthetic NAs at US cycle times of 1s/20s and 1s/10s.

Synthetic NAs US Cycle Time: Unfrozen Portion				
	1s/20s		1s/10s	
	Mean	Std. Dev	Mean	Std. Dev
pH	1.01173	0.01521	1.00042	0.0089
Conductivity	3.42611	0.24579	3.12755	0.20357
TS	5.18842	0.36365	4.95856	0.21344
COD	4.80123	0.40259	4.51946	0.27222
Synthetic NAs US Cycle Time: Unfrozen Portion				
	1s/20s		1s/10s	
	Mean	Std. Dev	Mean	Std. Dev
pH	0.57657	0.00533	0.5768	0.00487
Conductivity	0.00443	0.00126	0.00395	0.00072
TS	0.01142	0.02285	0.04668	0.05395
COD	0.03445	0.00674	0.01534	0.01172

Table 0-134: Results of pH, conductivity, TS, and COD ratios of progressive freeze concentration of synthetic NAs with inorganics at varying concentrations.

Inorganic Contaminates: Unfrozen Portion								
	Chloride at 40mg/L		Chloride and Sulfate at 40mg/L		Chloride at 500mg/L		Chloride and Sulfate at 500mg/L	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.97891	0.00179	0.94541	0.054	0.93926	0.02241	0.8295	0.03097
Conductivity	4.25226	0.35076	3.77779	0.23804	OR	OR	OR	OR
TS	4.84495	0.62592	4.67828	0.18113	3.49888	0.20102	2.72455	0.11552

	4.70879	0.35464	4.33928	0.24713	3.02246	0.09272	2.24533	0.10674
COD								

Inorganic Contaminates: Frozen Portion								
	Chloride at 40mg/L		Chloride and Sulfate at 40mg/L		Chloride at 500mg/L		Chloride and Sulfate at 500mg/L	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
pH	0.61497	0.01437	0.61798	0.02499	0.74754	0.02154	0.76535	0.05028
Conductivity	0.01647	0.00968	0.04871	0.05711	0.2795	0.03884	OR	OR
TS	0.00358	0.00716	0.0683	0.09296	0.29224	0.03192	0.53774	0.03355
COD	0.00912	0.01107	0.07983	0.06998	0.41027	0.02394	0.64584	0.03467

7.7 Statistical Analysis from Chapter 6

Table 0-135: ANOVA comparing the effect of solution type (synthetic NAs solution or three NAs mixture) on COD for the liquid portion of progressive freeze concentration.

COD Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Solution Type	2	201.35	100.67	1724	2.00E-16
Residuals	61	3.56	0.06		

Table 0-136: Tukey HSD test for factor solution type for Table 0-135.

Comparison of Factor: Solution Type					
Comparison of Factor: Solution Type		Mean Diff	Lower Bound	Upper Bound	P Value
Synthetic NAs	Control	3.4988441	3.3211025	3.6765760	0.0000000
Three NAs	Control	3.5947447	3.4170031	3.7724860	0.0000000
Three NAs	Synthetic NAs	0.0959006	-0.1093377	-0.1093377	0.5040623

TS Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Solution Type	2	237.8	118.9	1011	2.00E-16
Residuals	61	7.17	0.12		

Comparison of Factor: Solution Type					
Comparison of Factor: Solution Type		Mean Diff	Lower Bound	Upper Bound	P Value
Synthetic NAs	Control	4.0814808	3.8292469	4.3337147	0.0000000
Three NAs	Control	3.5986320	3.3463982	3.8508659	0.0000000
Three NAs	Synthetic NAs	-0.4828487	-0.7741033	-0.1915942	0.0005341

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Solution Type	2	96.98	48.49	658.9	2.00E-16
Residuals	61	4.49	0.07		

Comparison of Factor: Solution Type					
Comparison of Factor: Solution Type		Mean Diff	Lower Bound	Upper Bound	P Value
Synthetic NAs	Control	2.2383999	2.0388657	2.4379340	0.0000000

Three NAs	Control	2.6508104	2.4512763	2.8503446	0.0000000
Three NAs	Synthetic NAs	0.4124106	0.1820084	0.6428128	0.0001832

Table 0-141: ANOVA comparing the effect of solution type (synthetic NAs solution or three NAs mixture) on pH for the liquid portion of progressive freeze concentration.

pH Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Solution Type	2	0.007818	0.003909	29.35	1.18E-09
Residuals	61	0.008124	0.000133		

Table 0-142: Tukey HSD test for factor solution type for Table 0-141.

Comparison of Factor: Solution Type					
Comparison of Factor: Solution Type		Mean Diff	Lower Bound	Upper Bound	P Value
Synthetic NAs	Control	0.0030988	-0.0053895	0.0115871	0.6567818
Three NAs	Control	-0.0243246	-0.0328129	-0.0158363	0.0000000
Three NAs	Synthetic NAs	-0.0274234	-0.0372248	-0.0176219	0.0000000

Table 0-143: ANOVA comparing the effect of solution type (synthetic NAs solution or three NAs mixture) on COD for the solid portion of progressive freeze concentration.

COD Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Solution Type	2	14.984	7.492	9251	2.00E-16
Residuals	61	0.049	0.001		

Table 0-144: Tukey HSD test for factor solution type for Table 0-143.

Comparison of Factor: Solution Type					
Comparison of Factor: Solution Type		Mean Diff	Lower Bound	Upper Bound	P Value
Synthetic NAs	Control	-0.9616657	-0.9825974	-0.9407339	0.0000000
Three NAs	Control	-0.9736977	-0.9946295	-0.9576593	0.0000000
Three NAs	Synthetic NAs	-0.0120320	-0.0362020	0.0121379	0.4601892

Table 0-145: ANOVA comparing the effect of solution type (synthetic NAs solution or three NAs mixture) on TS for the solid portion of progressive freeze concentration.

TS Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Solution Type	2	14.881	7.44	10175	2.00E-16
Residuals	61	0.045	0.001		

Table 0-146: Tukey HSD test for factor solution type for Table 0-145.

Comparison of Factor: Solution Type					
Comparison of Factor: Solution Type		Mean Diff	Lower Bound	Upper Bound	P Value
Synthetic NAs	Control	-0.9785491	-0.9984385	-0.9586598	0.0000000
Three NAs	Control	-0.9498003	-0.9696897	-0.9299110	0.0000000
Three NAs	Synthetic NAs	0.0287488	0.0057826	0.0517151	0.0105426

Table 0-147: ANOVA comparing the effect of solution type (synthetic NAs solution or three NAs mixture) on conductivity for

the solid portion of progressive freeze concentration.

Conductivity Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Solution Type	2	15.695	7.847	107485	2.00E-16
Residuals	61	0.004	0		

Table 0-148: Tukey HSD test for factor solution type for Table 0-147.

Comparison of Factor: Solution Type					
Comparison of Factor: Solution Type		Mean Diff	Lower Bound	Upper Bound	P Value
Synthetic NAs	Control	-0.9927108	-0.9989955	-0.9864261	0.0000000
Three NAs	Control	-0.9881054	-0.9943901	-0.9818207	0.0000000
Three NAs	Synthetic NAs	0.0046054	-0.0026516	0.0118624	0.2866956

Table 0-149: ANOVA comparing the effect of solution type (synthetic NAs solution or three NAs mixture) on pH for the solid

portion of progressive freeze concentration.

pH Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Solution Type	2	2.6188	1.3094	6169	2.00E-16
Residuals	61	0.0129	0.0002		

Table 0-150: Tukey HSD test for factor solution type for Table 0-149.

Comparison of Factor: Solution Type				
Comparison of Factor: Solution Type	Mean Diff	Lower Bound	Upper Bound	P Value

Synthetic NAs	Control	-0.4162551	-0.4269714	-0.4055388	0.0000000
Three NAs	Control	-0.3921657	-0.4028820	-0.3814493	0.0000000
Three NAs	Synthetic NAs	0.0240895	0.0117153	0.0364636	0.0000490

Table 0-151: ANOVA comparing the effect of cycle time on COD for the liquid portion of progressive freeze concentration of synthetic NAs solution.

COD Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Cycle Time	2	53.75	26.876	493.1	5.53E-13
Residuals	13	0.71	0.055		

Table 0-152: Tukey HSD test for factor cycle time for Table 0-151.

Comparison of Factor: Off Cycle Time					
Comparison of Factor: Cycle Time		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	0.2817662	-0.1541198	0.7176522	0.2397180
Control	10s	-3.5194590	-3.8969740	-3.1419706	0.0000000
Control	20s	-3.8012252	-4.1787135	-3.4237368	0.0000000

Table 0-153: ANOVA comparing the effect of cycle time on TS for the liquid portion of progressive freeze concentration of synthetic NAs solution.

TS Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Cycle Time	2	66.48	33.24	810.1	2.27E-14
Residuals	13	0.53	0.04		

Comparison of Factor: Off Cycle Time					
Comparison of Factor: Cycle Time		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	0.2298645	-0.1483305	0.6080595	0.2784588
Control	10s	-3.9585557	-4.2860821	-3.6310292	0.0000000
Control	20s	-4.1884202	-4.5159467	-3.8608937	0.0000000

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Cycle Time	2	20.914	10.457	444.9	1.07E-12
Residuals	13	0.306	0.024		

Comparison of Factor: Off Cycle Time					
Comparison of Factor: Cycle Time		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	0.2985598	0.0123117	0.5848078	0.0406792
Control	10s	-2.1275511	-2.3754492	-1.8796530	0.0000000
Control	20s	-2.4261109	-2.6740090	-2.1782128	0.0000000

pH Unfrozen Portion

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Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Cycle Time	2	0.0004035	0.00020170	2.814	9.65E-02
Residuals	13	0.0009318	0.00007168		

Table 0-158: Tukey HSD test for factor cycle time for Table 0-157.

Comparison of Factor: Off Cycle Time					
Comparison of Factor: Cycle Time		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	0.0113113	-0.0044961	0.0271186	0.1809239
Control	10s	-0.0004184	-0.0141079	0.0132712	0.9964176
Control	20s	-0.0117296	-0.0254192	0.0019600	0.0975367

Table 0-159: ANOVA comparing the effect of cycle time on COD for the solid portion of progressive freeze concentration of synthetic NAs solution.

COD Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Cycle Time	2	3.804	1.902	45094	2.00E-16
Residuals	13	0.001	0		

Table 0-160: Tukey HSD test for factor cycle time for Table 0-159.

Comparison of Factor: Off Cycle Time					
Comparison of Factor: Cycle Time		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	0.0191089	0.0069831	0.0312347	0.0029843
Control	10s	0.9846609	0.9741597	0.9951622	0.0000000
Control	20s	0.9655520	0.9550507	0.9760533	0.0000000

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TS Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Cycle Time	2	3.773	1.8867	2382	2.00E-16
Residuals	13	0.01	0.0008		

Table 0-162: Tukey HSD test for factor cycle time for Table 0-161.

Comparison of Factor: Off Cycle Time					
Comparison of Factor: Cycle Time		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	-0.0352555	-0.0878033	0.0172922	0.2173699
Control	10s	0.9533197	0.9078121	0.9988274	0.0000000
Control	20s	0.9885753	0.9430676	1.0340829	0.0000000

Table 0-163: ANOVA comparing the effect of cycle time on conductivity for the solid portion of progressive freeze concentration of synthetic NAs solution.

Conductivity Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Cycle Time	2	3.967	1.983	4075333	2.00E-16
Residuals	13	0	0		

Table 0-164: Tukey HSD test for factor cycle time for Table 0-163.

Comparison of Factor: Off Cycle Time					
Comparison of Factor: Cycle Time		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	0.0004820	-0.0008205	0.0017845	0.6034044

Control	10s	0.9960500	0.9949220	0.9971780	0.0000000
Control	20s	0.9955680	0.9944400	0.9966959	0.0000000

Table 0-165: ANOVA comparing the effect of cycle time on pH for the solid portion of progressive freeze concentration of synthetic NAs solution.

pH Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Cycle Time	2	0.7168	0.3584	29758	2.00E-16
Residuals	13	0.0002	0		

Table 0-166: Tukey HSD test for factor cycle time for Table 0-165.

Comparison of Factor: Off Cycle Time					
Comparison of Factor: Cycle Time		Mean Diff	Lower Bound	Upper Bound	P Value
20s	10s	-0.0002321	-0.0067115	0.0062473	0.9950822
Control	10s	0.4231977	0.4175864	0.4288090	0.0000000
Control	20s	0.4234298	0.4178185	0.4290411	0.0000000

Table 0-167: ANOVA comparing the effect of synthetic NAs concentration on COD for the liquid portion of progressive freeze concentration of synthetic NAs solution.

COD Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Synthetic NAs Concentration	2	97.96	48.98	683.5	2.00E-16
Residuals	29	2.08	0.07		

Comparison of Factor: Concentration					
Comparison of Factor: Concentration		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	0.0715856	-0.2589602	0.4021315	0.8549070
Control	120mg/L	-3.4630513	-3.7493124	-3.1767902	0.0000000
Control	60mg/L	-3.5346369	-3.8208980	-3.2483758	0.0000000

Table 0-169: ANOVA comparing the effect of synthetic NAs concentration on TS for the liquid portion of progressive freeze concentration of synthetic NAs solution.

TS Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	2	133.65	66.82	529	2.00E-16
Residuals	29	3.66	0.13		

Table 0-170: Tukey HSD test for factor concentration for Table 0-169.

Comparison of Factor: Concentration					
Comparison of Factor: Concentration		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	0.3079250	-0.1309309	0.7467809	0.2103654
Control	120mg/L	-3.9275180	-0.4307579	-3.5474580	0.0000000
Control	60mg/L	-4.2354430	-4.6155036	-3.8553830	0.0000000

Table 0-171: ANOVA comparing the effect of synthetic NAs concentration on conductivity for the liquid portion of progressive freeze concentration of synthetic NAs solution.

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	2	40.09	20.045	858.4	2.00E-16
Residuals	29	0.68	0.023		

Table 0-172: Tukey HSD test for factor concentration for Table 0-171.

Comparison of Factor: Concentration					
Comparison of Factor: Concentration		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	-0.0382204	-0.2269177	0.1504770	0.8717724
Control	120mg/L	-2.2575100	-2.4209267	-2.0940930	0.0000000
Control	60mg/L	-2.2192897	-2.3827064	-2.0558730	0.0000000

Table 0-173: ANOVA comparing the effect of synthetic NAs concentration on pH for the liquid portion of progressive freeze concentration of synthetic NAs solution.

pH Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	2	0.0001524	0.00007618	0.847	0.439
Residuals	29	0.002608	0.00008993		

Table 0-174: Tukey HSD test for factor concentration for Table 0-173.

Comparison of Factor: Concentration				
Comparison of Factor: Concentration	Mean Diff	Lower Bound	Upper Bound	P Value

60mg/L	120mg/L	-0.0043456	-0.0160556	0.0073643	0.6344218
Control	120mg/L	-0.0052716	-0.0154127	0.0048695	0.4154584
Control	60mg/L	-0.0009260	-0.0110671	0.0092152	0.9723842

Table 0-175: ANOVA comparing the effect of synthetic NAs concentration on COD for the solid portion of progressive freeze concentration of synthetic NAs solution.

COD Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	2	7.4	3.7	3538	2.00E-16
Residuals	29	0.03	0.001		

Table 0-176: Tukey HSD test for factor concentration for Table 0-175

Comparison of Factor: Concentration					
Comparison of Factor: Concentration		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	-0.0221477	-0.0620810	0.0177855	0.3695740
Control	120mg/L	0.9505918	0.9160086	0.9851750	0.0000000
Control	60mg/L	0.9727395	0.9381564	1.0073227	0.0000000

Table 0-177: ANOVA comparing the effect of synthetic NAs concentration on TS for the solid portion of progressive freeze concentration of synthetic NAs solution.

TS Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	2	7.665	3.832	9615	2.00E-16
Residuals	29	0.012	0		

Table 0-178: Tukey HSD test for factor concentration for Table 0-177.

Comparison of Factor: Concentration					
Comparison of Factor: Concentration		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	0.0320367	0.0073842	0.0566891	0.0088203
Control	120mg/L	0.9945675	0.9732178	1.0159171	0.0000000
Control	60mg/L	0.9625308	0.9411811	0.9838805	0.0000000

Table 0-179: ANOVA comparing the effect of synthetic NAs concentration on conductivity for the solid portion of progressive freeze concentration of synthetic NAs solution.

Conductivity Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	2	7.884	3.942	70009	2.00E-16
Residuals	29	0.002	0		

Table 0-180: Tukey HSD test for factor concentration for Table 0-179.

Comparison of Factor: Concentration					
Comparison of Factor: Concentration		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	-0.0046001	-0.0138659	0.0046657	0.4477534
Control	120mg/L	0.9904107	0.9823863	0.9984352	0.0000000
Control	60mg/L	0.9950108	0.9869864	1.0030353	0.0000000

Table 0-181: ANOVA comparing the effect of synthetic NAs concentration on pH for the solid portion of progressive freeze concentration of synthetic NAs solution.

pH Frozen Portion					
Source of Variation	DF	Sum	Mean	F	p Value

		Sq	Sq		
Concentration	2	1.3866	0.6933	2950	2.00E-16
Residuals	29	0.0068	0.0002		

Table 0-182: Tukey HSD test for factor concentration for Table 0-181.

Comparison of Factor: Concentration					
Comparison of Factor: Concentration		Mean Diff	Lower Bound	Upper Bound	P Value
60mg/L	120mg/L	-0.0101135	-0.0290442	0.0088171	0.3961053
Control	120mg/L	0.4111983	0.3948039	0.4275927	0.0000000
Control	60mg/L	0.4213119	0.4049175	0.4377063	0.0000000

Table 0-183: ANOVA comparing the effect of freezing method on COD for the liquid portion of progressive freeze concentration of synthetic NAs solutions.

COD Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Synthetic NAs Freezing Method	2	98.35	49.18	848.3	2.00E-16
Residuals	29	1.68	0.06		

Table 0-184: Tukey HSD test for factor freezing method for Table 0-183.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	3.3373461	3.0798629	3.5948290	0.0000000
Ultrasound	Control	3.6603421	3.4028589	3.9178250	0.0000000
Ultrasound	Mechanical	0.3229959	0.0256799	0.6203120	0.0310788

TS Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Synthetic NAs Freezing Method	2	133.27	66.63	478.2	2.00E-16
Residuals	29	4.04	0.14		

Table 0-186: Tukey HSD test for factor freezing method for Table 0-185.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	4.0894736	3.6902722	4.4886751	0.0000000
Ultrasound	Control	4.0734879	3.6742865	4.4726894	0.0000000
Ultrasound	Mechanical	-0.0159857	-0.4769438	0.4449725	0.9959647

Table 0-187: ANOVA comparing the effect of freezing method on conductivity for the liquid portion of progressive freeze concentration of synthetic NAs solutions.

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Synthetic NAs Freezing Method	2	40.11	20.054	881.9	2.00E-16
Residuals	29	0.66	0.023		

Table 0-188: Tukey HSD test for factor freezing method for Table 0-187.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	2.1999687	2.0387125	2.3612249	0.0000000
Ultrasound	Control	2.2768310	2.1155748	2.4380872	0.0000000

| Ultrasound | Mechanical | 0.0768623 | -0.1093404 | 0.2630649 | 0.5708002 |

Table 0-189: ANOVA comparing the effect of freezing method on pH for the liquid portion of progressive freeze concentration of synthetic NAs solutions.

pH Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Synthetic NAs Freezing Method	2	0.0002185	0.0001092	1.246	0.303
Residuals	29	0.0025419	0.00008765		

Table 0-190: Tukey HSD test for factor freezing method for Table 0-189.

Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	0.0001236	-0.0098883	0.0101354	0.9994880
Ultrasound	Control	0.0060740	-0.0039378	0.0160858	0.3065116
Ultrasound	Mechanical	0.0059504	-0.0056102	0.0175111	0.4224160

Table 0-191: ANOVA comparing the effect of freezing method on COD for the frozen portion of progressive freeze concentration of synthetic NAs solutions.

COD Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Synthetic NAs Freezing Method	2	7.401	3.701	3650	2.00E-16
Residuals	29	0.029	0.001		

Table 0-192: Tukey HSD test for factor freezing method for Table 0-191.

Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.9482249	-0.9822746	-0.9141751	0.0000000
Ultrasound	Control	-0.9751065	-1.0091562	-0.9410567	0.0000000
Ultrasound	Mechanical	-0.0268816	-0.0661989	0.0124357	0.2266278

Table 0-193: ANOVA comparing the effect of freezing method on TS for the frozen portion of progressive freeze concentration of synthetic NAs solutions.

TS Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Synthetic NAs Freezing Method	2	7.661	3.831	7537	2.00E-16
Residuals	29	0.015	0.001		

Table 0-194: Tukey HSD test for factor freezing method for Table 0-193.

Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.9861508	-1.0102597	-0.9620418	0.0000000
Ultrasound	Control	-0.9709475	-0.9950565	-0.9468385	0.0000000
Ultrasound	Mechanical	0.0152033	-0.0136354	0.0430419	0.3805181

Table 0-195: ANOVA comparing the effect of freezing method on conductivity for the frozen portion of progressive freeze concentration of synthetic NAs solutions.

Conductivity Frozen Portion					
Source of Variation	DF	Sum	Mean	F	p Value

			Sq	Sq		
Synthetic NAs Freezing Method		2	7.884	3.942	73095	2.00E-16
Residuals		29	0.002	0		

Table 0-196: Tukey HSD test for factor freezing method for Table 0-195.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.9896126	-0.9974658	-0.9817594	0.0000000
Ultrasound	Control	-0.9958090	-1.0036622	-0.9879557	0.0000000
Ultrasound	Mechanical	-0.0061964	-0.0152645	0.0028717	0.2269951

Table 0-197: ANOVA comparing the effect of freezing method on pH for the frozen portion of progressive freeze concentration of synthetic NAs solutions.

pH Frozen Portion						
Source of Variation		DF	Sum Sq	Mean Sq	F	p Value
Synthetic NAs Freezing Method		2	1.3869	0.6935	3129	2.00E-16
Residuals		29	0.0064	0.0002		

Table 0-198: Tukey HSD test for factor freezing method for Table 0-197.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.4091964	-0.4251173	-0.3932756	0.0000000
Ultrasound	Control	-0.4233138	-0.4392346	-0.4073929	0.0000000
Ultrasound	Mechanical	-0.0141173	-0.0325011	0.0042665	0.1577624

COD Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Freezing Method with Inorganics	2	53.28	26.64	47.33	7.36E-10
Residuals	29	16.32	0.563		

Table 0-200: Tukey HSD test for factor freezing method for Table 0-199.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	2.5125123	1.7102518	3.3147730	0.0000000
Ultrasound	Control	2.6454163	1.8431557	3.4476770	0.0000000
Ultrasound	Mechanical	0.1329039	-0.7934667	1.0592750	0.9332998

Table 0-201: ANOVA comparing the effect of freezing method on TS for the liquid portion of progressive freeze concentration of NAs solutions containing inorganics.

TS Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Freezing Method with Inorganics	2	69	34.5	73.7	4.27E-12
Residuals	29	13.57	0.47		

Table 0-202: Tukey HSD test for factor freezing method for Table 0-201.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	2.9209161	2.1892745	3.6525578	0.0000000
Ultrasound	Control	2.9524093	2.2207677	3.6840510	0.0000000
Ultrasound	Mechanical	0.0314932	-0.8133338	0.8763202	0.9953389

Table 0-203: ANOVA comparing the effect of freezing method on conductivity for the liquid portion of progressive freeze concentration of NAs solutions containing inorganics.

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Freezing Method with Inorganics	2	48.51	24.257	531.7	2.00E-16
Residuals	21	0.96	0.046		

Table 0-204: Tukey HSD test for factor freezing method for Table 0-203.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	2.9525106	2.6515491	3.2534722	0.0000000
Ultrasound	Control	3.0775414	2.7765798	3.3785029	0.0000000
Ultrasound	Mechanical	0.1250307	-0.2556588	0.5057203	0.6902918

Table 0-205: ANOVA comparing the effect of freezing method on pH for the liquid portion of progressive freeze concentration of NAs solutions containing inorganics.

pH Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Freezing Method with Inorganics	2	0.04788	0.023942	11.04	2.72E-04
Residuals	29	0.06289	0.002169		

Table 0-206: Tukey HSD test for factor freezing method for Table 0-205.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.0837420	-0.1335428	-0.0339412	0.0007500

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Ultrasound	Control	-0.0697132	-0.1195140	-0.0199125	0.0047136
Ultrasound	Mechaical	0.0140288	-0.0434762	0.0715337	0.8198773

Table 0-207: ANOVA comparing the effect of freezing method on COD for the frozen portion of progressive freeze concentration of NAs solutions containing inorganics.

COD Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Freezing Method with Inorganics	2	4.082	2.0408	55.29	1.27E-10
Residuals	29	1.071	0.0369		

Table 0-208: Tukey HSD test for factor freezing method for Table 0-207.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.6939247	-0.8993870	-0.4884625	0.0000000
Ultrasound	Control	-0.7335478	-0.9390100	-0.5280856	0.0000000
Ultrasound	Mechanical	-0.0396230	-0.2768704	0.1976243	0.9107780

Table 0-209: ANOVA comparing the effect of freezing method on TS for the frozen portion of progressive freeze concentration of NAs solutions containing inorganics.

TS Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Freezing Method with Inorganics	2	4.8	2.3999	94.62	1.95E-13
Residuals	29	0.736	0.0254		

Table 0-210: Tukey HSD test for factor freezing method for Table 0-209

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.7683177	-0.9386277	-0.5980076	0.0000000
Ultrasound	Control	-0.7807536	-0.9510636	-0.6104435	0.0000000
Ultrasound	Mechanical	-0.0124359	-0.2090930	0.1842212	0.9866501

Table 0-211: ANOVA comparing the effect of freezing method on conductivity for the frozen portion of progressive freeze concentration of NAs solutions containing inorganics.

Conductivity Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Freezing Method with Inorganics	2	5.374	2.6871	379.5	2.00E-16
Residuals	25	0.177	0.0071		

Table 0-212: Tukey HSD test for factor freezing method for Table 0-211.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.8714997	-0.9718351	-0.7711643	0.0000000
Ultrasound	Control	-0.8987119	-0.9990473	-0.7983765	0.0000000
Ultrasound	Mechanical	-0.0272122	-0.1482212	0.0937969	0.8422554

Table 0-213: ANOVA comparing the effect of freezing method on pH for the frozen portion of progressive freeze concentration of NAs solutions containing inorganics.

pH Frozen Portion

Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Freezing Method with Inorganics	2	0.7877	0.3939	128	4.07E-15
Residuals	29	0.0892	0.0031		

Table 0-214: Tukey HSD test for factor freezing method for Table 0-213.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Mechanical	Control	-0.3047061	-0.3640260	-0.2453862	0.0000000
Ultrasound	Control	-0.3223786	-0.3816985	-0.2630587	0.0000000
Ultrasound	Mechaical	-0.0176725	-0.0861692	0.0508242	0.8009697

Table 0-215: ANOVA comparing the effect of inorganics on COD for the unfrozen portion of progressive freeze concentration of NAs solutions containing inorganics.

COD Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Presence Inorganics	2	141.19	70.6	202.8	2.00E-16
Residuals	53	18.45	0.35		

Table 0-216: Tukey HSD test for factor inorganics for Table 0-215.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
No Inorganics	Control	3.7293200	3.2384890	4.2201511	0.0000000
Inorganics	Control	2.5789640	2.1331450	3.0247839	0.0000000
Inorganics	No Inorganics	-1.1503560	-1.6936060	-0.6071049	0.0000135

TS Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Presence Inorganics	2	156.32	78.16	273.2	2.00E-16
Residuals	53	15.16	0.29		

Table 0-218: Tukey HSD test for factor inorganics for Table 0-217.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
No Inorganics	Control	3.7636000	3.3186260	4.2085732	0.0000000
Inorganics	Control	2.9366630	2.5324960	3.3408299	0.0000000
Inorganics	No Inorganics	-0.8269370	-1.3194320	-0.3344417	0.0004883

Table 0-219: ANOVA comparing the effect of inorganics on conductivity for the unfrozen portion of progressive freeze concentration of NAs solutions containing inorganics.

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Presence Inorganics	2	87.37	43.68	990.1	2.00E-16
Residuals	45	1.99	0.04		

Table 0-220: Tukey HSD test for factor inorganics for Table 0-219.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
No Inorganics	Control	2.5200910	2.3444437	2.6957383	0.0000000
Inorganics	Control	3.0150260	2.8109423	3.2191097	0.0000000
Inorganics	No Inorganics	0.4949350	0.2625755	0.7272946	0.0000158

Table 0-221: ANOVA comparing the effect of inorganics on conductivity for the unfrozen portion of progressive freeze

concentration of NAs solutions containing inorganics.

pH Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Presence Inorganics	2	0.06004	0.030019	23.46	5.03E-08
Residuals	53	0.06781	0.001279		

Table 0-222: Tukey HSD test for factor inorganics for Table 0-221.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
No Inorganics	Control	-0.0310835	-0.0608419	-0.0013251	0.0387765
Inorganics	Control	-0.0767276	-0.1037570	-0.0496982	0.0000000
Inorganics	No Inorganics	-0.0456442	-0.0785807	-0.0127076	0.0043036

Table 0-223: ANOVA comparing the effect of inorganics on COD for the frozen portion of progressive freeze concentration of

NAs solutions containing inorganics.

COD Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Presence Inorganics	2	10.061	5.03	245	2.00E-16
Residuals	53	1.088	0.021		

Table 0-224: Tukey HSD test for factor inorganics for Table 0-223.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
No Inorganics	Control	-0.9785037	-1.0977113	-0.8592962	0.0000000
Inorganics	Control	-0.7137363	-0.8220119	-0.6054606	0.0000000

Inorganics	No Inorganics	0.2647675	0.1328289	0.3967060	0.0000344

Table 0-225: ANOVA comparing the effect of inorganics on TS for the frozen portion of progressive freeze concentration of NAs solutions containing inorganics.

TS Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Presence Inorganics	2	10.351	5.175	363.2	2.00E-16
Residuals	53	0.755	0.014		

Table 0-226: Tukey HSD test for factor inorganics for Table 0-225.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
No Inorganics	Control	-0.9524502	-0.1051761	-0.8531389	0.0000000
Inorganics	Control	-0.7745356	-0.8647396	-0.6843317	0.0000000
Inorganics	No Inorganics	0.1779146	0.0679972	0.2878320	0.0007785

Table 0-227: ANOVA comparing the effect of inorganics on conductivity for the frozen portion of progressive freeze concentration of NAs solutions containing inorganics.

Conductivity Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Presence Inorganics	2	11.405	5.702	1535	2.00E-16
Residuals	49	0.182	0.004		

Table 0-228: Tukey HSD test for factor inorganics for Table 0-227.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
No Inorganics	Control	-	-	-	0.0000000

		0.9884554	1.0392767	0.9376341	
Inorganics	Control	-0.8851058	-0.9359271	-0.8342845	0.0000000
Inorganics	No Inorganics	0.1033496	0.0432171	0.1634821	0.0003778

Table 0-229: ANOVA comparing the effect of inorganics on pH for the frozen portion of progressive freeze concentration of NAs solutions containing inorganics.

pH Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Presence Inorganics	2	1.73	0.8648	467.8	2.00E-16
Residuals	53	0.098	0.0018		

Table 0-230: Tukey HSD test for factor inorganics for Table 0-229.

Comparison of Factor: Freezing Method					
Comparison of Factor: Freezing Method with Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
No Inorganics	Control	-0.3919909	-0.4277611	-0.3562206	0.0000000
Inorganics	Control	-0.3135423	-0.3460323	-0.2810524	0.0000000
Inorganics	No Inorganics	0.0784485	0.0388581	0.1180390	0.0000425

Table 0-231: ANOVA comparing the effect of inorganic concentration on COD for the liquid portion of progressive freeze concentration of NAs solutions containing inorganics.

COD Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	5	98	19.6	397.7	2.00E-16
Residuals	34	1.68	0.049		

Table 0-232: Tukey HSD test for factor inorganic concentration for Table 0-231.

Comparison of Factor: Concentration					
Comparison of Factor: Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Cl 500mg/L	Cl 40mg/L	-1.6863369	-2.1601369	-1.2125369	0.0000000
Cl & Sulfate 40mg/L	Cl 40mg/L	-0.3695082	-0.8433081	0.1042918	0.2013191
Cl & Sulfate 500mg/L	Cl 40mg/L	-2.4634660	-2.9372660	-1.9896661	0.0000000
Control	Cl 40mg/L	-3.708792	-4.0757959	-3.341788	0.0000000
None	Cl 40mg/L	-0.029135	-0.5029354	0.4446646	0.9999664
Cl & Sulfate 40mg/L	Cl 500mg/L	1.3168287	0.8430288	1.7906287	0.0000000
Cl & Sulfate 500mg/L		-0.777129	-1.2509291	-0.303329	0.0002689
Control	Cl 500mg/L	-2.022455	-2.389459	-1.655451	0.0000000
None	Cl 500mg/L	1.6572015	1.1834015	2.1310015	0.0000000
Cl & Sulfate 500mg/L	Cl & Sulfate 40mg/L	-2.093958	-2.5677578	-1.620158	0.0000000
Control	Cl & Sulfate 40mg/L	-3.339284	-3.7062878	-2.97228	0.0000000
None	Cl & Sulfate 40mg/L	0.3403728	-0.1334272	0.8141727	0.2785760
Control	Cl & Sulfate 500mg/L	-1.245326	-1.6123299	-0.878322	0.0000000
None	Cl & Sulfate 500mg/L	2.4343306	1.9605307	2.9081306	0.0000000
None	Control	3.6796567	3.3126528	4.0466605	0.0000000

Table 0-233: ANOVA comparing the effect of inorganic concentration on TS for the liquid portion of progressive freeze concentration of NAs solutions containing inorganics.

TS Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	5	108.46	21.69	309.6	2.00E-16
Residuals	34	2.38	0.07		

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Comparison of Factor: Concentration					
Comparison of Factor: Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Cl 500mg/L	Cl 40mg/L	-1.3460765	-1.9110350	-0.7811179	0.0000004
Cl & Sulfate 40mg/L	Cl 40mg/L	-0.1666780	-0.7316366	0.3982806	0.9462140
Cl & Sulfate 500mg/L	Cl 40mg/L	-2.1204066	-2.6853652	-1.5554481	0.0000000
Control	Cl 40mg/L	-3.844953	-4.282568	-3.407338	0.0000000
None	Cl 40mg/L	-0.203113	-0.7680718	0.3618453	0.8838962
Cl & Sulfate 40mg/L	Cl 500mg/L	1.1793985	0.6144399	1.7443571	0.0000050
Cl & Sulfate 500mg/L		-0.77433	-1.3392887	-0.209372	0.0027677
Control	Cl 500mg/L	-2.498877	-2.9364915	-2.061262	0.0000000
None	Cl 500mg/L	1.1429632	0.5780046	1.7079218	0.0000089
Cl & Sulfate 500mg/L	Cl & Sulfate 40mg/L	-1.953729	-2.5186872	-1.38877	0.0000000
Control	Cl & Sulfate 40mg/L	-0.678275	-4.11589	-3.24066	0.0000000
None	Cl & Sulfate 40mg/L	-0.036435	-0.6013939	0.5285233	0.9999575
Control	Cl & Sulfate 500mg/L	-1.724546	-2.1621614	-1.286931	0.0000000
None	Cl & Sulfate 500mg/L	1.9172934	1.3523348	2.4822519	0.0000000
None	Control	3.6418397	3.2042247	4.0794547	0.0000000

Conductivity Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	3	49.52	16.507	294.9	2.00E-16
Residuals	20	1.12	0.056		

Table 0-236: Tukey HSD test for factor inorganic concentration for Table 0-235.

Comparison of Factor: Concentration					
Comparison of Factor: Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Cl & Sulfate 40mg/L	Cl 40mg/L	-0.4744723	-0.9426844	-0.0062602	0.0463078
Control	Cl 40mg/L	-3.2522622	-3.6345557	-2.8699686	0.0000000
None	Cl 40mg/L	-0.7692574	-1.2374695	-0.3010453	0.0009234
Control	Cl & Sulfate 40mg/L	-2.77779	-3.1600834	-2.395496	0.0000000
None	Cl & Sulfate 40mg/L	-0.294785	-0.7629972	0.173427	0.3197969
None	Control	2.4830047	2.1007112	2.8652983	0.0000000

Table 0-237: ANOVA comparing the effect of inorganic concentration on pH for the liquid portion of progressive freeze concentration of NAs solutions containing inorganics.

pH Unfrozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	5	0.10315	0.020629	52.54	5.00E-15
Residuals	34	0.01335	0.000393		

Table 0-238: Tukey HSD test for factor inorganic concentration for Table 0-237.

Comparison of Factor: Concentration					
Comparison of Factor: Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Cl 500mg/L	Cl 40mg/L	-0.0396544	-0.0819447	0.0026358	0.0765935
Cl & Sulfate 40mg/L	Cl 40mg/L	-0.0335046	-0.0757948	0.0087856	0.1878708
Cl & Sulfate	Cl 40mg/L	-	-0.1917003	-0.1071198	0.0000000

500mg/L		0.1494100			
Control	Cl 40mg/L	0.0210854	-0.0116725	0.0538432	0.3950021
None	Cl 40mg/L	-0.004183	-0.0464733	0.0381072	0.9996510
Cl & Sulfate 40mg/L	Cl 500mg/L	0.0061498	-0.0361404	0.0484401	0.9977536
Cl & Sulfate 500mg/L		-0.109756	-0.1520459	-0.067465	0.0000001
Control	Cl 500mg/L	0.0607398	0.02798189	0.0934977	0.0000401
None	Cl 500mg/L	0.0354714	-0.0068189	0.0777616	0.1433368
Cl & Sulfate 500mg/L	Cl & Sulfate 40mg/L	-0.115905	-0.1581957	-0.073615	0.0000000
Control	Cl & Sulfate 40mg/L	0.0545899	0.02183207	0.0873478	0.0002132
None	Cl & Sulfate 40mg/L	0.0293215	-0.0129687	0.0726118	0.3149902
Control	Cl & Sulfate 500mg/L	0.1704954	0.13773751	0.2032533	0.0000000
None	Cl & Sulfate 500mg/L	0.145227	0.10293672	0.1875172	0.0000000
None	Control	-0.025268	-0.0580263	0.0074895	0.2109769

Table 0-239: ANOVA comparing the effect of inorganic concentration on COD for the solid portion of progressive freeze concentration of NAs solutions containing inorganics.

COD Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	5	7.093	1.4187	1603	2.00E-16
Residuals	34	0.03	0.0009		

Table 0-240: Tukey HSD test for factor inorganic concentration for Table 0-239.

Comparison of Factor: Concentration					
Comparison of Factor: Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Cl 500mg/L	Cl 40mg/L	0.4011495	0.3376564	0.4646427	0.0000000
Cl & Sulfate 40mg/L	Cl 40mg/L	0.0707073	0.0072141	0.1342005	0.0217989

Cl & Sulfate 500mg/L	Cl 40mg/L	0.6367265	0.5732333	0.7002196	0.0000000
Control	Cl 40mg/L	0.9908821	0.94170048	1.0400637	0.0000000
None	Cl 40mg/L	0.026289	-0.0372042	0.0897821	0.8092762
Cl & Sulfate 40mg/L	Cl 500mg/L	-0.330442	-0.3939354	-0.266949	0.0000000
Cl & Sulfate 500mg/L		0.2355769	0.17208376	0.2990701	0.0000000
Control	Cl 500mg/L	0.5897325	0.54055094	0.6389141	0.0000000
None	Cl 500mg/L	-0.374861	-0.4383537	-0.311367	0.0000000
Cl & Sulfate 500mg/L	Cl & Sulfate 40mg/L	0.5660192	0.50252601	0.6295123	0.0000000
Control	Cl & Sulfate 40mg/L	0.9201748	0.87099319	0.9693564	0.0000000
None	Cl & Sulfate 40mg/L	-0.044418	-0.1079115	0.0107485	0.3056648
Control	Cl & Sulfate 500mg/L	0.3541556	0.30497402	0.4033372	0.0000000
None	Cl & Sulfate 500mg/L	-0.610437	-0.6739306	-0.546944	0.0000000
None	Control	-0.964593	-0.1013775	-0.915412	0.0000000

Table 0-241: ANOVA comparing the effect of inorganic concentration on TS for the solid portion of progressive freeze concentration of NAs solutions containing inorganics.

TS Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	5	7.318	1.4636	1149	2.00E-16
Residuals	34	0.043	0.0013		

Table 0-242: Tukey HSD test for factor inorganic concentration for Table 0-241.

Comparison of Factor: Concentration				
Comparison of Factor: Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Cl 500mg/L	Cl 40mg/L	0.2886663	0.2124793	0.3648534	0.0000000
Cl & Sulfate	Cl 40mg/L	0.0647180	-0.0114690	0.1409051	0.1343757

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40mg/L				
Cl & Sulfate 500mg/L	Cl 40mg/L	0.5341631	0.4579760	0.6103501	0.0000000
Control	Cl 40mg/L	0.9964225	0.93740827	1.0554367	0.0000000
None	Cl 40mg/L	0.0554732	-0.0207139	0.1316602	0.2651944
Cl & Sulfate 40mg/L	Cl 500mg/L	-0.223948	-0.3001353	-0.147761	0.0000000
Cl & Sulfate 500mg/L		0.2454967	0.1693097	0.3216838	0.0000000
Control	Cl 500mg/L	0.7077562	0.64874193	0.7667704	0.0000000
None	Cl 500mg/L	-0.233193	-0.3093802	-0.157006	0.0000000
Cl & Sulfate 500mg/L	Cl & Sulfate 40mg/L	0.469445	0.39325801	0.5456321	0.0000000
Control	Cl & Sulfate 40mg/L	0.9317045	0.87269025	0.9907187	0.0000000
None	Cl & Sulfate 40mg/L	-0.009245	-0.0854319	0.0669422	0.9990573
Control	Cl & Sulfate 500mg/L	0.4622594	0.4032452	0.5212736	0.0000000
None	Cl & Sulfate 500mg/L	-0.47869	-0.5548769	-0.402503	0.0000000
None	Control	-0.940949	-0.9999636	-0.881935	0.0000000

Table 0-243: ANOVA comparing the effect of inorganic concentration on conductivity for the solid portion of progressive freeze concentration of NAs solutions containing inorganics.

Conductivity Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	3	6.797	1.6993	2724	2.00E-16
Residuals	20	0.017	0.0006		

Table 0-244: Tukey HSD test for factor inorganic concentration for Table 0-243.

Comparison of Factor: Concentration				
Comparison of Factor: Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Cl 500mg/L	Cl 40mg/L	0.2630257	0.2114418	0.3146096	0.0000000

Cl & Sulfate 40mg/L	Cl 40mg/L	0.0322426	-0.0193413	0.0838265	0.3803216
Control	Cl 40mg/L	0.9835286	0.9427479	1.0243092	0.0000000
None	Cl 40mg/L	0.0040495	-0.0475344	0.0556334	0.9993461
Cl & Sulfate 40mg/L	Cl 500mg/L	-0.230783	-0.282367	-0.179199	0.0000000
Control	Cl 500mg/L	0.7205029	0.67972224	0.7612835	0.0000000
None	Cl 500mg/L	-0.258976	-0.3105601	-0.207392	0.0000000
Control	Cl & Sulfate 40mg/L	0.9512859	0.9105053	0.9920666	0.0000000
None	Cl & Sulfate 40mg/L	-0.028193	-0.079777	0.0233907	0.5123468
None	Control	-0.979479	-1.0202597	-0.938698	0.0000000

Table 0-245: ANOVA comparing the effect of inorganic concentration on pH for the solid portion of progressive freeze concentration of NAs solutions containing inorganics.

pH Frozen Portion					
Source of Variation	DF	Sum Sq	Mean Sq	F	p Value
Concentration	5	1.153	0.23055	654.4	2.00E-16
Residuals	34	0.012	0.00035		

Table 0-246: Tukey HSD test for factor inorganic concentration for Table 0-245.

Comparison of Factor: Concentration					
Comparison of Factor: Inorganics		Mean Diff	Lower Bound	Upper Bound	P Value
Cl 500mg/L	Cl 40mg/L	0.1325658	0.0925062	0.1726254	0.0000000
Cl & Sulfate 40mg/L	Cl 40mg/L	0.0030067	-0.0370529	0.0430663	0.9999101
Cl & Sulfate 500mg/L	Cl 40mg/L	0.1503749	0.1103153	0.1904345	0.0000000
Control	Cl 40mg/L	0.3850292	0.35399917	0.4160592	0.0000000
None	Cl 40mg/L	0.0100499	-0.0300097	0.0501095	0.9727840
Cl & Sulfate 40mg/L	Cl 500mg/L	-0.129559	-0.1696186	-0.089499	0.0000000
Cl & Sulfate	Cl 500mg/L	0.0178091	-0.0222505	0.0578687	0.7600160

500mg/L					
Control	Cl 500mg/L	0.2524634	0.22143339	0.2834934	0.0000000
None	Cl 500mg/L	-0.122516	-0.1625755	-0.082456	0.0000000
Cl & Sulfate 500mg/L	Cl & Sulfate 40mg/L	0.1473682	0.10730859	0.1874278	0.0000000
Control	Cl & Sulfate 40mg/L	0.3820225	0.35099243	0.4130525	0.0000000
None	Cl & Sulfate 40mg/L	0.0070432	-0.0330164	0.0471027	0.9945082
Control	Cl & Sulfate 500mg/L	0.2346543	0.20362426	0.2656843	0.0000000
None	Cl & Sulfate 500mg/L	-0.140325	-0.1803846	-0.100265	0.0000000
None	Control	-0.374979	-0.4060093	-0.343949	0.0000000