Effect of water chemistry on Cold Lake and Athabasca bitumen

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ABSTRACT

Unconventional oil reserves are taking an increasing importance globally due to the decrease of conventional sources of hydrocarbons. Oil sands industry plays an important role in the production of unconventional bitumen, through proven technologies such as surface mining and in situ extraction processes.

Water use is an important part of both the surface mining and in situ production methods. The separation of the bitumen from the sand is assisted using water at different temperatures (75°C for surface mining and 200°C for in situ process). Therefore, it is expected that the water chemistry influences the bitumen separation during these processes.

The objective of this study was to investigate the effect of pH, salt concentration and equilibrium separation stages on some bitumen properties, by washing the bitumen while manipulating these variables. Also, it was of interest to determine and quantify the removed ions through this washing. A first phase of experimental work was performed by an one-step washing at room temperature Cold Lake bitumen with deionized water and 0.03M HCl, while increasing the concentration of dissolved NaCl from 0 to 1000 mg/L in both the deionized water and the acid solution. Three phases were obtained: aqueous, emulsion and organic (recovered bitumen) phase. Analyses of the recovered aqueous phase included: cation determination by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES), anion determination by High Performance Liquid Chromatography (HPLC), pH and conductivity. Viscosity and water content of the raw and the recovered bitumen was measured, and the remaining solvent content of the recovered bitumen was determined by Fourier Transform Infrared Spectroscopy and the viscosity was corrected for residual solvent content. The emulsion phase was not analyzed.

It was found that the increase of salt concentration in neutral aqueous solutions increased the viscosity of the bitumen after being washed, while the opposite effect was observed when washing the bitumen with acid solutions, where the increase of salt concentration led to the decrease of the viscosity. On the other hand, the one-step washing of Cold Lake bitumen resulted in the removal of mainly Cl^- (over 11000 µg/g bitumen vs 7000 µg/g bitumen initially added) and cations of Na (around 503 µg/g bitumen vs 90 µg/g bitumen initially added). Lesser quantities of HPO_4^{2-} (up to 40 µg/g bitumen approximately) and CO_3^{2-} (over 100 µg/g bitumen) were quantified. The removal of CO_3^{2-} was favored in the bitumen washing with 0.03 M HCl, while the higher removal of HPO_4^{2-} was obtained from the bitumen washing with deionized water. The increase of NaCl concentration decreased the removal of these anions.

A second phase of the experimental work consisted of the washing of Cold Lake bitumen. A four-step washing procedure at 75°C was developed, by removing the free water after each washing step and adding fresh water for the subsequent step. Two phases were obtained: aqueous phase and organic emulsion. The same analyses of the one-step washing procedure were performed on the aqueous phase samples. In the organic emulsion the cation content, asphaltenes, water and remaining solvent content were determined, as well as simulated distillation was performed.

Removal of ions of Cl (996 ± 227 µg/g bitumen) and Na (415 ± 65 µg/g bitumen) resulted from the four-step washing of Cold Lake bitumen. Cations of Ca, K were also removed. CO_3^{2-} and cations of elements such Ca and K were detected in lower concentrations. The ion removal could be explained to come from the connate water; however, it was found that the experimental concentrations obtained after each washing step were lower than those calculated from dilution of the connate water, indicating that the salts were retained in some way by the organic phase.

A third phase of experimental work was performed, with the goal to determine if the use of a low-water content bitumen could lead to differences in the ion removal, and if the removed ions could be linked to the bitumen. Washing of Athabasca bitumen under the same conditions of the second phase of experimental work was developed. The removal of ions after the washing of Athabasca bitumen was linked to the bitumen, with a higher removal of SO_4^{2-} (up to 62 µg/g bitumen) and CO_3^{2-} (up to 63 µg/g bitumen). Cations of elements such as Al and Fe were also removed in lower concentrations. Ions of Na and Cl were removed in lower concentrations compared to the quantities removed by washing the Cold Lake bitumen (16 ± 1 µg/g bitumen for cations of Na, and 4 ± 1 µg/g bitumen for Cl^-).

DEDICATION

To God, for always guide my steps, for giving me hope and show me the way in the most difficult moments.

To my husband Alejandro, for being my unconditional support, for all his love and understanding during these years.

To my parents, for always being present despite the distance. Thanks mom, for all your prayers, for giving me the courage and the strength to believe in myself.

To my brothers, specially to Andres, for holding my hand my entire life and making me know that you always will be there for me.

To my son, Alejandro, you are my big motivation. Specially dedicated to you.

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1. INTRODUCTION

1.1 Introduction

Oil sands are defined as naturally occurring bitumen impregnated sands. These heavy oil and bitumen resources, will become the principal source of crude oils with the decrease of light crude oil sources (Strausz and Lown, 2003). Alberta's oil sands has the third largest oil reserves in the world, after Venezuela and Saudi Arabia, as of 2016, it has proven reserves of 174 billion barrels (Canada's Oil and Natural Gas Producers, 2017). The majority of the oil sands deposits in Canada are located in Alberta, specifically in three main deposits: Peace River, Cold Lake and Athabasca (Woynillowicz et al., 2005).

While conventional sources of hydrocarbons are becoming less frequent and existing reserves are being produced at an ever-increasing rate, unconventional oil reserves are becoming more important to the global oil market. Furthermore, declines in the reserves of lighter crude oil have reduced the average quality of global conventional crude oil. Changes to the average viscosity of today's global crude oil is influencing refineries to adapt to heavier crudes, creating an environment that ensures a market for larger amounts of heavy and extra heavy crude oil. Many energy-producing companies are predicting a profitable future through investment in these unconventional reserves. Crude bitumen, a type of extra heavy oil, is a viscous mixture of hydrocarbons that in its natural state does not flow very easily (Rahnama et al., 2008).

Oil sands extraction is mainly achieved by two methods: in situ, or surface mining. Both extraction methods are extensively used, being 53% of production obtained by in situ technology, and 47% by surface mining (Canada's Oil and Natural Gas Producers, 2017).

Both surface mining and in situ processes use considerable amounts of water. Surface mining processes use water and organic solvents to dilute the oil sands and make them transportable, while in situ processes use steam at relatively high pressures to help the mixture of bitumen/water to come out from the well (Schumacher and Booz, 1982; Alberta Chamber of Resources, 2004).

It is clear that the oil sands production involves water as an important part of the process. Therefore, it is expected that the water chemistry plays a role in the bitumen separation and recovery. Previous work about the effect of the quality of water has been developed, some findings are:

- Bitumen liberation and bitumen-bubble attachment is negatively affected by the presence of salts, more so at higher pH of processing water. Furthermore, increasing pH by adding caustics can lead to an increased concentration of carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-) as a result of increased dissolution of CO_2 in the process water. Carbonate ions are known to precipitate the divalent cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in the process water. The oil sands industry is concerned that increasing the salinity of recycle process water will potentially affect the recovery of bitumen from the mined oil sands ores. (Chen et al., 2017).

- While high pH facilitated bitumen liberation, the presence of excessive salts (over 16000 ppm sodium) was found to be detrimental to bitumen liberation, in particular at high pH (Srinivasa et al., 2012).

- Washing of bitumen with acid solutions was found to decrease the viscosity of the bitumen. However, it was observed that washing of bitumen with deionized water was also able to decrease the bitumen viscosity. This decrease in viscosity could not be attributed only to an asphaltenes content reduction, and the water retention by some of the samples complicated the interpretation of the results (Gonzalez, 2015).

This work studied the impact of water chemistry on some bitumen properties, as well as the removal of ions by washing the bitumen with deionized water and manipulating the pH and concentration of dissolved salts on aqueous solutions.

1.2 Objectives and scope of work

1.2.1 Objective

Investigate the effect of pH, temperature and salt concentration on some bitumen properties, by washing the bitumen while manipulating these variables. Also, it was of interest to determine and quantify the removed ions through this washing.

1.2.2 Scope of work

Literature of oil sands extraction processes and the role of water in these processes was reviewed (**Chapter 2)**. Additionally, understanding of the water chemistry, acid-base interaction, effect of ion content on solubility and the formation of water-in-oil emulsions after the bitumen is in contact with water as part of the extraction process was also part of the literature review. Finally, a look on the inorganic compounds in the bitumen, the methods to properly determine and quantify these compounds, and an approach to quantify remaining solvent in previous diluted bitumen samples was presented. All the reviewed concepts and procedures, were focused to facilitate the execution of the experimental work and the interpretation of the results.

The experimental work was divided into three main sections: In **Chapter 3**, the observations posed by Gonzalez (2015) about the decrease of viscosity when the bitumen was washed with acid solutions (and even with deionized water) were taken as base for this section. Cold Lake bitumen was washed with different neutral and acid solutions, manipulating the concentration of dissolved salts. The objective was to investigate if the increase of dissolved salts could affect the bitumen viscosity in both cases (acid and neutral solutions). Viscosity measurements of the recovered bitumen were made, and prediction of viscosity by discounting the remaining solvent content was done using three different methods (Mehrotra, 1990; Riazi, 2005; Zachariah and de Klerk, 2017).

In **Chapter 4**, a four-step washing of Cold Lake bitumen was performed with deionized water. Typical temperature for surface mining process was used for this section. It was of interest to elucidate if the ion removal observed in **Chapter 3** could change by increasing the washing steps and the temperature. Also, it was intended to clarify if the removed ions were linked to the connate water or the bitumen.

In **Chapter 5**, washing of Athabasca bitumen under the same conditions of **Chapter 4** was developed. This experimental work aimed to evaluate if the removal of ions from Athabasca bitumen was comparable to the obtained in **Chapter 4** (Cold Lake bitumen). Also, the use of a low-water content bitumen allowed to further investigate if some ion removal was linked to the bitumen.

Final conclusions and recommendations for future work are presented in **Chapter 6**.

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2. LITERATURE REVIEW

2.1 Introduction

This chapter contains three main sections, all of them addressed to provide a background needed to pursue this study. The first section aims to give a general description of the oil sands, its production and bitumen recovery methods and the role that water plays during both processes, how the quality of water is affected by solids and bitumen by surface mining and *in situ* technologies, and how bitumen is affected by water and solids due to the same technologies. The second section is focused on water chemistry, the main ion interactions and equilibrium present in natural water. The third section is addressed to cover the inorganic content on bitumen and the best practices to determine these constituents.

2.2 Oil Sands

Oil Sands are defined as naturally occurring bitumen-impregnated sands. Other given designations are tar sands or bituminous sands, despite of the technical difference in the definition of tars as "dark brown-black viscous liquid product of the destructive distillation of petroleum, coal, and another carbonaceous materials" (Strausz and Lown, 2003)

The nature and properties of the oil sands determine the optimum process to separate the bitumen from the mineral matter. For example, most Alberta oil sands, unlike most American oil sands, break up easily after being in contact with hot water (called water wetting). It was found that the presence of a water film covering each sand grain allows the bitumen to be easily separated from the sand (Strausz and Lown, 2003).

2.2.1 Oil Sands Production Methods and Bitumen recovery

The oil sands extraction process can be achieved by two distinctive methods: *in situ* (sub-surface recovery), or open-pit mining (surface recovery). The bitumen extracted using the surface mining method is close to the surface and only counts for 20% of the total Canadian oil sands reserves. The other 80% is extracted using different *in situ* techniques: steam-assisted gravity drainage (SAGD), cyclic steam stimulation (CSS), vapor recovery extraction (VAPEX). (Poveda and Lipsett, 2014). By 2012, 60% of bitumen production is done through open-pit surface mining (Banerjee, 2012); however, this trend has changed and by 2016 *in situ* technology took 53% of bitumen production, and surface mining is accounted for the remaining 47% (Canada’s Oil and Natural Gas Producers, 2017).

Oil sands operations use water to separate oil from sand in the mining operations and to make steam for *in-situ* extraction. Smaller volumes are used in upgraders. In 2002, the Oil & Gas Industry was licensed to draw 4.1% of surface water, and 28% of groundwater of the 438 million cubic meters per year of fresh water allocated to this industry (Alberta Chamber of Resources, 2004).

Unconventional oil and gas extraction and production from any of the different sources raises a variety of concerns. Social, economic, health, and especially environmental impacts are expected; however, finding a balance among the three pillars of sustainability offers a feasible sustainable path. The primary affected pillar of sustainability noticed by stakeholders refers to environmental impacts; in unconventional oil and gas extraction and production, those impacts of major concerns include waste management, use of chemicals and energy, and air pollution. Major concerns arise due to the large amounts of mildly hazardous tailings and waste in the mining process during oil extraction and production. In addition to the concerns in light oil production, heavy oil requires the use of heat to pump the product out of the ground (Poveda and Lipsett, 2014).

It was mentioned that currently there are two main oil sands production and recovery methods, and the general characteristics of each are described in **Section 2.2.1.1** and **2.2.1.2**.

2.2.1.1 Surface mining

Surface mining is used generally for shallow deposits or outcrops, because the removal of overburden usually becomes uneconomic for depths of greater than 75 meters (Schumacher and Booz, 1982). In **Figure 2.1** a general description of oil sands mining process is shown.

Similar to coal mining operations, the surface mining processes, uses large electric and hydraulic shovels with capacities up to 45 m^3 to scoop the oil sand into trucks with capacities up to 400 tons. Heavy haulers transport the mined oil sands material to then unload it into crushers and sizers where the material (i.e., large clumps of earth) is broken down. The mixture is diluted using water and is transported to a plant in which the bitumen is separated from the other components, e.g. clay, sand and water, which will be described in more detail in subsequent paragraphs. The bitumen continues its course for upgrading to become synthetic crude oil (SCO), or dilution to become diluted bitumen (Dilbit).

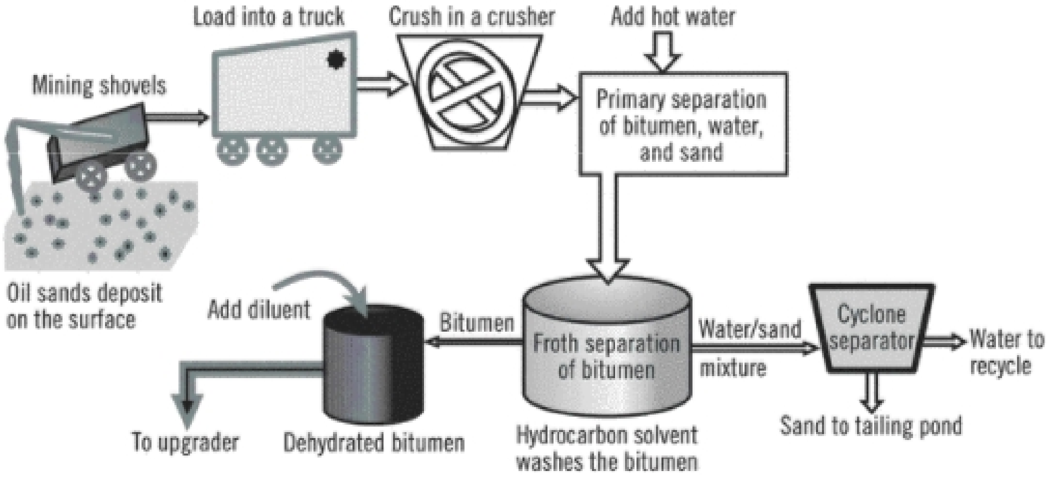

Figure 2.1 Generalized scheme of a commercial oil sands mining process in northern Alberta.

Reprinted from Banerjee, D. K. *Oil Sands, Heavy Oil and Bitumen: From Recovery to Refinery*, 2012. Copyright © 2012 PennWell Corp.

The fact that the mineral matter in the oil sands are wetted by water and not by bitumen, leads to the ability to use water in extraction processes for surface-mined oil sands. Hot water extraction, based on K.A. Clark's method, is the most common extraction process to recover bitumen from surface-mined oil sands (Schumacher and Booz, 1982). Process begins with crushing of the excavated ore, which is then conditioned with warm to hot water, steam, and aided with caustic or sodium citrate. The resulting mixture is then transported through a pipeline to an extraction plant (Oil Sands Research and Information Network, 2012).

The operating slurry temperature ranges from about 75°C in tumblers to as low as 35°C in Syncrude's Aurora hydrotransport based operation. Typically, a 40–55°C slurry temperature is used in the current operations. A typical overall bitumen recovery in commercial operations is about 88–95%. The recovered bitumen in the form of froth, which normally contains around 60% bitumen, 30% water and 10% solids (Masliyah et al., 2008).

Bitumen is separated, dehydrated and deaerated, and recovered from the coarse fraction as a floating froth through gravity. Dirty water and sand are directed to a cyclone separator. The water is cleaned and recycled. Wet sand is sent to tailing ponds, where larger particles separate by themselves through gravity settling; however, fine particles remain in suspension for a longer period of time and create challenges for land reclamation (Banerjee, 2012).

2.2.1.2 *In situ* (sub-surface) extraction

Subsurface recovery of heavy bitumen from oil sands through *in situ* technologies, consists in the injection of steam at relatively high pressures to increase the reservoir temperature and improve bitumen fluidity. By doing so the bitumen can be produced as liquid product from an oil well analogous to production of conventional crude oil.

One mature process for deep, thicker reserves, such as in Cold Lake and Peace River, involves cycling at single vertical injector/producer wells. An alternative incorporates steam drive between injectors and producers. While these processes originally depended on vertical well, combinations of vertical and horizontal wells are now used (Alberta Chamber of Resources, 2004).

Even when there are several in situ technologies as it was mentioned before, SAGD is considered the fastest growing technology in Alberta. In the SAGD process, two L-shaped wells (upper injection well and lower production well) are placed one above the other. Steam is pumped through the injection well (200ºC, saturation pressure over 3,000 kPa), while hydrocarbons are produced from the parallel, horizontal production well. Both wells are located close to the bottom of the hydrocarbon deposit, about 300-600 m in depth (**Figure 2.2**).

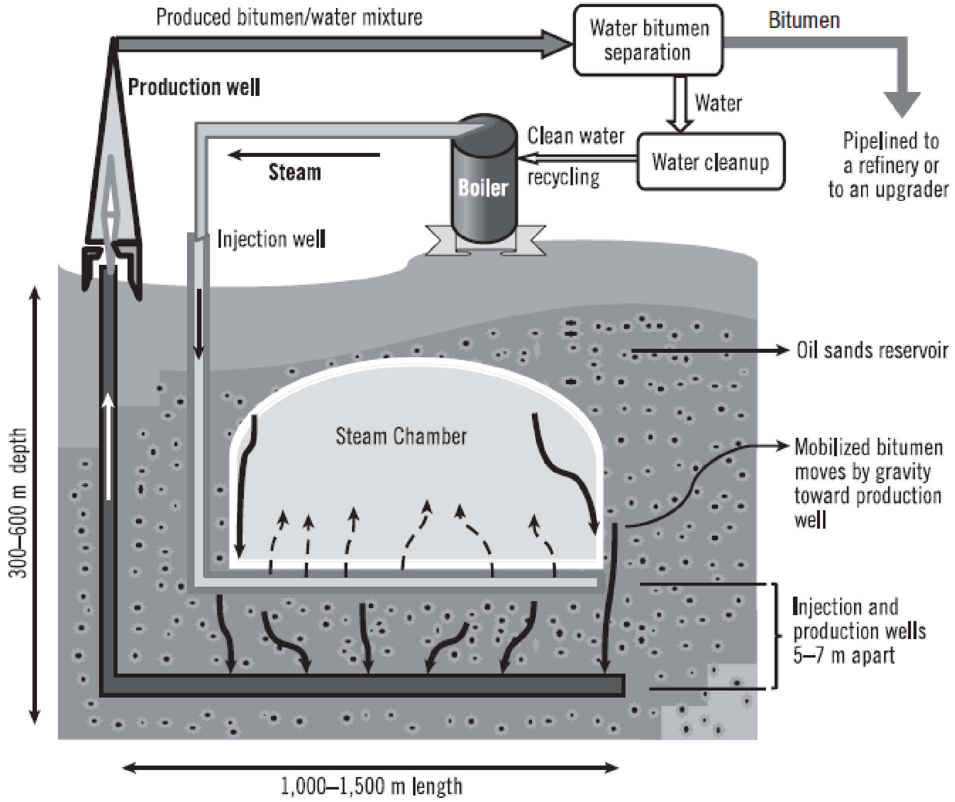

Figure 2.2 Cross-sectional view of the SAGD concept.

Reprinted from Banerjee, D. K. *Oil Sands, Heavy Oil and Bitumen: From Recovery to Refinery*, 2012. Copyright © 2012 PennWell Corp.

A steam chamber is created through around and above the injection well, helping to improve fluidity of the hydrocarbons, that after being mobilized with the condensed water, drain to bottom and are collected in the production well. The rate of steam injection and the rate of hydrocarbon production may be controlled by the growth of the steam chamber (Banerjee, 2012).

2.2.2 Water usage in Oil Sands

In surface mining, for every unit volume of bitumen recovered, there are 7 to 8 volume units of wet sand and mature fine tailings that need to be handled, and 10 volume units of water (recycle and make up) that are pumped around the system (Oil Sands Research and Information Network, 2012). Alkaline hot water extraction produces large volumes of surface-mining water that must be stored in onsite tailings ponds to prevent environmental pollution. On the other hand, in SAGD, the process water recycling efficiency for reuse in steam generation is higher. Produced water, recovered with formation water, is deoiled and then treated for use as boiler feedwater through hot lime softening, filtration, and weak acid cation exchange. Overall, more than 90% of the water injected as steam is recycled at a SAGD plant (Kawaguchi et al., 2012).

Previous work about the influence of salts on bitumen recovery from oil sands has been developed (Clark and Pasternack, 1932; Zhao, 2009), where it has been found that recycling of water has negative effects on bitumen recovery due to soluble salts. The soluble salts are carried from the bituminous beds from the overburden by ground water (sodium, calcium, magnesium and ferrous sulphates). Also, it has been found that separation of the oil sands is affected by the acidity; most of the sand in the deposit is somewhat acid, probably due to hydrolysis of ferrous sulfate. The separation is improved once the acidity is neutralized, when this is done, a good recovery of bitumen, comparatively free from mineral matter, follows on washing. On the other hand, some salts seemed to affect adversely the separation of the bitumen from the sand; through the addition of different sodium, magnesium and calcium compounds (chlorides, sulphates and oxides) to bituminous sands, it was found that the mineral content in the recovered bitumen increased and, in some cases, it affected the yield and efficiency of bitumen separation. Other salts, such as calcium and sodium carbonates, were not found to be detrimental in small quantities on the bitumen separation.

Produced water in the SAGD method contains various contaminants. By repeated recycling, contaminants such as dissolved organic compounds (DOCs), which include significant amounts of organic acids and organic acid salts, accumulate in the process water, severely interfering with subsequent reuse due to scaling and corrosion of pipelines and heat exchangers (Jennings et al., 2007; Kawaguchi et al., 2012)

2.2.3 Oil Sands Process Affected Water (OSPW)

Oil sands Process Affected Water (OSPW) is defined as any water that has been in contact with oil sands. Consequently, there is a high variability in the chemical composition of different OSPW. Process water includes many different water types including fresh OSPW retained in active settling basins or tailing ponds, consolidated tailings (CT), released water after treatment or fine tailings with chemical/physical separation techniques, seepage or dyke drainage water collected from surrounding the active settling basins, and aged or treated OSPW from wetlands and reclamation ponds (Li et al., 2017).

Tailings composed of water, salts, organics, minerals, and bitumen are pumped from separation vessels and froth treatment facilities to a series of settling basins and tailing ponds. The composition of these tailings varies with ore quality, source, extraction processes, and age, but generally contain ~70 to 80 % w/w water, ~20 to 30 % w/w mineral matter and ~1 to 3 % w/w organic material. Despite variability in the origin and processes involved in generating OSPW, OSPW always contains several major classes of contaminants. The contaminants include naphthenic acids (NAs), polycyclic aromatic hydrocarbons (PAHs), BTEX (benzene, toluene, ethyl benzene, and xylene), phenols, dissolved trace metals (Al, As, Cd, Cr, Cu, Fe, Pb, Mo, Ti, V, Zn) and abundant ions (Ca^{+2}, Mg^{+2}, HCO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-}). The concentration of these contaminants depends on the composition of the oil sands ore, the degree of water recycling, and the type of bitumen cleaning process used (either paraffinic or naphtha based).

2.2.4 Bitumen in contact with water: Emulsions

The contact of bitumen and water is part of the oil sands production and recovery methods. During the recovery process, the removal of solids and water is performed in both surface and *in situ* technologies. However, after the separation, around 2% of water and up to 0.8% solids remain in the bitumen. These emulsions are highly stable, and usually formed by the mechanical agitation from pumps or other transportation and handling devices (Masliyah et al., 2011).

Several contributors of the high stability of water in oil emulsions has been postulated. It is believed that water is involved in hydrogen bonding with asphaltenes at the water/oil interface, enhancing the stability of water-in-oil emulsions. On the other hand, the remarkable stability of water-in-diluted bitumen emulsions is due to the presence of a complex adsorbed layer at the surfaces of the dispersed droplets. Except for its role as a steric barrier, little is known about the properties of this interfacial layer (Czarnecki, 2001).

The wettability of the solids present in the emulsion has been postulated as a contributing factor in the water in oil emulsion stability. Experimental work showed that the presence of hydrophilic solids has a significantly lower potency in forming a water-in-oil emulsions compared to a mixture containing hydrophobic solids. Solids that were hydrophilic could be rendered hydrophobic due to adsorption of bitumen/asphalthenes (Gu et al., 2007)

To reduce the water and solid content in the bitumen, paraffinic or naphthenic solvents are added to help the separation by gravity settling, or by cycloning or centrifugation. The emulsified droplets can disperse stably in naphtha-diluted bitumen but flocculate with asphaltenes when paraffinic solvents are used as diluents (Wang, 2011).

2.3 Chemistry of water

2.3.1 Properties of acids and bases

Acids and bases can be classified as Brønsted and/or Lewis acids and bases. A Brønsted acid is defined as a proton donor, and a Brønsted base is a proton acceptor; in this context, a donated proton from an acid must be accepted by a proton acceptor (base). In aqueous solutions, a Brønsted acid donates the proton while the water acts as the base by accepting it. Similarly, a Lewis acid is an electron acceptor, while a Lewis base is an electron donor. (Brezonik and Arnold, 2011).

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad \text{or} \quad HCO_3^- + H^+ \rightarrow H_2CO_3^*$$

Equation 2.1

Some species are both Brønsted acids and Brønsted bases, like bicarbonate. Some metal ions also act as Brønsted acids, for example ferric ion (Fe^{3+}), when added to water, can lead to the release of protons (Brezonik and Arnold, 2011):

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_{3(s)} + 3H^+$$

Equation 2.2

2.3.2 The carbonate system

In water, the three dissolved carbonate species are $H_2CO_3^*$ + HCO_3^- and CO_3^{2-}, and total dissolved carbonate is given by $C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$. Concentrations of $CO_{2(aq)}$ and H_2CO_3 cannot be individually determined via titration, and collectively are expressed as $H_2CO_3^*$ (Benefield et al., 1982; Brezonik and Arnold, 2011):

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

Equation 2.3

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

Equation 2.4

$$[CO_{2(aq)}] + [H_2CO_3] = [H_2CO_3^*]$$

Equation 2.5

Since only a small fraction of the total CO_2 dissolved in water is hydrolyzed to H_2CO_3, it is convenient to sum the concentrations of dissolved CO_2 and H_2CO_3 to define the concentration term $H_2CO_3^*$ according to **Equation 2.5**.

2.3.3 Common ion effect

The concentration of a particular ion in an ionic reaction can be increased by the addition of a compound that produces the ion upon dissociation. The particular ion is thus derived from the compound already in the solution and from the added reagent, then called the common ion. The result is usually that there is higher concentration of this ion in solution than that derived from the original compound alone, and new equilibrium conditions will be produced (Vogel, 1961). These new conditions are related to Le Châtelier’s principle, due to the higher concentration of one of the ions in solution. If one ion pair exceeded its solubility limit, the equilibrium will be shifted toward the precipitation of a solid phase, decreasing its concentration as consequence.

A common ion can cause that other species present in the solution that have the same ion in common, to precipitate if the common ion concentration is increased. When the ion is already present in solution, it lowers the solubility of any solid that contains that ion as part of its structure (Brezonik and Arnold, 2011).

2.3.4 Indifferent Electrolyte Effect

The formation or dissolution of a precipitate always occurs in the presence of indifferent electrolytes. These indifferent ions do not take part in the solubility equilibrium reaction, they do affect the solubility behavior by affecting the activity coefficient of the ions in solution. The activity coefficient approaches unity as the solution approaches infinite dilution because the magnitude of the chemical and physical interactions which occur due to the presence of the ionic species become insignificant. The greater the concentration of indifferent electrolytes, the greater will be the ionic strength of the solutions and the smaller the value of the activity coefficient (Benefield et al., 1982).

2.4 Inorganic compounds in bitumen

Many different metallic elements have been reported in crude petroleum. The metals that are the most prevalent are aluminum, calcium, iron, nickel, silicon, sodium and vanadium. Additionally, it has been found that crude petroleum also contains some chromium, copper, lead, magnesium and manganese, and some traces of boron, cobalt, molybdenum, platinum, potassium, silver, strontium and titanium. Metals may occur in the same crude in more than one form, and inorganic forms may be present in highly dispersed suspensions, or in the colloidal state (McCoy, 1962). The geochemistry of metal complexes in fossil fuels and their precursors is almost entirely that of the metalloporphyrins, mainly related to Ni^{2+} and VO^{2+} porphyrins, although Cu^{2+} porphyrins can also be found (Filby and Branthaver, 1987).

The mineral composition of an oil sand has considerable impact on its quality with respect to processability. Since most of the minerals have low solubilities, the solution chemistry of minerals does not directly affect the hot water process. Nonetheless, the role of the small amount of minerals which can undergo ion exchange reactions liberating Ca^{2+} and Mg^{2+} ions and establish equilibrium with exchangeable ions can be important. Actually, there is a correlation between the loss of recovery with oil sands fines in the aging process, and the decrease in recovery as function of the concentration of soluble divalent ions due to aging in secondary tailings (Strausz and Lown, 2003).

In addition to the metallic elements originally present in crude oil, several others are introduced during the process of removing it from the ground. Emulsified brine and drilling muds are associated with the presence of salts of aluminum, barium, calcium, iron, magnesium and sodium, combined with bicarbonate, chloride, silicate and sulfate. These salts are extractable with hot water if a demulsifier is added (McCoy, 1962)

2.4.1 Preparation of samples and analysis for inorganic compounds in bitumen

In order to analyze the inorganic compounds present in bitumen, they need to be separated from the organic fraction. To achieve this separation, different methods have been developed specifically for each element to be analyzed. The preparation of the sample depends on the type of material to be examined, concentration, volatility, presence or absence of other elements and required accuracy (McCoy, 1962).

Due to these considerations, different approaches have been tested to determine and quantify inorganic compounds in bitumen. In **Table 2.1** the recommended preparation and analysis methods for the most common inorganic elements are summarized.

Table 2.1 Preparation of samples and analysis of inorganic compounds in bitumen

Cation	Sample preparation	Analysis for determination - quantification	Considerations
Aluminum [a]	Soft ashing and wet oxidation, followed by acid oxidation of carbonaceus residue (H_2SO_4 and HNO_3)	Colorimetric, gravimetric	Recommended removal of vanadium, iron and copper with chloroform to avoid interferences. Insolubility of ignited Aluminum oxide is inconvenient if the ash must be dissolved for further treatment
Arsenic [a]	Arsenic is extracted, and arsine is evolved. Molybdate reagent and acidity for color development is added. Absorption with iodine-bicarbonate solution	Colorimetric	Usually low concentrations (around 30 ppb) Forms trioxide which is lost during burning due to its volatility
Boron [a]	Liquid extraction for low concentrations (10-50 ppm). For high concentrations (4-6%), ignition in an oxigen bomb containing a solution of sodium carbonate is applied, followed by acid digestion	Colorimetric (low concentrations) - Alkalimetric (high concentrations)	
Barium [a]	Ignition up to 800°C and acid digestion, filtration and ignition to 900°C	Gravimetric	Coprecipitation of Cr^{3+} and Fe^{3+}, Calcium due to calcium sulphate solubility

[a]: (McCoy, 1962) [b]: (Khuhawar et al., 2012)

Table 2.1 cont Preparation of samples and analysis of inorganic compounds in bitumen

Cation	Sample preparation	Analysis for determination - quantification	Considerations
Calcium [a]	Ignition up to 500°C, followed by acid digestion with HCl. Dilution and addition of ammonium oxalate and methyl red indicator. Titration with NH_4OH, and subsequents washing and precipitation steps.	Gravimetric - Flame photometry	Possible interferences in the presence of sodium and barium
Cadmiun [b]	1. Wet digestion assisted by microwave radiation. 2. Dilution with organic solvent	Inductively Coupled Plasma - Optical and Mass Spectroscopy	
Cobalt [a]	H_2SO_4 pretreatment followed by soft ashing and wet oxidation. Oxidation by ferricyanide is also applied.	Colorimetric, volumetric, electrolytic	
Chromium [a]	Wet oxidation with $H2SO_4$, soft ashing with HNO_3, use of phosphoric and perchloric acid may be needed in some stages of the process.	Colorimetric,	Iron, molybdenum and vanadium can interfer in the colometric determination
Copper [a]	Pretreatment with fuming sulfuric acid, followed by soft ashing, and iodometric procedure (reduction of iodides to iodine by copper ions)	Colorimetric	

[a]: (McCoy, 1962) [b]: (Khuhawar et al., 2012)

Table 2.1 cont Preparation of samples and analysis of inorganic compounds in bitumen

Cation	Sample preparation	Analysis for determination - quantification	Considerations
Iron [a]	Pretreatment with fuming sulfuric acid, followed by soft ashing, and wet oxidation	Colorimetric using potassium thiocyanate (low concentrations). Zimmermann-Reinhardt volumetric method (high concentrations)	Decomposes at 480°C. Interefering elements: Aluminum, chromium, copper and vanadium
Potassium [b]	Wet digestion assisted by microwave radiation.	inductively Coupled Plasma - Mass Spectroscopy	
Lithium [b]	Wet digestion assisted by microwave radiation.	inductively Coupled Plasma - Mass Spectroscopy	
Magnessium [b]	Wet digestion assisted by microwave radiation.	inductively Coupled Plasma - Optical and Mass Spectroscopy	
Manganese [b]	1. Wet digestion assisted by microwave radiation. 2. Dilution with organic solvent	Electrothermal Atomic Absorption Spectrometry	
Molybdene [b]	Wet digestion assisted by microwave radiation.	Inductively Coupled Plasma - Optical and Mass Spectroscopy	Forms oxide which sublimes during burning due to its volatility

[a]: (McCoy, 1962) [b]: (Khuhawar et al., 2012)

Table 2.1 cont Preparation of samples and analysis of inorganic compounds in bitumen

Cation	Sample preparation	Analysis for determination - quantification	Considerations
Sodium [a]	Direct ashing in platinum ware, wet oxidation is not recommended as much sodium is always introduced from attack the glassware	Gravimetric by acid digestion and precipitation, Flame photometry (no precipitation)	
Nickel [a]	Wet ashing and acid digestion	Spectrometry	Use of sodium citrate to precipitate hydrous ferric oxide. Separation of bromide might be needed
Phosphorous [a]	1. Decomposition by ashing in the presence of zinc oxide. 2. Heteropoly Molybdenum Blue Colorimetric Method	Spectrometry, Colorimetric	
Lead [a]	Rapid wet oxidation in relatively large excess of sulfuric acid. Filtration of insoluble lead sulfate formed, followed by dry time and weighing. Ashing is not recommended		Platinum and silica ware can not be used (forms lead silicate).
Antimony [b]	Wet digestion assisted by microwave radiation.	Chemical vapour generation AAS, Inductively coupled plasma - Mass Spectroscopy	

[a]: (McCoy, 1962) [b]: (Khuhawar et al., 2012)

Table 2.1 cont Preparation of samples and analysis of inorganic compounds in bitumen

Cation	**Sample preparation**	**Analysis for determination - quantification**	**Considerations**
Selenium [a]	Oxidation in Parr oxygen bomb (low concentration). Wet oxidation, with initial digestion under a reflux condenser to avoid selenium volatilization	Colorimetric (low concentration), volumetric (high concentration)	
Silicon [a]	Wet ashing and acid digestion. Ignition in platinum crucible at 1100°C and weighing		
Strontium [b]	Wet digestion assisted by microwave radiation.	Inductively coupled plasma - Mass Spectroscopy	
Titanium [b]	Wet digestion assisted by microwave radiation.	Inductively coupled plasma - Optical and Mass Spectroscopy	
Vanadium [a]	1. Wet ashing and acid digestion. 2. Dilution with organic solvent	Volumetric, Inductively coupled plasma - optical emission spectroscopy	Vanadium can be found in two types of porphyrins, volatile and non-volatile. Samples prepared by dry-ashed will give lower results than a sample treated by wet-ashing.
Zinc [a]	Decomposition by fusion with potassium pyrosulphate.	Potentiometic titration with potassium ferrocyanide	Forms oxide which sublimes during burning due to its volatility

[a]: (McCoy, 1962) [b]: (Khuhawar et al., 2012)

2.5 Organic compounds in bitumen: Solvents

The use of solvents in bitumen is often encountered in industrial and laboratory applications. The dilution of heavy oils to improve the fluid and transport properties, as well as the dilution during laboratory experiments to favor the conditions (increase contact area with certain reagents, decrease viscosity to perform further experiments) of the bitumen is widely used. It is also common to remove these solvents before further processing of the bitumen in upgraders, or to determine the effects of the experimental work done in the laboratory on the bitumen. However, the total removal of solvents in bitumen is barely achieved. Therefore, the use of analytical techniques to quantify the remaining solvent content are used.

2.5.1 Quantitative Infrared Spectroscopy

Infrared spectra are used to determine the concentrations of chemical species in samples. The prediction of the concentration in a sample is based on the assumption that the calibration applies equally well to the standards and the unknown samples (Smith, 2011).

The relationships concerning the absorption of radiation can be given in mathematical form by the Bouguer-Lambert-Beer law. Assume that a collimated monochromatic beam of intensity I_0 passes through a layer of sample of thickness L, perpendicular to the parallel boundary planes. Part of the radiation is absorbed, while the rest passes through the layer. The resulting decrease in intensity is proportional to the incident intensity and the thickness of the layer (Pataki and Zapp, 1980).

2.5.1.1 Beer's Law

Beer's Law relates concentration, a sample property, to absorbance, a spectral property, and forms the basis for many quantitative spectroscopic analyses. The infrared beam impinges on a thin film of sample of pathlength L. The sample absorbs some of the infrared beam, and the light that passes through the sample is focused onto a detector to obtain the sample's spectrum. Beer's Law applies to the absorbance process, before interacting with a light beam a molecule is in low energy state.

When molecules absorb energy from a light beam they are promoted to an upper energy level. The amount of energy lost by the light beam equals the amount of energy gained by the molecule since the law of conservation of energy must be followed. The FTIR detects the decrease in light intensity, giving a peak in the sample's absorbance (Smith, 2011).

The Beer's Law can be explained by the **Equation 2.6**

$$A = \mathcal{E} * L * C$$

Equation 2.6

Where

A: Absorbance, is measured as the peak height or peak area in a spectrum. Percent transmittance spectra (%T) should *not* be used for quantitative analysis since the relationship between %T and concentration is complex and nonlinear.
$\mathcal{E}$: Absorptivity, a proportionality constant between concentration and absorbance
L: Pathlength, is the thickness of sample seen by the infrared beam.
C: Concentration of analyte in the sample

2.6 Relevance of the literature review to the study

The literature aspects explained in this Chapter, as it was previously mentioned, provided background useful to elucidate aspects of interest for this study:

The bitumen production from oil sands made clear the importance and impact of water usage in the current production processes (surface mining and in situ). The influence of the presence of different salts, naturally occurring in the oil sands, as well as the negative impact of acidity on the bitumen separation and yield. Since our investigation dealt with the use of bitumen coming from oil sands industry, this knowledge was taken into consideration during the development of **Chapter 3**, **Chapter 4** and **Chapter 5**.

The chemistry of water was considered fundamental in this study. The impact of acidity as well as the concentration of dissolved salts in water on some bitumen properties was studied. Solubility and effect of ion concentrations on the ion removal from the bitumen was determined. Additionally, the effect of ions present in the connate water was investigated in **Chapter 3** and **Chapter 4**. Removal of ions by water washing was studied in **Chapter 3**, **Chapter 4** and **Chapter 5.**

In **Chapter 4** and **Chapter 5**, the cations were quantified not only in the water after washing, but in the organic phase. For this reason, the determination of inorganic elements in the bitumen was of interest, as well as the preparation of the sample to pursue this quantification.

Washing of bitumen resulted in the formation of water-in-oil emulsions. The stability of these emulsions is also known as result of the bitumen separation from oil sands. The water content of the recovered organic emulsions was considered in **Chapter 3**, **Chapter 4** and **Chapter 5**. Additionally, the effect of the remaining solvent in the bitumen was quantified by FTIR Spectroscopy using the Beer's Law to quantify it.

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3. EFFECT OF ACID WASHING ON COLD LAKE BITUMEN

ABSTRACT

Water recycling during oil sands recovery and upgrading processes affects the quality of process water that may have an influence on bitumen upgrading. With a high volume of water recycling with the aim of reducing fresh water consumption, the increase of dissolved organic compounds (naphthenic acids, benzene, phenols) as well as the increase in dissolved inorganic materials, such as Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, and SO_4^{2-}, may increase to a level where it can affect downstream processes.

To evaluate the potential impact of dissolved inorganic materials on bitumen, a necessary first step is to determine the nature and quantity of the inorganic species present. It was of interest to determine how effectively these species could be removed by aqueous washing at neutral and acid pH. Furthermore, to determine how acid solutions and the presence of highly soluble ions can affect this removal. Separation of aqueous, organic and water-in-oil emulsion phases were made.

The aqueous samples were analyzed using High Performance Liquid Chromatography (HPLC) and Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). Removal of anions such as Cl^{-}, HPO_4^{2-} and CO_3^{2-} was detected, with a higher removal of Cl^{-} (over 11000 μg/g bitumen vs 7000 μg/g bitumen initially added), and cations of Na (around 503 μg/g bitumen vs 90 μg/g bitumen initially added). Lesser quantities of HPO_4^{2-}(up to 40 μg/g bitumen approximately) and CO_3^{2-} (over 100 μg/g bitumen) were quantified. The addition of NaCl had an influence on the removal of the anions HPO_4^{2-} and CO_3^{2-}, decreasing the removal of these anions until they were not longer detected. Removal of cations of elements such as Ca, K, Si was detected; however; the removal of these ions seemed not to be related to the addition of NaCl.

The viscosity of the recovered bitumen was measured and corrected based on the residual methylene chloride. It was found that the results had high variability, and the addition of NaCl, or the pH variation did not seem to be the only variables affecting the viscosity. The prediction

methods were found to be sensitive to slight variations in the solvent content. Additionally, it was noted that the formation of emulsions and the possible migration of some compounds from the bitumen to the emulsion phase could affect the bitumen viscosity.

Keywords: anion, cation, ion transfer, bitumen, washing, emulsion, ICP, HPLC, Cold Lake, viscosity.

3.1 Introduction

Mineral content of bitumen has been subject of a broad variety of studies. For example, the nature of the bitumen and its characterization, the effect of this elements on downstream refining processes, and the environmental impact of secondary streams after bitumen production processes such as hot water extraction, surface mining or SAGD (Pedenaud et al., 2005; Skierszkan et al., 2013; Aubertin and McKenna, 2016). Water is a common factor in the Oil Sands industry, in a major or minor extent, water is used to enhance bitumen production. For this reason, water recycling is used to minimize the consumption of fresh water, leading to the increase of some organic and inorganic elements in the oil sands process affected water (Allen, 2008).

Some studies have been performed to elucidate the effect of aqueous treatment on some key characteristics of bitumen (Gonzalez, 2015; Prado and de Klerk, 2016). Gonzalez concluded that bitumen washing with deionized water affected the viscosity of bitumen; also, it was found that bitumen washing with low acid concentrations was able to promote a higher decrease in viscosity of the bitumen. Correction of the measured viscosity based on the residual solvent used during the experiments was done through two different approaches.

However, in previous studies a baseline was not established of the elements that can be removed through water washing from bitumen, and how dissolved ions can affect this removal. For this reason, this study went through the determination of the ions that can be effectively removed by washing Cold Lake bitumen with deionized water (MilliQ water) and 0.03 M HCl, with controlled concentrations of NaCl (0-1000 mg/L). Cold Lake bitumen was specifically selected for this study to build on the previous studies that employed Cold Lake bitumen. Additionally, the viscosity of the recovered bitumen was analyzed, and three prediction methods from literature to correct the residual solvent were used.

It was intended to determine if the washing of bitumen using deionized water, as well as 0.03 M HCl solution, both with different concentrations of dissolved NaCl, can promote some ion transfer from the bitumen. If so, it was of main interest to evaluate if this ion transfer was able to change the viscosity of the bitumen.

3.2 Experimental Section

3.2.1 Materials

The main characterization of Cold Lake bitumen can be found in **Table 3.1**, properties of experimental interest of the bitumen used were measured and reported as part of the results. Deionized Water was obtained from a MilliPore Milli-Q Integral 5, with an ion conductivity of 1.28 ± 0.17 µS/cm and pH 7.04 ± 0.11. The deionized water was analyzed as blank for calibration purposes and the ionic content is considered as baseline for the ion quantification made for the analyzed samples reported in **Section 3.3**.

Table 3.1 Cold Lake bitumen characterization

Property		Value
Elemental composition [%]	C	66.5 ± 0.2
	H	10.8 ± 0.1
	N	0.4
	O	18.9 ± 0.2
	S	3.5
Viscosity [Pa.s]	10 °C	203 ± 3
	20°C	79 ± 13
Vanadium [ppm w/w]		124 ± 22
Nickel [ppm w/w]		50 ±4
Asphaltenes [% w/w]		11 ± 1

The rest of materials used in this study are described in **Table 3.2**, were commercially obtained and used without any further purification.

Table 3.2 Material used during calibration and reaction stages

Compound	Formula	CASRN [a]	Mass fraction purity % [b]	Supplier
Methylene Chloride	CH_2Cl_2	75-09-2	99.9	Fisher Scientific
Sodium Chloride	NaCl	7647-14-5	≥99.0	Fisher Scientific
Argon	Ar	7440-37-1	99.999 [c]	Praxair
Sodium Gluconate	$C_6H_{11}NaO_7$	527-07-1	≤100	Sigma Aldrich
Boric Acid	H_3BO_3	10043-35-3	≥90.0	Merck
Sodium Tetraborate Decahydrate	$Na_2B_4O_7 \cdot 10H_2O$	1303-96-4	≥99.5	Merck
Glycerin	$C_3H_8O_3$	56-81-5	≥99.5	Sigma Aldrich
Butanol	$C_4H_{10}O$	71-36-3	≥99.4	Anachemia
Acetonitrile	C_2H_3N	75-05-8	≥99.9	Sigma Aldrich
Sodium Fluoride	NaF	7681-49-4	≥99.5	Sigma Aldrich
Sodium Chloride	NaCl	7647-14-5	≥99.0	Fisher Scientific
Sodium Nitrite	$NaNO_2$	7632-00-0	≥97.0	Sigma Aldrich
Potassium Bromide	KBr	7758-02-3	99.9	Fisher Scientific
Sodium Nitrate	$NaNO_3$	7631-99-4	≥99.5	Merck
Sodium carbonate	Na_2CO_3	497-19-8	≥99.0	Sigma Aldrich
Potassium Phosphate Monobasic	KH_2PO_4	7778-77-0	≥99.0	Sigma Aldrich
Sodium Sulfate	Na_2SO_4	7757-82-6	≥99.0	Sigma Aldrich
ICP-OES wavelength calibration solution	NA	NA	NA	Agilent
TRACE-CERT multi-element standard solution 6 for ICP	NA	NA	NA	Agilent
Hydrochloric Acid	HCl	7647-01-0	3.06 (1N)	Fisher Scientific
pH buffer solution 4.0	NA	NA	3.99-4.01 [d]	Fisher Scientific
Tetrahydrofuran	C_4H_8O	109-99-9	NA	Fisher Scientific
Hydranal ® Composite 5	NA	NA	NA	Fluka
pH buffer solution 7.0	NA	NA	6.99-7.01 [d]	Fisher Scientific

[a] CASRN = Chemical Abstracts Services Registry Number, [b] This is the purity of the material guaranteed by the supplier; material was not further purified. [c] molar fraction purity %, [d] pH range.

3.2.2 Equipment and Procedure

Washing of the bitumen was performed using different aqueous reagents:

- Deionized (MilliQ) water
- 0.03 M HCl

To each of these aqueous reagents were added different NaCl concentrations, according to **Table 3.3**.

Table 3.3 Prepared aqueous solutions for Cold Lake bitumen washing

pH Adjustment	**NaCl concentration [mg/L)**			
	1	**2**	**3**	**4**
Deionized water	0	10	100	1000
0.03 M HCl aqueous solution	0	10	100	1000

The aqueous washing at different NaCl concentrations was performed following the procedure performed in a previous study (Gonzalez, 2015). The blank, deionized water at different NaCl concentrations and the acid solutions at different NaCl concentrations will be called "water/aqueous solutions", and it can be summarized as follows:

20 g of Cold Lake bitumen were dissolved in 100 mL of methylene chloride (CH_2Cl_2) in a 250 mL flask. After the bitumen was dissolved, 100 mL of water/aqueous solution was added to the flask. The compounds were mixed and stirred for 2 hours at 400 rpm and room temperature, using a 5 cm octagonal magnetic bar, and a Heidolph MR Hei – Standard hot plate. After the stirring was completed, the mixture was left overnight in a 500 mL separation funnel, to improve the separation of phases. Three different phases were recovered: aqueous, organic emulsion (water in oil emulsion), and organic phase. The sample that remained in the separation funnel and flask was washed with 30 mL of fresh CH_2Cl_2, and the volume was added to the organic emulsion phase.

The organic phase was placed in a Heidolph rotary evaporator for 17 hours at 45 ºC under vacuum at 55 kPa (abs), in order to remove the CH_2Cl_2. Then, the recovered bitumen and the organic emulsion phases were left overnight in the fumehood to allow the evaporation of any remaining CH_2Cl_2. The emulsion phase was also taken to the rotavap at the same conditions to remove the solvent; however, no further evaporation in the fumehood was performed for the emulsion phase. Weighing of all the separated phases was performed for material balance purposes using a Mettler Toledo ML-3002E/03 balance (capacity 3.2 kg, readability 0.1 g).

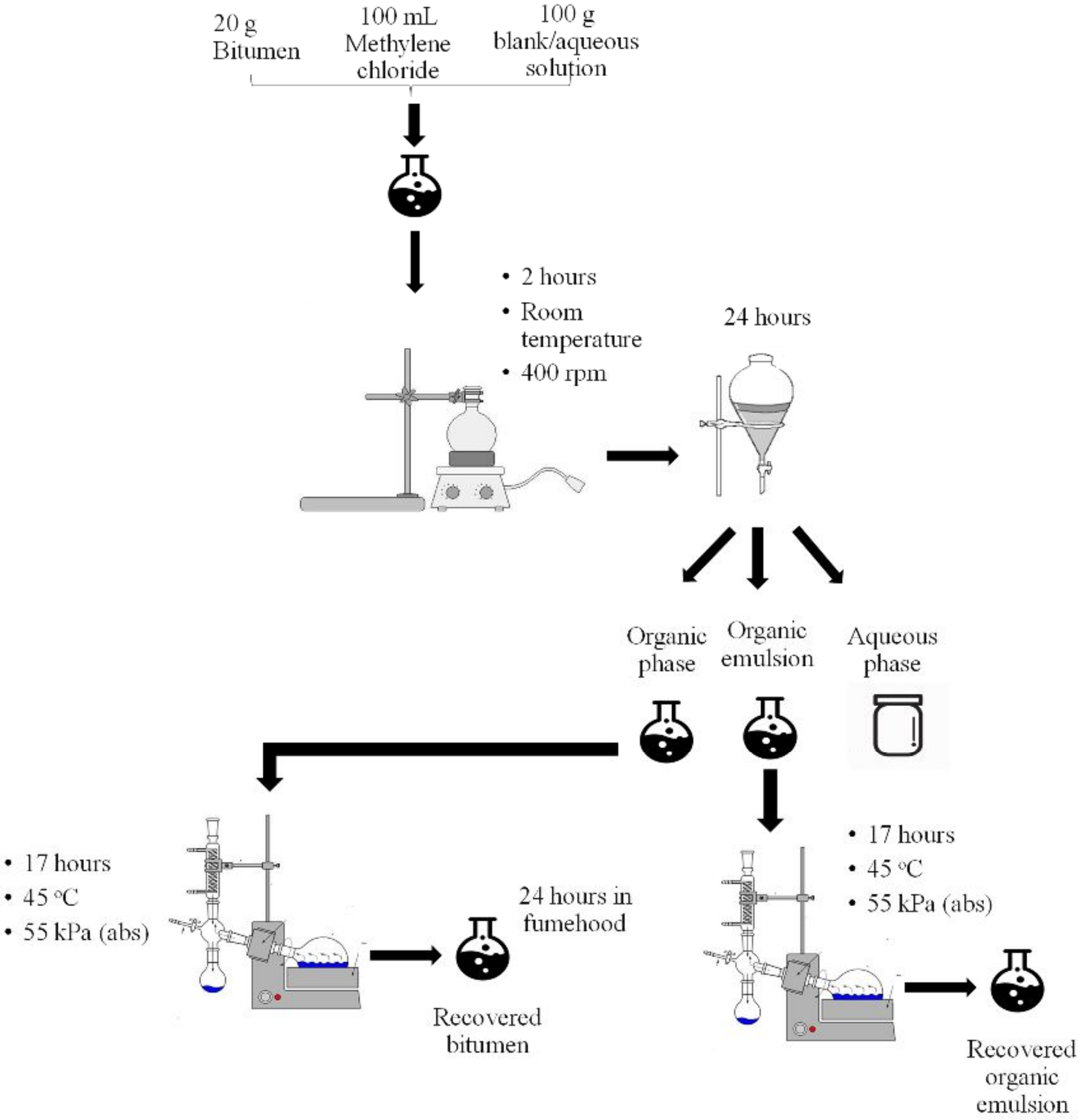

Figure 3.1 Experimental procedure – Aqueous washing of Cold Lake bitumen

3.2.3 Analyses

3.2.3.1 Anion determination of aqueous phase samples through HPLC

The aqueous phase was analyzed using a HPLC Waters Alliance e2695 model, coupled to a conductivity detector Waters 2432. The column used was an IC-Pak Anion HR. The eluent phase was a borate-gluconate solution. The injection volume was 100 µL, the eluent flow rate was set constant at 1.0 mL/min, and the temperature was kept at 30ºC. The samples were filtered to remove bitumen and toluene traces using Waters Sep-Pak C18 Classic cartridges.

Different standard solutions were prepared to build calibration curves, so that quantitative analysis of different anions could be done. Detailed calibration as well as the eluent phase preparation procedure can be found in **Section 3.2.5.1**.

3.2.3.2 Cation determination of acid and aqueous phase samples through ICP-OES

The aqueous phase samples were analyzed using an Agilent ICP-OES 5100 and SPS3 autosampler, an easy-fit torch, a Seaspray nebulizer, a double-pass spray chamber, and ultra-high purity compressed Argon gas. The conditions for the analysis were: radial viewing mode, pump speed 12 rpm, nebulizer flow 0.7 L/min, plasma flow 12 L/min, auxiliary flow 1 L/min, delay time 26 s, stabilization time 15 s, read time 5 s, power 1.2 kW. The aqueous phase samples were not acidified for this analysis. Each sample was measured in triplicate.

Standard solutions at different concentrations were prepared to build calibration curves. The calibration procedure can be found in **Section 3.2.5.2**.

3.2.3.3 pH and conductivity of aqueous phase

The aqueous phase samples obtained were analyzed for pH and conductivity using an Oakton® PC700 benchtop meter. The performed calibration can be found in **Section 3.2.5.3.**

3.2.3.4 Water content in organic phase

The water content was determined using a Karl-Fisher titrator Model V20S manufactured by Mettler Toledo. This analysis uses tetrahydrofuran as solvent and hydranal® as titrator agent. The water content of the tetrahydrofuran must be determined as a "blank".

The water content was determined in the raw Cold Lake bitumen, and some samples of recovered bitumen after washing were randomly picked and analyzed to determine if there was any remaining water in the bitumen. To determine the water content, the following procedure was developed:

0.500 g of sample was weighted using a Mettler Toledo XS105 dual range balance (capacity 41 g/120 g, readability 0.01 mg/0.1 mg). The sample was dissolved in 10 mL (8.890 g approximate) of tetrahydrofuran (proper care to avoid the volatilization of tetrahydrofuran after weighing must be taken). The mixture is then analyzed to determine the water content.

The calculation of water content of the organic phase is described in **Section 3.2.4.3**.

3.2.3.5 Viscosity of recovered bitumen

Viscosity measurements were performed using in an Anton Paar RheolabQC viscometer. A concentric cylinder CC17/QC-LTC measuring cup was used (internal diameter is 16.664 mm, length is 24.970 mm). For this analysis, 4 g approximately of sample was required. Viscosity measurements were performed at 10 and 20 ºC, at a constant shear rate of $10s^{-1}$. The temperature was controlled by a Julabo F25-EH circulating heater/chiller. Calibration of the viscometer was not experimentally verified by use of a reference with known viscosity.

3.2.3.6 Fourier Transform Infrared Spectroscopy (FTIR)

The recovered bitumen samples were analyzed using an ABB MB3000 instrument equipped with a MIRacleTM Reflection Attenuated Total Reflectance (ATR) diamond crystal plate and pressure clamp. The conditions for the analysis were: Resolution 4 cm^{-1}, 60 scans, detector gain of 81 and spectral region between 4000 and 400 cm^{-1}. A calibration curve was built for CH_2Cl_2, details are reported in **Section 3.2.5.4**.

3.2.3.7 Elemental composition

Elemental analysis of the raw bitumen and some of the recovered bitumen samples was performed using a Carlo Erba Model EA1108 Elemental Analyzer for CHNS (Triad Scientific, Inc., Manasquan, NJ, USA). Sampling for analysis of the raw bitumen was performed in triplicate and each sample was analyzed two times, the recovered bitumen samples were sampled for analyses once and each sample was analyzed two times. The oxygen content was determined by difference to reach 100% of the composition. The calibration and analyses were performed by the Analytical and Instrumentation Laboratory in the department of Chemistry of the University of Alberta.

3.2.4 Calculations

3.2.4.1 Material Balance

The material balance was checked by the percentage of difference between the total mass of bitumen and aqueous reagent used at the beginning of the experimental procedure, and the mass of bitumen, organic emulsion and aqueous solution recovered after the separation in the funnel and methylene chloride evaporation in the rotavap. To perform this calculation, the mass of recovered bitumen was corrected after determining the content of CH_2Cl_2 remaining in the sample, using the following equation:

$$M_{bit,corrected} = M_{bit} * (1 - \%_{CH_2Cl_2})$$

Equation 3.1

Where

$M_{bit,corrected}$: Corrected mass of bitumen [g]

M_{bit}: Mass of recovered bitumen [g]
$\%_{CH_2Cl_2}$: Percentage of CH_2Cl_2 remaining in the recovered bitumen [% w/w]

The content of CH_2Cl_2 remaining in the recovered bitumen was determined by a calibration curve built based on mixtures of raw bitumen with different percentages of CH_2Cl_2 and analyzed by FTIR. The calibration procedure and curve can be found in **Section 3.2.5.4**

The percentage of difference after correcting the CH_2Cl_2 content is calculated as follows:

$$\%_{difference,corrected} = \left(\frac{\left(M_{bit,0} + M_{aq,0}\right) - \left(M_{bit,corrected} + M_{org} + M_{aq}\right)}{M_{bit,o} + M_{aq,0}}\right) * 100$$

Equation 3.2

$\%_{difference,corrected}$: Percentage of difference of mass balance [% w/w]
$M_{bit,0}$: Initial mass of bitumen [g]
$M_{aq,0}$: Initial mass of aqueous solution [g]
M_{org}: Recovered mass of organic emulsion [g]
M_{aq}: Recovered mass of aqueous phase [g]

Due to the low boiling point of the CH_2Cl_2, some losses occurred during the handling of the samples, and during the experimental work. For this reason, this compound was not considered in the material balance; however, the remaining CH_2Cl_2 in the recovered bitumen was substracted from the mass of recovered bitumen.

3.2.4.2 Ion content in aqueous phase

The ion content of the aqueous phase is calculated according to:

$$M_{x\,aq} = \frac{C_{x\,aq} * M_{aq} * 1000\mu g}{\rho_{H_2O} * M_{bit,0} * 1mg}$$

Equation 3.3

$M_{x\,aq}$: Mass of element x in the aqueous phase [µg/g bitumen]

$C_{x\,aq}$: Concentration of element *x* in aqueous phase sample [mg/L]

M_{aq}: Mass of recovered aqueous phase sample (**Figure 3.1**) [g]

ρ_{H_2O}: Density of water. For simplification and calculation purposes, it was assumed the density to remain constant at 1000 g/L.

3.2.4.3 Water content in bitumen

The water content by Karl Fisher titration is calculated from:

$$M_{mixture} = M_{sample} + M_{THF}$$

Equation 3.4

$$DF_{sample} = \frac{M_{sample}}{M_{total}}$$

Equation 3.5

$$DF_{THF} = \frac{M_{THF}}{M_{total}}$$

Equation 3.6

$$\%water_{THF} = \%water_{THF,blank} * DF_{THF}$$

Equation 3.7

$$\%water_{sample} = (\%water_{mixture} - \%water_{THF}) * DF_{org}$$

Equation 3.8

Where:

$M_{mixture}$: Total mass of sample and solvent (tetrahydrofuran) [g]
M_{sample}: Mass of sample (organic emulsion/raw bitumen) [g]
M_{THF}: Mass of tetrahydrofuran [g]
DF_{sampel}: Dilution factor for the sample [dimensionless]
DF_{THF}: Dilution factor for tetrahydrofuran fraction [dimensionless]
$\%water_{THF}$: Percentage of water in tetrahydrofuran in the sample [% w/w]
$\%water_{THF,blank}$: Percentage of water in tetrahydrofuran when running as blank [%w/w]
$\%water_{sample}$: Percentage of water in the sample (organic emulsion/raw bitumen) [% w/w]
$\%water_{mixture}$: Percentage of water obtained running the mixture of sample/tetrahydrofuran [% w/w]

On the other hand, the water content by elemental composition was determined from:

$$\%_{water,oxygen\ content} = (\%_{oxygen,sample} - \%_{oxygen,Cold\ Lake}) * \frac{1\ mol\ H_2O}{16\ g\ O} * \frac{18\ g\ H_2O}{1\ mol\ H_2O}$$

Equation 3.9

Where

$\%_{water,oxygen\ content}$: Percentage of water based on the oxygen content of the sample [%] w/w
$\%_{oxygen,sample}$: Percentage of oxygen in the sample [%] w/w

$\%_{oxygen,Cold\ Lake}$: Typical percentage of oxygen in the Cold Lak bitumen. It is reported in the literature an oxygen content between 0.7 – 1.1 % w/w (Strausz and Lown, 2003; Gonzalez, 2015). To be conservative, 1.1 % w/w was taken for the calculation purposes.

3.2.4.4 Prediction of viscosity of recovered bitumen

The viscosity of the recovered bitumen was corrected considering the remaining content of CH_2Cl_2 determined using the calibration curve made through FTIR analysis (**Section 3.2.5.4**). Different equations were used to predict the viscosity of the recovered bitumen.

Viscosity prediction A:

Equation 3.4 (Riazi, 2005) was used by Gonzalez (2015) to predict the viscosity of the recovered bitumen after the removal of methylene chloride:

$$\mu_m = \left(\sum_{i=1}^{N} X_i * \mu_i^{1/3} \right)^3$$

Equation 3.10

Where

μ_m: Viscosity of the mixture [cP]
X_i: Molar fraction of component *i*
μ_i: Viscosity of component *I* [cP]
N: total number of components

Viscosity prediction B:

Using **Equation 3.10** (Mehrotra, 1990), Gonzalez (2015) predicted the viscosity of the bitumen after solvent removal, and compared these results with the ones obtained through the **Equation 3.9** used in **Prediction A:**

$$\log(\mu_m + 0.8) = \sum_{i=1}^{N} X_i \, [\frac{M_i}{M_a}]^{0.5} \log(\mu_i + 0.8)$$

Equation 3.11

$$M_a = \sum_{i=1}^{N} X_i M_i$$

Equation 3.12

Where

μ_m: Viscosity of the mixture, mPa.s
X_i: Molar fraction of component *i*
M_i: Molar mass of component *i* [g/mol]
M_a: Average molar mass [g/mol]

Viscosity prediction C

Prediction of viscosity in partial upgrading bitumen was investigated to determine the impact of process sequence of solvent deasphalting and visbreaking (Zachariah and de Klerk, 2017). In this study, several equations were used to determine the bitumen viscosity considering the addition of low viscosity solvents and the changes in density due to the temperature. Temperature adjustments of density were made using **Equation 3.12.**

$$\rho = a_1 + \; a_2 T'$$

Equation 3.13

Where

ρ: Density [kg/m^3]
a_1, a_2: Temperature correlation coefficients
T': Temperature [ºC]

Coefficient a_2 was found to be between -0.612 to -0.602; it was used a value of a_2=-0.607 (Zachariah and de Klerk, 2017). Using known values of density and temperature for Cold Lake bitumen, a_1 was found to be $a_1 = 1036$.

The density of the mixture of the mixture of bitumen and the remaining solvent was determined through **Equation 3.13**:

$$\frac{1}{\rho_m} = \frac{1 - X_D}{\rho_B} + \frac{X_D}{\rho_D} - X_D(1 - X_D)\left(\frac{1}{\rho_B} + \frac{1}{\rho_D}\right)\beta_{B,D}$$

Equation 3.14

Where

ρ_m: Density of the mixture [kg/m^3]
X_D: Mass fraction of diluent
ρ_B: Density of bitumen [kg/m^3]
ρ_D: Density of diluent [kg/m^3]
$\beta_{B,D}$: Binary interaction parameter, it was used -0.0812, which corresponds to the interaction between methylene chloride and Cold Lake bitumen using the experimental data for densities of Cold Lake bitumen at different residual methylene chloride fractions (Gonzalez, 2015).

Equation 3.15 and **Equation 3.16** were used to calculate the viscosity of bitumen:

$$ln\,(\nu_m) = \exp[\alpha(1 - X_D^n)] + \ln(\nu_D) - 1$$

Equation 3.15

$$\exp(\alpha) = \ln(\nu_B) - \ln(\nu_D) + 1$$

Equation 3.16

$$n = \frac{\nu_D}{[0.9029\nu_D + 0.1351]}$$

Equation 3.17

Where

ν_m: Kinematic viscosity of the mixture [cSt]
ν_B: Kinematic viscosity of the bitumen [cSt]
ν_D: Kinematic viscosity of the diluent [cSt]
n: Viscosity reduction parameter
α: Viscosity interaction parameter
X_D: Mass fraction of diluent

3.2.4.5 Viscosity of bitumen and effect of water content

Several models have been proposed to predict the viscosity of water-in-oil emulsions (Pal, 2001; Li et al., 2016; Nasery et al., 2016). The water content of the raw bitumen and some recovered bitumen samples after washing was determined according to **Section 3.2.3.4** and **3.2.4.3**. If there was water emulsified in the bitumen, the viscosity was corrected according to the water content through the following equation:

$$\mu_r = 1 + 2.5\emptyset\left(\frac{a + 0.4}{a + 1}\right)$$

Equation 3.18

$$\mu_r = \frac{\mu}{\mu_c}$$

Equation 3.19

$$a = \frac{\mu_d}{\mu_c}$$

Equation 3.20

$$\emptyset = \%water_{sample} * \frac{\rho_{w-o\ emulsion}}{\rho_{H_2 0}}$$

Equation 3.21

Where

μ_r: Relative viscosity
$\emptyset$: Volume fraction of water (water cut) [% v/v]
μ: Viscosity of water-in-oil emulsion [Pa.s]
μ_c: Viscosity of the continuous phase (bitumen) [Pa.s]
μ_d: Viscosity of the disperse phase (water) [Pa.s]
$\rho_{w-o\ emulsion}$: Density of water-in-oil emulsion [kg/m^3]
$\rho_{H_2 0}$: Density of water [kg/m^3]

3.2.5 Calibrations

3.2.5.1 HPLC calibration

Calibration curves were made for different anions to determine the concentration in the aqueous phase during each washing. The prepared standards were F^-, Cl^-, CO_3^{2-}, Br^-, SO_4^{2-}, HPO_4^{2-}, NO_3^-, NO_2^-. Since the carbonates exist in equilibrium in aqueous phase, both HCO_3^- and CO_3^{2-} are expressed and quantified as CO_3^{2-}.

3.2.5.1.1 Eluent preparation

Borate/Gluconate concentrate preparation:

To a one-liter, polypropylene Corning® volumetric flask, add:

16 g sodium gluconate
18 g boric acid
25 g sodium tetraborate decahydrate

Add approximately 500 mL of MilliQ water and mix until dissolved, then add:

250 mL glycerin

Fill the flask to the mark with MilliQ water and mix thoroughly. Concentrate may be stored refrigerated for up to six months before replacement.

Borate/Gluconate eluent

Place approximately 500 mL of MilliQ water into a one-liter, polypropylene Corning® volumetric flask and add:

20 mL Borate/Gluconate concentrate
20 mL butanol
120 mL acetonitrile

Fill the flask to the mark with MilliQ water and mix. Filter through a 0.22 µm membrane.

3.2.5.1.2 Standard preparation

Concentrated standard

It was prepared separated standards by diluting each of the chemical compounds listed in **Table 3.4**, to 100 mL with MilliQ water.

Table 3.4 Standard preparation for HPLC

Anion	Retention time [min]	Chemical compound	Weight [g]	Concentration [ppm] [a]
F^-	2.1	NaF	0.221	1000
CO_3^{2-} [b]	2.6	Na_2CO_3	0.246	1400
Cl^-	3.6	NaCl	0.329	2000
NO_2^-	4.6	$NaNO_2$	0.600	4000
Br^-	5.8	KBr	0.596	4000
NO_3^-	6.8	$NaNO_3$	0.548	4000
HPO_4^{2-}	10.1	KH_2PO_4	0.854	6000
SO_4^{2-}	14.3	Na_2SO_4	0.592	4000

[a]: by diluting up to 100 mL with deionized water

[b]: HCO_3^-/CO_3^{2-} reported as CO_3^{2-}

3.2.5.1.3 Working standard

Through dilution of the concentrated standard with MilliQ water, different concentrations of working standards were prepared according to **Table 3.5**.

Table 3.5 Prepared standards for HPLC calibration curve

Anion	Retention time [min]	Concentration [ppm]			
		Blank	Standard 1	Standard 2	Standard 3
F^-	2.1	0	1	10	20
CO_3^{2-} [a]	2.6	0	7	14	140
Cl^-	3.6	0	20	20	40
NO_2^-	4.6	0	4	40	80
Br^-	5.8	0	4	40	80
NO_3^-	6.8	0	4	40	80
HPO_4^{2-}	10.1	0	6	60	120
SO_4^{2-}	14.3	0	4	40	80

[a]: HCO_3^-/CO_3^{2-} reported as CO_3^{2-}

Working standards were prepared and run once to get the calibration curves. The curve linearity for each element is shown in **Table 3.6**.

Table 3.6 Calibration curve linearity for HPLC

Anion	Retention time [min]	Correlation Coefficient (R^2)
F^-	2.1	0.9987
$CO_3^{2-\ a}$	2.6	0.9999
Cl^-	3.6	0.9922
NO_2^-	4.6	0.9933
Br^-	5.8	0.9912
NO_3^-	6.8	0.9967
HPO_4^{2-}	10.1	0.9972
SO_4^{2-}	14.3	0.9972

[a]: Correlation coefficient, based on the regression line built using the prepared standards.

[b]: HCO_3^-/CO_3^{2-} reported as CO_3^{2-}

3.2.5.2 ICP calibration

Calibration curves were made for different cations to determine the concentration in the aqueous phase during each washing. The prepared standards contained cations of the elements Al, As, Ba, Cd, Co, Cr, Cu, K, Mn, Mo, Ni, Pb, Se, Sb, B, Ca, Fe, Li, Mg, Na, P, Si, Ti, V and Zn.

3.2.5.2.1 Standard preparation

To build the calibration curves, two standard solutions were used:

- ICP-OES wavelength calibration solution containing 50 mg/L of cations of the elements Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Zn, and 500 mg/L K in 5 % w/w HNO_3.

- TRACE-CERT multi-element standard solution 6 for ICP, containing 100 mg/L of cations of the elements Al, Sb, Ba, Pb, B, Ca, Cd, Cr, Co, Fe, K, Cu, Li, Mg, Mn, Mo, Na, Ni, P, Si, Ti, Vn and Zn in 5 % w/w HNO_3 and < 0.1 % w/w HF, both supplied by Agilent.

The prepared standards, as well as the emission wavelength that was selected for calibration and analysis, are listed in **Table 3.7**.

Table 3.7 Prepared standards for ICP calibration curve

Cation of the element	Wavelength [nm]	Concentration [ppm]				
		Blank	Standard 1	Standard 2	Standard 3	Standard 4
Al	396.152	0	1	5	10	20
As	188.980	0	-	5	10	-
B	249.772	0	1	-	10	20
Ba	455.403	0	1	-	10	20
Ca	396.847	0	1	-	10	20
Cd	214.439	0	1	5	10	20
Co	238.892	0	1	5	10	20
Cr	267.716	0	1	5	10	20
Cu	327.395	0	1	5	10	20
Fe	238.204	0	1	-	10	20
K	766.491	0	1	50	100	20
Li	670.783	0	1	-	10	20
Mg	279.553	0	1	-	10	20
Mn	257.61	0	1	5	10	20
Mo	202.032	0	1	5	10	20
Na	589.592	0	1	-	10	20
Ni	216.555	0	1	5	10	20
P	213.618	0	1	-	10	20
Pb	220.353	0	1	5	10	20
Sb	206.834	0	1	-	10	20
Se	196.026	0	-	5	10	-
Si	251.611	0	1	-	10	20
Ti	336.122	0	1	-	10	20
V	292.401	0	1	-	10	20
Zn	213.857	0	1	5	10	20

-: not present

The prepared standards were run in triplicates to obtain the calibration curves for each element. The linearity of the calibration curves can be found in **Table 3.8**.

Table 3.8 Calibration curve linearity for ICP-OES

Cation of the element	Wavelength [nm]	Correlation coefficient (R^2) [a]
Al	396.152	0.99975
As	188.98	0.99997
B	249.772	0.99887
Ba	455.403	0.99984
Ca	396.847	0.99980
Cd	214.439	0.99984
Co	238.892	0.99992
Cr	267.716	0.99977
Cu	327.395	0.99995
Fe	238.204	0.99992
K	766.491	0.99994
Li	670.783	0.99996
Mg	279.553	0.99998
Mn	257.61	0.99980
Mo	202.032	0.99972
Na	589.592	0.99975
Ni	216.555	0.99943
P	213.618	0.99937
Pb	220.353	0.99983
Sb	206.834	0.99973
Se	196.026	0.99999
Si	251.611	0.99537
Ti	336.122	0.99996
V	292.401	0.99977
Zn	213.857	0.99960

[a]: Correlation coefficient, based on the regression line built using the prepared standards.

3.2.5.3 pH and conductivity calibration

To perform the pH/conductivity measurements, new pH and conductivity electrodes were installed. Calibration for both electrodes was done following the instructions given in the manufacturer manual (Thermo Scientific, 2010). The pH electrode was calibrated using pH buffer solutions (4.0 and 7.0).

The conductivity electrode was calibrated preparing standard solutions of NaCl (**Table 3.9**). The correlation coefficient (R^2) based on the linear regression obtained from the prepared standards was calculated to be 0.9981.

Table 3.9 Conductivity of NaCl standard solutions

Standard	Cl^- concentration [ppm]	Conductivity [µS/cm]
0	0	0.64
1	152	471
2	303	919
3	606	1771
4	1212	3860

3.2.5.4 CH_2Cl_2 content by FTIR calibration

An internal calibration curve with Cold Lake bitumen at different concentrations of CH_2Cl_2 was built, based on the application of the Beer-Lambert Law (**Chapter 2**, **Section 2.4.1**). The calibration curve was used to determine quantitatively the remaining content of this solvent after the evaporation in the Rotavap (**Figure 3.1**).

To correct the potential variances in the path length during the measurements, the calibration curve was built considering the ratio between the height of absorption around 1265 cm^{-1} related to CH_2Cl_2 wagging in the methylene chloride, and the height of absorption around 1450 cm^{-1} related to methylene groups (CH_2). The height of these peaks was obtained by the use of line segments to parallel the baseline of the spectrum within the wavelength range of interest (for the CH_2Cl_2 wagging was used the 1251-1278 cm^{-1} range, while for the CH_2 group was used the 1485-1442 cm^{-1} range).

The correlation coefficient obtained from the quadratic regression was found to be 0.9966 and the curve can be observed in **Figure 3.2**.

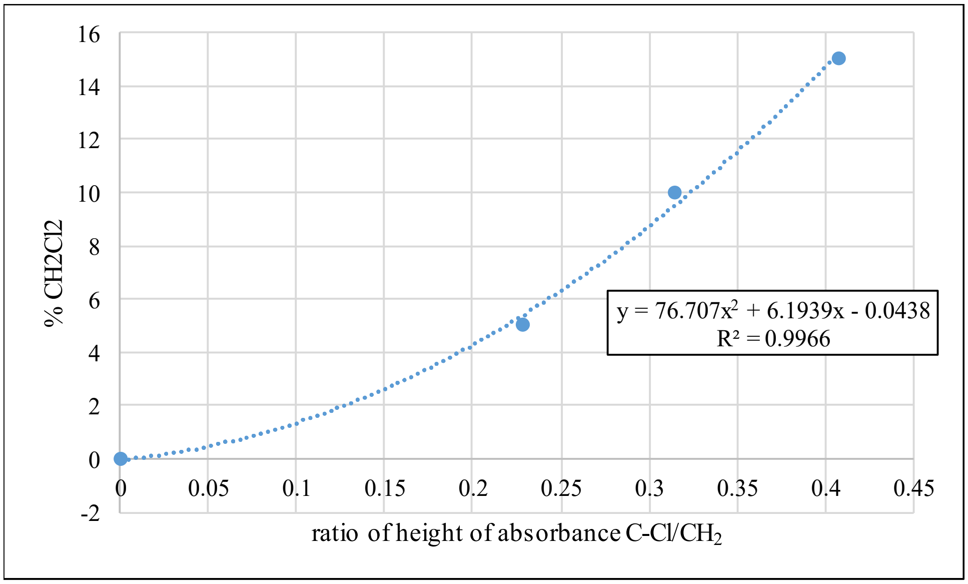

Figure 3.2 Calibration curve of CH_2Cl_2 by FTIR, R^2: correlation coefficient

3.3 Results

3.3.1 Methylene chloride content in recovered bitumen

The content of CH_2Cl_2 remaining in the recovered bitumen after its removal in the rotavap was determined by FTIR. The ratio between the intensity of the peak at 1265 cm^{-1} corresponding to the C-Cl stretching, and the peak at 1450 cm^{-1} corresponding to methylene groups (CH_2) was used to determine the solvent content based on the calibration curve built at different CH_2Cl_2 concentrations (**Figure 3.2**). The CH_2Cl_2 content for the bitumen washed with different NaCl concentrations dissolved in deionized water can be found in **Table 3.10**. It can be observed that the residual methylene chloride in each sample, despite of being evaporated in the Rotavap under the same conditions, exhibited a high variability. The residual methylene chloride in the recovered bitumen seemed to increase in the samples washed with higher NaCl aqueous solutions.

Table 3.10 Methylene chloride content in recovered bitumen – Cold Lake bitumen washing with deionized water and different NaCl concentrations

Sample		**Absorbance C-Cl peak**	**Absorbance CH_2 peak**	**CH_2Cl_2 content in bitumen by FTIR** [% w/w]
Deionized (MilliQ) water	1	nd	0.0428	nd
	2	0.0033	0.040753	0.8655
	3	nd	0.04284	nd
	Average	**0.00112**	**0.0421**	**0.2885**
	s	**0.0019**	**0.0012**	**0.4997**
10 mg/L NaCl in deionized (MilliQ) water	1	0.0007	0.0438	0.083
	2	0.0038	0.0418	1.031
	3	0.0022	0.0431	0.413
	Average	**0.0023**	**0.0429**	**0.5090**
	s	**0.0016**	**0.0010**	**0.4813**
100 mg/L NaCl in deionized (MilliQ) water	1	0.0022	0.0431	0.4134
	2	0.0085	0.0395	4.2617
	2	0.0073	0.0452	2.6217
	Average	**0.0060**	**0.0426**	**2.4323**
	s	**0.0034**	**0.0029**	**1.9311**
1000 mg/L NaCl in deionized (MilliQ) water	B43	nd	0.04	nd
	B44	0.0049	0.0397	1.6424
	B45	0.0071	0.0441	2.5944
	Average	**0.0040**	**0.0427**	**1.4123**
	s	**0.0036**	**0.0026**	**1.3124**

s: sample standard deviation, nd: not detected, considered as "0" for calculation of average and standard deviation

The remaining content of CH_2Cl_2 in the recovered bitumen after washing with 0.03 M HCl at different NaCl concentrations is showed in **Table 3.11**. For the acid washings, it can be noticed that the residual methylene chloride increased compared to the neutral washings (**Table 3.10**). Methylene chloride was detected in all the recovered bitumen samples.

Table 3.11 Methylene Chloride content in recovered bitumen – Cold Lake bitumen washing with 0.03 M HCl at different NaCl concentrations

Sample		**Absorbance C-Cl peak**	**Absorbance CH_2 peak**	**C-Cl/CH_2 peak ratio**	**C-Cl/CH_2 peak ratio**	**CH_2Cl_2 content in bitumen by FTIR** [%] w/w
0.03 M HCl in deionized (MilliQ) water	1	0.0037	0.0409	0.22	0.09	0.9943
	2	0.0057	0.0435	0.15	0.13	1.8314
	3	0.0085	0.0441	0.22	0.19	3.5631
	Average	**0.0060**	**0.0428**	**0.1965**		**2.1296**
	s	**0.0024**	**0.0017**	**0.0386**		**1.3101**
10 mg/L NaCl in 0.03 M HCl	1	0.0026	0.0434	0.14	0.06	0.5410
	2	0.0099	0.0499	0.24	0.20	3.4250
	3	0.0179	0.0450	0.03	0.40	0.2900
	Average	**0.0101**	**0.0461**	**0.1374**	**0.2185**	**1.4187**
	s	**0.0076**	**0.0034**	**0.1031**	**0.1690**	**1.7421**
100 mg/L NaCl in 0.03 M HCl	1	0.0027	0.0411	0.16	0.06	0.5989
	2	0.0074	0.0442	0.19	0.17	2.7721
	3	0.0048	0.0434	0.13	0.11	1.4084
	Average	**0.0050**	**0.0429**	**0.1617**	**0.1146**	**1.5931**
	s	**0.0024**	**0.0016**	**0.0306**	**0.0515**	**1.0983**
1000 mg/L NaCl in 0.03 M HCl	1	0.003028	0.041071	0.19	0.07	0.7313
	2	0.009678	0.040234	0.26	0.24	5.1983
	3	0.005758	0.044956	0.13	0.13	1.7662
	Average	**0.0062**	**0.0421**	**0.1946**	**0.1474**	**2.5653**
	s	**0.0033**	**0.0025**	**0.0621**	**0.0851**	**2.3382**

s: sample standard deviation, nd: not detected, considered as "0" for calculation of average and standard deviation

3.3.2 Material Balance

Table 3.12 shows the material balance of the Cold Lake bitumen washing with deionized water at different concentrations of NaCl, according to the experimental procedure detailed in **Section 3.2.2**. The average and the standard deviation of each set of 3 experiments were reported in **Table 3.12**. It can be observed, that the percentage of difference between the mass of added bitumen and aqueous reagent compared to the mass of recovered bitumen, organic emulsion and aqueous phase

(**Equation 3.2**) for the individual experiments was found to be up to 4 % w/w, and for the set of experiments (average) the percentage of difference was placed below 2 % w/w. However, it is important to highlight that it was observed that there was a high variation in the recovered mass of the aqueous (M_{aq}) and organic emulsion (M_{org}) phases as can be noticed in their respective standard deviations. The recovered bitumen exhibited lower standard deviation within each set of experiments than the recovery of aqueous and organic phases.

The material balance corresponding to the washing with 0.03 M HCl at different NaCl concentrations is reported in **Table 3.13**. The percentage of difference between the mass of bitumen and acid solution added for the washing, and the recovered mass of bitumen, organic emulsion and aqueous phase samples, was found to be up to 2 % w/w. Like it was observed for the treatment with NaCl aqueous solutions, there was a high variation of the recovery of aqueous and organic emulsion phases for the acid washing. Similarly, the variation of the mass of recovered bitumen was found to be lower than the obtained in the recovered organic emulsion and aqueous phases.

Table 3.12 Material balance – Cold Lake bitumen washing with deionized water and different NaCl concentrations

Sample		**CH_2Cl_2 content in bitumen by FTIR**	**Bitumen** $M_{bit,0}$	**Methylene Chloride** [a]	**Aqueous Reagent** $M_{aq,0}$	**Recovered bitumen** M_{bit}	**Recovered aqueous solution** M_{aq}	**Recovered organic emulsion** M_{org}	**Total** $M_{bit}+M_{aq}+M_{org}$	**Diference**	**CH_2Cl_2 content in bitumen by FTIR**	**Corrected bitumen mass (Eq. 3.1)**	**Total mass corrected**	**Percentage of difference**
		[% w/w]	[g]	[mL]	[g]	[g]	[g]	[g]	[g]	(g)	[% w/w]	[g]	[g]	[% w/w]
Deionized (MilliQ) water	1	nd	20	100	100	16	62	43	121	0.00	nd	16	121	<1
	2	0.8655	20	100	100	17	68	37	122	0.87	1	17	122	<2
	3	nd	20	100	100	14	62	43	120	0.00	nd	14	120	<-1
	Average	**0.2885**	**20**	**100**	**100**	**16**	**64**	**41**	**121**	0.29	<1	**16**	**121**	**<1**
	s	**0.4997**	**0**	**0**	**0**	**1**	**4**	**3**	**1**	0.50	<1	**1**	**1**	**<1**
10 mg/L NaCl in deionized (MilliQ) water	1	0.083	20	100	100	15	83	23	121	0.08	<1	15	121	<1
	2	1.031	20	100	100	24	83	14	121	1.03	1	24	121	<1
	3	0.413	20	100	100	16	76	33	125	0.41	<1	16	125	4
	Average	**0.5090**	**20**	**100**	**100**	**18**	**81**	**23**	**122**	0.51	<1	**18**	**122**	**<2**
	s	**0.4813**	**0**	**0**	**0**	**4**	**3**	**8**	**2**	0.48	<1	**4**	**2**	**2**
100 mg/L NaCl in deionized (MilliQ) water	1	0.4134	20	100	100	16	88	16	120	0.41	<1	16	120	<1
	2	4.2617	20	100	100	17	51	52	119	4.26	2	16	118	-1
	2	2.6217	20	100	100	16	0	104	120	2.62	3	16	120	<-1
	Average	**2.4323**	**20**	**100**	**100**	**16**	**46**	**57**	**120**	2.43	2	**16**	**120**	**<-1**
	s	**1.9311**	**0**	**0**	**0**	**0**	**44**	**44**	**1**	1.93	2	**0**	**1**	**<1**
1000 mg/L NaCl in deionized (MilliQ) water	1	nd	20	100	100	15	91	16	121	0.00	nd	15	121	<1
	2	1.6424	20	100	100	15	74	30	119	1.64	2	15	119	<-1
	3	2.5944	20	100	100	17	30	76	122	2.59	3	16	121	1
	Average	**1.4123**	**20**	**100**	**100**	**15**	**65**	**40**	**121**	1.41	1	**15**	**120**	**<1**
	s	**1.3124**	**0**	**0**	**0**	**1**	**32**	**31**	**1**	1.31	1	**1**	**1**	**<1**

[a]: CH_2Cl_2 was not considered for material balance purposes, apart from correcting for the mass of bitumen based on residual solvent

[b]: sample standard deviation, nd: not detected, considered as “0” for calculation purposes

Table 3.13 Material balance – Cold Lake bitumen washing with 0.03 M HCl and different NaCl concentrations

Sample		Bitumen $M_{bit,0}$ [g]	Methylene Chloride [a] [mL]	Aqueous Reagent $M_{aq,0}$ [g]	Recovered bitumen M_{bit} [g]	Recovered aqueous solution M_{aq} [g]	Recovered organic emulsion M_{org} [g]	Total $M_{bit}+M_{aq}+M_{org}$ [g]	CH_2Cl_2 content in bitumen by FTIR [% w/w]	Corrected bitumen mass (Eq. 3.1) [g]	Total mass corrected [g]	Percentage of difference [% w/w]
0.03 M HCl in deionized (MilliQ) water	1	20	100	100	16	66	37	119	1	16	119	<1
	2	20	100	100	17	88	15	119	2	17	119	<1
	3	20	100	100	15	92	13	120	4	14	119	<1
	Average	**20**	**100**	**100**	**16**	**82**	**22**	**120**	2	**16**	**119**	**<1**
	s	**0**	**0**	**0**	**1**	**14**	**13**	**<1**	1	**1**	**1**	**<1**
10 mg/L NaCl in 0.03 M HCl	1	20	100	100	17	77	27	121	1	17	121	1
	2	20	100	100	15	80	27	122	3	15	121	<1
	3	20	100	100	15	86	19	120	<1	15	120	<1
	Average	**20**	**100**	**100**	**16**	**81**	**24**	**121**	1	**15**	**121**	**<1**
	s	**0**	**0**	**0**	**1**	**<5**	**<5**	**1**	2	**1**	**1**	**<1**
100 mg/L NaCl in 0.03 M HCl	1	20	100	100	18	83	22	123	1	18	123	2
	2	20	100	100	16	85	22	122	3	15	121	1
	3	20	100	100	17	83	22	122	1	17	122	<2
	Average	**20**	**100**	**100**	**17**	**84**	**22**	**122**	2	**17**	**122**	**<2**
	s	**0**	**0**	**0**	**1.00**	**<1**	**<1**	**<1**	1	**1**	**1**	**<1**
1000 mg/L NaCl in 0.03 M HCl	1	20	100	100	17	90	14	121	1	17	120	<1
	2	20	100	100	18	85	19	122	5	17	121	<1
	3	20	100	100	18	86	19	122	2	18	122	<2
	Average	**20**	**100**	**100**	**17**	**87**	**17**	**121**	3	**17**	**121**	**<1**
	s	**0**	**0**	**0**	**<1**	**<3**	**<3**	**<1**	2	**<1**	**<1**	**1**

[a]: CH_2Cl_2 was not considered for material balance purposes, apart from correcting for the mass of bitumen based on residual solvent

[b]: sample standard deviation

3.3.3 Anion determination

The anion determination in the aqueous solution after the bitumen washing, was done by HPLC as mentioned in **Section 3.2.3.1**. The anions that were not observed in the chromatogram were reported as "not detected" (nd), while those anions that were detected but in such low concentrations that could not be quantified, were reported as "not quantified" (nq). The **Figure 3.3** shows the chromatogram corresponding to the recovered aqueous phase sample after washing the bitumen with a 1000 mg/L NaCl solution. It can be observed the around the first minute the release of cations since they are ejected first from the column. At 2.5 minutes, the peak corresponding to CO_3^{2-}/HCO_3^- can be noticed, followed by the Cl^- peak at 3.6 minutes. Then, at 9.8 minutes the HPO_4^{2-} are released from the column. Finally, at 14 minutes approximately it is detected the release of SO_4^{2-}; however, the intensity of the peak is too low that it could not be quantified.

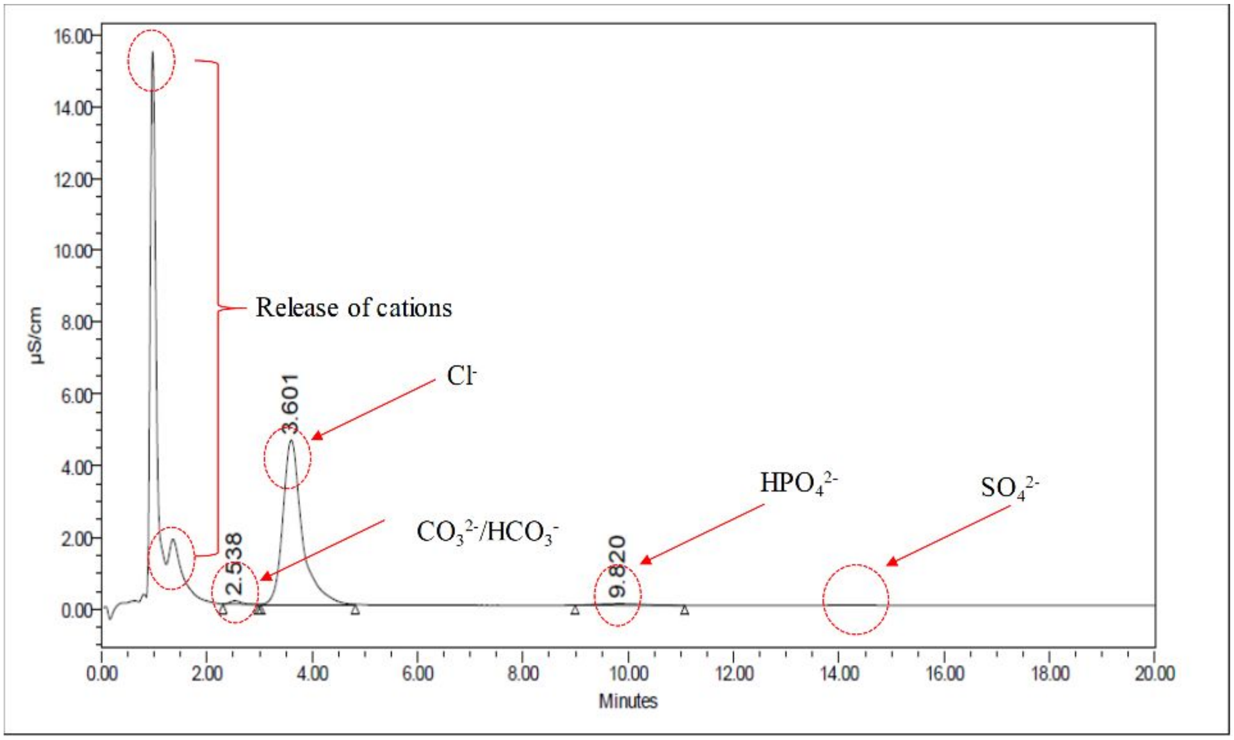

Figure 3.3 HPLC chromatogram for one recovered aqueous sample – Cold Lake bitumen washing with deionized water (1000 mg/l NaCl)

3.3.3.1 Anion determination on aqueous solutions at different concentrations of NaCl

The anion determination for the bitumen washing with deionized water can be observed in **Table 3.14**. In all the aqueous solutions, Cl^- was mainly quantified. It can be observed that chlorides were washed from the bitumen in higher amount (784 ± 362 µg/g bitumen) and CO_3^{2-} and HPO_4^{2-} were washed from the bitumen in lower extent (113 ± 22 and 41 ± 5 µg/g bitumen respectively). SO_4^{2-} was detected but the intensity of the peaks in the chromatogram was too low that it could not be quantified. No other anions were detected.

Due to the high concentration of Cl^-, the samples were diluted before being analyzed by HPLC. Therefore, it is important to highlight that a percentage of error of the obtained results might be introduced based on the linearity of the calibration curve and the dilution of the sample.

Table 3.14 Anion determination on aqueous phase – Cold Lake bitumen washing with deionized water

Sample	**Deionized water**							
	1		**2**		**3**		**Average**	
Recovered aqueous solution M_{aq} [g]	62		68		62		64 ± 3	
Initial bitumen [g]	20		20		20		20	
Added Cl^- [µg/g bitumen]	-		-		-		-	
Anion	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass Mx,aq [µg/g bitumen]**
F^-	nd	-	nd	-	nd	-	nd	-
CO_3^{2-}	35	108	40	136	30	93	35 ± 5	113 ± 22
Cl^-	217	673	350	1188	158	490	242 ± 98	784 ± 362
NO_2^-	nd	-	nd	-	nd	-	nd	-
Br^-	nd	-	nd	-	nd	-	nd	-
NO_3^-	nd	-	nd	-	nd	-	nd	-
HPO_4^{2-}	14	43	13	45	11	35	13 ± 1	41 ± 5
SO_4^{2-}	nq	-	nq	-	nq	-	nq	-

nd: not detected element, nq: not quantified element, -: not calculated

The **Table 3.15** shows the anion determination for the washing of Cold Lake bitumen with an aqueous solution of 10 mg/L NaCl. The anions that could be quantified were Cl^- (833 ± 306 µg/g bitumen), the removal of CO_3^{2-} and HPO_4^{2-} decreased in comparison to the bitumen washing with deionized water. It is important to mention that an amount of 24 ± 1 µg/g bitumen of Cl^- was added with the NaCl. The removal of Cl^- were by far higher than the added amount of this anion.

Table 3.15 Anion determination on aqueous phase – Cold Lake bitumen washing with aqueous solution (10 mg/L NaCl)

Sample	10 mg/L of NaCl in deionized water (6 mg Cl^-/L approximate)							
	1		2		3		Average	
Recovered aqueous solution M_{aq} [g]	83		83		76		81 ± 4	
Initial bitumen [g]	20		20		20		20	
Added Cl^- [µg/g bitumen]	25		25		23		24 ± 1	
Anion	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass Mx,aq [µg/g bitumen]
F^-	nd	-	nd	-	nd	-	nd	-
CO_3^{2-}	25	105	28	115	18	67	24 ± 5	96 ± 26
Cl^-	191	791	279	1157	145	549	205 ± 68	833 ± 306
NO_2^-	nd	-	nd	-	nd	-	nd	-
Br^-	nd	-	nd	-	nd	-	nd	-
NO_3^-	nd	-	nd	-	nd	-	nd	-
HPO_4^{2-}	7	30	4	15	1	4	4 ± 3	16 ± <1
SO_4^{2-}	nq	-	nq	-	nq	-	nq	-

nd: not detected element, nq: not quantified element, -: not calculated

The **Table 3.16** shows the anion determination for the washings performed with aqueous solution at 100 mg/L of NaCl. Higher concentrations of Cl^- was removed from the bitumen (1582 ± 703 µg/g bitumen), considering that the addition of Cl^- related to the NaCl concentrations in the initial aqueous solutions was 212 ± 80 µg/g bitumen. On the other hand, HPO_4^{2-} was detected in one of the samples, representing a washing from the bitumen of less than 1 µg/g bitumen. SO_4^{2-}, as in the previous experiments, was detected but the intensity of the peaks in the chromatogram was too low that it could not be quantified. Again, a reduction in the amount of CO_3^{2-} washed from the bitumen was observed.

Table 3.16 Anion determination on aqueous phase – Cold Lake bitumen washing with aqueous solution (100 mg/L NaCl)

Sample	**100 mg/L of NaCl in deionized water (61 mg Cl^-/L approximate)**							
	1		**2**		**3**		**Average**	
Recovered aqueous solution M_{aq} [g]	0		88		51		46 ± 44	
Initial bitumen [g]	20		20		20		20	
Added Cl^- [µg/g bitumen]	-		268		156		212 ± 80	
Anion	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**
F^-	nd	-	nd	-	nd	-	nd	-
CO_3^{2-}	nd	-	24	104	29	73	26 ± 3	89 ± 22
Cl^-	-	-	473	2079	426	1085	449 ± 33	1582 ± 703
NO_2^-	-	-	nd	-	nd	-	nd	-
Br^-	-	-	nd	-	nd	-	nd	-
NO_3^-	-	-	nd	-	nd	-	nd	-
HPO_4^{2-}	-	-	1	6	nd	-	<1	<1
SO_4^{2-}	-	-	nq	-	nq	-	nq	-

nd: not detected element, nq: not quantified element, -: not calculated

For the washing with aqueous solution containing 1000 mg/L of NaCl (**Table 3.17**) it can be observed that only Cl^- was quantified. The removal of Cl^- during these experiments was considerably higher than the obtained with lower NaCl concentrations (40112 ± 19798 µg/g bitumen). The amount of Cl^- added with the NaCl was estimated in 1973 ± 955 µg/g bitumen, and the removal of this anion was determined to be 4011 ± 1980 µg/g bitumen in the aqueous phase samples.

Other anions such as HPO_4^- and SO_4^{2-} were detected when analyzing samples diluted up to 100 times. However, due to the low concentration of these anions, they could not be quantified. On the other hand, CO_3^{2-} were not detected in any of the samples. It seems that at high Cl^- concentrations, the anions of HPO_4^-, SO_4^{2-} and CO_3^{2-} were not detected by the instrument. This could be related to the saturation of the column due to the Cl^- content.

Table 3.17 Anion determination on aqueous phase – Cold Lake bitumen washing with aqueous solution (1000 mg/L NaCl)

Sample	1000 mg/L of NaCl in deionized water (607 mg Cl^-/L approximate)							
	1		2		3		Average	
Recovered aqueous solution M_{aq} [g]	91		74		30		65 ± 31	
Initial bitumen [g]	20		20		20		20	
Added Cl^- [µg/g bitumen]	2762		2246		911		1973 ± 955	
Anion	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**
F^-	nd	-	nd	-	nd	-	nd	-
CO_3^{2-}	nd	-	nd	-	nd	-	nd	-
Cl^-	1264	5749	1197	4429	1237	1856	1233 ± 34	4011 ± 1980
NO_2^-	nd	-	nd	-	nd	-	nd	-
Br^-	nd	-	nd	-	nd	-	nd	-
NO_3^-	nd	-	nd	-	nd	-	nd	-
HPO_4^{2-}	nq	-	nq	-	nq	-	nq	-
SO_4^{2-}	nq	-	nd	-	nq	-	nq	-

nd: not detected element, nq: not quantified element, -: not calculated

3.3.3.2 Anion determination on acid solutions at different concentrations of NaCl

The anion determination corresponding to the Cold Lake washing with 0.03 M HCl at different NaCl concentrations were analyzed by HPLC, and the results reported in this section.

The **Table 3.18** shows the anion determination for the washing of Cold Lake bitumen with 0.03 M HCl. Mainly Cl^- were quantified in the recovered aqueous solutions (6898 ± 1481 µg/g bitumen). Considering that the addition of Cl^- within the HCl was 4353 ± 729 µg/g bitumen, the analyzed samples resulted in a Cl^- removal of over 1000 µg/g bitumen.

On the other hand, CO_3^{2-} was removed in lower extent (176 ± 62 µg/g bitumen), while HPO_4^{2-} was only detected in one of the samples with a concentration of 2 mg/L. Finally, while SO_4^{2-} were detected, it could not be quantified due to the low intensity of the peaks.

Table 3.18 Anion determination on acid solution – Cold Lake bitumen washing with acid solution (0.03 M HCl)

Sample	0.03 M HCl (1064 mgCl$^-$/L approximate)							
	1		2		3		Average	
Recovered aqueous solution M_{aq} [g]	66		88		92		82 ± 11	
Initial bitumen [g]	20		20		20		20	
Added Cl^- [µg/g bitumen]	3521		4660		4877		4353 ± 729	
Anion	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]
F^-	nd	-	nd	-	nd	-	nd	-
CO_3^{2-}	36	120	55	242	36	165	43 ± 11	176 ± 62
Cl^-	1594	5275	1654	7244	1784	8176	1677 ± 97	6898 ± 1481
NO_2^-	nd	-	nd	-	nd	-	nd	-
Br^-	nd	-	nd	-	nd	-	nd	-
NO_3^-	nd	-	nd	-	nd	-	nd	-
HPO_4^{2-}	nd	-	nd	-	2	7	1 ± 1	2 ± 4
SO_4^{2-}	nq	-	nq	-	nq	-	nq	-

nd: not detected element, nq: not quantified element, -: not calculated

In **Table 3.19**, corresponding to the washing with 0.03 M HCl and 10 mg/L of NaCl, it was noticed that similar to the findings for the 0.03 M HCl (no NaCl added), only Cl^- and CO_3^{2-} were quantified (SO_4^{2-} were detected but the intensity of the peak was not enough to be quantified). However, it was observed that the removal of Cl- was higher (7131 ± 213 µg/g bitumen). Taking into account that around 4339 ± 248 µg/g bitumen were added due to the HCl and NaCl presents in the solution, all the analyzed samples were found to have a considerable removal of this element.

Table 3.19 Anion determination on acid solution – Cold Lake bitumen washing with acid solution (0.03 M HCl, 10 mg/L NaCl)

Sample	10 mg/L of NaCl in 0.03 M HCl (1070 mg Cl^-/L approximate)							
	1		2		3		Average	
Recovered aqueous solution M_{aq} [g]	77		80		86		81 ± 4	
Initial bitumen [g]	20		20		20		20	
Added Cl^- [µg/g bitumen]	4126		4280		4611		4339 ± 248	
Anion	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass Mx,aq [µg/g bitumen]
F^-	nd	-	nd	-	nd	-	nd	-
CO_3^{2-}	44	168	38	152	42	181	41 ± 3	167 ± 11
Cl^-	1753	6759	1765	7060	1758	7574	1758 ± 6	7131 ± 213
NO_2^-	nd	-	nd	-	nd	-	nd	-
Br^-	nd	-	nd	-	nd	-	nd	-
NO_3^-	nd	-	nd	-	nd	-	nd	-
HPO_4^{2-}	nd	-	nd	-	nd	-	nd	-
SO_4^{2-}	nq	-	nd	-	nq	-	nq	-

nd: not detected element, nq: not quantified element, -: not calculated

In the **Table 3.20** the same behavior was observed, with the bitumen washing using 0.03 M HCl and 100 mg/L NaCl. The increase in the removal of Cl^- occurred, and the decrease of the CO_3^{2-} removal was also noticed.

Table 3.20 Anion determination on acid solution - Cold Lake bitumen washing with acid solution (0.03 M HCl, 100 mg/L NaCl)

Sample	100 mg/L of NaCl in 0.03 M HCl (1125 mg Cl^-/L approximate)							
	1		2		3		Average	
Recovered aqueous solution M_{aq} [g]	83		85		83		84 ± 1	
Initial bitumen [g]	20		20		20		20	
Added Cl^- [µg/g bitumen]	-		4755		4668		4712 ± 61	
Anion	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]
F^-	nd	-	nd	-	nd	-	nd	-
CO_3^{2-}	31	128	42	179	28	118	34 ± 7	141 ± 33
Cl^-	1627	6755	1877	7931	1904	7901	1803 ± 152	7529 ± 670
NO_2^-	nd	-	nd	-	nd	-	nd	-
Br^-	nd	-	nd	-	nd	-	nd	-
NO_3^-	nd	-	nd	-	nd	-	nd	-
HPO_4^{2-}	nd	-	nd	-	nd	-	nd	-
SO_4^{2-}	nq	-	nq	-	nq	-	nq	-

nd: not detected element, nq: not quantified element, -: not calculated

The washing of the bitumen with acid solution (0.03 M HCl) and 1000 mg/L of NaCl was reported in **Table 3.21**. In this case, only Cl^- were obtained (over 11000 µg/g bitumen). The removal of this anion exhibited the same response as the initial Cl^- concentration increased; while around 7000 µg/g bitumen of Cl^- were added, it was obtained a removal of over 4000 µg/g bitumen through the bitumen washing. On the other hand, it was observed that, no CO_3^{2-} was detected in any of the samples, while HPO_4^- and SO_4^{2-} were detected but only in the analyzed samples after dilution, and in such low concentrations that it could not be quantified.

It seemed that, as it was mentioned in the anion determination of the washings with 1000 mg/L of NaCl dissolved in water, the high concentration of Cl^- given the contribution of HCl and NaCl in the acid solutions, led to the column saturation and, therefore, the quantification of anions present in low concentrations (such as CO_3^{2-}, HPO_4^- and SO_4^{2-}) was not possible.

Table 3.21 Anion determination on acid solution - Cold Lake bitumen washing with acid solution (0.03 M HCl, 1000 mg/L NaCl)

Anion	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [μg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [μg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [μg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [μg/g bitumen]
F^-	nd	-	nd	-	nd	-	nd	-
CO_3^{2-}	nd	-	nd	-	nd	-	nd	-
Cl^-	2473	11129	2799	11928	2717	11657	2663 ± 170	11571 ± 406
NO_2^-	nd	-	nd	-	nd	-	nd	-
Br^-	nd	-	nd	-	nd	-	nd	-
NO_3^-	nd	-	nd	-	nd	-	nd	-
HPO_4^{2-}	nq	-	nq	-	nq	-	nq	-
SO_4^{2-}	nd	-	nq	-	nd	-	nq	-

nd: not detected element, nq: not quantified element, -: not calculated

3.3.4 Cation determination on aqueous and acid samples

The aqueous phase samples obtained from the separation after the bitumen washing with aqueous and acid solutions, were analyzed by ICP-OES to determine the cation content. The spectra obtained by the ICP-OES were checked to determine interferences that might affect the cation quantification. Elements such as Ar, C, H, N and O may be observed as part of the baseline, and this could be observed in elements such as Al, Li and Mo. The discussion of the spectra for one of the samples is attached for reference (**Figure 3.4**):

Aluminum: The observed peak was well defined, with no interferences in the analyzed wavelength.

Arsenic: The observed emission was too close to the baseline, that it could not be properly quantified.

Boron: The observed peak was well defined, with no interferences in the analyzed wavelength.

Barium: No interferences were observed.

Calcium: No interferences were observed.

Cadmium: The observed emission was associated to baseline noise: therefore, this element was not detected.

Cobalt: The observed emission was too close to the baseline, that it could not be properly quantified for most of the samples.

Chromium: The intensity of the emission was too low that according to the built calibration curve this element was not quantified.

Copper: There was no interference regarding this element.

Iron: There was no interference regarding this element.

Potassium: No interferences were observed

Lithium: A well defined peak was observed. As it was mentioned previously, background emissions of Ar could be observed, and considered as part of the baseline of the spectrum.

Magnesium: No interferences were observed.

Manganese: No interferences were observed.

Molybdenum: The observed peak was well defined, neighbor emissions are considered as part of the baseline, so no interferences were observed.

Sodium: No interferences were observed

Nickel: Emission was not observed at the specified wavelength (216.55 nm).

Phosphorous: The observed emission was associated to baseline noise: therefore, this element was not detected. However, for different samples, it was observed a well-defined peak with low intensity, being quantified below 1 mg/L.

Lead: The element was not detected.

Antimony: The observed emission was associated to baseline noise: therefore, this element was not detected.

Selenium: The element was not detected.

Silicon: No interference was observed for this element.

Titanium: It was observed that there was emission at the wavelength of interest. However, due to the intensity of the emission, it was not quantified.

Vanadium: The observed emission was associated to baseline noise: therefore, this element was not detected.

Zinc: The observed emission was associated to baseline noise: therefore, this element was not detected. However, in the case of the acid washing samples, a clear peak was obtained, and the quantification of the element could be made.

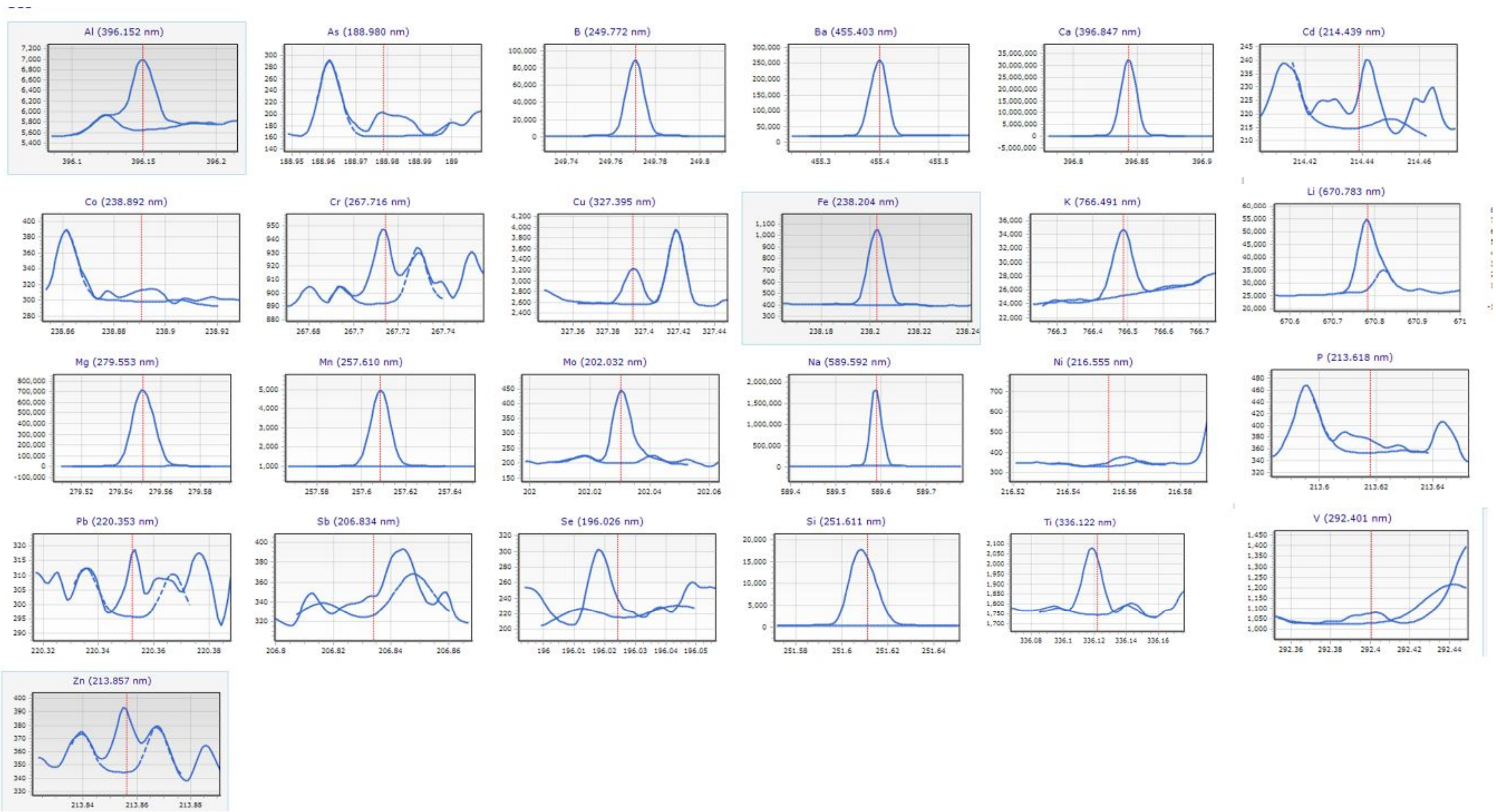
Al (396.152 nm)
As (188.980 nm)
B (249.772 nm)
Ba (455.403 nm)
Ca (396.847 nm)
Cd (214.439 nm)
Co (238.892 nm)
Cr (267.716 nm)
Cu (327.395 nm)
Fe (238.204 nm)
K (766.491 nm)
Li (670.783 nm)
Mg (279.553 nm)
Mn (257.610 nm)
Mo (202.032 nm)
Na (589.592 nm)
Ni (216.555 nm)
P (213.618 nm)
Pb (220.353 nm)
Sb (206.834 nm)
Se (196.026 nm)
Si (251.611 nm)
Ti (336.122 nm)
V (292.401 nm)
Zn (213.857 nm)

Figure 3.4 ICP-OES Spectra for aqueous phase sample - Cold Lake bitumen washing with deionized water

3.3.4.1 Cation determination on aqueous solutions at different NaCl concentrations

The cation determination corresponding to the washing of Cold Lake bitumen with deionized water at different NaCl concentrations is reported from **Table 3.22** to **Table 3.25**. It can be observed that for all the performed washings, most of the elements were detected at low concentrations (<1 mg/L), while others were not detected or could not be quantified, as it was explained previously (**Figure 3.4**). Cations of elements such as B, Ca, K, and Si were obtained in concentrations up to 6 mg/L. For example, the washing of Ca resulted in a removal from 16 ± 8 to 21 ± 1 µg/g bitumen for the washing with deionized water at different NaCl concentrations. The cation of element K was removed from 8 ± 1 to 11 ± 6 µg/g bitumen. Considering the sample standard deviation of the different experiments, it is clear that the removal of these cations remained nearly constant for the different washings, and the same behavior was observed for the cations B, Mg, and Si.

On the other hand, the cations of Na exhibited the highest removal from the bitumen, increasing the amount removed while increasing the NaCl concentration in the initial aqueous solution from 0 to 100 mg/L. As it was observed in the **Section 3.3.3.1**, the removal of Na showed the same trend of the anion Cl^-. The washings with deionized water and the solutions of deionized water with 10 mg/L NaCl and 100 mg/L (**Table 3.22**, **Table 3.23** and **Table 3.24**), exhibited a removal of Na of 248 ± 129, 257 ± 105 and 503 ± 216 µg/g bitumen respectively; while the amount of added Na in the corresponding initial aqueous solutions was 0, 16 ± 1, 90 ± 51 µg/g bitumen respectively. It is clear that the removal of Na in these washings increased while increasing the NaCl concentration in the aqueous solution.

But, regarding the washing with the aqueous solution with 1000 mg/L of NaCl in deionized water the total removal of cations of Na was determined as 1200 ± µg/g bitumen (**Table 3.25**), being the amount of added Na equal to 1277 ± 619 µg/g bitumen. It seems that at the highest NaCl concentration, the removal of Na from the bitumen was not observed.

Table 3.22 Cation determination on aqueous phase – Cold Lake bitumen washing with deionized water

Sample	Deionized water							
	1		2		3		Average	
Recovered aqueous solution M_{aq} [g]	62		68		62		64 ± 3	
Initial bitumen [g]	20		20		20		20	
Added Na$^+$ [µg/g bitumen]	-		-		-		-	
Cation of element	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass Mx,aq [µg/g bitumen]**
Al	<1	<1	<1	<1	<1	<1	<1	<1
As	nq	-	nq	-	nq	-	nq	nq
B	3	8	3	10	2	7	3	8 ± 1
Ba	<1	<1	<1	<1	<1	<1	<1	<1
Ca	6	18	5	17	6	18	5	17 ± 1
Cd	nd	-	nd	-	nd	-	nd	-
Co	nq	-	nq	-	nq	-	nq	-
Cr	nq	-	nq	-	nq	-	nq	-
Cu	<1	<1	nd	-	nd	-	nd	-
Fe	<1	<1	<1	<1	nd	-	nd	-
K	3	9	5	16	2	6	3 ± 1	10 ± 5
Li	<1	<1	<1	1	<1	<1	<1	<1
Mg	1	4	1	3	1	3	1	3 ± 1
Mn	<1	<1	nd	-	<1	<1	<1	<1
Mo	<1	<1	<1	<1	<1	<1	<1	<1
Na	67	207	115	392	47	144	76 ± 35	248 ± 129
Ni	nd	-	nd	-	nd	-	nd	-
P	<1	<1	<1	<1	nd	-	nd	-
Pb	nd	-	nd	-	nd	-	nd	-
Sb	nd	-	nd	-	nd	-	nd	-
Se	nd	-	nd	-	nd	-	nd	-
Si	2	6	3	9	1	<1	2 ± 1	7 ± 2
Ti	nq	-	nq	-	nq	-	nq	-
V	nd	-	nd	-	nd	-	nd	-
Zn	nd	-	nd	-	nd	-	nd	-

nd: not detected, nq: not quantified; considered as "0" for calculation purposes, -: not calculated

Table 3.23 Cation determination on aqueous phase – Cold Lake bitumen washing with aqueous solution (10 mg/L NaCl)

Sample	**10 mg/L of NaCl in deionized water (4 mg Na^+/L approximate)**							
	1		**2**		**3**		**Average**	
Recovered aqueous solution M_{aq} [g]	83		83		76		81 ± 4	
Initial bitumen [g]	20		20		20		20	
Added Na^+ [µg/g bitumen]	17		17		15		16 ± 1	
Cation of element	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass Mx,aq [µg/g bitumen]**
Al	<1	<1	<1	<1	<1	<1	<1	<1
As	nq	-	nq	-	nq	-	nq	-
B	2	10	3	12	2	9	2	10 ± 2
Ba	nd	-	<1	<1	<1	<1	nd	-
Ca	5	21	5	22	5	20	5	21 ± 1
Cd	nd	-	nd	-	nd	-	nd	-
Co	nq	-	nq	-	nq	-	nq	-
Cr	nq	-	nq	-	nq	-	nq	-
Cu	nd	-	nd	-	nd	-	nd	-
Fe	nd	-	<1	<1	nd	-	nd	-
K	2	9	3	14	1	6	2 ± 1	9 ± 4
Li	<1	<1	<1	<1	<1	<1	nd	-
Mg	1	4	1	4	1	3	1	4 ± 1
Mn	nd	-	nd	-	<1	<1	nd	-
Mo	nd	-	<1	<1	<1	<1	nd	-
Na	57	238	89	370	43	163	63 ± 24	257 ± 105
Ni	nd	-	nd	-	nd	-	nd	-
P	nd	-	nd	-	nd	-	nd	-
Pb	nd	-	nd	-	<1	<1	nd	-
Sb	nd	-	nd	-	nd	-	nd	-
Se	nd	-	nd	-	nd	-	nd	-
Si	1	6	2	8	1	3	1 ± 1	6 ± 2
Ti	nq	-	nq	-	nq	-	nq	-
V	nd	-	nd	-	nd	-	nd	-
Zn	nd	-	nd	-	nd	-	nd	-

nd: not detected, nq: not quantified; considered as “0” for calculation purposes, -: not calculated

Table 3.24 Cation determination on aqueous phase – Cold Lake bitumen washing with aqueous solution (100 mg/L NaCl)

Sample	**100 mg/L of NaCl in deionized water (39 mg Na$^+$/L approximate)**							
	1		**2**		**3**		**Average**	
Recovered aqueous solution M_{aq} [g]	0		88		51		46 ± 44	
Initial bitumen [g]	20		20		20		20	
Added Na$^+$ [µg/g bitumen]	-		172		99		90 ± 51	
Cation of element	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**
Al	-	-	<1	<1	<1	<1	<1	<1
As	-	-	nq	-	nq	-	nq	-
B	-	-	3	15	3	7	3	11 ± 6
Ba	-	-	<1	<1	<1	<1	nd	-
Ca	-	-	6	27	5	13	6 ± 1	20 ± 10
Cd	-	-	nd	-	nd	-	nd	-
Co	-	-	nq	-	nq	-	nq	-
Cr	-	-	nq	-	nq	-	nq	-
Cu	-	-	<1	<1	nd	-	nd	-
Fe	-	-	<1	<1	<1	<1	nd	-
K	-	-	5	20	4	11	4	16 ± 7
Li	-	-	<1	1	<1	<1	nd	-
Mg	-	-	1	5	1	2	1	4 ± 2
Mn	-	-	<1	<1	nd	-	nd	-
Mo	-	-	1	<1	1	<1	1	<1
Na	-	-	149	656	138	350	143 ± 8	503 ± 216
Ni	-	-	nd	-	nd	-	nd	-
P	-	-	nd	-	<1	<1	<1	<1
Pb	-	-	nd	-	nd	-	nd	-
Sb	-	-	nd	-	nd	-	nd	-
Se	-	-	nd	-	nd	-	nd	-
Si	-	-	2	11	2	6	2	8 ± 3
Ti	-	-	nq	-	nq	-	nq	-
V	-	-	nd	-	nd	-	nd	-
Zn	-	-	nd	-	nd	-	nd	-

nd: not detected, nq: not quantified; considered as “0” for calculation purposes, -: not calculated

Table 3.25 Cation determination on aqueous phase – Cold Lake bitumen washing with aqueous solution (1000 mg/L NaCl)

Sample	1000 mg/L of NaCl in deionized water (393 mg Na^+/L approximate)							
	1		2		3		Average	
Recovered aqueous solution M_{aq} [g]	91		74		30		65 ± 31	
Initial bitumen [g]	20		20		20		20	
Added Na^+ [µg/g bitumen]	1788		1454		590		1277 ± 619	
Cation of element	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]
Al	<1	<1	<1	<1	<1	<1	<1	<1
As	nq	-	nq	-	nq	-	nq	nq
B	3	13	3	10	3	4	3	9 ± 4
Ba	<1	<1	<1	<1	<1	<1	<1	<1
Ca	5	23	5	19	5	7	5	16 ± 8
Cd	nd	-	nd	-	nd	-	nd	-
Co	nq	-	nq	-	nq	-	nq	-
Cr	nq	-	nq	-	nq	-	nq	-
Cu	<1	<1	nd	-	nd	-	<1	<1
Fe	<1	<1	<1	<1	<1	<1	<1	<1
K	4	20	3	10	3	5	4 ± 1	12 ± 8
Li	<1	1	<1	<1	<1	<1	<1	<1
Mg	1	5	<1	3	1	1	1	3 ± 2
Mn	<1	<1	nd	-	nd	-	<1	<1
Mo	<1	<1	<1	<1	<1	<1	<1	<1
Na	376	1708	361	1343	372	548	370 ± 8	1200 ± 593
Ni	nd	-	nd	-	nd	-	nd	-
P	<1	<1	nd	-	<1	<1	<1	<1
Pb	nd	-	nd	-	nd	-	nd	-
Sb	nd	-	nd	-	nd	-	nd	-
Se	nd	-	nd	-	nd	-	nd	-
Si	2	11	2	7	2	3	2	7 ± 4
Ti	nq	-	nq	-	nq	-	nq	-
V	nd	-	nd	-	nd	-	nd	-
Zn	nd	-	nd	-	nd	-	nd	-

nd: not detected, nq: not quantified; considered as “0” for calculation purposes, -: not calculated

3.3.4.2 Cation determination on acid solutions at different NaCl concentrations

The recovered aqueous phase after the washing with acid solutions at different NaCl concentrations was performed, was analyzed by ICP-OES to determine the cation content. The results are reported from **Table 3.26** to **Table 3.29**. Similar to the washings with neutral aqueous solutions (**Section 3.3.4.1**), it was observed that cations of the elements B, Ca, K and Si were quantified in the recovered aqueous samples. The removed amount of these cations was found to be like that removed with the washings with deionized water at different NaCl concentrations.

Regarding the removal of Na, it was observed an increasing trend in the removal of this cation while the NaCl increased in the acid solution (0.03 M HCl), removing 247 ± 70, 264 ± 35 and 413 ± 35 µg/g bitumen for the washings with this solution and 0, 16 ± 1, and 164 ± 2 mg/L of Na added respectively. However, for the highest NaCl concentration (1000 mg/L) it was observed that there was not removal of this element (1461 ± 67 µg/g bitumen vs 1710 ± 51 µg/g bitumen of Na added).

The rest of the cations were quantified in low concentrations (<1 mg/L). Others, such as As, Co, Cr and Ti, were detected but in such low concentration that they could not be quantified. And cations of Cd, Mo, Sb and V were not detected in the spectra.

Table 3.26 Cation determination on acid solution - Cold Lake bitumen washing with acid solution (0.03 M HCl)

Sample	0.03 M HCl in deionized (MilliQ) water							
	1		2		3		Average	
Recovered aqueous solution M_{aq} [g]	66		88		92		82 ± 11	
Initial bitumen [g]	20		20		20		20	
Added Na$^+$ [µg/g bitumen]	-		-		-		-	
Cation of element	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]
Al	<1	<1	<1	<1	<1	<1	<1	<1
As	nq	-	nq	-	nq	<1	nq	-
B	3	9	2	11	3	13	3	11 ± 2
Ba	<1	<1	<1	<1	<1	<1	<1	<1
Ca	3	10	2	9	3	14	3	11 ± 3
Cd	nd	-	nd	-	nd	-	nd	-
Co	nq	-	nq	-	nq	-	nq	-
Cr	nq	-	nq	-	nq	-	nq	-
Cu	<1	<1	<1	<1	<1	<1	<1	<1
Fe	<1	<1	<1	<1	<1	1	<1	<1
K	3	10	2	8	3	14	3	10 ± 3
Li	<1	<1	<1	<1	<1	<1	<1	<1
Mg	<1	2	<1	1	<1	2	<1	2
Mn	nd	-	nd	-	<1	<1	<1	-
Mo	nd	-	nd	-	nd	-	nd	-
Na	67	222	44	194	71	326	61 ± 15	247 ± 70
Ni	<1	<1	<1	<1	<1	<1	<1	<1
P	<1	<1	nd	-	nd	-	<1	<1
Pb	<1	<1	<1	<1	nd	-	<1	<1
Sb	nd	-	<1	<1	nd	-	nd	-
Se	<1	<1	<1	<1	<1	<1	<1	<1
Si	<1	2	<1	2	<1	3	<1	3 ± 1
Ti	nq	-	nq	-	nq	-	nq	-
V	nd	-	nd	-	nd	-	nd	-
Zn	<1	<1	<1	<1	<1	<1	<1	<1

nd: not detected, nq: not quantified; considered as “0” for calculation purposes, -: not calculated

Table 3.27 Cation determination on acid solution - Cold Lake bitumen washing with acid solution (0.03 M HCl, 10 mg/L NaCl)

Sample	**10 mg/L of NaCl in 0.03 M HCl**							
	1		**2**		**3**		**Average**	
Recovered aqueous solution M_{aq} [g]	77		80		86		81 ± 4	
Initial bitumen [g]	20		20		20		20	
Added Na^+ [µg/g bitumen]	15		16		17		16 ± 1	
Cation of element	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**
Al	<1	<1	<1	<1	<1	<1	<1	<1
As	nq	nq	nq	-	nq	-	nq	-
B	3	11	2	10	2	11	3	10 ± 1
Ba	<1	<1	<1	<1	<1	<1	<1	<1
Ca	3	11	3	12	2	10	3	11 ± 1
Cd	nd	-	nd	-	nd	-	nd	-
Co	nq	-	nq	-	nq	-	nq	-
Cr	nq	-	nq	-	nq	-	nq	-
Cu	<1	<1	<1	<1	<1	<1	<1	<1
Fe	<1	<1	<1	<1	<1	<1	<1	<1
K	2	9	3	11	3	11	3	10 ± 1
Li	<1	<1	<1	<1	<1	<1	<1	<1
Mg	<1	2	<1	2	<1	1	<1	2
Mn	nd	-	nd	-	nd	-	nd	-
Mo	nd	-	nd	-	nd	-	nd	-
Na	58	223	71	285	66	283	65 ± 7	264 ± 35
Ni	<1	<1	<1	<1	<1	<1	<1	<1
P	<1	<1	nd	-	nd	-	nd	-
Pb	nd	-	<1	<1	<1	<1	<1	<1
Sb	nd	-	<1	<1	<1	<1	<1	<1
Se	nd	-	nd	<1	nd	-	<1	<1
Si	<1	2	<1	3	<1	3	<1	3
Ti	nq	-	nq	-	nq	-	nq	-
V	nd	-	nd	-	nd	-	nd	-
Zn	<1	<1	<1	<1	<1	<1	<1	<1

nd: not detected, nq: not quantified; considered as “0” for calculation purposes, -: not calculated

Table 3.28 Cation determination on acid solution - Cold Lake bitumen washing with acid solution (0.03 M HCl, 100 mg/L NaCl)

Sample	**100 mg/L of NaCl in 0.03 M HCl**							
	1		**2**		**3**		**Average**	
Recovered aqueous solution M_{aq} [g]	83		85		83		84 ± 1	
Initial bitumen [g]	20		20		20		20	
Added Na^+ [µg/g bitumen]	162		165		162		164 ± 2	
Cation of element	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**
Al	<1	<1	<1	<1	<1	<1	<1	<1
As	nq	-	nq	-	nq	-	nq	-
B	3	11	3	12	3	11	3	11 ± 1
Ba	<1	<1	<1	<1	<1	<1	<1	<1
Ca	3	12	3	11	3	14	3	12 ± 2
Cd	nd	-	nd	-	nd	-	nd	-
Co	nq	-	nq	-	nq	-	nq	-
Cr	nq	-	nq	-	nq	-	nq	-
Cu	<1	<1	<1	<1	<1	<1	<1	<1
Fe	<1	<1	<1	<1	<1	1	<1	<1
K	3	13	3	11	4	15	3	13 ± 2
Li	<1	<1	<1	<1	<1	<1	<1	<1
Mg	<1	2	<1	1	<1	2	<1	2
Mn	nd	-	nd	-	<1	<1	<1	<1
Mo	nd	-	nd	-	nd	-	nd	-
Na	94	392	92	393	109	453	99 ± 9	413 ± 35
Ni	<1	<1	<1	<1	<1	<1	<1	<1
P	<1	<1	<1	<1	<1	<1	<1	<1
Pb	nd	-	nd	-	nd	-	nd	-
Sb	nd	-	nd	-	nd	-	nd	-
Se	<1	<1	<1	<1	<1	<1	<1	<1
Si	<1	<1	<1	3	<1	3	<1	3
Ti	nq	-	nq	-	nq	-	nq	-
V	nd	-	nd	-	nd	-	nd	-
Zn	<1	<1	<1	<1	<1	<1	<1	<1

nd: not detected, nq: not quantified; considered as “0” for calculation purposes, -: not calculated

Table 3.29 Cation determination on acid solution - Cold Lake bitumen washing with acid solution (0.03 M HCl, 1000 mg/L NaCl)

Sample	1000 mg/L of NaCl in deionized (MilliQ) water							
	1		2		3		Average	
Recovered aqueous solution M_{aq} [g]	90		85		86		87 ± 2	
Initial bitumen [g]	20		20		20		20	
Added Na^+ [µg/g bitumen]	1769		1675		1686		1710 ± 51	
Cation of element	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**
Al	<1	<1	<1	<1	<1	<1	<1	<1
As	nq	-	nq	-	nq	-	nq	-
B	2	11	3	11	2	10	2 ± 0	11 ± 1
Ba	<1	<1	<1	<1	<1	<1	<1	<1
Ca	3	12	3	14	2	7	3 ± 1	11 ± 3
Cd	nd	-	nd	-	nd	-	nd	-
Co	nq	-	nq	-	nq	-	nq	-
Cr	nq	-	nq	-	nq	-	nq	-
Cu	<1	<1	<1	<1	<1	<1	<1	<1
Fe	<1	<1	<1	1	<1	<1	<1	<1
K	3	15	3	12	2	9	3 ± 1	12 ± 3
Li	<1	<1	<1	<1	<1	<1	<1	<1
Mg	<1	2	<1	3	<1	1	<1	2 ± 1
Mn	nd	-	nd	-	nd	-	nd	-
Mo	nd	-	nd	-	nd	-	nd	-
Na	314	1415	361	1538	333	1430	336 ± 23	1461 ± 67
Ni	<1	<1	<1	<1	<1	<1	<1	<1
P	<1	<1	<1	<1	<1	<1	<1	<1
Pb	<1	<1	nd	-	<1	<1	<1	<1
Sb	<1	<1	nd	-	<1	<1	<1	<1
Se	<1	<1	nd	-	<1	<1	<1	<1
Si	<1	3	<1	3	<1	2	<1	3 ± 1
Ti	nq	-	nq	-	nq	-	nq	-
V	nd	-	nd	-	nd	-	nd	-
Zn	<1	<1	<1	<1	<1	<1	<1	<1

nd: not detected, nq: not quantified; considered as “0” for calculation purposes, -: not calculated

3.3.5 pH and conductivity on aqueous solutions

All the aqueous solutions recovered after the separation of phases were taken to measure pH and conductivity. The **Table 3.30** shows the results corresponding to the bitumen washing with deionized water at different NaCl concentrations; additionally, the Cl^- concentration determined by HPLC as well as the calculated Cl^- concentration based on the calibration curve of the conductivity meter is attached. It can be noticed that the Cl- concentration obtained by HPLC is consistently higher than the one obtained by the benchtop conductivity meter. However, the trend observed in both set of results is the same.

Table 3.30 pH and conductivity on aqueous solutions – Cold Lake bitumen washing with deionized water at different NaCl concentrations

Sample		pH	Conductivity [µS/cm]	Cl^- concentration (HPLC) [mg/L]	Calculated Cl^- concentration * [mg/L]
Deionized (MilliQ) water	1	6.85	285	217	102
	2	7.63	443	350	152
	3	7.16	166	158	65
	Average	7.21	298	242	106
	s	0.32	113	80	36
10 mg/L of NaCl in deionized (MilliQ) water	1	6.94	481	185	164
	2	7.58	362	273	126
	3	7.19	170	139	66
	Average	7.24	338	199	119
	s	0.26	128	56	40
100 mg/L of NaCl in deionized (MilliQ) water	1	7.50	557	413	188
	2	7.59	450	366	154
	3	-	-	-	-
	Average	7.55	504	390	171
	s	0.04	54	24	17
1000 mg/L of NaCl in deionized (MilliQ) water	1	7.60	2850	1264	910
	2	7.62	1116	1197	364
	3	7.54	786	1237	260
	Average	7.59	1584	1233	511
	s	0.03	905	28	285

s: sample standard deviation, *: based on the conductivity meter calibration curve, -: not determined/calculated

In the **Table 3.31** it can be found the results for the experiments corresponding to the bitumen washing with 0.03 M HCl at different NaCl concentrations.

Table 3.31 pH and conductivity on aqueous solutions – Cold Lake bitumen washing with 0.03 M HCl at different NaCl concentrations

Sample		**pH**	**Conductivity [mS/cm]**	**Cl^- concentration (HPLC) [mg/L]**	**Calculated Cl^- concentration * [mg/L]**
0.03 M HCl	1	1.73	6	1594	1902
	2	1.72	11	1654	3476
	3	1.77	12	1784	3791
	Average	1.74	10	1677	3056
	s	0.02	3	79	827
10 mg/L of NaCl in 0.03 M HCl	1	1.75	6	1753	1902
	2	1.77	6	1765	1902
	3	1.78	12	1758	3791
	Average	1.77	8	1759	2532
	s	0.01	3	5	891
100 mg/L of NaCl in 0.03 M HCl	1	1.77	6	1627	1902
	2	1.79	6	1877	1902
	3	1.76	10	1904	3161
	Average	1.77	7	1803	2322
	s	0.01	2	125	594
1000 mg/L of NaCl in 0.03 M HCl	1	1.75	9	2473	2846
	2	1.71	12	2799	3791
	3	1.77	13	2717	4106
	Average	1.74	11	2663	3581
	s	0.02	2	138	535

s: sample standard deviation, *: based on the conductivity meter calibration curve, -: not determined/calculated

3.3.6 Water content in bitumen

As it was mentioned in **Section 3.2.3.4**, the raw bitumen as well as some of the recovered bitumen samples after washing, were analyzed to determine the water content by Karl Fisher titration. On the other hand, elemental composition of the raw bitumen was determined. Three samples of Cold Lake bitumen were taken, and each sample was analyzed twice (**Table 3.32**). By using the oxygen content and as it was described in **Equation 3.9**, the water content was also determined based on this analysis. Additionally, in **Appendix 3.1**, experiments to determine the water content by gravimetry of the raw Cold Lake bitumen were performed. The results of water content through the three methods can be observed in **Table 3.33**.

Table 3.32 Elemental composition of Cold Lake bitumen

Sample*	Wt. (mg.)	%N	%C	%H	%S	%O
Cold Lake bitumen 01	1.61	0.39	66.63	10.71	3.52	18.75
Cold Lake bitumen 01	1.75	0.39	66.78	10.82	3.44	18.57
Cold Lake bitumen 02	1.89	0.38	66.42	10.88	3.58	18.75
Cold Lake bitumen 02	1.79	0.38	66.28	10.82	3.53	18.99
Cold Lake bitumen 03	1.53	0.39	66.22	10.61	3.53	19.25
Cold Lake bitumen 03	1.56	0.39	66.35	10.79	3.64	18.82
Average	**1.69**	**0.39**	**66.45**	**10.77**	**3.54**	**18.86**
s	**0.14**	**0.01**	**0.22**	**0.10**	**0.07**	**0.24**

s: sample standard deviation, *: three samples of Cold Lake were taken, and each sample was analyzed twice

Table 3.33 Water content determination in Cold Lake bitumen

Sample	***%water* determined by Karl-Fisher titration [%] w/w**	***%water* determined by gravimetry [%] w/w**	***%water* determined by oxygen content [%] w/w**
Cold Lake bitumen	9.29 ± 0.1	27.1 ± 1.9	20.1 ± 0.3

It can be observed that the water content in the raw bitumen was found to be considerably higher by gravimetry (>27% w/w) than the content determined by Karl-Fisher titration (>9 % w/w). It seems that the batch of Cold Lake bitumen used for the experiments, contained a lot of water, meaning this, that the Cold Lake bitumen that was used, consisted in a water-in-oil emulsion, with a high content of water. Additionally, some samples of recovered bitumen after washing were randomly chosen and its water content was analyzed by Karl Fisher titration and elemental content (**Table 3.34**). It was found that the recovered bitumen samples contained a very low amount of water. Since the emulsion layer was separated from the recovered bitumen as described in **Figure 3.1**, low water content was expected in these samples.

Table 3.34 Elemental composition of recovered bitumen samples, and water content based on oxygen content and by Karl Fisher titration

Recovered bitumen from	**Experiment**	**%N [%] w/w**	**%C [%] w/w**	**%H [%] w/w**	**%S [%] w/w**	**%O [%] w/w**	**%water based on oxygen content [%] w/w**	***%water* determined by Karl-Fisher titration [%] w/w**
Washing with deionized water	1	0.45	83.12	10.55	4.33	1.54	0.61	-
		0.47	83.19	10.66	4.43	1.25	0.29	-
Washing with 10 mg/L NaCl in deionized water	1	0.45	83.25	10.66	4.49	1.15	0.17	-
		0.47	83.12	10.69	4.52	1.20	0.23	-
Washing with 100 mg/L NaCl in deionized water	1	0.47	83.18	10.68	4.52	1.16	0.18	-
		0.46	83.24	10.70	4.51	1.09	0.10	0.04 ± 0.05
Washing with 1000 mg/L NaCl in deionized water	1	0.47	83.49	10.68	4.58	0.78	-0.24	0.05 ± 0.01
		0.49	83.48	10.67	4.58	0.78	-0.24	-
Washing with 0.03 M HCl and 10 mg/L NaCl	1	0.46	82.80	10.59	4.46	1.69	0.77	-
		0.46	82.72	10.77	4.42	1.64	0.72	-
Washing with 0.03 M HCl and 100 mg/L NaCl	1	0.46	82.61	10.57	4.44	1.91	1.02	-
		0.46	82.82	10.64	4.52	1.55	0.62	-
Washing with 0.03 M HCl and 100 mg/L NaCl	1	0.45	82.20	10.56	4.30	2.50	1.68	-
		0.46	82.33	10.59	4.46	2.17	1.31	-
Washing with 0.03 M HCl and 100 mg/L NaCl	1	0.46	82.69	10.50	4.46	1.88	0.99	-
		0.46	82.67	10.59	4.36	1.91	1.03	-
Average		**0.46**	**82.93**	**10.63**	**4.46**	**1.51**	**0.58**	-
s		**0.01**	**0.38**	**0.07**	**0.08**	**0.49**	**0.55**	-

s: sample standard deviation, -: not analyzed

3.3.7 Prediction of viscosity of recovered bitumen

The viscosity of the recovered bitumen was measured corrected based on the residual amount of methylene chloride. In **Table 3.35** can be found the measured viscosities of the recovered bitumen, and the viscosity calculated through the predictions A, B and C detailed in **Section 3.2.4.4**, for the washings with deionized water at different NaCl concentrations. It was observed a high variation between the predicted viscosity within each set of experiments for the applied methods. While viscosity prediction methods A and B led to similar results, from method C were predicted higher viscosity results.

Table 3.35 Viscosity prediction of recovered bitumen - Cold Lake bitumen washing with aqueous solution at different NaCl concentrations

Sample		Methylene chloride content [% w/w]	Measured viscosity at 20 °C μ_m [Pa.s]	Viscosity prediction A μ_B [Pa.s]	Viscosity prediction B μ_B [Pa.s]	Viscosity prediction C μ_B [Pa.s]
Deionized (MilliQ) water	1	nd	19	19	19	19
	2	1	5	6	5	10
	3	nd	38	38	39	38
	Average	**<1**	**20**	**21**	**21**	**22**
	s	**<1**	**14**	**16**	**17**	**14**
10 mg/L of NaCl in deionized (MilliQ) water	1	<1	59	60	60	70
	2	1	7	8	8	17
	3	<1	14	15	15	23
	Average	**<1**	**27**	**28**	**28**	**37**
	s	**<1**	**23**	**28**	**29**	**29**
100 mg/L of NaCl in deionized (MilliQ) water	1	<1	21	22	22	34
	2	2	7	15	4	154
	3	3	5	9	7	37
	Average	**2**	**11**	**15**	**11**	**75**
	s	**2**	**7**	**7**	**10**	**69**
1000 mg/L of NaCl in deionized (MilliQ) water	1	nd	87	87	87	89
	2	2	46	63	58	246
	3	3	7	11	9	47
	Average	**1**	**66**	**53**	**51**	**128**
	s	**1**	**33**	**39**	**40**	**105**

s: sample standard deviation

Comparison of each prediction method and the raw bitumen viscosity is shown in **Figure 3.5**.

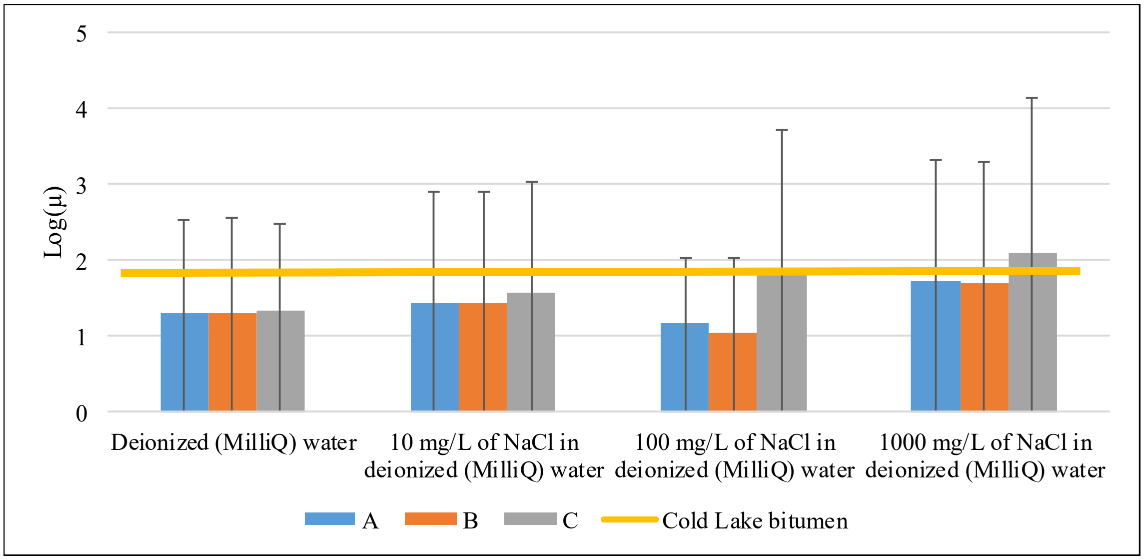

Figure 3.5 Predicted viscosity through methods A,B and C - Cold Lake bitumen washing with deionized water at different NaCl concentrations

It can be observed that the prediction of viscosity through methods A and B resulted in lower viscosity results compared to the ones obtained through prediction C. When the residual methylene was found to be up to 1% w/w, the three methods are in agreement, with similar predicted viscosities. However, when the residual methylene chloride content increases over 2% w/w, the method C estimated higher viscosity results compared to methods A and B. On the other hand, from prediction C, in some cases it was obtained viscosity results higher than the raw bitumen (washings with deionized water at 1000 mg/L NaCl).

The measured viscosity and the prediction of viscosity corresponding to the bitumen washing with acid NaCl solutions was reported in **Table 3.36**. Similarly, the comparison between the prediction methods is shown in **Figure 3.6**.

Table 3.36 Viscosity prediction of recovered bitumen - Cold Lake bitumen washing with aqueous solution at different NaCl concentrations

Sample		**Methylene chloride content [% w/w]**	**Measured viscosity at 20^{o}C μ_m [Pa.s]**	**Viscosity prediction A μ_B [Pa.s]**	**Viscosity prediction B μ_B [Pa.s]**	**Viscosity prediction C μ_B [Pa.s]**
0.03 M HCl	1	1	8	10	9	21
	2	2	5	6	5	18
	3	4	37	72	61	932
	Average	**2**	**17**	**30**	**25**	**324**
	s	**1**	**18**	**37**	**31**	**527**
10 mg/L of NaCl in 0.03 M HCl	1	1	6	7	7	11
	2	3	36	39	70	564
	3	<1	34	36	35	51
	Average	**1**	**25**	**27**	**37**	**208**
	s	**2**	**17**	**17**	**32**	**308**
100 mg/L of NaCl in 0.03 M HCl	1	1	5	6	5	9
	2	3	23	39	33	262
	3	1	3	4	4	10
	Average	**2**	**10**	**16**	**14**	**94**
	s	**1**	**11**	**19**	**16**	**146**
1000 mg/L of NaCl in 0.03 M HCl	1	1	12	14	13	26
	2	5	2	6	3	58
	3	2	2	3	2	7
	Average	**3**	**6**	**8**	**6**	**31**
	s	**2**	**6**	**6**	**6**	**26**

s: sample standard deviation

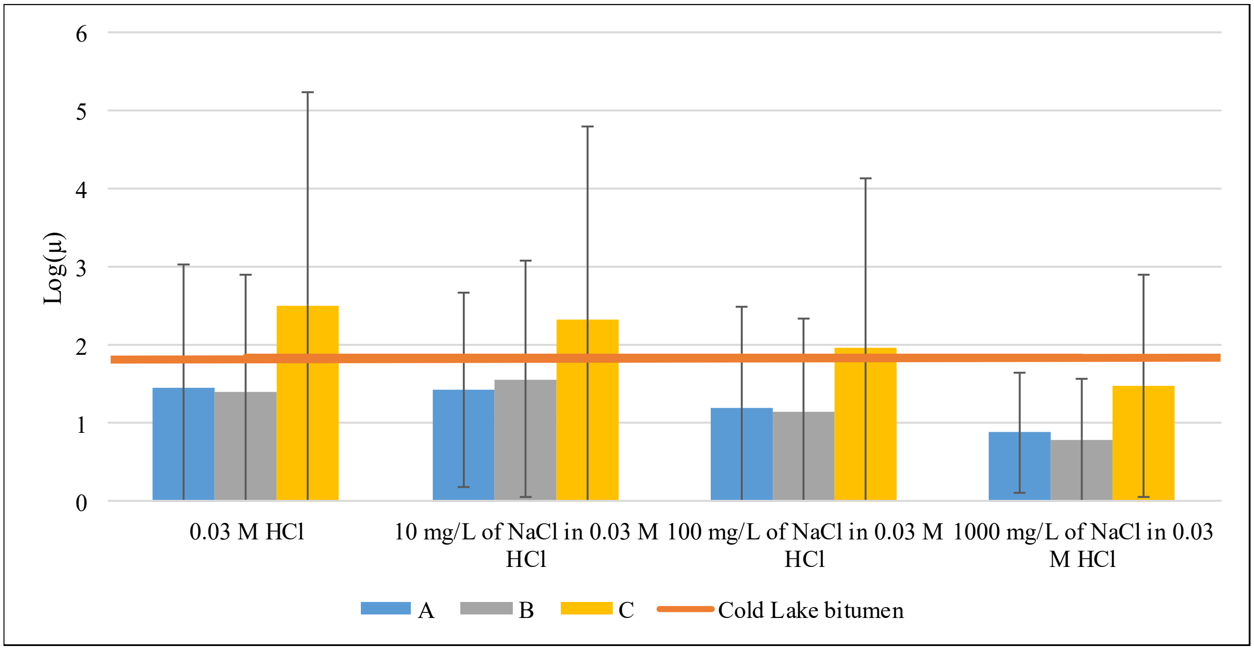

Figure 3.6 Predicted viscosity through methods A, B and C - Cold Lake bitumen washing with 0.03 M HCl at different NaCl concentrations

From **Figure 3.6** it can be noticed that prediction of viscosity through method C, resulted in values by far higher than the viscosity of the raw bitumen, while viscosity prediction through method A and B was lower than the viscosity of raw bitumen. As it was mentioned previously, the remaining content of methylene chloride, was highly influenced by the remaining content of methylene chloride. Additionally, it is important to mention the high variability of the results in each set of experiments.

3.3.8 Viscosity of bitumen and effect of water content

The **Table 3.33** showed the water content in the raw bitumen and two selected samples of recovered bitumen after washing was done. Considering that the raw bitumen exhibited high water content, correction of the measured viscosity based on the water content by Karl-Fisher titration was made to these samples as detailed in **Section 3.2.4.5** (**Table 3.37**).

Table 3.37 Viscosity correction of Cold Lake bitumen due to water content

Sample	Cold Lake viscosity at 20°C [Pa.s]	Corrected viscosity at 20°C μ_c [Pa.s]
1	69	63
2	88	81
3	79	72
Average	**79**	**72**
s	**8**	**7**

s: sample standard deviation

3.4 Discussion

3.4.1 Material Balance

From the material balance reported in the **Table 3.12** and **Table 3.13** for the washings performed with different aqueous solutions, it can be stated that the average losses for each set of experiments (triplicate), was found to be lower than 2 % w/w. Considering the nature of the experiments, involving the transfer and separation of the different phases, the losses can be considered to be within the acceptable range. However, it is important to highlight the variability in the mass of recovered aqueous and emulsion. It can be inferred that some not controlled variables affected the emulsion formation, and in consequence, the amount of resolved aqueous phase. The mass of recovered bitumen was consistently between 15 and 18 g (average) for the different experiments.

3.4.2 Ion removal from bitumen

The **Table 3.38** summarizes the ions that were obtained in concentrations >1 mg/L. When comparing the removed ions with the literature, it can be highlighted that the concentration of ions such as Ca^{2+} and Mg^{2+}, is directly related to the oil sands production process, being reported the presence of Ca^{2+} from 15 to 25 mg/L, Mg^{2+} from 5 to 10 mg/L, Na^{+} over 500 mg/L, and Cl^{-} from

75 to 550 mg/L for tailings pond water (Allen, 2008). On the other hand, the sum of Ca^{2+} and Mg^{2+} was estimated from 30-80 mg/L for oil sands process affected water (Sadrzadeh et al., 1983).

Considering that the washings were performed with bitumen (not oil sands), it was expected to obtain lower concentrations when comparing to OSPW. Concentrations reported in the literature indicates that bicarbonates (700- 1000 mg/L), sodium (500-700 mg/L), sulfates (200-300 mg/L), and chlorides (75- 550 mg/L) have the highest concentrations among all dissolved solids present in OSPW (Pourrezaei, 2013). The removal of ions of the elements Na and Cl in a higher extent compared to the rest of the quantified ions, supports these findings.

On the other hand, determination of trace elements in Athabasca oil sands is reported in the literature (Jacobs and Filby, 1983). It was found large differences in trace elements when analyzing different Athabasca oil sand samples (homogenized and non-homogenized), and the differences were attributed to the presence of entrained mineral matter and not due to the bitumen itself.

The low CO_3^{2-}/HCO_3^{2-} removal from the bitumen was observed during all the washings. This ion was removed from the bitumen mainly through the washings with deionized water and aqueous solutions with low NaCl concentrations. The same behavior was observed for the HPO_4^{2-} removal. Both ions are highly insoluble, and it seems that increase in Na^+ and Cl^- concentration due to the addition of NaCl, affected the ability to remove these ions from the bitumen. This behavior can occur due to solubility differences, while NaCl is highly soluble in water, CO_3^{2-}/HCO_3^- and HPO_4^{2-} are not. Additionally, solubility can be affected due to the “common ion effect”, where a common electrolyte present in the aqueous phase (in this case Na^+) can shift the equilibrium reaction to the undissociated ionic compounds, according to Le Châtelier’s principle (Benefield et al., 1982). It is also important to highlight that, when the concentration of ions of Na and Cl increased (due to the addition of NaCl and HCl, the detection of HPO_4^{2-}, SO_4^{2-} and CO_3^{2-} in most of the cases was achieved when analyzing samples diluted up to 100 times. The presence of high concentrations of Cl^- could have promoted the saturation of the column during the analysis and therefore, the detection of these low concentrated ions could not be achieved.

On the other hand, cations of Na were removed in higher proportion than the added amount of these ions in the aqueous solutions. After discounting the added amount of Na in the form of NaCl for the washings with deionized water with 0, 10 and 100 mg/L NaCl, it can be observed that the removed amount of this ion is around 250 µg/g bitumen. It seems that the addition of NaCl did not affect the removal of Na since it remained nearly constant. However, the washing performed with deionized water and 1000 mg/L NaCl showed that no Na was removed from the bitumen, since no additional cations of Na were observed in the aqueous phase. When comparing this removal to the quantification of Na made to the connate water in **Appendix 3.1**, it can be inferred that the presence of Na in the bitumen may be associated to connate water, and after reaching an equilibrium with the washing solution, no more ion transfer occurred.

Regarding the removal of Cl^-, it was observed that there was an increasing trend when the added Cl^- increased. This could be due to the presence of Cl^- in the form of NaCl, and other compounds such as $CaCl_2$, $MgCl_2$, $SrCl_2$, $FeCl_2$ and $FeCl_3$ (De Oliveira Souza et al., 2015), some of the corresponding cations were also found in the recovered aqueous samples such as those of elements Ca, Mg and Fe (**Table 3.38**). The removal of organic chlorides seems unlikely due to the low levels of chlorides bonded to the bitumen (Jacobs and Filby, 1983).

To further investigate this, the ions that were quantified in higher concentrations (Na and Cl) were compared to the concentration determined in the water that was separated from the Cold Lake and analyzed in **Appendix 3.1**. Based on the water content determined by Karl Fisher and by gravimetry, two theoretical dilution curves were built considering both water content results (**Figure 3.7**), by adding 100 g of water. Then, the curves were compared to the concentrations in the recovered water obtained from the washing of the bitumen with deionized water (**Table 3.14** and **Table 3.22**). This allowed to simulate the effect of the washing performed to the bitumen. The **Figure 3.7** shows the projection of dilution for the cations of Na based on the experimental concentration of the connate water (**Appendix 3.**1) as well as the experimental Na from the bitumen through the washing with deionized water.

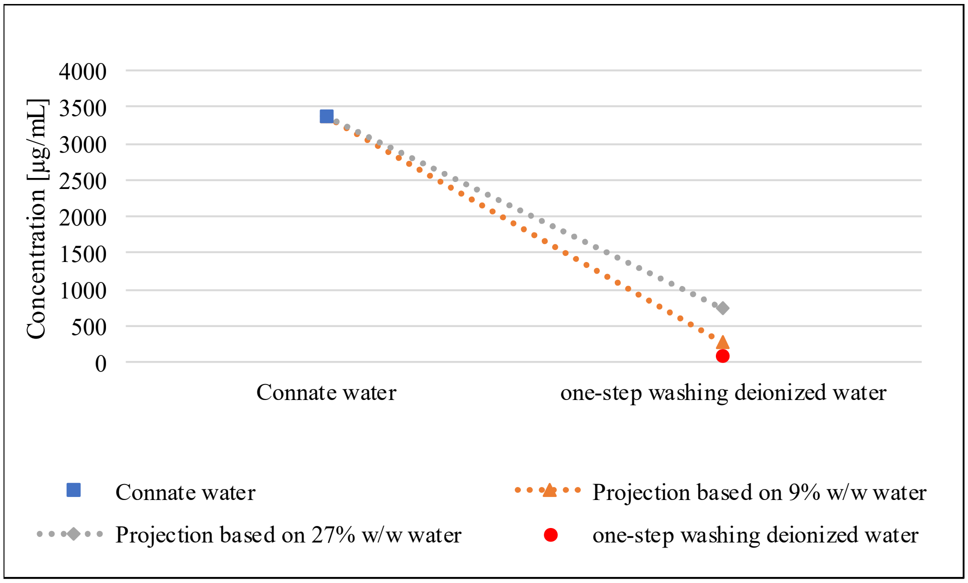

Figure 3.7 Concentration of cations of Na in water.
In the connate water is shown the measured concentration in the water separated from Cold Lake bitumen (**Appendix 3.1**). The one-step washing with deionized water shows the theoretical concentration that should have been found depending on the water content of the bitumen, as well as the actual experimental measured concentration after the bitumen washing.

It can be observed that, the concentration of cations of Na was lower than the theoretical dilution curve. Similarly, the **Figure 3.8** shows the projection of dilution of Cl^- based on the experimental concentration of the connate water, as well as the experimental concentration in the recovered aqueous phase after the bitumen washing. It can be observed that the concentration of Cl^- in the recovered water after the bitumen washing was found to be below the dilution profile of the connate water.

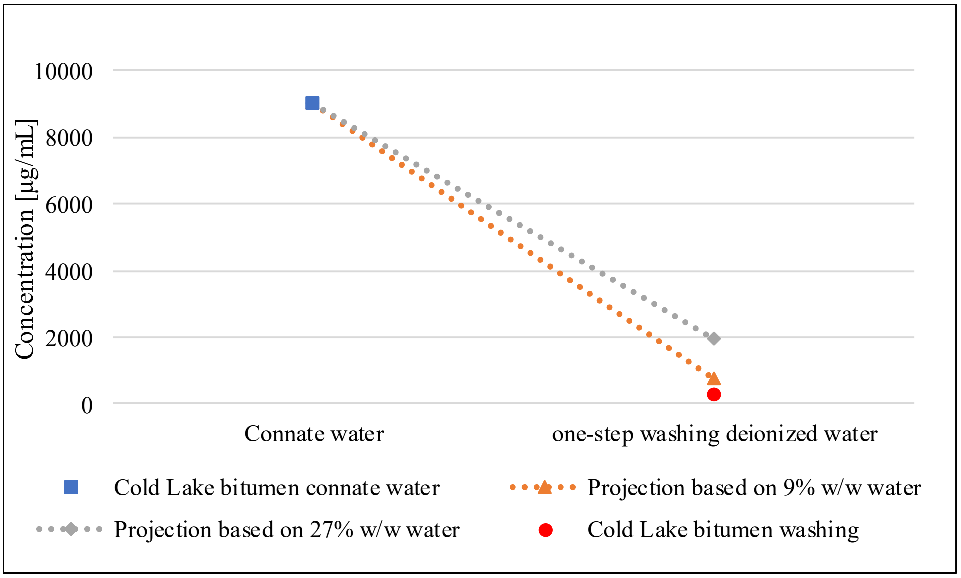

Figure 3.8 Concentration of Cl$^-$ in water.

In the connate water is shown the measured concentration in the water separated from Cold Lake bitumen (**Appendix 3.1**). The one-step washing with deionized water shows the theoretical concentration that should have been found depending on the water content of the bitumen, as well as the actual experimental measured concentration after the bitumen washing.

The **Figure 3.9** shows the concentration of cations of Ca in the connate water, as well as the theoretical concentrations based on the water content of the Cold Lake bitumen. It can be noticed that the experimental concentration of cations of Ca in the aqueous phase after the bitumen washing, was located between the two theoretical concentrations depending on the water content of the Cold Lake bitumen, closer to the projection basedon a water content of 9% w/w.

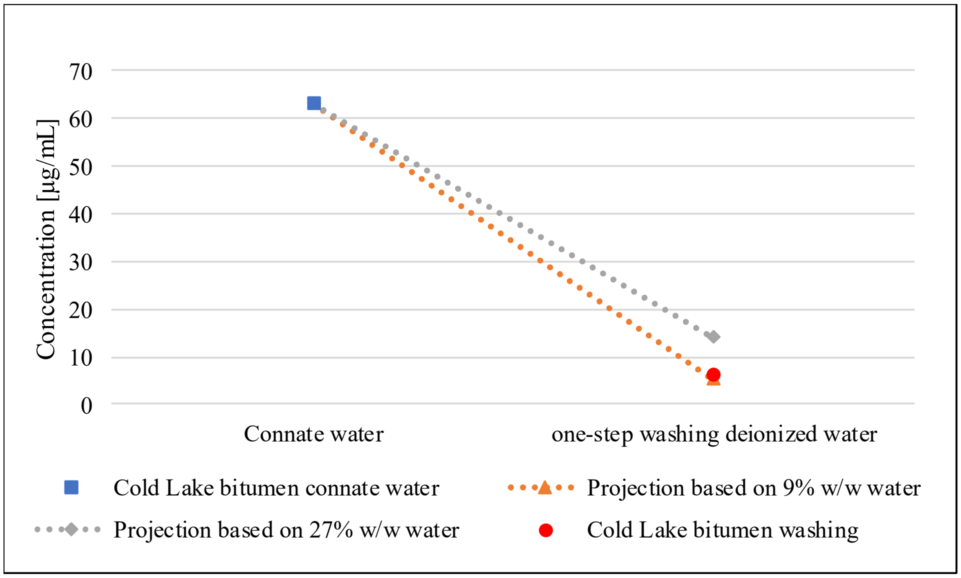

Figure 3.9 Concentration of cations of Ca in water.

In the connate water is shown the measured concentration in the water separated from Cold Lake bitumen (**Appendix 3.1**). The one-step washing with deionized water shows the theoretical concentration that should have been found depending on the water content of the bitumen, as well as the actual experimental measured concentration after the bitumen washing.

Based on the **Figure 3.7** to **Figure 3.9**, it appears that the assumption of complete mixing is not valid. If it was valid, the bitumen should have contained less than 9% w/w of water, or that the salts partitioned unequally between the water separated and retained during the **Appendix 3.1** analysis. In the case of the ions of Na (**Figure 3.7**) and Cl (**Figure 3.8**) the concentration in the recovered aqueous phase after the bitumen washing was consistently lower than the theoretical dilution curves; while in **Figure 3.8** the experimental concentration of cations of Ca exceeded the theoretical curve (6 µg/mL vs 5 µg/mL respectively).

The **Table 3.39** summarizes the main ions that were removed from the bitumen after performing washings with 0.03 M HCl at different NaCl concentrations. It was observed an increase in the removal of CO_3^{2-}/HCO_3^- with the acid aqueous solutions in comparison to the washings with neutral aqueous solutions. The solubility of carbonates increases in acid media, this explains the higher presence of these anion in the recovered aqueous samples. However, in both cases (neutral and acid washing) when the Cl^- concentration increased due to the addition of NaCl, a decrease of the concentration of this anion was observed, being detected only in very diluted samples when the NaCl concentration was 1000 mg/L in the aqueous solutions. This could occur due to the saturation of the column when analyzing samples with high Cl^- concentrations.

Other cations of elements such as Ca, K and Na exhibited the same behavior explained for the washings with neutral aqueous solutions (**Table 3.38**). The removal of HPO_4^{2-} was barely detected in the acid washings compared to the neutral ones; it has been reported that the solubility of some phosphates vary inversely with the pH, demonstrating that the hydrogen ions play an important role in the solubility of this compound (Huffman et al., 1957).

The removal of Cl^-, as it was discussed for the washings with deionized water at different NaCl concentrations, showed an increasing trend when the concentration of NaCl increased. The extent of the removal was higher when acid aqueous solutions were applied for the washing, this can be related to the ability of the acid to disrupt some chemical weak interactions and promote the ion exchange (Gonzalez, 2015).

Table 3.38 Removal of ions – Cold Lake bitumen washing with deionized water at different NaCl concentrations

Sample	Deionized water		10 mg/L of NaCl in deionized water		100 mg/L of NaCl in deionized water		1000 mg/L of NaCl in deionized water	
	Average		Average		Average		Average	
Recovered aqueous solution M_{aq} [g]	64 ± 3		81 ± 4		46 ± 44		65 ± 31	
Initial bitumen [g]	20		20		20		20	
Added Na^+ [µg/g bitumen]	-		16 ± 1		90 ± 51		1277 ± 619	
Added Cl^- [µg/g bitumen]	-		24 ± 1		212 ± 80		1973 ± 955	
Ion	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]	Concentration $C_{x,aq}$ [mg/L]	Total mass $M_{x,aq}$ [µg/g bitumen]
CO_3^{2-}	35 ± 5	113 ± 22	24 ± 5	96 ± 26	26 ± 3	89 ± 22	nd	-
Cl^-	242 ± 98	784 ± 362	205 ± 68	833 ± 306	449 ± 33	1582 ± 703	12326 ± 335	40112 ± 19798
HPO_4^{2-}	13 ± 1	41 ± 5	4 ± 3	16 ± <1	<1	<1	nd	-
Ca^{2+}	5	17 ± 1	5	21 ± 1	6 ± 1	20 ± 10	5	16 ± 8
K^+	3 ± 1	10 ± 5	2 ± 1	9 ± 4	4	16 ± 7	4 ± 1	12 ± 8
Na^+	76 ± 35	248 ± 129	63 ± 24	257 ± 105	143 ± 8	503 ± 216	370 ± 8	1200 ± 593
Si^+	2 ± 1	7 ± 2	1 ± 1	6 ± 2	2	8 ± 3	2	7 ± 4
Mg^{2+}	1	3 ± 1	1	4 ± 1	1	4 ± 2	1	3 ± 2

nd: not detected element, -: not calculated

Table 3.39 Removal of ions – Cold Lake bitumen washing with 0.03 m HCl at different NaCl concentrations

Sample	**0.03 M HCl**		**10 mg/L of NaCl in 0.03 M HCl**		**100 mg/L of NaCl in 0.03 M HCl**		**1000 mg/L of NaCl in 0.03 M HCl**	
	Average		**Average**		**Average**		**Average**	
Recovered aqueous solution M_{aq} [g]	82 ± 11		81 ± 4		84 ± 1		87 ± 2	
Initial bitumen [g]	20		20		20		20	
Added Cl^- [µg/g bitumen]	4353 ± 729		4339 ± 248		4712 ± 61		7270 ± 219	
Added Na^+ [µg/g bitumen]	-		16 ± 1		164 ± 2		1710 ± 51	
Ion	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass Mx,aq [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass Mx,aq [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**
CO_3^{2-}	43 ± 11	176 ± 62	41 ± 3	167 ± 11	34 ± 7	141 ± 33	nd	-
Cl^-	1677 ± 97	6898 ± 1481	1758 ± 6	7131 ± 213	1803 ± 152	7529 ± 670	2663 ± 170	11571 ± 406
HPO_4^{2-}	1 ± 1	2 ± 4	nd	-	nd	-	nd	-
Ca^{2+}	3	11 ± 3	3	11 ± 1	3	12 ± 2	3 ± 1	11 ± 3
K^+	3	10 ± 3	3	10 ± 1	3	13 ± 2	3 ± 1	12 ± 3
Na^+	61 ± 15	247 ± 70	65 ± 7	264 ± 35	99 ± 9	413 ± 35	336 ± 23	1461 ± 67

nd: not detected element, -: not calculated

Regarding the pH and conductivity measurements, results reported in **Table 3.30** for the washings of Cold Lake bitumen with aqueous solutions at different NaCl concentrations, showed that there was little variation of pH between the samples obtained from the washing with deionized water and 10 mg/L NaCl (7.21 and 7.23 ± 0.3 respectively) and the samples obtained from the washings with 100 and 1000 mg/L NaCl (7.5 and 7.6 respectively). Considering the standard deviation of the first group of results, it can be said that the pH of the recovered aqueous samples remained neutral. Due to the low basicity of the Cl^- ion and given that this ion was found in higher concentration, it was expected that no pH variation would occur.

The pH and conductivity measurements for the washing of bitumen with 0.03 M HCl at different NaCl concentrations was reported in **Table 3.31**. Since pH is defined in terms of the hydrogen ion activity, and considering the HCl dissociation in H^+ and Cl^- ions, the pH can be calculated by (Karastogianni et al., 2016):

$$pH = -log_{10}[H^+]$$ **Equation 3.22**

Having a HCl concentration of 0.03 M, the pH of the initial aqueous solution is estimated in a pH of 1.5. The pH of the recovered aqueous phase samples was measured and remained between 1.7 and 1.8 approximately. Considering that some CO_3^{2-}/HCO_3^- was removed from the bitumen and transferred to the aqueous phase, and knowing that this ion exert a buffering effect on aqueous solutions (Strausz and Lown, 2003), the slight increase in the pH can be attributed to its presence.

The effect of anions and cations on soils pH has been studied (Tavakkoli et al., 2015), and it has been determined that the presence of cations Na^+, K^+, Mg^{2+}, and Ca^{2+}, as well as anions such as Cl^-, SO_3^{2-}, HCO_3^- and CO_3^{2-}, are usually found in alkaline soil, dominating in the pH range from 7.0 to 8.5. The presence of some of these ions also supports the increase of pH when compared to the initial aqueous solution.

Additionally, a comparison of the chloride concentration determined by the HPLC analyses and the calculated concentration using the calibration curve built for the pH/conductivity meter is made. The calibration curve of both instruments, the HPLC and the pH/conductivity meter, was made using standard solutions of NaCl. However, it was noticed that the differences between the HPLC and conductivity meter concentrations was more pronounced when analyzing samples with high concentrations of Cl^- (neutral solutions at 1000 mg/L NaCl and the acid aqueous solutions).

It can be also noticed that the sample standard deviation obtained from each set of experiments (**Table 3.30** and **Table 3.31**) was higher in the calculated Cl^- concentration from the conductivity meter for the same cases (high Cl^- concentration). This can be attributed to the cell size (K=1); at higher conductivities (order of mS/cm) it is recommended the use of larger cell sizes (K=10) (ISO 7888:1985:, 1985). For this reason, it can be considered that the HPLC results are more accurate, particularly for the acid aqueous measurements. The chloride concentration calculated indirectly from the conductivity can be used for reference purposes.

3.4.3 Viscosity of raw bitumen and recovered bitumen after washing

Methods for the prediction of the viscosity of liquids are less accurate than the methods for gases, especially for the estimation of viscosity of undefined petroleum fractions and crude oils. Errors of 20–50% or even 100% in prediction of liquid viscosity are not unusual (Riazi, 2005).The applied methods in this chapter (**Section 3.2.4.4**), considered the molar fraction of each component to predict the viscosity of the mixture, defined as component concentration, as well as the individual viscosity of each component (Mehrotra, 1990). In addition, the viscosity prediction through method C, considered the binary viscosity interaction between the solvent and the bitumen, the temperature and the density as contributors to determine the viscosity of the mixture.

The viscosity prediction of the bitumen (after correction of the solvent content) from the measured viscosity of the recovered bitumen was found to be highly variable, the standard deviation obtained from viscosity prediction methods A, B and C (**Table 3.35** and **Table 3.36**) indicated that, while all the equations are influenced by the solvent content, method C is more sensitive to any variation of this content.

The remaining content of methylene chloride was determined by FTIR (**Section 3.3.1**). It was determined up to 5% w/w of methylene chloride in the analyzed samples, with most of the results being between 2-4% w/w. According to the calibration curve for methylene chloride (**Section 3.2.5.4**) the relationship is not linear specially below 3% w/w of methylene chloride, this could lead to errors at low solvent concentrations; therefore, the investigation of the behavior of the curve in more detail between 0-3 % w/w might be necessary.

Through viscosity prediction methods A and B lower viscosity results were obtained, compared with method C which in some cases led to viscosity predictions higher than the raw bitumen. This indicates the high sensitivity of this method to the methylene chloride content.

The **Figure 3.5** provided some valuable information. Despite the variability of the predicted viscosity results through the different methods, two main observations can be pointed out: First, the average predicted viscosities were found to be lower than the viscosity of the raw bitumen, except by method C, which at 100 and 1000 mg/L of NaCl equaled or was higher than the raw bitumen viscosity. As it was mentioned previously, the high dependence of the method on the solvent content led to the obtention of results in some cases higher than the viscosity of the raw bitumen. Second, it was observed an increment in the average viscosity when the NaCl concentration of the aqueous phase increased; this behavior was consistently observed specifically in the viscosity prediction method C. It can be inferred that the washing of the bitumen, as it was pointed by Gonzalez (2015), reduced the viscosity of the bitumen. On the other hand, it can be stated that the increment of dissolved salts exerted a negative effect on the viscosity compared to the washings made with “cleaner” water (less concentration of dissolved salts).

Similarly, in the viscosity prediction after the washing of bitumen with acid solutions was obtained a high standard deviation, which made difficult the interpretation of the results. As it was mentioned previously, it is speculated that the determination of the remaining methylene chloride content could affect the calculations.

The **Figure 3.6** also provided important findings to be discussed: First, it could be observed that the average predicted viscosity in most of the cases was lower than the raw bitumen viscosity, except by the method C (this was observed also in **Figure 3.5** with the neutral washings). This supported the strong dependence of the prediction method to the solvent content compared to methods A and B. Regarding the behavior of the viscosity when increasing the dissolved salts content, the opposite trend was found in the acid washings; the average predicted viscosity tended to decrease when the NaCl concentration increased. Again, the conclusion posed by Gonzalez (2015) was supported since the predicted viscosity of the recovered bitumen through methods A and B (used in that study) were consistently lower than the raw bitumen viscosity. Regarding the decrease in the predicted viscosity when the NaCl concentration increased, it seems that the fact of being in an acid media caused the contrary effect to the viscosity. Even when it was not clear the reasons of this behavior, further investigation on this area might be recommended.

The viscosity seems to respond to some other variables not controlled in this study. The viscosity of organic liquids mixed with solvents has been subject of several studies (He et al., 2014; Li et al., 2016; Ma et al., 2016). Variables such as interfacial tension, nature of solvent, solubility and density are considered factors that affect the viscosity of organic liquids diluted by organic solvents. The prediction of viscosity in the presence of solvents poses a challenge, and the solvent itself affects considerably the binary viscosity interactions.

It is important to highlight also, as it was shown in the material balances for both the deionized water and acid washings (**Table 3.12** and **Table 3.13**), an emulsion resulted after the separation of phases. This emulsion, containing mainly water and bitumen, and traces of methylene chloride, was not further treated or analyzed. Knowing the nature and composition of the bitumen contained in the emulsion can be of interest, if there are differences between the recovered bitumen and the one contained in the emulsion. From the previous experimental work (Gonzalez, 2015), the asphaltenes content in the bitumen present in emulsion phase was higher than the asphaltenes content of the raw bitumen (52 vs 16.8 % w/w). This result might suggest that a migration of asphaltenes is occurring to the emulsion phase, and it can be speculated that the asphaltenes have an impact on the resulting viscosity.

3.5 Conclusions

The objective of this Chapter was to determine if the presence of ions in the water can influence the bitumen viscosity, by washing Cold Lake bitumen with different neutral and acid NaCl solutions. Analysis of anions and cations in the recovered aqueous phase, and viscosity determination through different methods were performed. Based on the findings, the conclusions are:

- The bitumen used for these experiments contained a high amount of water (>9 % w/w). This was confirmed by three different approaches: Karl Fisher titration, oxygen content and gravimetry. The water content influenced the viscosity of the raw bitumen, and the removal of the ions through washing from the connate water.

- The bitumen washing resulted in the removal of mainly NaCl (cations of Na and Cl^-) from the bitumen. The removal of cations of Na seemed to be equilibrium constrained, being nearly constant while increasing the NaCl concentration, and stopping once the equilibrium was reached.

- Anions such as HCO_3^-/CO_3^{2-} (expressed as CO_3^{2-}) and HPO_4^{2-} were removed in low extent (176 ± 62 µg CO_3^{2-}/g bitumen and 41 ± 5 µg HPO_4^{2-}/g bitumen). The removal of CO_3^{2-} was favored in the bitumen washing with 0.03 M HCl, while the higher removal of HPO_4^{2-} was obtained from the bitumen washing with deionized water. The increase of NaCl concentration decreased the removal of these anions, due to solubility and equilibrium constraints.

- Removal of cations was focused mainly on those of elements Ca and K, and it was not related to the increase of NaCl.

- The viscosity prediction of the bitumen after the washings exhibited a high variability, this was attributed to the high dependence of the applied methods to the solvent content. However, the average viscosity decreased when the NaCl concentration increased for neutral washings. The contrary effect was observed in the washings with 0.03 M HCl, where the average viscosity decreased when the NaCl concentration increased. Further investigation of the cause of this behavior was not made.

- The viscosity prediction of organic liquids depends of some variables not controlled during this study, such as interfacial interactions, solubility of compounds, nature of the solvent and binary viscosity interactions. Additionally, a fraction of the bitumen migrated to the obtained emulsion phase, possibly affecting the measured viscosity, and the predicted viscosity in consequence.

- The different viscosity prediction methods resulted in differences in the viscosity of the recovered bitumen, while two methods (Mehrotra, 1990; Riazi, 2005) estimated viscosities below the one obtained for the raw bitumen, the third method (Zachariah and de Klerk, 2017) predicted viscosity results in some cases higher than the raw bitumen viscosity. This confirmed that the third method, was more sensitive to the solvent content than the other two applied methods.

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4 EFFECT OF WATER WASHING ON COLD LAKE BITUMEN

ABSTRACT

In **Chapter 3**, it was found that the washing at room temperature of Cold Lake bitumen with neutral and acid solutions and different NaCl concentrations, led to the removal of quantifiable amounts of mainly cations of elements such as Na, Ca, K, and anions such as Cl^-, CO_3^{2-}/HCO_3^-, HPO_4^{2-} as well as the detection of SO_4^{2-}. These ions confirmed those ones reported in the literature for Oil Sands Process Affected Water (Allen, 2008; Huang, 2016; Li et al., 2017).

In this section, Cold Lake bitumen, was washed four times at 75ºC and an inert atmosphere. Separation of the aqueous and organic emulsion phases was performed before the following washing step. Analysis of the ion content (anions and cations), was done by High Liquid Performance Chromatography (HPLC) and Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), removal of the solvent from the organic emulsion phase and analysis of the water content and cation content was done. Finally, the cation determination of the raw bitumen and the recovered aqueous and organic phases were compared. Other properties of the bitumen were also investigated to determine if the ion removal affected them.

Removal of ions of Cl (996 ± 227 µg/g bitumen) and Na (415 ± 65 µg/g bitumen) was obtained. Cations of Ca, K were also removed. Ions of elements such as Ni, Ti, V and Zn were not removed. The presence of ions of B and Si could have originated occurred from borosilicate glassware. The removal of ions could be explained to come from the connate water; however, the ions were retained in some way in the organic phase.

Decrease of pH and conductivity, as well as a decrease in the Cl^- concentration occurred after each washing step, indicating that each washing reached an equilibrium stage, and further removal of ions was achieved when fresh water was added to the system.

Keywords: anion, cation, ion transfer, bitumen, washing, emulsion, ashing, ICP, HPLC, Cold Lake

4.1 Introduction

The effect of bitumen washing with neutral and acid solutions at known concentrations of a highly soluble salt (NaCl), was investigated. It was found that the Cold Lake bitumen used in the experiments had a high water content, and after the different washings were performed, mainly ions of elements Na and Cl were obtained. Also, anions such as HCO_3^-/CO_3^{2-}, HPO_4^{2-}, and cations of elements Ca and K were removed. Measurements of viscosity of the recovered organic phase was done, and prediction of the bitumen viscosity after treatment was performed through different methods; however, there was a high variation between the different approaches and a strong dependence on the remaining solvent content.

But, there are some other questions that need to be answered: To what extent are the removed ions linked only to the connate water? Is it possible to further remove ions when applying subsequent washing steps and separations instead of using a single stage washing? If we analyze the ion content in the raw bitumen, and the ion content in all the recovered aqueous phases and the final organic phase; will these contents be consistent? Can a washing temperature increase exert some effect on the ion removal?

In this chapter, it was of main interest to determine if water washing of Cold Lake bitumen in subsequent steps can promote the same ion removal observed in **Chapter 3**.

4.2 Experimental Section

4.2.1 Materials

The basic characterization of Cold Lake bitumen was reported in **Chapter 3, Table 3.1**. The rest of materials used in this study (see **Table 4.1**) were commercially obtained and used without any further purification. The washings were performed using deionized water obtained from a MilliPore Milli-Q Integral 5, with an ion conductivity of 1.28 ± 0.17 µS/cm and pH 7.04 ± 0.11. The deionized water was analyzed as a blank for calibration purposes and its ionic content was considered as baseline for the quantification that was made for anions (HPLC) and cations (ICP-OES).

Table 4.1 Material used during calibration and reaction stages

Compound	Formula	CASRN [a]	Mass fraction purity % [b]	Supplier
Toluene	C_6H_5-CH_3	108-88-3	99.9	Fisher Scientific
Argon	Ar	7440-37-1	99.999 [c]	Praxair
Nitrogen	N_2	7727-37-9	99.998 [c]	Praxair
Sodium Gluconate	$C_6H_{11}NaO_7$	527-07-1	≤100	Sigma Aldrich
Boric Acid	H_3BO_3	10043-35-3	≥90.0	Merck
Sodium Tetraborate Decahydrate	$Na_2B_4O_7 \cdot 10H_2O$	1303-96-4	≥99.5	Merck
Glycerin	$C_3H_8O_3$	56-81-5	≥99.5	Sigma Aldrich
Butanol	$C_4H_{10}O$	71-36-3	≥99.4	Anachemia
Acetonitrile	C_2H_3N	75-05-8	≥99.9	Sigma Aldrich
Sodium Fluoride	NaF	7681-49-4	≥99.5	Sigma Aldrich
Sodium Chloride	NaCl	7647-14-5	≥99.0	Fisher Scientific
Sodium Nitrite	$NaNO_2$	7632-00-0	≥97.0	Sigma Aldrich
Potassium Bromide	KBr	7758-02-3	99.9	Fisher Scientific
Sodium Nitrate	$NaNO_3$	7631-99-4	≥99.5	Merck
Potassium Phosphate Monobasic	KH_2PO_4	7778-77-0	≥99.0	Sigma Aldrich
Sodium Sulfate	Na_2SO_4	7757-82-6	≥99.0	Sigma Aldrich
Tetrahydrofuran	C_4H_8O	109-99-9	NA	Fisher Scientific
Hydranal ® Composite 5	NA	NA	NA	Fluka
ICP-OES wavelength calibration solution	NA	NA	NA	Agilent
TRACE-CERT multi-element standard solution 6 for ICP	NA	NA	NA	Agilent
Pentane	C_5H_{12}	109-66-0	99.6	Fisher Scientific
Nitric acid	HNO_3	7697-37-2	≥68.0	Fisher Scientific
Linear alkylbenzene sulfonic acid	$C_{12}H_{25}C_6H_4SO_3H$	27176-87-0	≥70.0	Sigma Aldrich
Ethyl alcohol	C_2H_6O	64-17-5	≤100	Commercial Alcohols
Hydrochloric Acid	HCl	7647-01-0	3.06 (1N)	Fisher Scientific
Carbon disulfide	CS_2	75-15-0	99.99	Fisher Scientific
pH buffer solution 4.0	NA	NA	3.99-4.01 [d]	Fisher Scientific
pH buffer solution 7.0	NA	NA	6.99-7.01 [d]	Fisher Scientific
Hydrogen	H_2	1333-74-0	99.999 [c]	Praxair
Helium	He	7440-59-7	99.999 [c]	Praxair
Air	-	132259-10-0	19.5-23.5 [e]	Praxair

[a] CASRN = Chemical Abstracts Services Registry Number, [b] This is the purity of the material guaranteed by the supplier; material was not further purified. [c] molar fraction purity %, [d] pH range, [e] molar % of O_2

4.2.2 Equipment and Procedure

The removal of ionic species from bitumen by stepwise water washing was performed through the following procedure:

100 g of bitumen was dissolved with 100 g of toluene in a 1000 mL round bottom flask. Both compounds were mixed and stirred at 500 rpm for 30 minutes at 75ºC under inert (N_2) atmosphere, to homogenize the mixture. The flask was connected to a top condenser cooled with a mixture of water/glycol at 3ºC supplied by a chiller Julabo model HE/F 25. Weighing was done using a Mettler Toledo ML-3002E/03 balance (capacity 3.2 kg, readability 0.1 g). For the stirring process a hot plate, Fisher Scientific model Isotemp and a Fisherbrand 38.1 mm octagonal stir bar, was used.

After 30 minutes, 100 g of MilliQ water was added and stirring at the previous conditions continued for 3 hours. Then, the sample was transferred to a 1000 mL separation funnel for 24 hours to improve the phase separation.

The phases were separated in free water and water/oil emulsion. The water/oil emulsion was washed again with 100 g of fresh MilliQ water and the same stirring and separation procedure was done, until four washing steps were completed (**Figure 4.1**).

To remove the toluene as well as decrease the water content from the water in oil emulsion, after the fourth washing step, the emulsion was taken to a Rotavap Heidolph for 12 hours at 45ºC and 70 kPa absolute. Due to the close boiling points of toluene and water, a mixture of toluene and some free water was recovered, however, not all the water was boiled off and transferred to the collector, some supernatant free water was observed in the organic phase (which at the same time still contained emulsified water). The toluene/water volume was transferred to a separation funnel and the toluene was separated from the water. The water was put together with the free recovered water from the organic phase for further analysis.

The free water phase obtained from each washing and the separation with the Rotovap was analyzed to determine anion content through High Performance Liquid Chromatography (HPLC). Cations were analyzed through Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). All the experiments were performed six times.

The organic phase was analyzed to determine water content through Karl Fisher titration. Also, it was analyzed by Fourier transform infrared (FTIR) spectroscopy and the asphaltenes content was determined. FTIR provided a chemical fingerprint of the oil, the asphaltenes content was measured to see whether the removal of ionic species affected the oil solubility characteristics. In addition, the cations of the organic phase samples were analyzed as explained in **Section 4.2.3.2**.

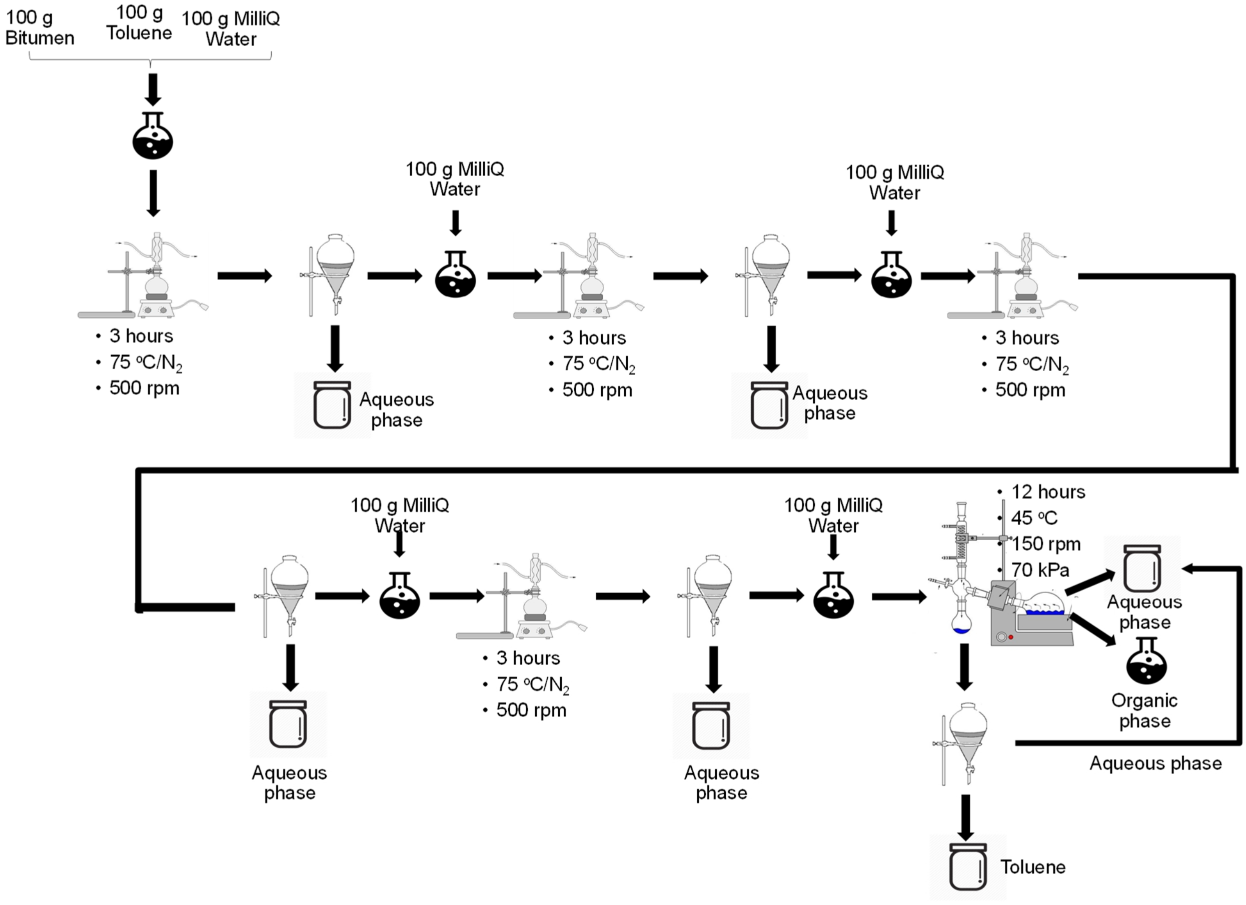

Figure 4.1 Experimental procedure – Washing of bitumen with MilliQ water

All the experiments were performed six times to have enough information and reduce the uncertainty associated with the results.

4.2.3 Analyses

4.2.3.1 Anion determination through HPLC

The aqueous phase was analyzed as it was described in **Chapter 3**, **Section 3.2.3.1**. The calibration and standards preparation can be found in **Chapter 3**, **Section 3.2.5.1**.

4.2.3.2 Cation determination through ICP-OES

Analysis of aqueous phase samples was performed as described in **Chapter 3**, **Section 3.2.3.2**. The samples were not further acidified for this analysis.

The organic samples (bitumen and organic emulsions) were prepared performing ashing with linear alkylbenzene sulfonic acid (LASA) in order to retain the volatile porphyrinic compounds, and ethyl alcohol to improve the dehydration during the procedure (Platteau and Carrillo, 1995). Acid digestion and dilution with deionized water was performed (**Figure 4.2**). The samples were analyzed under the same conditions of the aqueous phase samples. Each sample, as well as the raw bitumen, was measured in triplicate. The procedure was performed as follows:

A porcelain 100-mL crucible was cleaned adding 25 mL of 20% w/w HNO_3, covered with a watch glass and heated on a Fisher Scientific model Isotemp hot plate, until boiling was reached and kept for 15 minutes to allow the acid solution reflux on the walls of the crucible. Then, the acid solution was rejected, and the crucible was rinsed twice with hot MilliQ water. The procedure was repeated with fresh acid solution and fresh hot MilliQ water. After the treatment, the crucible was covered with clean watch glass and dried at 110ºC in a Carbolite CWF1100 oven for 30 minutes.

Since the organic phase contained a considerable amount of water (water in oil emulsion), it was pre-heated up to 90ºC and stirred at 350 rpm for 30 minutes to homogenize the emulsion before sampling, weighing before and after heating was performed to calculate the losses due to potential water evaporation, and it was determined that losses between 0.2 and 0.4% w/w occurred.

After homogenization, 9 g of sample was weighed in a clean crucible, then 0.9 g of linear alkylbenzene sulfonic acid (LASA) and 45 mL of ethyl alcohol were added. The crucible was placed in a BRANSON 2800 sonicator for 20 minutes to promote the contact between the acid, alcohol and organic phase. After sonicating the sample, the crucible was placed on a hot plate and progressively heated until 150ºC. After the aqueous phase is evaporated, heating continued up to 200ºC on the hot plate, then the crucible was transferred to the oven and was progressively heated (20 ºC/min) until 450ºC and kept for 30 minutes. Then, the crucible was taken from the oven and place on the hot plate at 200ºC in a fumehood, where 3 mL of HNO_3 was added drop by drop over the whole surface of the sample. Heating was continued until no brown nitrogen dioxide vapor was observed.

The crucible was taken to the oven and progressively heated (20ºC/min) until 550ºC. After reaching this temperature, the sample was kept in the oven for 2 hours. Then, the crucible was allowed to cool to room temperature, some drops of MilliQ water were added to moisten the ashes. First, 3 mL of HNO_3 and then 3 mL of HCl were added drop by drop and heating on the hot plate up to 70 ºC was applied to promote the dissolution of the ashes. When the ashes were dissolved, the solution was transferred to a 100 mL volumetric flask and diluted to the mark with MilliQ water, and then analyzed through Inductively Coupled Plasma – Optical Emision Spectrometry. The **Figure 4.2** illustrates the washing and ashing procedures respectively.

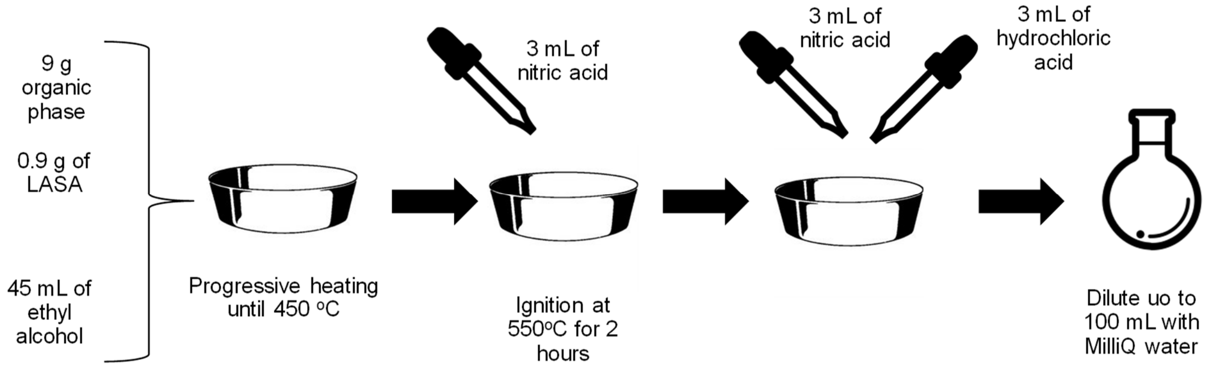

Figure 4.2 Ashing and acid digestion procedure

Standard solutions at different concentrations were prepared in order to build calibration curves. The calibration procedure can be found in **Chapter 3, Section 3.2.5.2**.

4.2.3.3 Water content in organic phase

Pre-heating of the sample for 30 minutes at 90ºC and stirring at 350 rpm for 30 minutes to homogenize the emulsion before sub-sampling was undertaken as it was mentioned in **4.2.2.**. The water content was determined only by Karl Fisher titration as described in **Chapter 3**, **Section 3.2.3.4**. The calculation was performed according to **Chapter 3, Section 3.2.4.3**.

4.2.3.4 pH/conductivity of aqueous phase

The aqueous phase samples obtained after each washing step and the evaporation in the Rotavap, were analyzed for pH and conductivity using an Oakton® PC700 benchtop meter. The peformed calibration can be found in **Chapter 3, Section 3.2.5.3**.

4.2.3.5 Asphaltenes content in organic phase

Asphaltenes content was determined on the Cold Lake bitumen as well as on the recovered emulsion using pentane and vacuum filtration, according to the following procedure:

1 g of bitumen was dissolved in 40 mL of *n*-pentane in a 100 mL flask and stirred for one hour, at 500 rpm with a Fisherbrand 38.1 mm octagonal stir bar and Fisher Scientific model Isotemp hot plate, followed by 24 hours without stirring. Then, the mixture was vacuum filtered through a Whatman 0.22 µm Millipore filter. The filtered cake was rinsed with fresh *n*-pentane until the eluent became colorless. The rinsed asphaltenes sample was left in the fumehood for 72 hours and then weighted. The weighing was performed using a Mettler Toledo XP1203S balance (capacity 1210 g, readability 1 mg).

4.2.3.6 Simulated distillation (SimDis) of organic phase

Organic phase samples after toluene removal (last procedure step) were analyzed through SimDis, in order to determine the effect of the washings in the distillation profile. The apparatus consisted of: Gas chromatograph – Agilent 7890B, Flame Ionization Detector (FID), Temperature programmable inlet – cool on column (COC), Cryogenic oven cooling to -20 ºC, Automatic sample injector, Column – DB-HT-SIMDIS 5m x 0.53 mm x 0.15 micron, OpenLAB GC software, Dragon SimDis software, carrier gas Hydrogen, Helium and Air grade 5.0 from Praxair. The method conditions can be found in the **Table 4.2**.

Table 4.2 Method conditions for SimDis

Oven	Initial temperature	-20 °C
	Temperature program	15 °C/min
	Final temperature	425 °C
	Final hold time	10 min
Inlet	Initial temperature	50 °C
	Temperature program	15 °C/min
	Final temperature	425 °C
Column	Column flow	20 mL/min
	Carrier flow	Constant flow
	Carrier control	435 °C
Detector	Temperature	40 mL/min
	Hydrogen	15 mL/min
	Air	350 mL/min
	Make-up (He)	15 mL/min
Volume injected		0.5 µL
Data acquisition rate		10 Hz
Total acquisition time		39.7 min

The instrument was calibrated as described in **Section 4.2.5.4**. The sample was prepared according to the following procedure:

0.100 g of sample was weighted in a 10 mL volumetric flask, using a Mettler Toledo ME204 balance (capacity 220 g, readability 0.0001 g) then the weighing balanced was tared. After this, 5 mL of CS_2 was added and the mixture was swirled until dissolving the sample (this step must be performed without inverting the flask to avoid sample losses). Once the sample was dissolved, the flask was filled to the mark with CS_2 and immediately closed with a stopper. The total mass of CS_2 is weighed. The solution was gently swirled and then, from the middle level of the flask, 1.5 mL of sample was taken using a 9” glass pipette into 3 vials (capacity 2mL). After each transfer the vial was immediately closed with its cap. The vials were stored in the freezer at -17ºC until the analysis was performed.

4.2.3.7 Fourier Transform Infrared Spectroscopy (FTIR)

The organic emulsion samples after evaporation in the Rotavap, as well as the Cold Lake bitumen were analyzed using an ABB MB3000 instrument equipped with a MIRacleTM Reflection Attenuated Total Reflectance (ATR) diamond crystal plate and pressure clamp. The conditions for the analysis were: Resolution 4 cm^{-1}, 60 scans, detector gain of 81 and spectral region between 4000 and 400 cm^{-1}. The data was collected for qualitative analysis; therefore, no calibration was performed.

4.2.4 Calculations

4.2.4.1 Ion content in bitumen, aqueous phase and organic emulsion:

It is speculated that the water washing can influence the cation removal from the organic phase, given by:

$$M_{x,org} = M_{x,bit} - M_{x\ aq,total}$$

Equation 4.1

Where

$M_{x,org}$: Mass of element x in the organic phase per mass of bitumen [µg/g bitumen]
$M_{x,bit}$: Mass of element x per mass of bitumen [µg/g bitumen]

$M_{x\ aq,total}$: Mass of element x removed through all the washing steps (aqueous phase) per mass of bitumen [µg/g bitumen]

To determine the mass of element x in each of the phases and in the raw bitumen, the following equations were used

$$M_{x,org} = \frac{C_{x,dig\ org} * V_{digested\ org}}{M_{ashing\ org} * (1 - \frac{\%_{water,org}}{100})}$$

Equation 4.2

$$M_{x,bit} = \frac{C_{x,dig\ bit} * V_{digested\ bitumen}}{M_{ashing\ bit} * (1 - \frac{\%_{water,bit}}{100})}$$

Equation 4.3

$$M_{x\ aq,total} = \sum_{1}^{n} M_{x\ aq,n}$$

Equation 4.4

$$M_{x\ aq,n} = \frac{C_{x\ aq,n} * M_{aq,n} * \rho_{H_2O}}{M_{bit}\ * (1 - \frac{\%_{water,bit}}{100})}$$

Equation 4.5

Where

$C_{x,dig\ org}$: Concentration of element x in the digested organic emulsion sample [µg/mL]

$V_{digested\ org}$: Volume of digested ashed organic emulsion sample (**Figure 4.2**) [mL]

$M_{ashing\ org}$: Mass of organic emulsion sample used for ashing procedure (**Figure 4.2**) [g]

$\%water_{org}$: Water content in the organic emulsion sample [% w/w]

$C_{x,dig\ bit}$: Concentration of element x in the digested bitumen [µg/mL]

$V_{digested\ bitumen}$: Volume of ashed digested bitumen (**Figure 4.2**) [mL]

$M_{ashing\ bit}$: Mass of bitumen sample used for ashing procedure (**Figure 4.2**) [g]

$\%water_{bit}$: Water content in the raw bitumen [% w/w]

$C_{x\ aq,n}$: Concentration of element *x* in aqueous phase sample in washing step *n* [µg/mL]

$M_{aq,n}$: Mass of aqueous phase sample in washing step *n* (**Figure 4.1**) [mg]

ρ_{H_2O}: Density of water. For simplification and calculation purposes, it was assumed the density to remain constant at 1 mg/mL.

M_{bit}: Mass of bitumen used for the washing procedure (**Figure 4.1**)

The percentage of difference in the material balance for each element is given by:

$$\%_{difference} = \frac{M_{x,bit} - (M_{x,aq} + M_{x,org)}}{M_{x,bit}} * 100$$

Equation 4.6

Where

$\%_{difference}$: Difference [%] between the mass of element *x* in the raw bitumen and the total mass of element *x* in both aqueous and organic emulsion phase.

The percentage of removal of each element from the bitumen is calculated by:

$$\%_{removal} = \frac{M_{x,aq}}{M_{x,bit}} * 100$$

Equation 4.7

Where

$\%_{removal}$: Removal [%] of element *x* from bitumen through washing.

Therefore, it is intended to determine if this removal follows in somehow a specific pattern with each washing step. The decision to base the percentage of removal on the amount recovered in the aqueous product was due to the emulsion-nature of the bitumen after washing.

4.2.4.2 Water content in organic phase

The water content was calculated as reported in **Chapter 3**, **Section 3.2.4.3**.

4.2.4.3 Asphaltenes content

The asphaltenes content, after weighting the asphaltenes obtained according to the procedure described in **Section 4.2.3.4**, is determined by:

$$\%_{asphaltenes} = \frac{M_{asphaltenes}}{M_{bitumen}} * 100$$

Equation 4.8

Where

$\%_{asphaltenes}$: Percentage [%] w/w of asphaltenes
$M_{asphaltenes}$: Mass of asphaltenes [g]
$M_{bitumen}$: Mass of bitumen [g]

For the organic emulsion samples, the content of water was discounted to compare the results based on the actual organic content of the sample, through the following equation:

$$\%_{asphaltenes} = \frac{M_{asphaltenes}}{M_{organic} * (1 - \frac{\%H_2O_{KF}}{100})} * 100$$

Equation 4.9

Where

$\%_{asphaltenes}$: Percentage of asphaltenes [% w/w]
$M_{asphaltenes}$: Mass of asphaltenes [g]
$M_{organic}$: Mass of organic emulsion [g]
$\%H_2O_{KF}$: Percentage [%] w/w of water by Karl Fisher titration

4.2.5 Calibrations

4.2.5.1 HPLC calibration

The calibration of the HPLC was performed as indicated in **Chapter 3, Section 3.2.5.1**.

4.2.5.2 ICP calibration

ICP calibration was performed as indicated in **Chapter 3**, **Section 3.2.5.2**.

4.2.5.3 pH/conductivity calibrations

The pH and conductivity calibrations were performed as indicated in **Chapter 3**, **Section 3.2.5.3**.

4.2.5.4 SimDis calibration

Calibration of the instrument was performed before running the analysis, and it is valid up to 13 analyses. The instrument calibration was performed using CS_2 as "blank" and two reference materials:

- Reference Material 5010, ASTM D6352/D7169, Supelco – used to determine the detector response factor which is used to calculate the amount of sample recovered.
- Retention time calibration mixture (Polywax 655, Neat, Supelco and Boiling point calibration sample #1 kit, Agilent technologies Part. No. 5080-8715) – used to

develop a retention time versus boiling point curve, then the boiling point distribution can be calculated up to the recovered amount.

4.2.5.4.1 Retention time calibration mixture 655 preparation

- Weigh 50 mg of Polywax 655 on a 10 mL volumetric flask.
- Add 8 mL of CS_2.
- Using a 13 mm magnetic stir bar, dissolve Polywax 655 while applying heat, i.e., place the capped flask under a fume hood in a hot plate magnetic stirrer set at 80 ºC (Note: this process can take up to 4 h).
- Once Polywax 655 is dissolved, add 50 µL of the boiling point calibration sample #1 kit and fill the flask up to the graduation mark with CS_2.
- Replace the stopper.
- Place the flask back in the hot plate magnetic stirrer set at 80 ºC to make the solution clear again.
- Once the solution is clear and without removing the flask from the hot plate magnetic stirrer, quickly transfer a 1.5 mL aliquot of the solution (from the center of the flask) to 6 (2 mL) vials, placing their screw cap firmly and immediately. Vials can be stored in the freezer, if they are not used on the same day they are prepared

4.2.5.4.2 Reference material 5010 preparation

- Weigh a 10 mL volumetric flask with its cap and record the weight.
- Tare the scale and add 0.100 g of reference material 5010 to the flask.
- Tare the scale and add 5 mL of CS_2 to the flask.
- Swirl the solution without inverting the flask.
- Fill the flask up to the graduation mark with CS_2 and place the stopper immediately.
- Quickly transfer a 1.5 mL aliquot of the solution (from the center of the flask) to 6 (2 mL) vials, placing their screw cap firmly and immediately.
- Vials can be stored in the freezer.

The blank (CS_2) is programmed to be run at the beginning of the sequence (three times), after each standard or sample injection (one time) to verify the absence of carryover from previous samples, and at the end of the sequence (one time). After the blank, the reference material 5010 is programmed, and then the retention time calibration mixture 655. This sequence will set the calibration of the instrument, after this the samples can be analyzed.

4.3 Results

4.3.1 Material Balance

Table 4.3 shows the average of the six individual material balances corresponding to each experiment. The individual material balances can be found in **Appendix 4.1** in. In the initial stage, the mass of toluene used as solvent, mass of bitumen (for the first washing step), and mass of MilliQ water added for washing purposes are considered. For the subsequent washing steps, the mass of organic emulsion that was obtained from the previous step is taken as the new "initial stage" in terms of the organic fraction used for the next washing. In the recovery stage, the mass of organic emulsion, as well as the aqueous phase obtained after the separation was registered. In the Rotavap the toluene used as solvent was recovered, as well as some aqueous phase and the final remaining organic emulsion with lower content of water.

The losses for each washing step were up to 2% w/w. However, it is important to mention that, despite the low percentage of losses, a high variability in the mass of aqueous phase between the same washing step for different experiments was observed. This is supported by the standard deviation (s) for the recovered aqueous phase, which was up to ± 47.57 g of 100 g of added water in the fourth washing step. Given the high variations in the recovered aqueous phase after each washing step, the organic emulsion exhibited standards deviation in the same order too.

In the aqueous phase samples recovered after each washing step (**Figure 4.3**), it was observed high turbidity. This condition was observed in the four washing steps, for the final evaporation in the Rotavap, no turbidity was found.

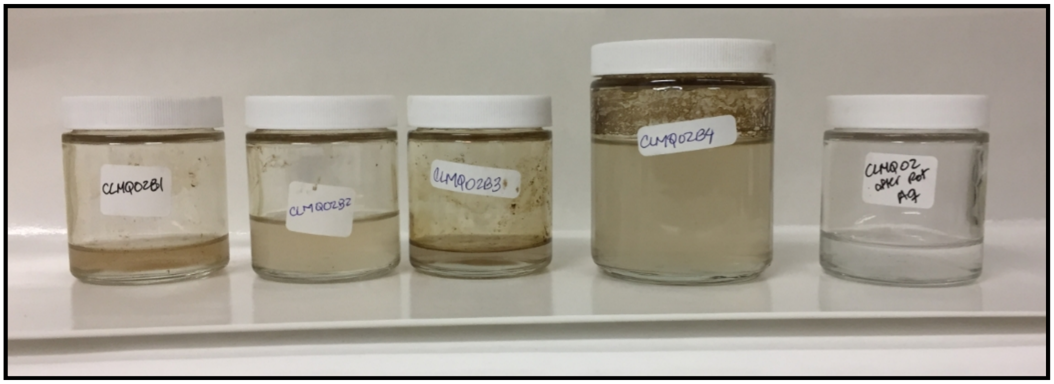

Figure 4.3 Aqueous phase samples for washing steps 1-4 and recovered after evaporation in a Rotavap – Experiment 5, Cold Lake bitumen washing

Table 4.3 Material balance – Cold Lake bitumen washings

Stage	Compound	Unit	Washing step				Rotavap
			1	2	3	4	
Initial	Bitumen (M_{bit})	[g]	100.37	-	-	-	-
		s	0.21	-	-	-	-
	Organic emulsion	[g]	-	271.70	293.48	341.47	339.60
		s	-	12.37	23.09	38.44	47.55
	Toluene	[g]	100.37	-	-	-	-
		s	0.23	-	-	-	-
	Deionized (MilliQ) water	[g]	100.33	100.22	100.15	100.04	-
		s	0.33	0.20	0.20	0.35	-
	Total	[g]	301.21	371.92	393.64	441.51	339.60
		s	0.59	12.44	23.03	38.52	47.55
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	26.30	76.55	47.97	97.65	27.87
		s	13.12	32.94	37.87	52.11	35.19
	Organic emulsion	[g]	271.88	295.09	341.47	342.26	201.71
		s	12.33	23.29	38.66	53.01	27.62
	Toluene	[g]	-	-	-	-	80.67
		s	-	-	-	-	7.75
	Total	[g]	299.68	373.24	391.24	441.92	334.18
		s	1.64	12.68	21.37	37.87	49.60
	Losses	[%]	0.51	-0.35	0.58	-0.10	1.72
		s	0.56	0.60	1.75	0.32	2.20

s: sample standard deviation, experiments were performed six times

4.3.2 Anion determination by HPLC

The anion chromatogram of one of the recovered aqueous samples after the first washing step of experiment 3, diluted by one hundred times, can be observed in **Figure 4.4**. The first peak (before 2 minutes) corresponds to the release of cations from the column Around 2.4 minutes, it can be observed a small peak, assigned to HCO_3^-/CO_3^{2-}. However, due to the dissociation equilibrium for HCO_3^-/CO_3^{2-} and the low intensities obtained for the analyzed samples, the quantification was made in terms of CO_3^{2-}. Around 3.3 – 3.6 minutes, it was noticed a prominent peak corresponding to Cl^-. Anions such as HPO_4^{2-} and SO_4^{2-} were detected in such low concentrations mainly in undiluted samples, that quantification could not be made.

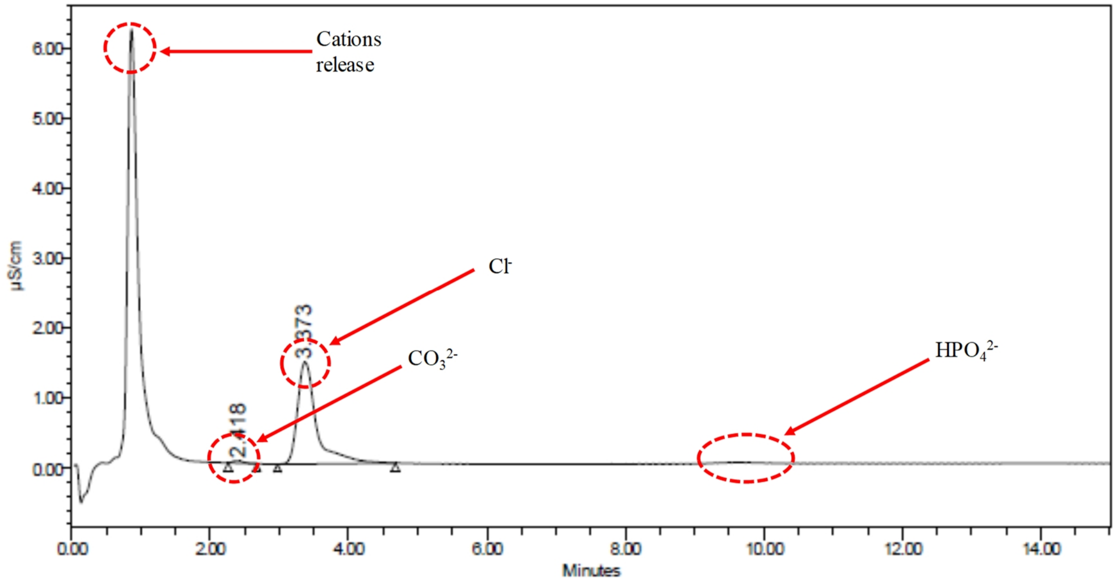

Figure 4.4 Anion determination by HPLC, experiment 3 1st washing step (dilution 1x100)– Cold Lake bitumen washing

The anion determination for experiment 1 – aqueous sample recovered from Cold Lake bitumen washing, can be found in **Table 4.4**. As it can be seen, the anions that were quantified in the aqueous phase after each washing were identified as Cl^- and CO_3^{2-}/HCO_3^-. Similarly, the **Table 4.5** illustrates the average anion removal for experiments 1-6. The same behavior was observed for all the experiments. Results of anion removal of experiments 2-6 can be found in **Appendix 4.2**.

Table 4.4 Anion determination through HPLC for experiment 1 – Cold Lake bitumen washing

	Washing step				Rotavap	
	1	2	3	4		
Recovered aqueous solution M_{aq} [g]	**44**	**41**	**89**	**62**	**31**	**Removed from bitumen**
Initial bitumen [g]	**100**					
Anion	$C_{x,aq\ 1}$ **[mg/L]**	$C_{x,aq\ 2}$ **[mg/L]**	$C_{x,aq\ 3}$ **[mg/L]**	$C_{x,aq\ 4}$ **[mg/L]**	$C_{x,aq\ rot}$ **[mg/L]**	**[µg/g bitumen]**
F^-	nd	nd	nd	nd	nd	-
CO_3^{2-}	<1	nd	<1	<1	nd	<1
Cl^-	683	456	324	280	nd	944
NO_2^-	nd	nd	nd	nd	nd	-
Br^-	nd	nd	nd	nd	nd	-
NO_3^-	nd	nd	nd	nd	nd	-
HPO_4^{2-}	nq	nq	nq	nq	nq	-
SO_4^{2-}	nq	nq	nq	nq	nq	-

nd: not detected, nq: not quantified -: not calculated

Table 4.5 Average anion determination through HPLC for experiments 1-6 – Cold Lake bitumen washing

	Washing step				Rotavap	
	1	2	3	4		
Recovered aqueous solution M_{aq} [g]	**42 ± 20**	**45 ± 46**	**60 ± 30**	**93 ± 50**	**28 ± 35**	**Removed from bitumen**
Initial bitumen [g]	**100**					
Anion	$C_{x,aq\ 1}$ **[mg/L]**	$C_{x,aq\ 2}$ **[mg/L]**	$C_{x,aq\ 3}$ **[mg/L]**	$C_{x,aq\ 4}$ **[mg/L]**	$C_{x,aq\ rot}$ **[mg/L]**	**[µg/g bitumen]**
F^-	nd	nd	nd	nd	nd	-
CO_3^{2-}	<1	<1	<1	<1	<1	<1
Cl^-	501 ± 243	516 ± 238	315 ± 143	225 ± 107	41 ± 71	996 ± 227
NO_2^-	nd	nd	nd	nd	nd	-
Br^-	nd	nd	nd	nd	nd	-
NO_3^-	nd	nd	nd	nd	nd	-
HPO_4^{2-}	nq	nq	nq	nq	nq	-
SO_4^{2-}	nq	nq	nq	nq	nq	-

nd: not detected, nq: not quantified, -: not calculated

As it was observed in Chapter 3, a high variation in the mass of recovered aqueous phase was found. The average standard deviation of the mass of Cl^- removed from the bitumen (**Table 4.5**) illustrates this behavior.

4.3.3 Cation determination through ICP-OES

The spectra obtained for the cation determination were reviewed to determine possible interferences. **Figure 4.5** shows the ICP-OES spectra of experiment 1 – aqueous phase for first washing step, the spectra were similar to the observed in Chapter 3, some differences were found for the following elements:

Aluminum: It is observed an interference at 396.13 nm approximately, which can be attributed to Fe. No interference was observed for the organic emulsion and raw bitumen samples.

Cadmium: For the recovered aqueous phase from the first washing step in experiment 1, it was observed a low emission at the specified wavelength; however, it could not be quantified. For the rest of the samples no emission was observed, therefore, the element was not detected.

Copper: The intensity of the emission was too low that according to the built calibration curve this element was not quantified.

Zinc: The detected emission was too low, that the element could not be quantified

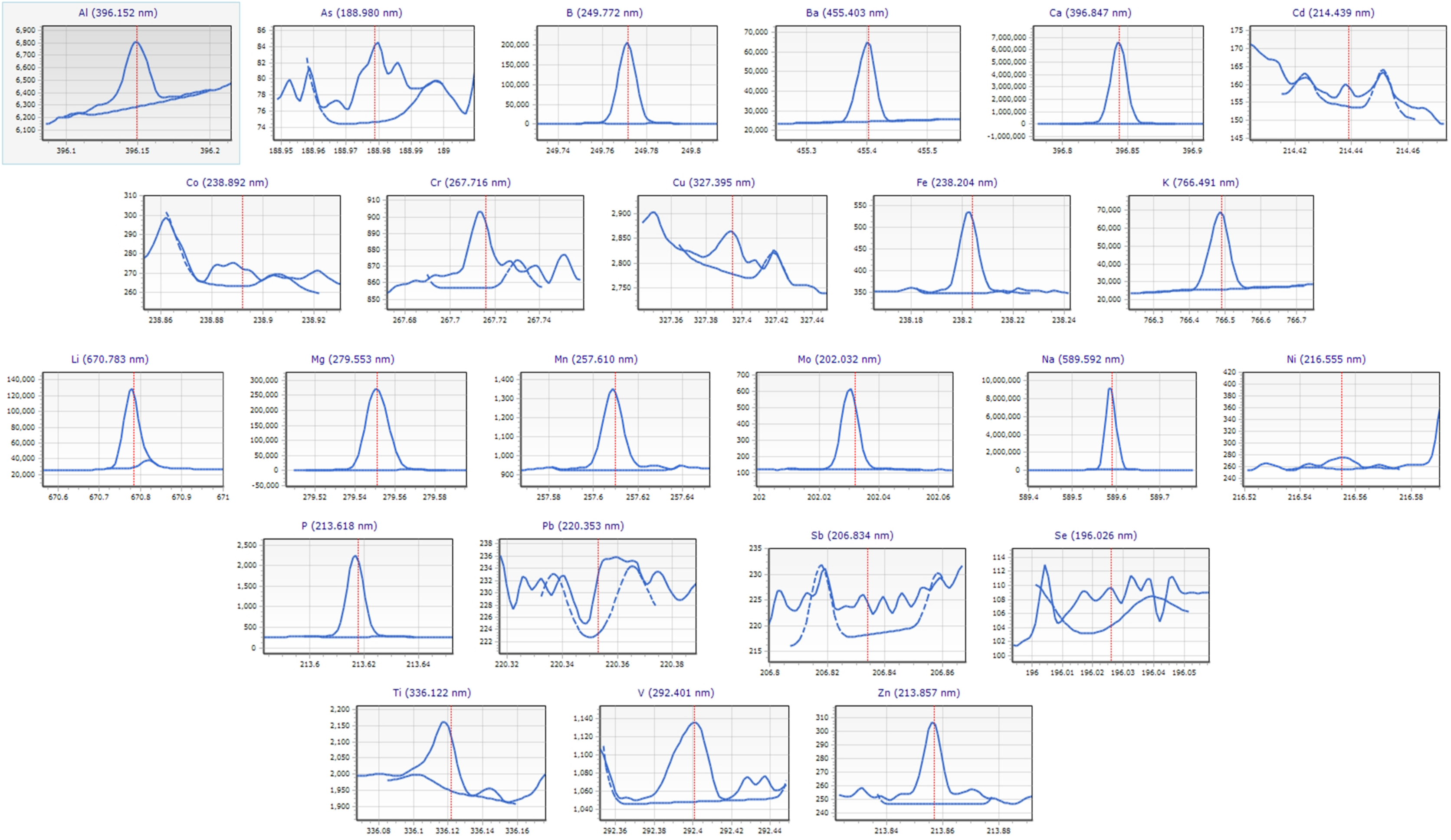

Figure 4.5 ICP-OES spectra of experiment 1 (aqueous phase 1st washing step) – Cold Lake bitumen washing

As it was previously mentioned in **Section 4.3.2**, the variation of aqueous phase after each washing step makes unadvisable the comparison between one washing step of one experiment, and the same step of another experiment. The cation removal for experiment 1 can be found in **Table 4.6**, while experiments 2-6 are reported in **Appendix 4.3**.

The elements reported as "nd" were not detected by the instrument and they were not observed in the spectra. On the other hand, the elements reported as 'nq" were observed in the spectra, but in such low concentrations that it could not be quantified.

The percentage of difference between the cation present in the raw bitumen, and the sum of the cation present in both the aqueous and organic recovered phases, was calculated according to **Equation 4.6**. The percentage of cation removal from bitumen was determined using the **Equation 4.7**. It can be observed from **Table 4.6** that the percentage of difference between $M_{x,bit}$ (mass of element x per mass of bitumen) and $M_{x,total}$ (mass of element x in both aqueous and organic phase per mass of bitumen) for most of the elements is below 37%, with the exception of cations of elements such as B and Si (>-1100% and >200% respectively). In cations of elements such Ca, Fe and Mo, the difference percentage of difference between the raw bitumen and the recovered phases after washing was -37%, 33% and 33% respectively. For the rest of the analyzed cations (except for B and Si as it was previously mentioned), the percentage of difference was lower than 25%.

Considering the cations with lower percentages of difference between the raw bitumen and the recovered phases after washing, the highest removal from the bitumen was observed for the cations of elements K (46% of removal), Mg (50%) and Na (57% removal). For these cations the percentage of difference between the raw bitumen and the sum of recovered aqueous and organic phases were lower than 10%.

The average cation determination is reported in **Table 4.7**. It can be observed that, like the observations made for experiment 1 (**Table 4.6**), the cations with higher percentage of difference between the raw bitumen and the recovered phases after washing were found to be those from elements B and Si (>-1100% and >-480%). Cations of elements such Al exhibited 50% of difference between the raw bitumen and the phases after washing was performed. However, considering the standard deviation of both the experiments and the raw bitumen analysis, it can be noticed that the values are within the same range. Same behavior was observed for Ca, Li, Mo and Ni, where the quantity of cations determined in the raw bitumen and the sum of the amount of cations in the recovered phases after washing, falls into the same range due to the standard deviation. For the rest of the cations, the percentage of difference when comparing before and after washing samples was calculated below 11%.

Table 4.6 Cation determination on aqueous and organic phase for experiment 1 – Cold Lake bitumen washing

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen ($M_{x\ aq,total}$)**	**Organic phase ($M_{x,org}$)**	**Total ($M_{x\ aq,total}$ + $M_{x,org}$)**	**Cold Lake bitumen ($M_{x,bit}$)**	*% difference*	*% removal*
Recovered aqueous solution M_{aq} [g]	**44**	**41**	**89**	**62**	**31**						
Cation of element	**$C_{x,aq\ 1}$ [mg/L]**	**$C_{x,aq\ 2}$ [mg/L]**	**$C_{x,aq\ 3}$ [mg/L]**	**$C_{x,aq\ 4}$ [mg/L]**	**$C_{x,aq\ rot}$ [mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**	**[%]**
Al	<1	<1	<1	<1	<1	<1	2	2	2 ± 2	0	*
As	nq	nq	nq	nq	nq	nq	nq	nq	nq	-	-
B	12	5	3	2	1	12	<1	12	<1	>-1100	-
Ba	<1	<1	<1	<1	nd	<1	<1	1	1 ± <1	0	*
Ca	5	6	4	3	2	11	26	37	27 ± 11	-37	39
Cd	nq	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Co	nd	nd	nd	nd	nd	nd	<1	<1	<1	*	*
Cr	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Cu	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Fe	<1	<1	<1	<1	<1	<1	6	6	9 ± <1	33	*
K	12	9	5	4	<1	16	16	32	34 ± 4	6	46
Li	<1	<1	<1	<1	nd	<1	1	2	2 ± <1	0	*
Mg	1	1	<1	<1	<1	2	2	4	4 ± 1	0	50
Mn	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Mo	<1	<1	<1	<1	<1	<1	3	4	6 ± 1	33	*
Na	300	221	111	94	4	380	241	621	664 ± 89	6	57
Ni	nq	nd	nd	nd	nd	nd	41	41	50 ± 4	18	0
P	2	<1	<1	<1	<1	1	<1	2	<1	*	*
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Sb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Si	19	15	10	9	1	30	4	34	11 ± 2	-209	270
Ti	nd	nd	nd	nd	nd	nd	1	1	1 ± <1	0	0
V	<1	<1	nd	<1	nd	<1	95	95	124 ± 22	23	*
Zn	nq	nq	nq	nq	nq	nq	1	1	1 ± <1	*	*

nd: not detected, nq: not quantified, -: not calculated, *: too low to be calculated, NA: not applicable

Table 4.7 Average cation determination on aqueous and organic phase for experiments 1-6 – Cold Lake bitumen washing

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen ($M_{x\ aq,total}$)**	**Organic phase ($M_{x,org}$)**	**Total ($M_{x\ aq,total}$ + $M_{x,org}$)**	**Cold Lake bitumen ($M_{x,bit}$)**	% $_{difference}$	% $_{removal}$
Recovered aqueous solution M_{aq} [g]	42 ± 20	45 ± 46	60 ± 30	93 ± 50	**28 ± 35**						
Cation of element	$C_{x,aq\ 1}$ **[mg/L]**	$C_{x,aq\ 2}$ **[mg/L]**	$C_{x,aq\ 3}$ **[mg/L]**	$C_{x,aq\ 4}$ **[mg/L]**	$C_{x,aq\ rot}$ **[mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**	**[%]**
Al	<1	<1	<1	<1	<1	<1	3 ± 1	3 ± 1	2 ± 2	-50	*
As	nq	nq	nq	nq	nq	nq	nq	nq	nq	NA	NA
B	12 ± <1	6 ± 1	3 ± <1	2 ± <1	<1	12 ± 1	<1	12 ± 1	1.0	>1100	-
Ba	<1	<1	<1	<1	nd	<1	1 ± <1	1 ± <1	1 ± <1	0	*
Ca	6 ± 3	6 ± 1	4 ± 1	4 ± 1	1 ± <1	11 ± 2	22 ± 6	33 ± 6	27 ± 11	-22	41
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Co	nd	nd	nd	nd	nd	nd	<1	<1	<1	*	0
Cr	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	0
Cu	nq	nq	nq	nq	nq	nq	1 ± <1	1 ± <1	<1	*	*
Fe	<1	<1	<1	nd	<1	<1	8 ± 2	8 ± 2	9 ± <1	11	*
K	14 ± 3	10 ± 1	6 ± 1	4 ± 1	<1	17 ± 3	13 ± 4	31 ± 3	34 ± 4	9	50
Li	1 ± <1	<1	<1	<1	nd	1 ± <1	1 ± <1	2 ± <1	2 ± <1	0	50
Mg	1 ± <1	1 ± <1	<1	<1	<1	1 ± <1	3 ± 1	4 ± <1	4 ± 1	0	25
Mn	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Mo	<1	<1	<1	<1	<1	1 ± <1	4 ± 1	4 ± 1	6 ± 1	33	17
Na	329 ± 53	237 ± 27	143 ± 26	102 ± 24	4 ± <1	415 ± 65	196 ± 83	611 ± 71	664 ± 89	8	63
Ni	nq	nd	nd	nd	<1	<1	41 ± 7	41 ± 7	50 ± 4	18	*
P	<1 ± 1	<1	<1	<1	<1	<1	<1	1 ± 1	<1	*	*
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Sb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Si	19 ± 4	11 ± 4	9 ± 4	6 ± 3	1 ± <1	24 ± 9	40 ± 28	64 ± 24	11 ± 2	-482	218
Ti	nd	nd	nd	nd	nd	nd	1 ± <1	1 ± <1	1 ± <1	0	0
V	<1	<1	<1	<1	nd	<1	111 ± 22	111 ± 22	124 ± 22	10	*
Zn	nq	nq	nq	nq	nq	nq	1 ± <1	1 ± <1	1 ± <1	*	*

nd: not detected, nq: not quantified, -: not calculated, *: too low to be calculated, NA: not applicable

4.3.4 Water content in raw bitumen organic emulsion

The water content in the raw bitumen was determined according to **Section 4.2.3.3**. The results are shown in **Table 4.8**. Free water was not observed; however, it was decided to analyze the water content as a "blank". It was determined that the water was emulsified and, the emulsion was found to be highly stable. Separation was not achieved through centrifugation or ultra-sonication.

On the other hand, the recovered organic phases after washing were also analyzed since, according to the material balance (**Table 4.3**), the organic phase retained a large amount of water. In these cases, it was decided to perform the heating and homogenization of the samples following the procedure explained in **Section 4.2.2**. However, it was found that despite following the preheating and homogenization procedure, some free water was present in the samples. Removal or decantation of free water was not done, since this would alter the composition of the emulsion, and it could lead to the misinterpretation of results of cation removal between those samples where more water could be removed, and those samples where no water could be removed due to the stability of the emulsion. Rather, homogenizing the organic emulsion to the maximum possible was decided to be a more accurate approach.

Table 4.8 Water content in organic phase by Karl Fisher titration – Cold Lake bitumen washing

Name	*%water* $_{(KF)}$ - homogenized sample [%] w/w
Cold Lake bitumen	9.29 ± 0.14
Experiment 1	50.12 ± 0.85
Experiment 2	52.89 ± 0.00
Experiment 3	30.29 ± 0.69
Experiment 4	65.45 ± 0.01
Experiment 5	63.65 ± 0.01
Experiment 6	47.27 ± 0.77

It can be observed that the organic emulsion samples retained a high percentage of water (up to 65% w/w). This finding is in agreement with the fact of having some washing steps with low or no recovery of aqueous phase after the 24 hours in the separation funnel or after the evaporation in the Rotavap according to the procedure described in **Section 4.2**.

4.3.5 pH/conductivity of aqueous phase

The results of pH measurements corresponding to experiment 1 are shown in **Figure 4.6**. In **Figure 4.7** the conductivity measurements were compared with the chloride concentration determined through HPLC. The three parameters (pH, conductivity and chloride concentration) decreased after each washing step.

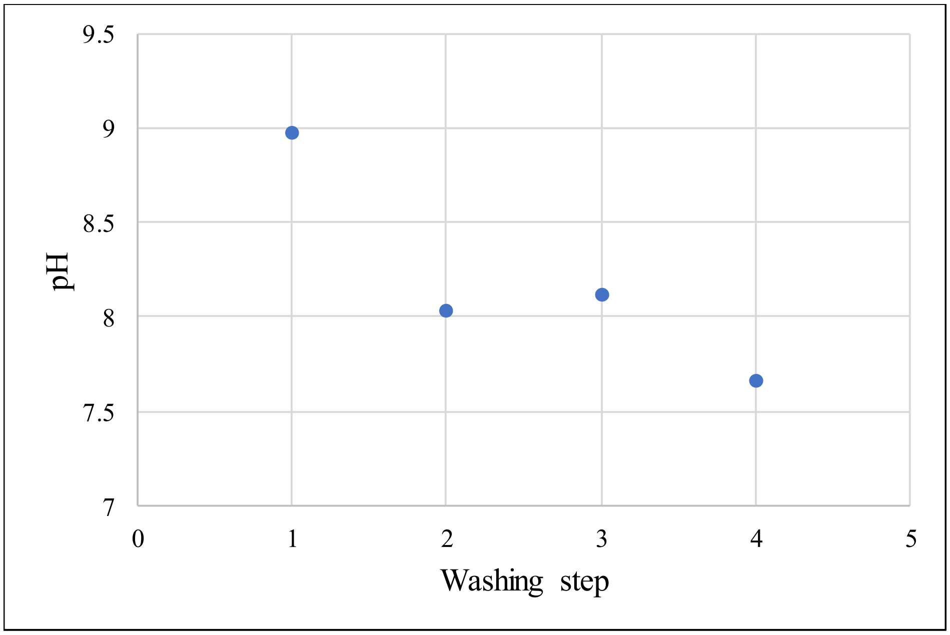

Figure 4.6 pH of aqueous phase for experiment 1 – Cold Lake bitumen washing

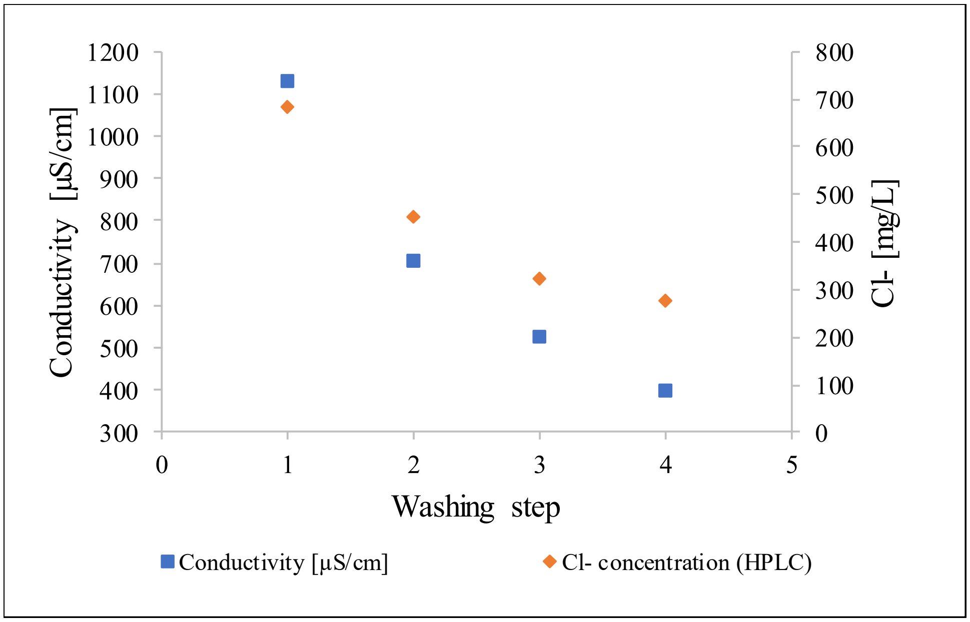

Figure 4.7 Conductivity of aqueous phase and Cl^- determination by HPLC for experiment 1 – Cold Lake bitumen washing

The **Table 4.9** shows the measured conductivity, and the measured chloride concentrations for experiments 2-6. Also, the calculated Cl^- concentration based on the calibration curve performed for the pH/conductivity meter was included. It can be observed that the pH and conductivity reduction occurred in all the performed experiments, as well as the decrease in the Cl^- concentration determined by HPLC. However, even when the calculated Cl^- concentration decreased as the washing steps were done, the calculated Cl^- concentration values were consistently lower than the measured Cl^- concentration by HPLC.

Table 4.9 pH, conductivity and chloride concentrations for aqueous phase samples, experiments 2-6

Experiment	Washing step	pH	Conductivity [µS/cm]	Cl^- concentration (HPLC) [mg/L]	Calculated Cl^- concentration * [mg/L]
2	1	-	-	517.2	-
	2	8.3	417.0	636.0	143.6
	3	7.9	402.0	332.5	138.9
	4	7.7	244.0	185.5	89.1
	Rotavap	6.5	14.8	0	17.0
3	1	-	-	742.5	-
	2	8.8	1388.0	639.8	449.4
	3	7.9	478.0	402.0	162.8
	4	7.8	463.0	240.0	158.1
	Rotavap	-	-	0	-
4	1	-	-	516.6	-
	2	7.63	1790	664.7	576.0
	3	-	-	380.5	-
	4	7.54	366	288.6	127.6
	Rotavap	4.32	64.6	123.3	32.7
5	1	7.87	918	454.9	301.4
	2	7.36	763	637.7	252.6
	3	-	-	403.6	-
	4	7.21	787	301.9	260.1
	Rotavap	-	-	0	-
6	1	-	-	592.5	-
	2	7.82	1430	579.9	462.6
	3	-	-	365.2	-
	4	7.26	739	282.1	245.0
	Rotavap	-	-	0	-

-: not measured/not calculated, *: calculated concentration based on the calibration curve of the conductivity meter

4.3.6 Asphaltenes content

The asphaltenes content of the Cold Lake bitumen and experiments 1-3 is listed in **Table 4.10**, the weight of the samples was corrected according to the water content (**Table 4.8**) using the **Equation 4.9**, and the analysis was performed once per sample. During the filtration of the asphaltenes as it was described in **Section 4.2.3.5**, it was found that the rinse of the asphaltenes cake with fresh *n*-

pentane was difficult to perform for the Cold Lake bitumen, and for the organic emulsion samples it was not possible to rinse the sample. It was observed that the *n*-pentane insoluble particles were fine and easily suspended in the liquid phase, as it can be observed in **Figure 4.8**. The dry resulting asphaltenes of the raw Cold Lake bitumen and the organic emulsion phase resulting from experiment 1 were observed under a Carl Zeiss SteREO Discovery V20 stereomicroscope. (**Figure 4.9**). This microscope has a zoom range of 20:1, high end magnification of up to 345x (with eyepiece 10x), with objective PlanApo S 1.0x FWD 60 mm. The camera is an AxioCam ERc5s and the software AxioVision Rel. 4.8.

Table 4.10 Asphaltenes content – Cold Lake bitumen washing

Name	Sample Weight [g]	Water content (by Karl-Fisher titration) [%] w/w	Asphaltenes weight [g]	% $_{asphaltenes}$ (not corrected)* [%] w/w	% $_{asphaltenes}$ (corrected)** [%] w/w
Cold Lake bitumen 1	0.96	9.29	0.10	10.44	11.51
Cold Lake bitumen 2	1.11	9.29	0.12	10.55	11.63
Cold Lake bitumen 3	1.00	9.29	0.12	12.01	13.24
Average	**1.02**	**9.29**	**0.11**	**11.00**	**12.12**
s	**0.08**	**0.00**	**0.01**	**0.87**	**0.96**
Experiment 1	1.13	0.50	0.09	7.72	15.47
Experiment 2	1.20	0.53	0.07	5.85	12.42
Experiment 3	1.08	0.30	0.07	6.38	9.15
Average	**1.14**	**0.44**	**0.08**	**6.65**	**12.35**
s	**0.06**	**0.12**	**0.01**	**0.96**	**3.16**

s: sample standard deviation, *: Asphaltenes content based on the total weight of sample, **: Asphaltenes content based on the "dry" weight of sample (discounting water content determined by Karl Fisher titration)

Figure 4.8 Asphaltenes filtration for experiment 1 – Cold Lake bitumen washing

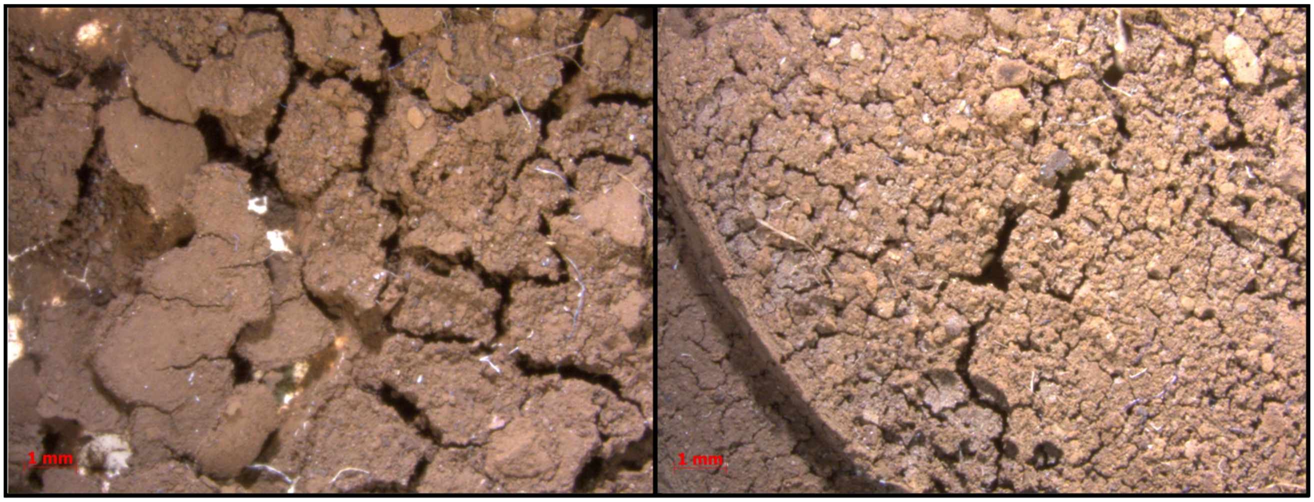

Figure 4.9 Asphaltenes for A: Cold Lake Bitumen, B: Organic emulsion sample of experiment 1. Pictures taken with a SteREO Discovery. V20 microscope

The calculated asphaltenes content in the organic samples showed a high variation between 9% w/w (experiment 3) and 15.5% w/w (experiment 1). The average was calculated to be 12.3% w/w with a standard deviation of ± 2.6% w/w. The asphaltenes content in the raw bitumen was determined between 11.5 and 13.2% w/w, with an average of 12.1 ± 0.96 % w/w. The weight of the sample was corrected according to the water content determined by Karl-Fisher titration. Considering the difficulties faced during the filtration and rising of the samples, it can be stated that the asphaltenes content of the organic emulsion did not showed a significant variation compared to the raw bitumen.

4.3.7 Simulated distillation (SimDis) of organic emulsion

Simulated distillation was performed on raw Cold Lake bitumen and 3 organic emulsion samples after all the washing steps and toluene/water removal by evaporation in a Rotavap (experiments 1-3). The weight of the organic emulsion samples was corrected according to the water content determined through Karl Fisher titration, to represent the distillation curve adjusted to the actual amount of organic fraction injected. **Figure 4.10** shows the distillation profile for these samples, whereas in **Figure 4.11** the distillation profiles were corrected in terms of the water content.

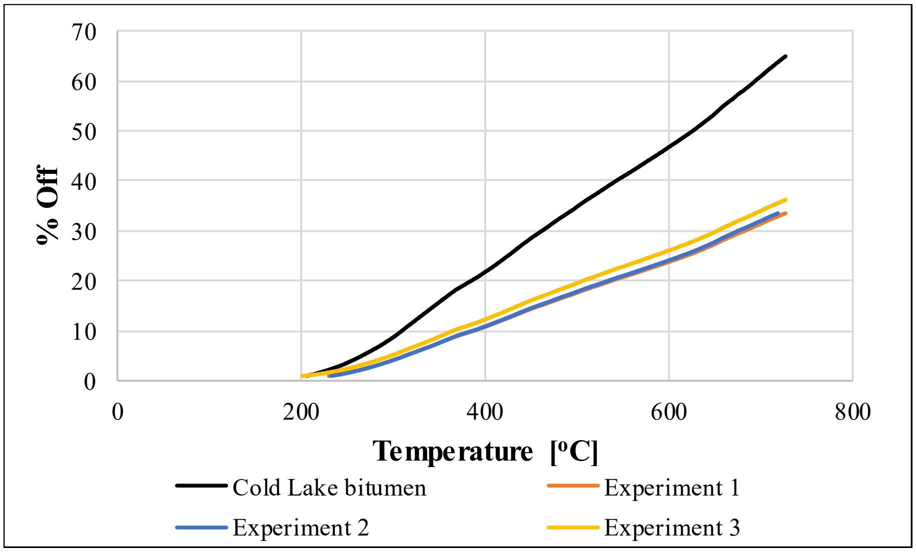

Figure 4.10 Simulated distillation of Cold Lake bitumen, and organic emulsion after washings and toluene/water removal, experiments 1-3

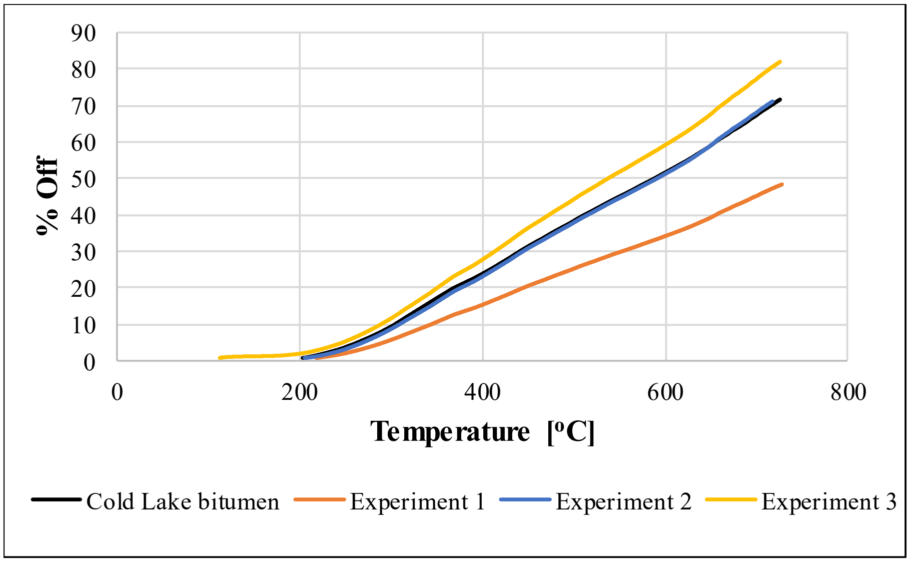

Figure 4.11 Simulated distillation of Cold Lake bitumen, and organic emulsion after washing and toluene/water removal (corrected water content determined by Karl Fisher titration)

4.3.8 Fourier Transform Infrared Spectroscopy (FTIR) of organic emulsion

The organic emulsion samples after evaporation in the Rotavap for experiments 1-3 were analyze by FTIR. **Figure 4.12** shows the FTIR spectra for the Cold Lake bitumen and the organic emulsion sample resulting from experiment 1. Results for experiments 2 and 3 are reported in **Appendix 4.4**

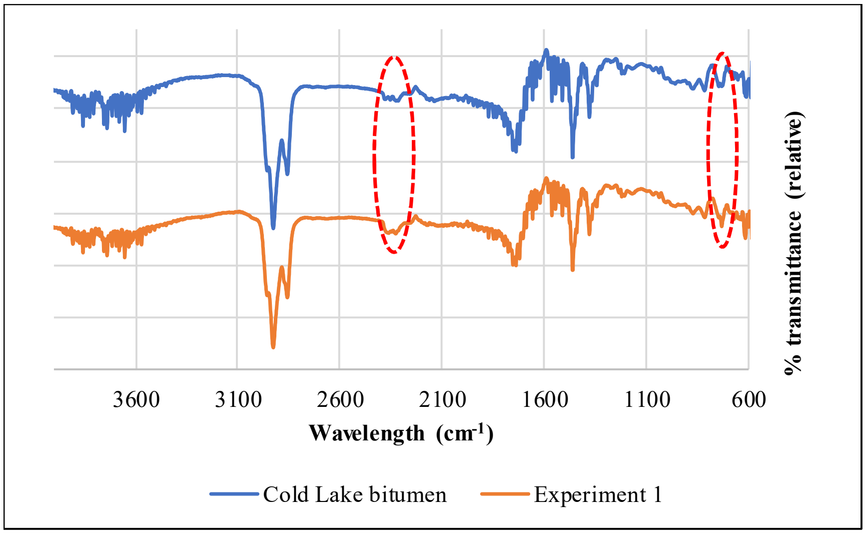

Figure 4.12 Fourier Transform Infrared Spectroscopy for Cold Lake bitumen and experiment 1 – Cold Lake bitumen washing

Variations at 2350 cm^{-1} approximately between the spectrum of Cold Lake bitumen and the one for the experiment 1 are observed, and it can be associated to CO_2 background. Also, it was observed a difference at 728 cm^{-1} between the raw bitumen and the organic emulsion from Experiment 1. Other differences in the intensity of the peaks can be attributed to differences in the path length between the analyses of each sample.

4.4 Discussion

4.4.1 Material Balance

The material balance in **Table 4.3** shows a low overall percentage of losses (less than 2 %). The percentage of losses can be considering as acceptable taking into account the sample manipulation during each washing step (removal of magnetic stir bar, transfer from flask to separation funnel and vice versa). Between each washing step, there was one to two days where the organic emulsion was covered with parafilm, during this time it was found that some minor losses occurred, this might be due to some toluene and water volatilization.

As it was shown in **Figure 4.3**, turbidity of the aqueous samples was observed in all the washing steps. This can be related to the high content of dissolved salts, and it was observed that suspended solids and particles were removed from the bitumen and transferred to the aqueous phase. The aqueous sample recovered after the evaporation in the Rotavap did not exhibit turbidity, this condition was expected since the aqueous phase for this stage was recovered through evaporation.

4.4.2 Ion transfer

As it was observed in **Table 4.4**, the water washing was able to promote a significant transfer of Cl^-. Also, the presence of CO_3^{2-}/HCO_3^- and SO_4^{2-} was detected; however, these anions were detected at so low concentrations that it could not be quantified. This finding is in agreement with the anions typically found in oil sands process affected water (OSPW) (Huang, 2016). It is clear, that the nature of the washed bitumen affects the species that can be removed through water washing. Chlorides were significantly removed in an average of 996 ± 227 μg/g bitumen for the six performed experiments. Analysis of the connate water by mixing hot water with Cold Lake bitumen and then separating it, is available in the literature (Strausz and Lown, 2003); it was reported that 2,761 mg/L of chlorides were found in the connate water of Cold Lake oil sand core.

When comparing the Cl^- removal to that one through the one-step washing of Cold Lake bitumen dissolved in methylene chloride in **Chapter 3**, **Table 3.14**, where the Cl^- removal was found to be of 784 ± 362 µg/g bitumen, it can be noticed that the removal seemed to be similar in both cases. However, the removal of cations of Na for the washings of Cold Lake bitumen in this Chapter (**Table 4.7**), compared to the one-step washing with deionized water in **Chapter 3** (**Table 3.22**), was higher (415 ± 65 µg/g bitumen vs 248 ± 129 µg/g bitumen respectively). It seems that the increase of temperature (from room temperature in the one-step washing, to 75ºC in this section washing), as well as the fact of performing 4 steps of washing, could influence the removal of these cations by increasing it. However, considering the standard deviation obtained from the experiments, it can be stated that both results are located within the same range and order.

The water content in the Cold Lake bitumen seemed to play an important role in the removal of ionic species. According to **Table 4.8**, the water content of the raw bitumen was around 9% w/w. This high-water content observed in the raw bitumen can contain dissolved salts and solids, which during the washing with deionized water could be easily removed since they were already present in an aqueous media.

The Cl^- concentration decreased after each washing step. It seems that after the deionized water is in contact with the bitumen, the system reaches an equilibrium stage for the ionic transfer, once the aqueous phase is separated and fresh water is added, a new equilibrium is reached, where the available ions that are susceptible to be removed. Anions such as CO_3^{2-}/HCO_3^- and SO_4^{2-}, despite of not being quantified, were detected mainly for the first washing step, the subsequent aqueous samples corresponding to washings 2-4, showed less intense or no peaks at the corresponding retention times.

To clarify if the removal is occurring mainly from the connate water, the ions quantified in higher proportions (Na and Cl) were compared to the concentration determined in the Cold Lake bitumen connate water (**Apendix 3.1**). Based on the water content in the Cold Lake bitumen determined by Karl Fisher titration (9% w/w) and by gravimetry (27% w/w) and reported in **Chapter 3**, **Table 3.33**, two projections curves of dilution were built. It was considered the removal of water after each water step to build these curves, since the experimental data was based not only on dilution but the removal of water (and ions) during each washing step (**Equation 4.10**):

$$[X]_n = \frac{[X]_{n-1} * (M_{aqbit,n-1} - M_{aqremoved,n})}{(M_{aqbit,n-1} - M_{aqremoved,n} + M_{aqadded,n})}$$

Equation 4.10

Where

$[X]_n$: Concentration of element *X* in after step washing *n*, (*n*=0 corresponds to the connate water) [µg/mL].

$[X]_{n-1}$: Concentration of element *X* in after step washing *n-1*, (*n*=0 corresponds to the connate water) [µg/mL].

$M_{aqbit,n-1}$: Mass of water present in the bitumen after washing step *n-1* [g].

$M_{aqremoved,n}$: Mass of water removed from the bitumen after washing step *n* [g].

$M_{aqadded,n}$: Mass of water added to the bitumen in step washing *n* [g].

The **Figure 4.13** shows the profile of dilution of cations of the element Na of the connate water, as well as the experimental concentrations obtained from the 4-step Cold Lake bitumen washing.

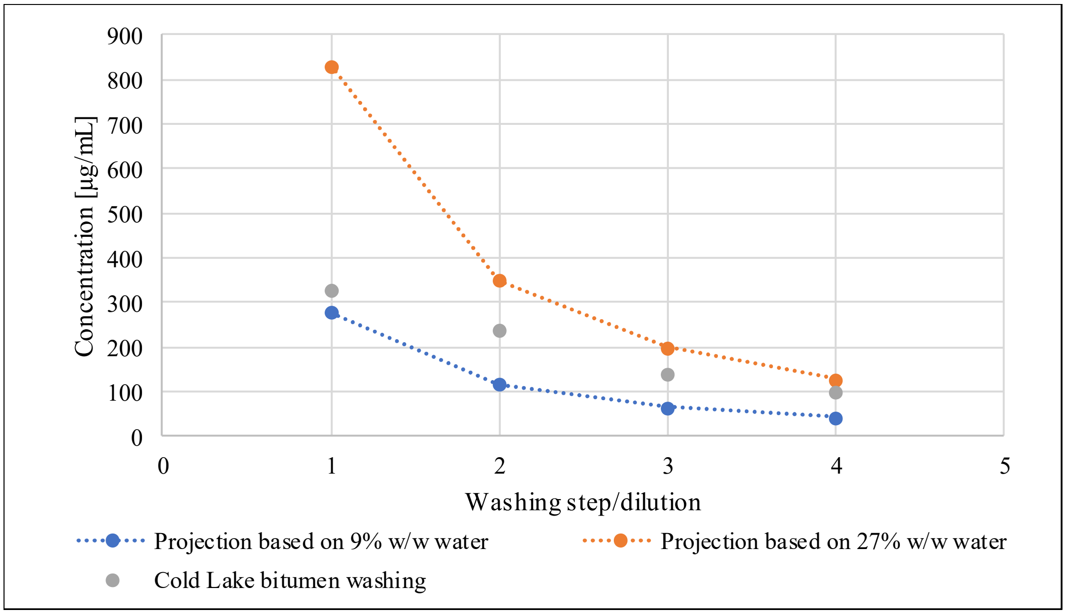

Figure 4.13 Concentration of cations of Na: Theoretical dilutions of the connate water depending on the bitumen water content (projection curves), and experimental concentrations after each washing step of Cold Lake bitumen.

On the other hand, the **Figure 4.14** shows the projection of the recovered mass of cations of Na present in the connate water, based on the water content determined by Karl Fisher titration and gravimetry (**Chapter 3**, **Table 3.33**), as well as the mass of cations of Na removed after each washing step. For this figure, it was assumed that the water remaining within the organic emulsion contained the same concentration of the water recovered in the last washing step.

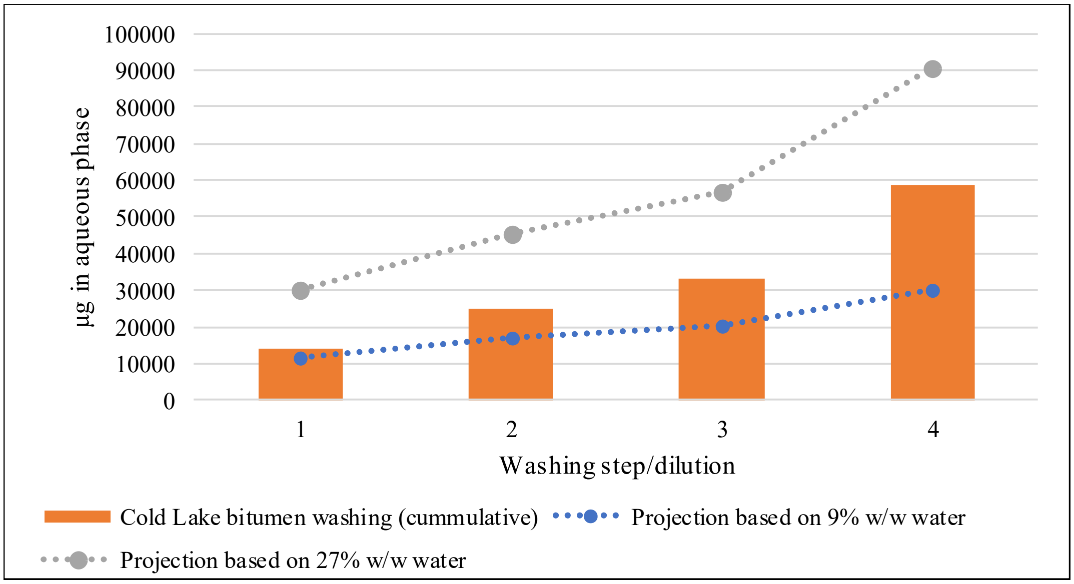

Figure 4.14 Mass of cations of Na: Theoretical mass in the aqueous phase after each washing step, and experimental mass based on the concentration after each washing step of Cold Lake bitumen

It can be noticed that the concentration obtained experimentally for each of the recovered aqueous samples is placed between the projections of the concentration in the connate water at 9% and 27% w/w. Since there were differences between the content of water obtained by Karl Fisher titration and by gravimetry, both projections were made. The experimental concentration profile, as well as the total amount of cations of Na recovered through washings suggests that, if the water content is 9% w/w, the removal of these cations occurred not only from the connate water but from the bitumen. However, if the water content is 27% w/w, the removal of these cations was related to connate water. Therefore, it is not possible to conclude beyond any uncertainty if removal of these cations from the bitumen was achieved.

Similarly, the **Figure 4.15** and **Figure 4.16** shows the projection of the concentration and mass respectively of Cl^- for the connate water and obtained experimentally through the 4-step washing. As it was explained for the **Figure 4.13** and **Figure 4.14**, the profiles were built considering not only the dilution but the extraction of free water after each washing step. Additionally, it was assumed that the all the water remaining in the organic emulsion could be recovered and the concentration of this water was the same of that one recovered in the last washing step.

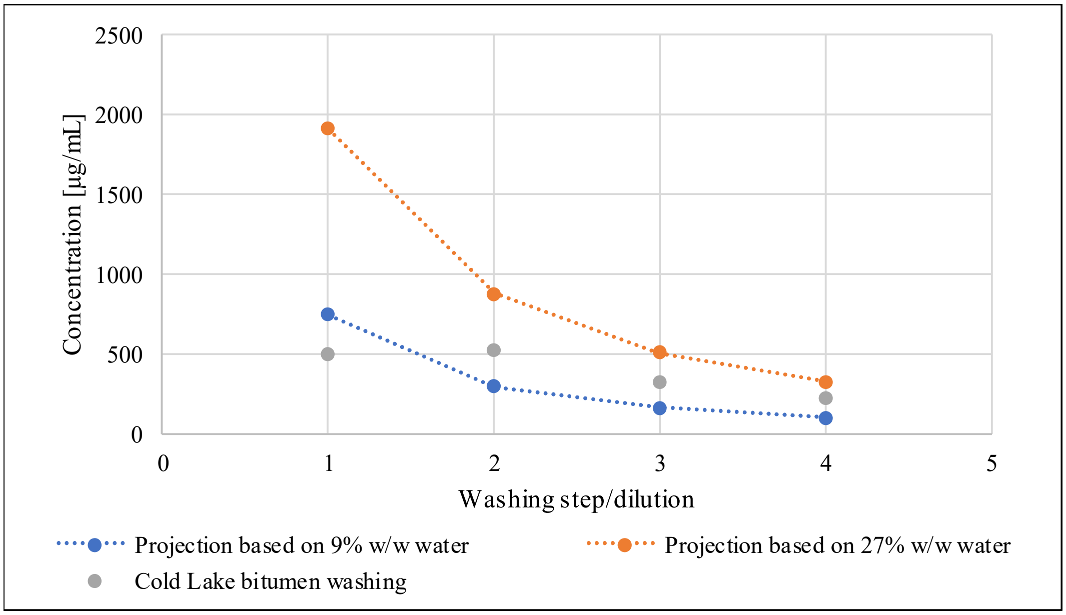

Figure 4.15 Concentration of Cl$^-$: Theoretical dilutions of the connate water depending on the bitumen water content (projection curves), and experimental concentrations after each washing step of Cold Lake bitumen.

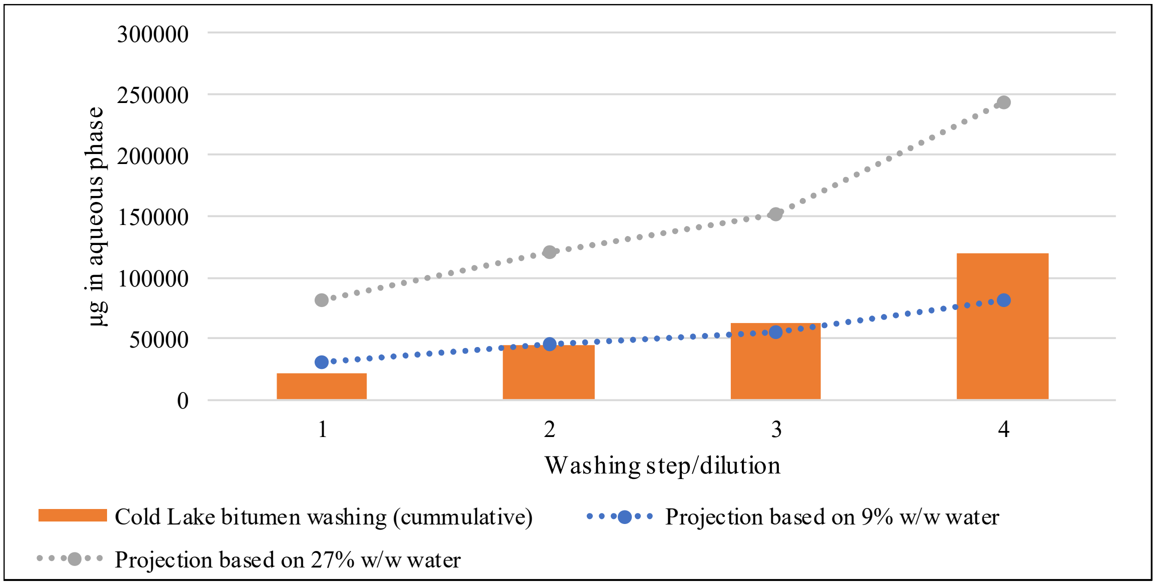

Figure 4.16 Mass of Cl$^-$: Theoretical mass in the aqueous phase after each washing step, and experimental mass based on the concentration after each washing step of Cold Lake bitumen

The same findings observed in **Figure 4.13** and **Figure 4.14** were observed for the Cl^- concentration profile and total recovered mass (**Figure 4.15** and **Figure 4.16**). The experimental concentration and total mass was located mainly in between the projection for the connate water at the two possible water contents (9% w/w and 27% w/w). The removal may or may not be related only to connate water.

On the other hand, in the **Table 4.7**, it was noticed that cations of elements B and Si were found in the aqueous phase in higher quantities than the ones found in the raw bitumen. This can be explained due to the glassware, which might introduce boron to the aqueous solutions. Release of boron in water, as well as basic and acid solutions has been studied. It has been found that over a month of storage in glass bottles, boron was detected in water; while for acid and basic solutions, boron was detected within the first 14 days of storage (Green et al., 1976). Leaching of ions of Na and Si was determined in several concentrations of Na_2O, B_2O_3 and SiO_2 glasses after being in contact with a buffering solution (pH of 8.5) of tris-hydroxymethylaminomethane (TRIS) in aqueous HCl at 90°C. The leached amount of cations of Na, Si and B reached stationary limits in all the cases; however, the time to reach the stationary limit as well as the leaching extent changed drastically as the glass composition changed the higher the Na_2O and B_2O_3 the concentration within the glass, the higher the leaching extent and the shorter the time to reach the stationary state (Ledieu et al., 2004). The experimental data did not show high differences between the quantity of cations of Na in the raw bitumen compared to the amount of this cation in the aqueous and organic emulsion phases. However, it is important to point out the high concentration of this ion in the connate water and the bitumen; if any leach occurred, the impact would be lesser than the one observed for the cations of B and Si.

To further investigate this, experimental work to determine the leaching of glassware to aqueous solutions was determined (**Appendix 4.5**). It was found that even when some leaching of ions occurred by the storage of samples in glassware, the concentration is very low (less than 2 mg/L after 16 days of storage). On the other hand, the concentration of cations of B and Si in the connate water was high, but after washing and acid digestion of the bitumen, the quantified concentrations were lower than the ones found in the connate water. Therefore, it can be inferred that the applied procedure to the raw bitumen and the organic phase is not suitable to determine these cations accurately.

Additionally, in the **Table 4.7** it was noticed a high variation between experiments for the determination of cations of Al. For experiment 1 (**Table 4.6**), there was no difference between the amount of cations of Al in the raw bitumen and the amount of this cation present in the recovered aqueous and organic samples; while the average of the six experiments (**Table 4.7**) led to an average of 50% of difference for this cation. It is important to mention that the quantity of cations of Al in the raw bitumen was low (2 ± 2 µg/g bitumen) and the average amount of cations of Al obtained from the phases after washing was found to be 3 ± 1 µg/g bitumen; therefore, considering the standard deviation the results are placed within the same range. The insolubility of ignited aluminum oxides that need to be dissolved for further analysis (McCoy, 1962), can bring an explanation to this high variation between analyses, as well as the difference between the raw bitumen and the phases after washing in consequence.

Variations in the determination of cations of Ca were also observed between experiments. It was removed consistently 11 ± 2 µg/g bitumen of cations of Ca (aqueous phase); however, some variations were found in the determination of cations of Ca in the raw bitumen (27 ± 11 µg/g bitumen) and the organic phase (33 ± 6 µg/g bitumen). It can be inferred that the variations occurred during the determination of this cation in the organic samples (raw bitumen and water-in-oil emulsions). Even when direct and wet ashing are recommended to determine calcium in crude oils, the ignition temperature may produce fused calcium residues, leading to some inaccuracies when the quantification is made (McCoy, 1962). On the other hand, experimental work to determine the leaching of Ca^{2+} by using porcelain crucibles when quantifying Ca^{2+} in beef liver (Meyer and Meyer, 1976), concluding that the use of porcelain crucibles during the dry ashing led to the release of calcium from the crucible. The high variation found during the determination of cations of Ca of both the raw bitumen and the recovered organic phase, makes the comparison of these values unadvisable.

It was observed that cations such as those of K, Li and Na were significantly removed from the bitumen (>50% w/w of the amount present in the raw bitumen). Some elements were not removed through bitumen water washing. Cations of Ni, Ti and V exhibited low or no removal (<1, 0 and <1% respectively). According to the literature, vanadium and nickel contents are present mainly in oil-soluble form (Strausz and Lown, 2003), additionally p/revious studies have determined that acid aqueous treatment does not remove these metals from bitumen (Prado and de Klerk, 2016).

The rest of the cations determined by ICP-OES were not removed or were removed in low quantities. Cations such as those of elements Al, Co, Cr, Cu, Fe and Mn were quantified up to 1 μg/g bitumen or less in the aqueous phase, in some cases the concentration was too low that it could not be quantified, or it was not detected.

4.4.3 pH/conductivity in aqueous phase

The pH results observed in **Figure 4.6**, as expected, decreased through each washing step. As it was mentioned in **Section 4.4.2**, it was detected through the review of the HPLC spectra that carbonates/bicarbonates were found in low concentrations. Carbonates are known for acting as buffers, reaching a pH of 9.5 the aqueous suspensions of $CaCO_3$, $CaMg(CO_3)_2$ and $MgCO_3$ (Strausz and Lown, 2003). The presence of carbonates could affect the pH of the aqueous solutions since the pH decreased after each washing step. On the other hand, the transfer of some organic acids from the bitumen to the aqueous phase has been reported in several studies (Clemente and Fedorak, 2005; Huang et al., 2017); therefore, it seems feasible that the naphthenic acids have been transferred from the bitumen through the washing with deionized water. On the other hand, it was determined that there was removal of cations of Fe (8 ±2 μg/g bitumen in the aqueous phase); and some acidity can be introduced due to the presence of dissociated ferric salts.

A comparison between the conductivity measured through the ph/conductivity meter, and the concentration of Cl^- is available in **Figure 4.7**, and in **Table 4.9**. It can be observed that the decrease of conductivity after each washing step for experiment 1 is supported by the decrease in the chloride concentration, indicating that the major contribution to the conductivity of the samples is given by fully ionized elements such as chlorides. In **Table 4.9**, the measured conductivity and Cl^- concentration for experiments 2-6 followed the same trend. It is important to mention that the conductivity measurements are highly influenced by the cell constant, presence of air bubbles in the sample, and temperature of the sample. In addition, as it was discussed in **Chapter 3, Section 3.4.4**, these differences can be also related to the ion separation that occurs in the HPLC column, making easier for the fully ionized elements such as Cl^-, to reach the negative terminal and, therefore, to bring more accurate results of this anion concentration.

Despite of the difference in the Cl^- concentrations obtained by the HPLC and the pH/conductivity meter, in both cases a clear decreasing trend was obtained. The Cl^- concentration calculated indirectly from the conductivity brings a good reference of how the system changes between each washing step, however, the concentration obtained by the HPLC analysis is more accurate and therefore, it was used for quantification purposes.

4.4.4 Water content in organic emulsion

The results shown in **Table 4.8** demonstrated the high water content retained by the organic emulsion after the washings and evaporation in the Rotavap was performed. The water content by Karl-Fisher titration was up to 65% w/w for experiment 4. According to the material balance (average for experiments 1-6), considering the mass for the final organic emulsion, and the recovered toluene (**Table 4.5**), it can be stated that more than 50% w/w of water was kept within the organic emulsion.

After the preheating and stirring procedure was performed to homogenize the samples (**Section 4.2.2**), some free water could not be re-emulsified. For this reason, the water content determined by Karl Fisher titration may not reflect the total amount of water that actually was contained in the samples. It was decided to maintain the same procedure for the homogenization in order to keep the losses due to water evaporation at a minimum. On the other hand, as it was mentioned in **Section 4.3.4**, the free water was not separated from the organic emulsion in order to keep the initial conditions of the previously separated phases to avoid some bias due to the decantation of the samples, since this procedure would be not uniform for all the samples.

4.4.5 Asphaltenes content

The asphaltenes content for the Cold Lake bitumen and organic emulsions samples of experiments 1-3 were reported in **Table 4.10**. The asphaltenes content before and after water content correction were found to be around 12% w/w for both the raw bitumen and the recovered organic emulsions, after the correction of water content was made. However, a higher standard deviation was obtained for the asphaltenes determination of the recovered organic emulsions (12.35 ± 3.16 % w/w). This can be due to:

- As it was mentioned in **Section 4.4.4**, the water content of the recovered organic emulsions was determined but non-homogeneities were observed after the samples were pre-heated and stirred. It could not be guaranteed that during the sub-sampling to determine asphaltenes, some of these non-homogeneities were also taken as part of the new sample.
- In **Section 4.3.6**, it was described that the asphaltenes rinsing with fresh *n*-pentane and vacuum filtration was found to be difficult to perform. For experiments 1-3 the asphaltenes cake was barely or no washed with fresh *n*-pentane due to the plugging of the paper filter. The size of the asphaltenes particles seemed to be so small that the paper got plugged, making not possible to perform the procedure as it was explained in **Section 4.2.3.5**.

Having stated that, it can be speculated that the asphaltenes content reported in **Table 4.10** is subject to some errors regarding the water content and the possible presence of *n*-pentane solubles in the asphaltenes cake.

The asphaltenes of the Cold Lake bitumen and the organic emulsion of experiment 1 were observed under the microscope (**Figure 4.9**). However, no significant differences were observed between the two samples.

4.4.6 Simulated distillation (SimDis) of organic emulsion phase

The water content in the organic emulsion samples had an important impact on the simulated distillation profile. In **Figure 4.10** the simulated distillation for the Cold Lake bitumen and the organic emulsion sample of experiments 1-3 is shown. The percentage of recovery is considerably low for the organic emulsion samples (less than 40% off for experiments 1-3 vs 65% off for the Cold Lake bitumen). The weight of the organic emulsion phase samples was corrected considering the water content determined in **Table 4.8**. The corrected simulated distillations are shown in **Figure 4.11**, it can be observed that the distillation profiles after water correction. Similar to the asphaltenes content in **Section 4.4.5**, the content of water exerted an important effect on the corrected results. For the simulated distillation (**Section 4.2.3.6**), the amount of sample needed for the analysis is 0.100 g, any inhomogeneity affects considerably the obtained result. Since it is known that the homogenization of the organic emulsion samples could not be achieved completely, it is expected that the corrected results of the simulated distillation may not represent the sample accurately.

According to **Figure 4.11**, the corrected result for experiment 2 matches with the distillation of the raw bitumen. The corrected distillation of experiments 1 and 3, under and over estimates the raw bitumen distillation respectively and, as it was mentioned, this could be due to the water content in the analyzed samples.

4.4.7 Fourier Transform Infrared Spectroscopy

The results of FTIR analysis for the Cold Lake bitumen and experiment 1 were reported in **Figure 4.12**. Little differences between the raw bitumen and the organic emulsion samples were found. For example, the region between 3600 – 3200 cm^{-1} (corresponding to the O-H stretching for free liquid water) resulted very similar for both the raw bitumen and the emulsion, despite the high water content that remained within the organic emulsion. Again, this was not expected for a sample containing 50.12 % w/w of water according to the results reported in **Table 4.8**. Some studies refer that the presence of certain anions can destroy or weaken the hydrogen-bonded network of water (Uchida et al., 2015). This might explain the absence of strong absorbance related to free water. On the other hand, the C-H stretching at 3032 cm^{-1} as well as the C-C stretching at 1506 cm^{-1} corresponding to aromatic ring were not observed in the different collected spectra. However, at 728 cm^{-1} it was observed a small peak in experiment 1, that suggest the presence of toluene in the sample, therefore, a small amount of toluene remained in the sample after the evaporation by Rotavap was performed.

4.5 Conclusions

The experiments and analysis of this chapter were undertaken with the purpose of determining if the ion removal observed in **Chapter 3** was mainly linked to the connate water, as well as investigate if the four-step washing was able to remove more ions that a one-step washing as it was performed in **Chapter 3**. Also, it was of interest to investigate if an increase of the temperature of washing influenced the ion transfer. The use of analytical tools such as anion and cation determination, and the thorough determination of water content and its contrast with the connate water was of special significance to answer the posed question of this chapter.

The main findings in this chapter are:

- The water washing of the Cold Lake bitumen, produced two main phases: an aqueous phase, and an organic emulsion containing more than 50% w/w of water. No separate organic phase was obtained.

- The pre-heating and homogenization of the organic emulsion samples, was not enough to achieve enough homogenization of the samples. Some free water was observed after this procedure was applied to the organic emulsion samples. This condition impacted considerably the determination of water content, and some complimentary analysis such as asphaltenes content and simulated distillation.

- Water washing of the Cold Lake bitumen was able to remove an important amount of Cl^-. It was detected minor concentrations of SO_4^{2-} and HCO_3^-/CO_3^{2-}.

- Washing of Cold Lake bitumen resulted in a higher removal of Cl^- and cations of Na. This removal was slightly higher to the obtained by the one-step washing of Cold

Lake bitumen. Temperature and the performing of subsequent washing steps seemed to play a role in the increased removal of ions of Na and Cl.

- The removal of ions could have taken place from the connate water present in the Cold Lake bitumen. However, since the water content of Cold Lake bitumen determined by Karl Fisher titration and by gravimetry was found to be different, it was not possible to establish this beyond any uncertainty.

- Cations of elements such as Ca, K, Li and Mg were also removed from the bitumen. The rest of the analyzed cations were not removed, or its removal was too low that it could not be quantified.

- High percentage of difference between the quantity of cations of B and Si present in the raw bitumen, and the amount present in the recovered phases after washing was found. This also affected the percentage of removal, by giving results of >100% of removal from the bitumen, which is not realistic. It was inferred that inaccuracies in the determination of these elements in the raw bitumen and the organic phase occurred.

- The analysis of pH and conductivity in the aqueous phase samples allowed to confirm the high concentration of chlorides obtained from the washing of the Cold Lake bitumen. In addition, it was confirmed the decrease of conductivity supported by the decrease of Cl^- after each washing step.

- No difference was observed between the asphaltenes content for the organic emulsion phase sample and that one of the raw bitumen. However, the difficulties during the filtration and rising of the organic emulsion samples, as well as the inhomogeneity due to the water contents, resulted in a high standard deviation.

- The simulated distillation of the recovered organic emulsion samples, was impacted by the inhomogeneity in the water content.

- It was detected that some toluene remained in the recovered organic emulsion samples, after being analyzed by FTIR. However, the spectra did not show the presence of free water in the organic emulsion, this could be attributed to the presence of anions that can destroy or weaken the hydrogen-bonded network of water (Uchida et al., 2015).

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5. EFFECT OF WATER WASHING ON ATHABASCA BITUMEN

ABSTRACT

In **Chapter 3** and **Chapter 4** it was found that the washing of Cold Lake bitumen, led to the removal of quantifiable amounts of mainly cations of elements such as Na, Ca, K, and anions Cl^-, CO_3^{2-}/HCO_3^-, HPO_4^{2-}; and the detection of SO_4^{2-}. The removal of ions seemed to be linked to the connate water, since the raw bitumen used for the experiments contained a high percentage of water (>9% w/w), but this could not be confirmed.

In this chapter, Athabasca bitumen was washed under the under the same procedure used in **Chapter 4**. In the same way, analysis by High Performance Liquid Chromatography (HPLC) and Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) was performed on the aqueous and organic emulsion phases. It was intended to determine if the use of a bitumen with low water content (<1% w/w) would help to verify if the removal of ions is mainly related to connate water or if it can be linked somehow to the bitumen.

Removal of anions such as CO_3^{2-}, Cl^-, HPO_4^{2-}, SO_4^{2-} were detected with higher quantification of SO_4^{2-} (up to 62 µg/g bitumen) and CO_3^{2-} (up to 63 µg/g bitumen). Cations of elements such as Al and Fe (up to 3 µg/g bitumen which corresponded to up to 50 % w/w respectively of the quantity present in the raw bitumen) were removed. Other cations of elements such as Ni, Ti and V were not removed from the bitumen.

A decrease of pH and conductivity, as well as a decrease in the Cl^- concentration occurred after each washing step. Asphaltenes content in the bitumen increased in the recovered bitumen after washing by around 2% w/w.

Keywords: Anion, Cation, Ion transfer, bitumen, washing, emulsion, ashing, ICP, HPLC, Athabasca.

5.1 Introduction

The washing of Cold Lake bitumen was investigated in **Chapter 3** and **Chapter 4**. Due to the high water content in the raw bitumen used for the experiments, it was speculated that the ion transfer to the aqueous phase after the washing, was linked mainly to the connate water.

In this chapter, it is intended to elucidate if the water content was effectively related to the extent of ion removal observed when the washing of Cold Lake bitumen was performed. Athabasca bitumen, with low water content (<1% w/w), was washed using the same procedure used in **Chapter 4**. Ion determination on both the aqueous and organic emulsion phases was done, in order to compare it with the behavior observed from the washing of Cold Lake bitumen.

5.2 Experimental Section

5.2.1 Materials

The basic characterization for Athabasca bitumen can be found in **Table 5.1**. Properties of experimental interest of the Athabasca bitumen used were measured and reported as part of the results. Deionized water was obtained from a MilliPore Milli-Q Integral 5, with an ion conductivity of 1.28 ± 0.17 µS/cm and pH 7.04 ± 0.11. The deionized water was analyzed as blank for calibration purposes and the ionic content is considered as baseline for the ion quantification made for the analyzed samples reported in **Section 5.3**. The materials used in this chapter can be found in **Chapter 4**, **Section 4.2.1**, **Table 4.2.**

Table 5.1 Athabasca bitumen characterization

Property		Value
Elemental composition [%]	C	83.1-83.86
	H	10.5-10.7
	N	0.4-0.56
	O	0.8-1.41
	S	4.48-5.23
	H/C	1.49-1.54
API Gravity		8.6-11.3
Density [kg/m^3]		0.991-1.010
Viscosity [cp]	15 °C	18,000-371000
	25 °C	6,090-113000
	60 °C	459-1240
	100 °C	72-119
Ash [% w/w]		0.44-0.65
Vanadium [ppm w/w]		151.1-200
Nickel [ppm w/w]		49-87.2
Asphaltene [% w/w]		13.9-16.2

Source: Strausz & Lown, 2003

5.2.2 Equipment and Procedure

The equipment and procedure performed for this chapter, is the same used for the Cold Lake bitumen washing. Detailed description can be found in **Chapter 4**, **Section 4.2.2**.

5.2.3 Analyses

The analyses performed on the aqueous and organic emulsion phases, were described in **Chapter 4**, **Section 4.2.3**, and it can be summarized as: cation determination through ICP-OES, water content in organic phase was determined by Karl Fisher titration and oxygen content, pH/conductivity of aqueous phase, asphaltenes content in organic phase, simulated distillation (SimDis) of organic phase and Fourier Transform Infrared spectroscopy (FTIR).

5.2.4 Calculations

The performed calculations are available in **Chapter 4**, **Section 4.2.4**.

5.2.5 Calibrations

5.2.5.1 HPLC calibration

The calibration of the HPLC was performed as indicated in **Chapter 3, Section 3.2.5.1**.

5.2.5.2 ICP calibration

ICP calibration was performed as indicated in **Chapter 3**, **Section 3.2.5.2**.

5.2.5.3 pH/conductivity calibrations

The pH and conductivity calibrations were performed as indicated in **Chapter 3**, **Section 3.2.5.3**.

5.2.5.4 SimDis calibration

SimDis calibration was performed as indicated in **Chapter 4**, **Section 4.2.5.4**.

5.3 Results

5.3.1 Material Balance

The **Table 5.2** shows the average of the six individual material balances corresponding to each experiment. The individual material balances can be found in **Appendix 5.1**. In the initial stage, the mass of toluene used as solvent, mass of bitumen (for the first washing step), and mass of MilliQ water added for washing purposes are considered. For the subsequent washing steps, the mass of organic emulsion that was obtained from the previous step is taken as the new “initial stage” in terms of the organic fraction used for the next washing. In the recovery stage, the mass of organic emulsion, as well as the aqueous phase obtained after the separation was registered. In the Rotavap the toluene used as solvent was recovered, as well as some aqueous phase and the final remaining organic emulsion with lower content of water.

The losses for each washing step are between 1.12 to 2.94 % w/w. However, it is important to mention that despite the low percentage of losses, a high variability in the mass of aqueous phase was observed, as it can be seen in the standard deviation (s) for the recovered aqueous phase, which it was up to ± 51.87 g of water in the fourth washing step. Given the high variations in the recovered aqueous phase, the organic emulsion exhibited standards deviation in the same order too.

Table 5.2 Average material balance – Athabasca Bitumen washings

Stage	**Compound**	**Unit**	**Washing step**				**Rotavap**
			1	**2**	**3**	**4**	
Initial	Bitumen (M_{bit})	[g]	100.19	-	-	-	-
		s	0.08	-	-	-	-
	Organic emulsion	[g]	-	249.08	327.59	378.52	395.11
		s	-	21.76	19.88	19.88	57.42
	Toluene	[g]	104.46	-	-	-	-
		s	4.74	-	-	-	-
	Deionized (MilliQ) water	[g]	100.09	99.98	100.01	100.05	-
		s	0.28	0.14	0.13	0.23	-
	Total	[g]	304.73	349.05	427.60	478.57	395.11
		s	4.96	21.73	19.92	21.81	57.42
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	50.47	16.09	41.54	76.54	178.19
		s	18.98	9.30	17.13	56.83	53.12
	Organic emulsion	[g]	249.90	327.77	379.36	396.70	131.93
		s	21.54	19.78	21.87	56.27	21.29
	Toluene	[g]	-	-	-	-	86.47
		s	-	-	-	-	11.46
	Total	[g]	300.37	343.86	420.90	473.24	396.58
		s	5.95	21.14	17.58	22.94	65.08
	Losses	[%]	1.43	1.48	1.55	1.12	2.94
		s	0.68	0.35	0.58	1.33	1.88

s: sample standard deviation, -:not calculated

5.3.2 Anion determination through HPLC

The anion concentration was determined based on the built calibration curves, those anions that were not observed in the chromatogram were reported as “not detected”, in the same way, those anions that could be detected, but the intensity of the peak was too low that could not be quantified, were reported as “not quantified”.

The chromatogram for experiment 1 – aqueous sample recovered from the first washing step, is shown in **Figure 5.1**. It can be seen that there are peaks corresponding to Cl^-, SO_4^{2-} and HCO_3^- /CO_3^{2-}, also it was detected a low peak corresponding HPO_4^{2-} and NO_3^- in some samples; however, this element could not be quantified. The higher peaks were found for the aqueous phases recovered after the first washing step, decreasing after each washing step. Due to the dissociation equilibrium of HCO_3^- and CO_3^{2-}, these anions were reported as CO_3^{2-}.

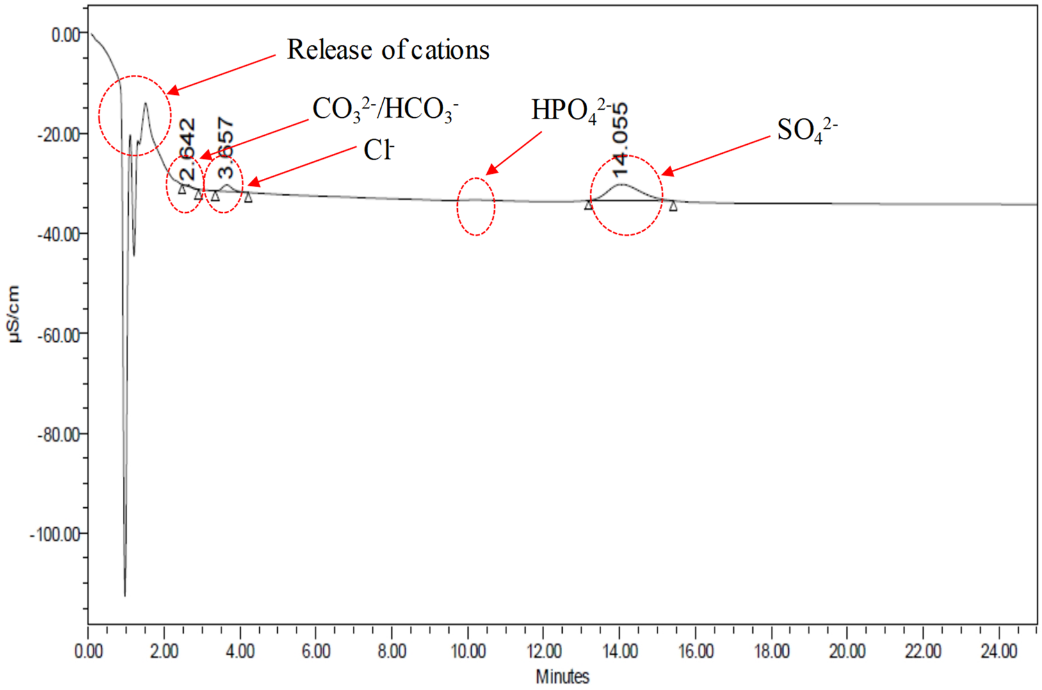

Figure 5.1 HPLC chromatogram for experiment 1, aqueous sample recovered from first washing step – Athabasca bitumen washing

Due to the high variation in the amount of recovered aqueous phase for each experiment, there were difficulties when comparing the removal of element *x* in the second washing step of experiment 1, with that of experiments 2 to 6. However, **Table 5.3** shows the anion removal for experiment 1. On the other hand, in the **Table 5.4** can be observed average of the six experiments corresponding to the anion concentrations for the washings steps 1-4, as well as the total anion removal, in the same way the anion removal for experiments 2-6 can be found in **Appendix 5.2**. As it can be seen, the anions that were found in the aqueous phase after each washing step were CO_3^{2-}, Cl^-, HPO_4^{2-}, SO_4^{2-}, with a higher contribution of CO_3^{2-} and SO_4^{2-}.

Table 5.3 Anion determination by HPLC for aqueous phase of experiment 1- Athabasca bitumen washing

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	
Recovered aqueous solution M_{aq} [g]	18	24	30	40	241	**Removed from bitumen**
Initial bitumen [g]			100			
Anion	**$C_{x,aq\ 1}$ [mg/L]**	**$C_{x,aq\ 2}$ [mg/L]**	**$C_{x,aq\ 3}$ [mg/L]**	**$C_{x,aq\ 4}$ [mg/L]**	**$C_{x,aq\ rot}$ [mg/L]**	**$(M_{x\ aq,total})$ [µg/g bitumen]**
F^-	nd	nd	nd	nd	nd	-
CO_3^{2-}	7	8	4	11	13	39
Cl^-	6	2	2	1	0	2
NO_2^-	nd	nd	nd	nd	nd	-
Br^-	nd	nd	nd	nd	nd	-
NO_3^-	nq	nd	nd	nq	nd	-
HPO_4^{2-}	nq	nq	nd	nq	1	-
SO_4^{2-}	75	33	25	21	10	62

nd: not detected, nq: not quantified, -: not calculated

Table 5.4 Average of anion determination for experiments 1-6 – Athabasca bitumen washing

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen**
Recovered aqueous solution M_{aq} [g]	50 ± 19	16 ± 9	42 ± 17	77 ± 57	178 ± 53	
Initial bitumen [g]			100			
Anion	$C_{x,aq\ 1}$ **[mg/L]**	$C_{x,aq\ 2}$ **[mg/L]**	$C_{x,aq\ 3}$ **[mg/L]**	$C_{x,aq\ 4}$ **[mg/L]**	$C_{x,aq\ rot}$ **[mg/L]**	**($M_{x\ aq,total}$) [µg/g bitumen]**
F^-	nd	nd	nd	nd	nd	-
CO_3^{2-}	25 ± 11	21 ± 14	17 ± 7	14 ± 10	12 ± 2	53 ± 8
Cl^-	6 ± <1	2 ± 1	1 ± <1	<1	<1	4 ± 1
NO_2^-	nd	nd	nd	nd	nd	-
Br^-	nd	nd	nd	nd	nd	-
NO_3^-	nq	nq	nq	nq	nd	-
HPO_4^{2-}	<1	<1	nd	nd	<1	<1
SO_4^{2-}	23 ± 25	18 ± 8	15 ± 5	14 ± 4	10 ± 2	46 ± 10

nd: not detected, nq: not quantified, -: not calculated

5.3.3 Cation determination through ICP-OES

For the cation determination, possible interferences during the analysis were reviewed through the spectra. **Figure 5.2** shows the ICP-OES spectra of the experiment 1 – aqueous phase for first washing step. The spectra were found to be similar to the described in the **Chapter 4**, **Section 4.3.3**, with the following exceptions:

Aluminum: The observed peak was well defined, with no interferences in the wavelength area corresponding to this element.

Cobalt: No interferences were observed.

Nickel: No interferences were observed.

Titanium: The existence a well defined peak at the wavelength of interest was not observed; therefore, it was considered that the element was not detected.

Zinc: No interferences were observed for this element.

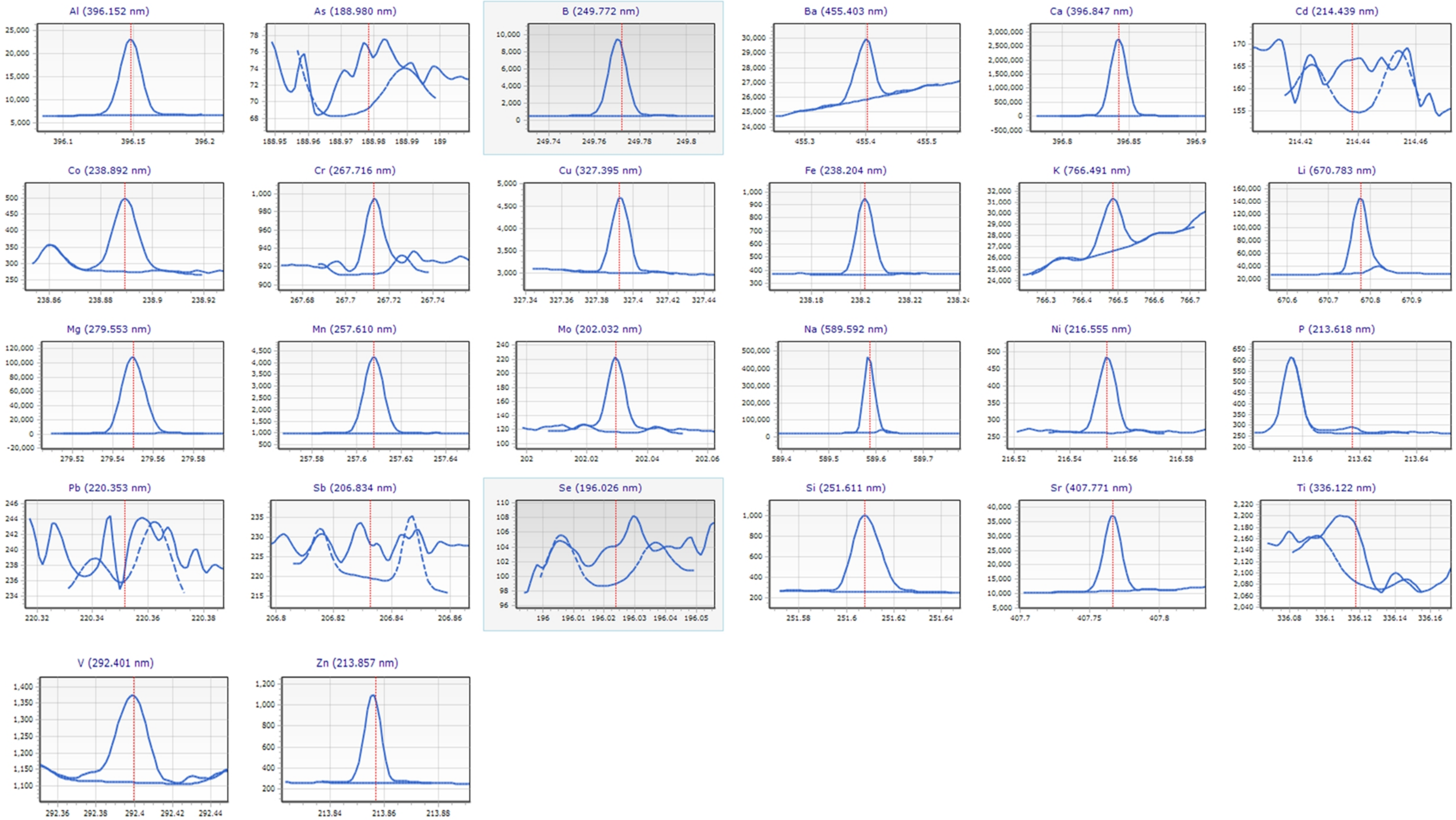

Figure 5.2 ICP-OES spectra of experiment 1 – aqueous phase first washing step – Athabasca bitumen washing

As it was mentioned for the anion determination in **Section 5.3.2**, the high variation in the amount recovered aqueous phase makes inadvisable to compare each washing step between experiments. However, the **Table 5.5** shows the cation determination for experiment 1 – aqueous phase for first washing step. In the **Table 5.6** the average of the cation determination on aqueous and organic phase of the experiments 1-6 can be found. Detailed information for experiments 2-6 is reported in **Appendix 5.3**.

The elements reported as "not detected" were not observed in the spectrum, while the elements reported as "not quantified", were detected in the spectrum but in such low concentration that it could not be quantified. Additionally, the spectrum around the wavelength of the emission used for each element was checked and for these cases, whether it was not observed variation on the baseline in the wavelength of interest, or the variation was too low in terms of intensity that were attributed to noise. The percentage of difference was calculated according to **Chapter 4, Equation 4.6**, and the percentage of removal was determined using **Equation 4.7** – **Chapter 4**.

When observing the cation determination for experiment 1 (**Table 5.5**), a high variation in the percentage of difference between the mass of element *x* per mass of bitumen and the sum of the mass of element *x* in both aqueous and organic phase per mass of bitumen was obtained. For this experiment, cations of elements such as B, Ca, Fe, K, Mg, Na, Si showed over 25% w/w of difference when comparing the amount of the element in the bitumen and the recovery after the washings.

Similarly, from the average determination (**Table 5.6**) it can be noticed that there was a high variation between $M_{x,bit}$ (mass of element *x* per mass of bitumen) and $M_{x,total}$ (mass of element *x* in both aqueous and organic phase per mass of bitumen). Cations of elements such as Al, B, Ca, Cu, K, Li, Mg, Na and Si exhibited differences over 25% w/w. On the other hand, lower differences between the raw bitumen and the sum of the aqueous and organic phase were obtained for cations of elements such as Fe, Ni, Ti and V (<15% w/w), with a percentage of removal through the washings of less than 2% w/w for the case of Fe and Ni, and no removal for Ti, V and Zn was observed.

It can be observed from **Table 5.5** and **Table 5.6** that some of the analyzed cations (elements Ba, Co, Cr, Li, Mn, P, Se) were removed in low quantities (≤1 μg/g bitumen). In these cases, the percentage of difference between the raw bitumen and the recovered aqueous and organic phases after washing, as well as the percentage of removal from bitumen through washing was not calculated due to the low cation concentrations reported for the aqueous and organic samples.

Table 5.5 Cation determination on aqueous and organic phase for experiment 1 – Athabasca bitumen washing

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen ($M_{x\ aq,total}$)**	**Organic phase ($M_{x,org}$)**	**Total ($M_{x\ aq,total}$ + $M_{x,org}$)**	**Athabasca bitumen ($M_{x,bit}$)**	**% *difference***	**% *removal***
Recovered aqueous solution M_{aq} [g]	18	24	30	40	241						
Cation of element	$C_{x,aq\ 1}$ [mg/L]	$C_{x,aq\ 2}$ [mg/L]	$C_{x,aq\ 3}$ [mg/L]	$C_{x,aq\ 4}$ [mg/L]	$C_{x,aq\ rot}$ [mg/L]	[µg/g bitumen]	[µg/g bitumen]	[µg/g bitumen]	[µg/g bitumen]	[%]	[%]
Al	2	<1	<1	<1	<1	<1	3	3	2 ± 1	-21	<50
As	nq	nq	nq	nq	nq	-	nq	-	nq	-	-
B	<1	<1	<1	<1	<1	1	1	2	1 ± 1	-100	100
Ba	nd	nd	nd	nd	nd	-	<1	<1	<1	*	*
Ca	2	1	1	1	1	4	27	31	8 ± 7	-288	45
Cd	nd	nd	nd	nd	nd	-	nd	-	nd	NA	NA
Co	<1	<1	<1	<1	<1	<1	<1	<1	<1	*	*
Cr	nq	nq	nq	nq	nq	-	<1	<1	<1	*	*
Cu	<1	<1	<1	<1	<1	<1	1	1	1 ± 2	*	*
Fe	<1	<1	nd	nd	<1	<1	4	4	3	-33	<33
K	1	1	<1	<1	<1	1	4	5	3 ± 1	-67	39
Li	1	<1	<1	nd	nd	<1	<1	<1	<1	*	*
Mg	<1	<1	<1	<1	<1	1	2	3	1 ± <1	-200	113
Mn	<1	<1	<1	<1	<1	<1	nd	<1	<1	*	*
Mo	<1	nd	nd	nd	nd	<1	8	8	9 ± 1	11	<11
Na	17	10	6	5	3	17	15	32	16 ± 6	-100	106
Ni	<1	<1	<1	<1	<1	<1	76	76	68 ± 7	-12	<2
P	<1	<1	<1	<1	<1	<1	5	5	<1	>-400	*
Pb	<1	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Sb	<1	<1	<1	<1	nd	<1	nd	<1	nd	NA	NA
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Si	<1	<1	<1	<1	<1	<1	1	2	10 ± 2	76	<10
Ti	nd	nd	nd	nd	nd	nd	3	3	2	-23	0
V	<1	nd	nd	nd	nd	<1	223	223	186 ± 31	-20	0
Zn	<1	<1	<1	<1	<1	<1	1	2	1 ± 1	*	*

nd: not detected, nq: not quantified, NA; not applicable, -: not calculated, *: not calculated due to the low concentration

Table 5.6 Average of cation determination on aqueous and organic phase for experiments 1-6 – Athabasca bitumen washing

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen ($M_{x\ aq,total}$)**	**Organic phase ($M_{x,org}$)**	**Total ($M_{x\ aq,total} + M_{x,org}$)**	**Athabasca bitumen ($M_{x,bit}$)**	***% difference***
Recovered aqueous solution M_{aq} [g]	50 ± 19	18 ± 9	42 ± 17	77 ± 50	178 ± 53					
Cation of element	**$C_{x,aq\ 1}$ [mg/L]**	**$C_{x,aq\ 2}$ [mg/L]**	**$C_{x,aq\ 3}$ [mg/L]**	**$C_{x,aq\ 4}$ [mg/L]**	**$C_{x,aq\ rot}$ [mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**
Al	<1	<1	<1	<1	<1	<1	3 ± <1	3 ± <1	2 ± <1	-50
As	nq	nq	nq	nq	nq	nq	nq	nq	nq	-
B	<1	<1	<1	<1	<1	<1	1 ± <2	2 ± <2	1 ± 1	-100
Ba	nd	nd	nd	nd	nd	nd	<1	<1	<1	*
Ca	1 ± <1	<1	<1	1 ± <1	1 ± <1	3 ± <1	12 ± 9	15 ± 9	8 ± 7	-88
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA
Co	<1	<1	<1	<1	<1	<1	<1	<1	<1	*
Cr	nq	nq	nq	nq	nq	nq	<1	<1	<1	*
Cu	<1	nd	<1	<1	<1	<1	2 ± 2	2 ± 2	1 ± 2	-100
Fe	<1	nd	nd	nd	<1	<1	3 ± <1	3 ± <1	3 ± <1	0
K	1 ± <1	<1	<1	<1	<1	1 ± <1	3 ± <1	4 ± <1	3 ± 1	-33
Li	<1	<1	<1	<1	<1	<1	<1	<1	<1	*
Mg	<1	<1	<1	<1	<1	<1	1 ± <1	2 ± <1	1 ± <1	-100
Mn	<1	<1	<1	<1	<1	<1	<1	<1	<1	*
Mo	<1	nd	nd	nd	<1	<1	7 ± 3	7 ± 3	9 ± <1	22
Na	13 ± 2	4 ± 4	5 ± 1	3 ± 1	3 ± 1	16 ± 1	13 ± 5	29 ± 6	16 ± 6	-81
Ni	<1	<1	<1	<1	<1	<1	67 ± 7	67 ± 7	68 ± 7	1
P	<1	<1	<1	<1	<1	<1	1 ± 2	1 ± 2	<1	*
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA
Sb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA
Se	nd	nd	nd	nd	nd	nd	<1	<1	nd	*
Si	<1	<1	<1	<1	2 ± 3	4 ± 4	3 ± 2	7 ± 6	10 ± 2	27
Ti	nd	nd	nd	nd	nd	nd	2 ± <1	2 ± <1	2 ± <1	2
V	<1	nd	nd	nd	nd	<1	197 ± 20	197 ± 20	186 ± 31.25	-6
Zn	<1	<1	<1	<1	<1	<1	1 ± <1	1 ± <1	1 ± <1	*

nd: not detected, nq: not quantified, NA; not applicable, -: not calculated, *: not calculated due to the low concentration

5.3.4 Water content in raw bitumen and organic emulsion

The water content in the Athabasca bitumen and the recovered organic emulsion samples was determined by Karl Fisher titration according to **Chapter 3**, **Section 3.2.3.4**. Additionally, the water content of the Athabasca bitumen was determined by elemental composition according to **Chapter 3, Section 3.2.3.7**. The results of water content by Karl Fisher titration are shown in **Table 5.7**. A first set of analyses was performed without homogenizing the sample, with high variability in the results. For this reason, it was decided to homogenize the samples following the procedure detailed in **Chapter 4**, **Section 4.2.2**. However, it was encountered that despite the preheating and homogenization procedure, some variations were found during the sub-sampling process for this analysis, but these variations resulted being lower than the analysis without homogenization. The samples analyzed by Karl Fisher titration were analyzed in triplicate, while the elemental composition of the Athabasca bitumen each of the three samples was analyzed two times.

Table 5.7 Water content by Karl Fisher titration in organic phase after toluene/water removal – Athabasca bitumen washing

Name	***%water* - non homogenized sample**		***%water* - homogenized sample**	
	[%] w/w	**s**	**[%] w/w**	**s**
Athabasca bitumen	0.01	0	**-**	**-**
Experiment 1	20.28	5.46	16.08	1.24
Experiment 2	24.86	7.45	26.55	1.17
Experiment 3	29.49	3.96	25.23	0.98
Experiment 4	-	-	13.49	2.90
Experiment 5	-	-	8.78	0.50
Experiment 6	-	-	6.14	0.07

[-]: Samples not analyzed

It can be noticed that the organic emulsion corresponding to the experiments 1-3 resulted in higher water content than the experiments 4-6. The experimental procedure for the bitumen washing (**Chapter 4**, **Figure 4.1**), was performed for experiments 1-3 at the same time; similarly, experiments 4-6 were done together. Findings regarding this difference were discussed in **Section 5.4.4.**

Table 5.8 shows the elemental composition of three samples of Athabasca bitumen. Each sample was analyzed twice. The oxygen content for the Athabasca bitumen (**Table 5.1**) was reported to be 0.8-1.41% w/w. The elemental analysis performed on the samples indicated that the oxygen content resulted to be between the range reported in the literature. For this reason, the water content was calculated according to **Chapter 3**, **Equation 3.9**, for those values of oxygen content over the range of reference. To be conservative, 1.41% w/w of oxygen as the reference value for calculations was taken.

Table 5.8 Elemental composition of Athabasca bitumen, and water content based on oxygen content

Sample	**Wt. (mg.)**	**%N [%] w/w**	**%C [%] w/w**	**%H [%] w/w**	**%S [%] w/w**	**%O [%] w/w**	**%water based on oxygen content [%] w/w**
Athabasca bitumen 01	1.84	0.51	83.18	10.25	4.51	1.55	0.15
	1.47	0.54	83.47	10.49	4.73	0.76	*
Athabasca bitumen 02	1.42	0.55	83.35	10.45	4.66	0.99	*
	1.88	0.52	83.40	10.44	4.70	0.93	*
Athabasca bitumen 03	1.70	0.53	83.34	10.45	4.74	0.94	*
	1.72	0.53	83.27	10.50	4.70	1.00	*
Average	**1.67**	**0.53**	**83.34**	**10.43**	**4.67**	**1.03**	**0.03**
s	**0.19**	**0.01**	**0.10**	**0.09**	**0.08**	**0.27**	**0.06**

*: too low to be quantified, used “0” for average and standard deviation purposes

From **Table 5.7** and **Table 5.8**, it can be noticed that the water content in the Athabasca bitumen was very low. The water content by Karl Fisher titration (**Table 5.7**) was found to be 0.01 % w/w, while the water content determined by oxygen content (**Table 5.8**) was calculated as 0.03 ± 0.06. Due to the low oxygen content calculated by difference from the elemental analysis, and using 1.41% w/w as the oxygen content for Athabasca bitumen, it can be stated that both analysis used to determine the water content are in agreement.

5.3.5 pH/conductivity of aqueous phase

The pH measurements for experiment 1 are shown in **Figure 5.3**. In **Figure 5.4**, it can be observed the conductivity measurements and the Cl^- concentration for each washing step corresponding to experiment 1 measured by HPLC. Individual results for experiments 1-3 are shown in **Table 5.9**. These parameters showed decreasing trends after each washing step.

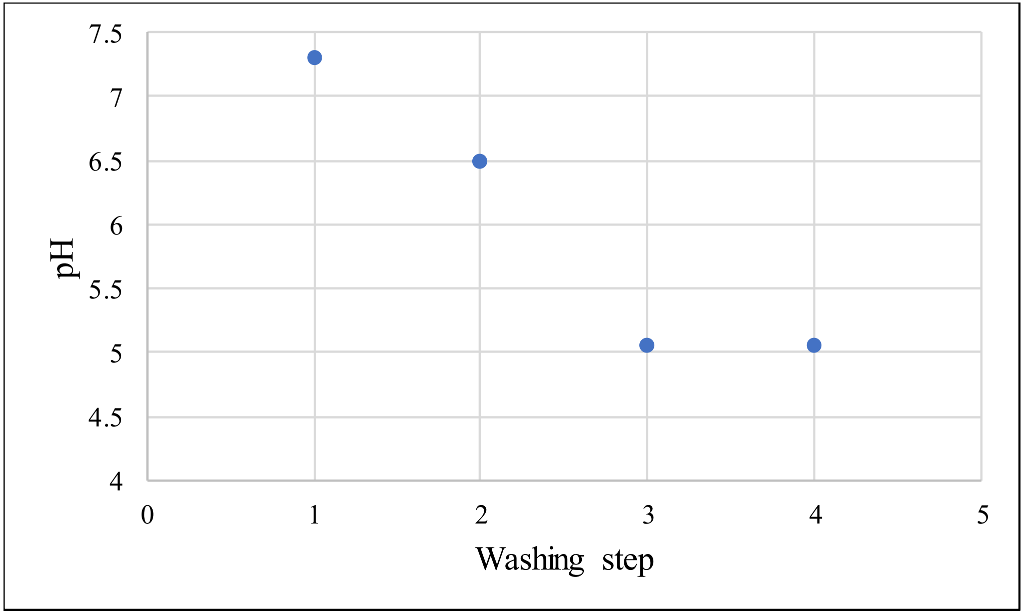

Figure 5.3 pH of aqueous phase for experiment 1 – Athabasca bitumen washing

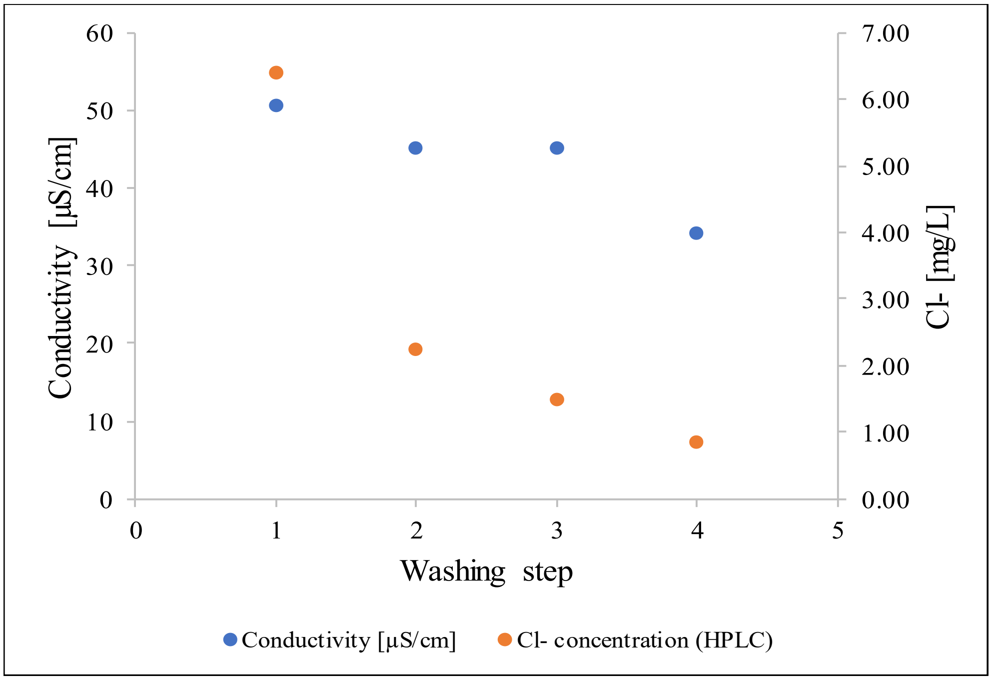

Figure 5.4 Conductivity and Cl$^-$ concentration determined by HPLC of aqueous phase for experiment 1 – Athabasca bitumen washing

Table 5.9 pH, conductivity and chloride concentration for aqueous samples, experiments 1-3

Experiment	**Washing step**	**pH**	**Conductivity [µS/cm]**	**Cl$^-$ concentration (HPLC) [mg/L]**	**Calculated Cl- [mg/L]** *
1	1	7.3	50.7	6.41	16.0
	2	6.5	45.3	2.25	14.3
	3	5.1	45.2	1.51	14.2
	4	5.1	34.3	0.88	10.8
2	1	7.3	50.6	4.7	15.9
	2	-	-	1.7	-
	3	5.3	38.0	0.8	12.0
	4	4.7	29.0	0.3	9.1
3	1	7.3	45.3	5.6	14.3
	2	6.3	50.2	1.3	15.8
	3	6.3	28.2	2.0	8.9
	4	6.4	27.9	0.7	8.8

-: not measured/not calculated, *: calculated concentration based on the calibration curve of the conductivity meter

5.3.6 Asphaltenes content

The asphaltenes content obtained and calculated based on the water content (**Table 5.7**) is listed in **Table 5.10**. The analyses were performed once for experiments 1-3.

Table 5.10 Asphaltenes content – Athabasca bitumen washing

Name	**Sample Weight**	**Water content (KF titration)**	**Asphaltenes weight**	**$\%_{asphaltenes}$ (not corrected)[*]**	**$\%_{asphaltenes}$ (corrected)[**]**
	[g]	**[%] w/w**	**[g]**	**[%] w/w**	**[%] w/w**
	1.12	0.01	0.19	17.34	17.51
Athabasca bitumen	1.09	0.01	0.17	15.19	15.34
	1.16	0.01	0.18	15.82	15.98
Average	**1.12**	**0.01**	**0.18**	**16.11**	**16.28**
s	**0.03**	**0.00**	**0.01**	**1.11**	**1.12**
Experiment 1	1.07	0.16	0.15	13.76	16.39
Experiment 2	1.06	0.27	0.14	13.51	18.50
Experiment 3	1.14	0.25	0.16	13.65	18.21
Average	**1.09**	**0.23**	**0.15**	**13.64**	**17.70**
s	**0.04**	**0.06**	**0.01**	**0.13**	**1.15**

s: standard deviation of experiments 1-3, [*]: Asphaltenes content based on the total weight of sample, [**]: Asphaltenes content based on the “dry” weight of sample (discounting water content determined by Karl Fisher titration)

The calculated asphaltenes content in the organic samples was consistently between 16 to 19 % w/w, with a standard deviation of ±1.15%. Compared to the Athabasca bitumen, there is an increase of around 2%. However, the sample standard deviation for both the Athabasca bitumen and the recovered organic emulsion was placed around 1% w/w. The weight of the sample was corrected according to the water content determined by Karl Fisher titration (**Table 5.7**).

5.3.7 Simulated distillation (SimDis) of organic emulsion

Simulated distillation was performed on raw Athabasca bitumen and 3 organic emulsion samples after all the washing steps and toluene/water removal by evaporation in a Rotavap. The weight of the organic emulsion samples was corrected according to the water content determined through Karl Fisher titration (**Table 5.7**), to represent the distillation curve adjusted to the actual amount of organic fraction injected. **Figure 5.5** shows the distillation profile for these samples, and **Figure 5.6** the distillation profiles that were corrected in terms of the water content.

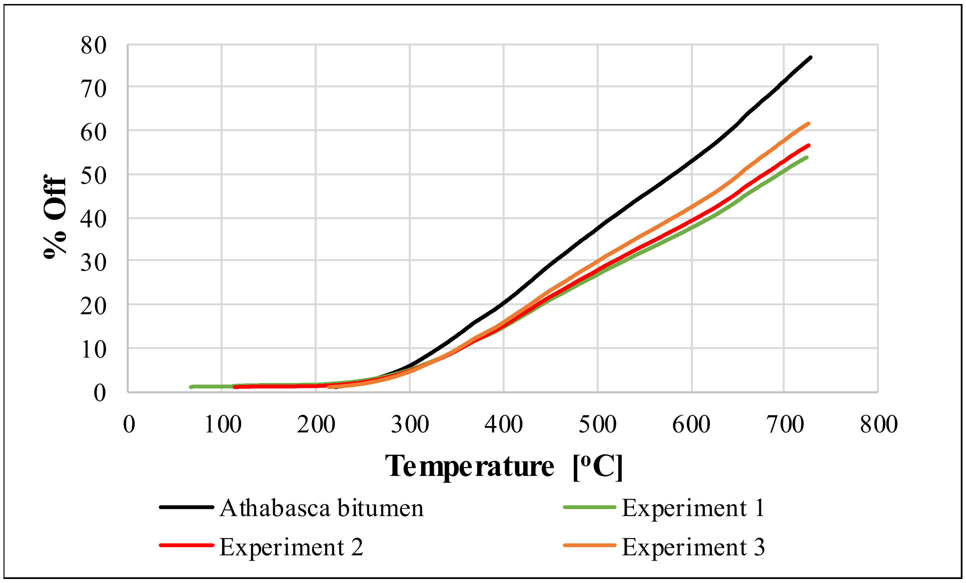

Figure 5.5 Simulated distillation of Athabasca bitumen, and organic emulsion samples for experiments 1-3

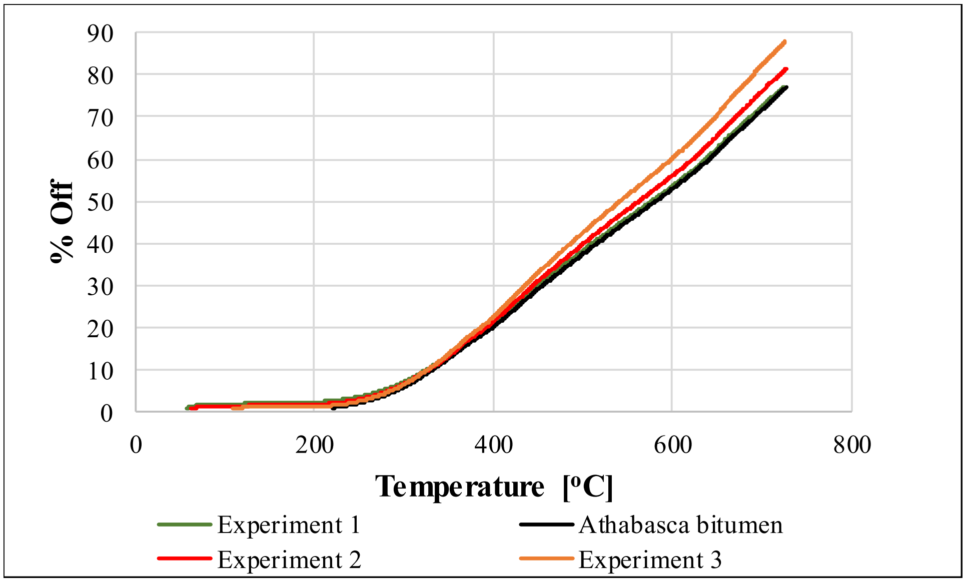

Figure 5.6 Simulated distillation of Athabasca bitumen, and organic emulsion after washing and toluene/water removal (corrected water content determined by Karl Fisher titration)

5.3.8 Fourier Transform Infrared Spectroscopy (FTIR) of organic emulsion

The organic emulsion samples after evaporation in the Rotavap were analyzed by FTIR. **Figure 5.7** shows the FTIR spectrogram for the Athabasca bitumen and the organic emulsion sample for experiment 1. It can be observed within 2400 and 2200 cm^{-1} some differences between the Athabasca bitumen and the recovered organic phase from experiment 1, corresponding to CO_2. Also, in the range of 1780-1740 cm^{-1} it is observed that the C=O interactions for the Athabasca bitumen looked to be more pronounced compared to the ones obtained for the recovered bitumen from experiment 1. Finally, it is observed that there is difference around 728 cm^{-1}. Spectra for experiments 2 and 3 can be found in **Appendix 5.4**.

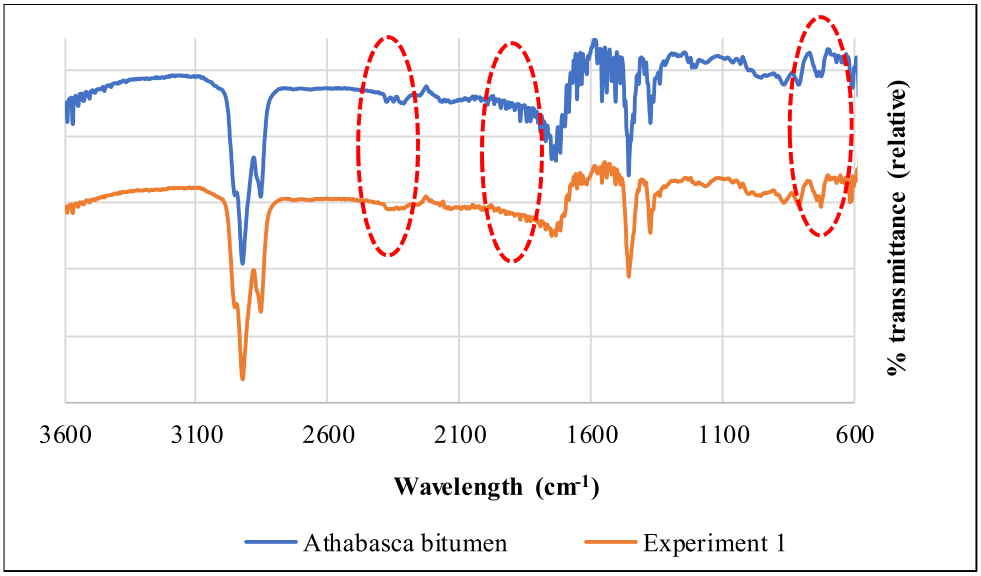

Figure 5.7 Fourier Transform Infrared Spectroscopy for Athabasca bitumen and experiment 1

5.4 Discussion

5.4.1 Material Balance

The material balance in **Table 5.2** shows low overall percentage of losses during the experimental procedure (up to 2.94 ± 1.72%) which is acceptable considering the sample manipulation during each washing step (removal of magnetic stir bar, transfer from flask to separation funnel and vice versa). Additionally, typically between the separation of aqueous phase from organic emulsion and the subsequent washing step, there was one to two days where the organic emulsion was covered with parafilm. The samples were weighted before and after this storage period and it was found that some losses occurred, this might be due to some toluene and water volatilization.

5.4.2 Ion transfer

As it was observed in **Table 5.4** for the experiment 1, the water washing was able to promote the transfer of anions. According to the literature (Allen, 2008), bicarbonates, chlorides, sulphates and phosphates are found in process affected water. The anions that were detected (HCO_3^-, CO_3^{2-}, Cl^-, HPO_4^{2-}, SO_4^{2-}) supported it. In the raw bitumen some anionic species remained after the production process (mining or steam assisted gravity drainage – SAGD), due to the nature of the bitumen source or to the quality of the water used for the bitumen production. At the experimental conditions, the removal of these anions occurred during all the washing, decreasing after each step. The mixture water/bitumen after being in contact seems to reach an equilibrium stage for the anion transfer, once the aqueous phase is separated from the organic emulsion and fresh water is added to the system, the transfer occurs again until reaching the equilibrium. Since the total amount of ions susceptible to be removed through this treatment decreases after each washing, the amount of anion removed in each stage becomes lower in consequence. Sulphates exhibited the highest removal (62 µg/g bitumen) followed by Chlorides (2 µg/g bitumen), both species are known for being harmful to refining processes as well as affecting the crude oil value (Gary and Handwerk, 2007). Considering that Alberta bitumen contains a high level of sulfur, in the range 4.1-6.2%, it is expected to find considerable amounts of sulphates as a result of oxidation processes and its presence in the connate water (Strausz and Lown, 2003).

On the other hand, when analyzing the average of the total amount of removed anions for experiments 1-6 (**Table 5.3**), it is noticed that the observed behavior in experiment 1 is valid for the experiments 2-6. Sulphates were removed in highest proportion (46 ± 9 µg/g bitumen) followed by Chlorides (4 ± 1 µg/g bitumen). Despite the high variations regarding the amount of water removed after each washing step for experiments 1-6, the trend of total Cl^- and SO_4^{2-} removed through the washings remained consistent.

The high percentages of difference between the Al in the raw bitumen and the recovered in the aqueous and organic phases can be attributed to the insolubility of ignited Aluminum oxides (**Chapter 2, Table 2.1**). Cations of elements such as B exhibited a high percentage of difference between the raw bitumen and the recovered phases after washing. The same behavior was observed in the determination of cations of Na and Si, where an important percentage of difference between these elements in the raw bitumen, and the amount of these elements obtained in the aqueous and organic phases after washing was found.

The determination of cations of Ca showed a high variability, for each individual experiment and, consequently, for the average of experiments 1-6. In the **Table 5.5**, it was observed an important standard deviation for the quantification of cations of Ca in the raw bitumen (8 ± 7 µg/g bitumen) and the recovered organic phase (12 ± 9 µg/g bitumen), while the quantification in the aqueous phase remained nearly constant (3 ± <1 µg/g bitumen). As it was mentioned in **Chapter 4**, the ignition temperature may produce fused calcium residues (McCoy, 1962), as well as the leaching of cations of Ca (Meyer and Meyer, 1976), could interfere in this measurement.

Some elements were not removed through bitumen water washing. Cations of elements such as Ni, Ti and V exhibited low or no removal (<2, 0 and <1% respectively). This behavor was also observed in **Chapter 3** during the washing of Cold Lake bitumen. However, it has been determined that nickel is associated to the organic and inorganic fractions with no apparent preference (Filby and Branthaver, 1987), this could explain the fact that some cations of Ni (<2%) were removed from the bitumen through water washing.

Other cations of elements such as As and Cr were detected in such low concentrations that they could not be quantified in the aqueous phase. Cations of Cr was detected in low amounts (<1 µg/g bitumen) in the raw bitumen and the organic phase. On the other hand, cations of elements such as Fe, K, Mg, Mn and Zn, were detected in low quantities (<1 µg/g bitumen) in the aqueous phase; therefore, an important removal of these elements was not observed.

To determine if the ions removed and quantified in the aqueous phase were related to the connate water in the Athabasca bitumen, theoretical dilution curves for SO_4^{2-} and Cl^- were built. Since the connate water could not be separated and analyzed due to the low content in the bitumen, reference values of these anions in the Athabasca bitumen connate water were used: 727 mg/L for SO_4^{2-} and 218 mg/L for Cl^- (Strausz and Lown, 2003). Additionally, the projection taking the concentration of Cl^- in the Cold Lake bitumen water determined experimentally and reported in **Appendix 3.1** is added (8977 mg/L). Since the Cl^- concentration in the Cold Lake bitumen connate water was much higher than the one found in the literature for the Athabasca bitumen, this projection was useful to compare the profiles in case of having higher concentrations of this anion. The **Figure 5.8** shows the projection of the concentration of Cl^- in the connate water, as well as the experimental concentrations obtained in the aqueous phase after each washing step.

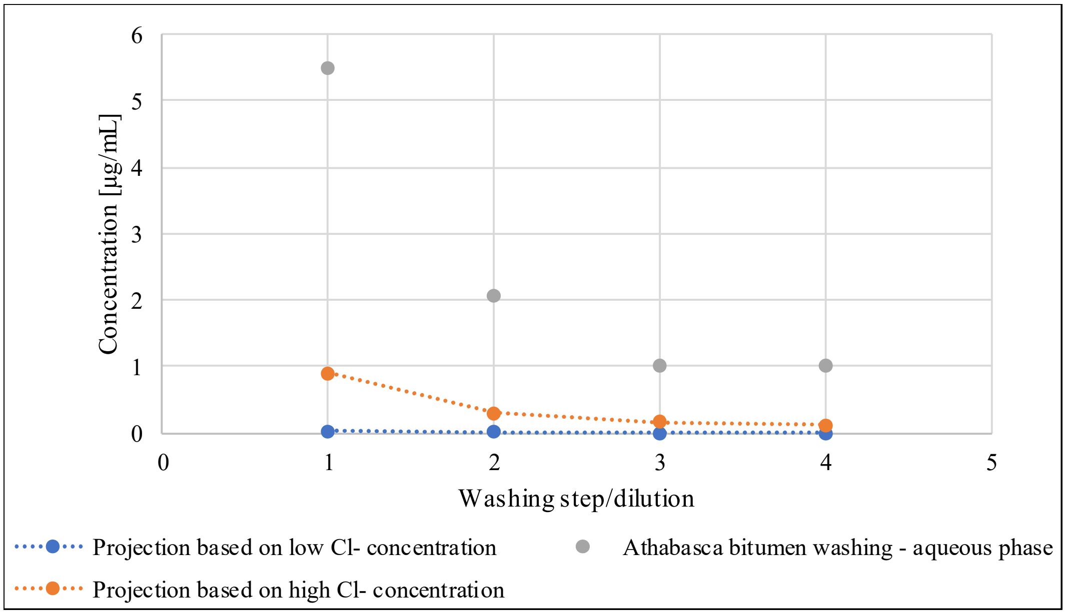

Figure 5.8 Concentration of Cl^-: Theoretical dilutions of the connate water depending the Cl^- concentration, and experimental concentrations after each washing step of Athabasca bitumen.

As it was previously mentioned, two theoretical dilution curves were built, using the literature reference value, and using the experimental value of the Cold Lake water which was higher than the reference, according to **Chapter 4**, **Equation 4.10**. However, due to the very low water content, it can be noticed that the experimental concentration of Cl^- in the recovered aqueous phase after each washing was higher than both projections. Additionally, it was calculated the total quantity of Cl^- present in the aqueous phase, and it was compared to the quantity of Cl^- in the connate water using both the low and high Cl^- concentrations. As it was done in **Chapter 4**, **Section 4.4.2**, it was assumed that the concentration of the water remaining within the organic phase was the same than that of the recovered aqueous phase. The **Figure 5.9** shows the results of this comparison.

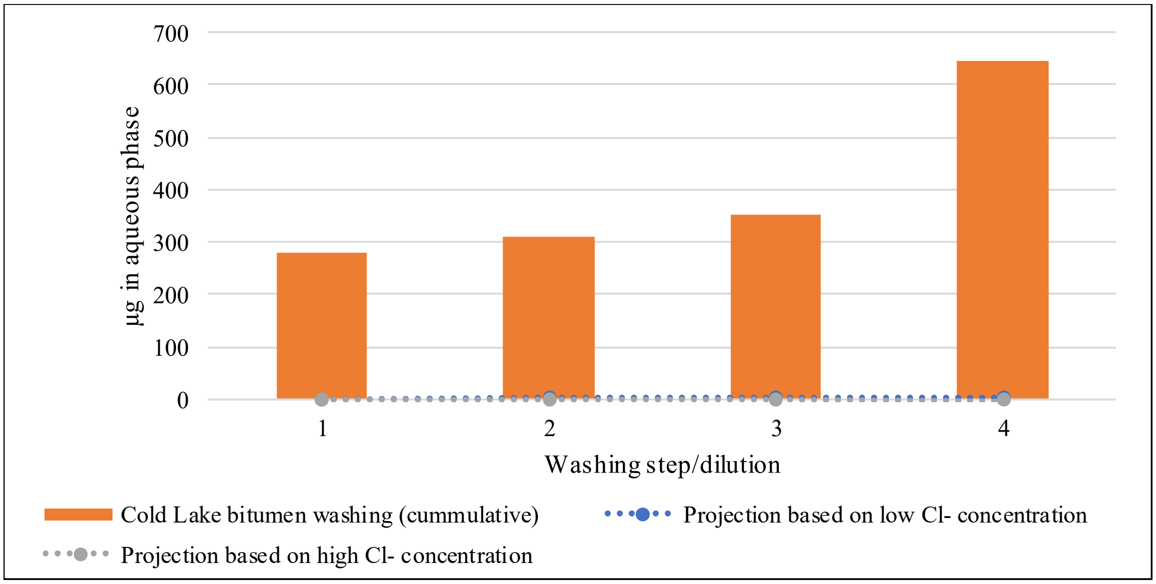

Figure 5.9 Mass of Cl^-: Theoretical mass in the aqueous phase after each washing step, and experimental mass based on the concentration after each washing step of Athabasca bitumen

The **Figure 5.9** demonstrates that the Cl^- present in the aqueous phase samples after each washing step, were related to the bitumen and not to the connate water. However, when comparing the extent of removal of this anion to the observed in the Cold Lake bitumen washing (**Chapter 4**, **Figure 4.16**), there is a high difference between the quantity of Cl^- in the Cold Lake bitumen and its connate water that were removed through the water washing.

Similarly, the **Figure 5.10** and **Figure 5.11** shows the concentration profiles for the removal of SO_4^{2-}. In this case, it was only used the reference concentration of SO_4^{2-} in the Athabasca bitumen connate water available in the literature (Strausz and Lown, 2003), since for the Cold Lake water no SO_4^{2-} were detected.

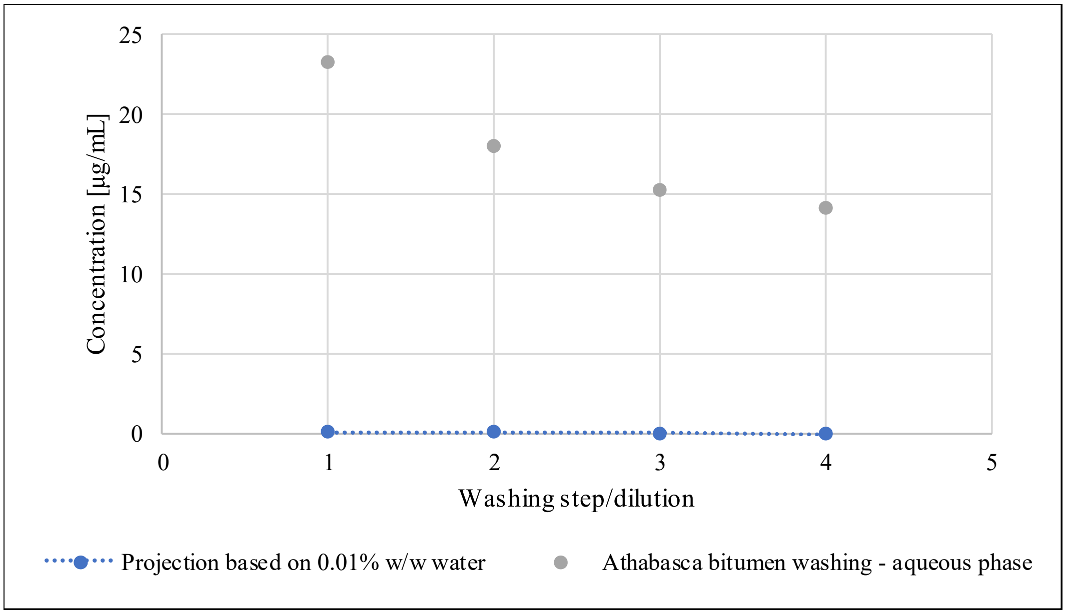

Figure 5.10 Concentration profile for SO_4^{2-} in the connate water and in after each washing step of Athabasca bitumen

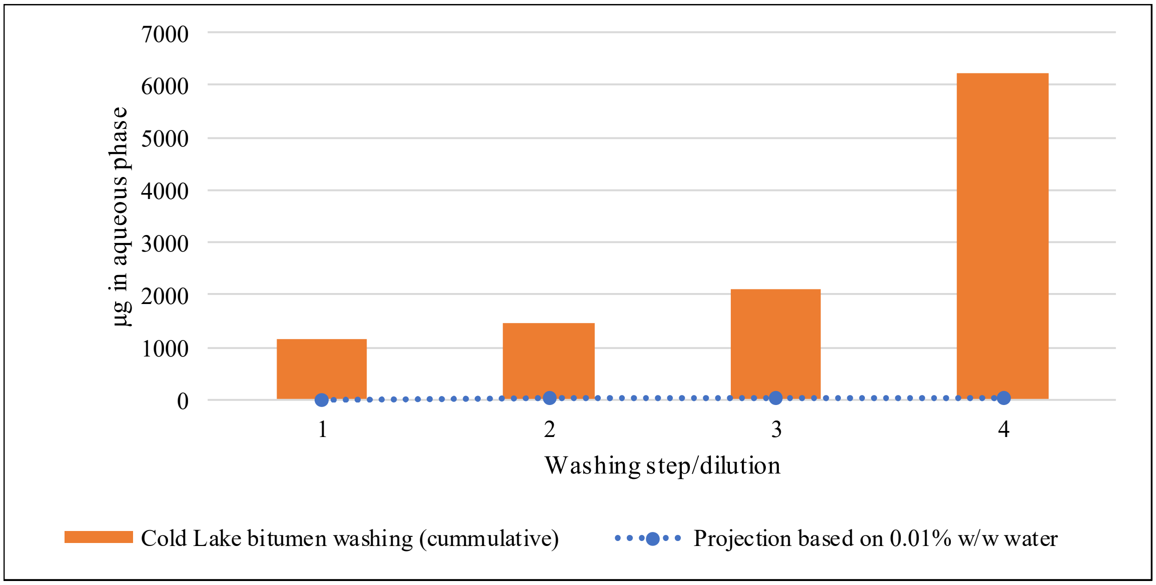

Figure 5.11 Mass of SO_4^{2-}: Theoretical mass in the aqueous phase after each washing step, and experimental mass based on the concentration after each washing step of Cold Lake bitumen

The **Figure 5.10** and **Figure 5.11**, supported the observations made from **Figure 5.8** and **Figure 5.9**. The SO_4^{2-} removed by the water washing was linked to the bitumen.

The projection of cations of Na was not presented since as it was discussed previously, inconsistencies between the quantity of Na in the raw bitumen, and the quantities of Na in both the recovered aqueous and organic emulsion samples was observed. The washing of Athabasca bitumen resulted in lower concentration of cations of Na (**Table 5.6**) compared to that observed from the washing of Cold Lake bitumen (**Chapter 4**, **Table 4.7**). Due to this, differences in the concentration of this cation had a higher influence in the percentage of difference between the raw bitumen and the recovered aqueous and organic emulsion phases. The comparison of this cation under these conditions in unadvisable.

5.4.3 pH/conductivity in aqueous phase

The pH results of the aqueous samples for experiment 1 observed in **Figure 5.3**, as expected, decreased through each washing step. Carbonates are known for acting as buffers, with a pH for aqueous suspensions of CaCO3, $CaMg(CO_3)_2$ and $MgCO_3$ between 8.9 and 9.5 (Strausz and Lown, 2003). Since carbonates/bicarbonates were found in higher concentration for the first washing step, the pH reduction for the subsequent steps can be attributed to the decrease/absence of this anion in the aqueous phase, as well as the presence of some acid salts, such as $KHSO_4$, $FeCl_3$ and some sodium phosphates. In the oil sands process affected water (OSPW), several studies have pointed the presence of naphthenic acids as a primary source of toxicity of these effluents (Mahaffey and Dubé, 2016). Therefore, it can be speculated that some organic acids can be released after the continued contact of the bitumen and the water, however, this hypothesis was not further developed, since it was not considered within the scope of this study.

Regarding the conductivity measurements, **Figure 5.4** described the decreasing behavior of conductivity in the aqueous phase during the water washing steps. The concentration reduction of ions such as chlorides in the aqueous phase explains the decrease of the conductivity and supports the fact of having a decrease in the total removed amount of ionic species after each stage of the washing process.

It was found that the calculated Cl^- concentration based on the calibration curve of the conductivity meter was consistently higher than the Cl^- concentration determined by HPLC. This could de related to the presence of some organic ionic species that may affect the total conductivity and are expressed as Cl^- concentration. For the measurement of pH and conductivity, the samples were not filtered to remove any organic compounds, while to analyze the samples in the HPLC, the sample was taken and filtered using a SepPak C18 cartridge, to avoid the pass of organic through the column.

5.4.4 Water in organic emulsion

The results shown in **Table 5.7** confirmed that the organic emulsion samples contained a high amount of water after the washing and evaporation in the Rotavap procedure. Additionally, it was found that the samples after being stored and then used for sub-sampling for analyses became stratified, as it can be seen in the non-homogenized sample's results (**Table 5.7**). A high standard deviation was obtained since during the sub-sampling process non-homogeneous amounts of water in oil emulsion were taken, considering that for most of the analysis the amount of sample required was lower than 1 g, these non-homogeneities could have led to inconsistent results. For this reason, it was decided to pre-heat and stir the samples for 30 minutes to promote the reconstitution of the original emulsion. As it can be seen in the homogenized column results (**Table 5.7**), the water content obtained by Karl-Fisher titration showed lower standard deviations (up to 2 % vs 7 %). However, some minor variances in the water content could affect in an important dimension some results such as asphaltenes content, simulated distillation, ionic content, etc.

It was mentioned that the water content by Karl Fisher titration was higher in experiments 1-3 compared to the results obtained for experiments 4-6. Checking the material balance (**Table 5.2**), looking for any differences during the washing steps, it was observed that for all the experiments, despite the high variability of the recovered phases, during the first 3 steps of the washing, the recovered mass of organic emulsion was similar between experiments. However, it could be noticed that in the washing step 4, the recovered organic emulsion for experiments 1-3 was higher than the one for experiments 4-6. The **Table 5.11** shows this difference.

Table 5.11 Recovered organic emulsion during washing steps for experiments 1-6

Sample	**Recovered organic phase [g]**			
	1	**2**	**3**	**4**
Experiment 1	286.47	356.39	416.47	466.09
Experiment 2	256.15	343.04	374.68	419.64
Experiment 3	239.10	306.70	358.03	395.27
Average	**260.57**	**335.38**	**383.06**	**427.00**
s	**23.99**	**25.72**	**30.11**	**35.98**
Experiment 4	253.76	325.20	357.57	416.40
Experiment 5	241.09	328.74	386.34	386.02
Experiment 6	222.82	306.52	383.05	296.78
Average	**239.22**	**320.15**	**375.65**	**366.40**
s	**10.05**	**11.21**	**5.47**	**46.90**

In the **Table 5.11**, the mass of recovered emulsion of experiments 1-3 and 4-6 is presented, and its average and standard deviation was calculated for both group of experiments. It can be noticed, that the mass of recovered organic emulsion for experiments 1-3 in the last washing step resulted in an average of 427.00 g, while the average of recovered emulsion for the experiments 4-6 in the last washing step was 366.40 g. After checking in detail, the differences between both group of experiments, it was detected that for experiments 4-6, 48 hours in the separation funnel, for decantation were given; compared to the 24 hours given for experiment 1-3 in this last washing step. This additional time allowed the emulsion to further separate, and hence to recover more free water as part of the aqueous phase.

5.4.5 Asphaltenes content

The asphaltenes content determined for three experiments (**Table 5.10**) showed that the asphaltenes after the correction due to the water content was made, was consistently around 18% w/w. It was found that the analyzed samples contained around 2% w/w more asphaltenes than the obtained in the Athabasca bitumen. It is important to mention that, despite the homogenization process performed for all the samples, it cannot be guaranteed that during the sub-sampling process (1g of sample is taken to determine asphaltenes) any inhomogeneity can be present and affect these results. However, considering that for the three experiments were obtained very similar results, it can be inferred that the washing process is affecting the asphaltenes content by increasing it, this can be supported by the fact of having around 1% of sample standard deviation in both the raw and the recovered bitumen. It can be speculated that the ion removal promoted new bonding between the asphaltenes and other bitumen structures (such as maltenes and resins), leading to a slight increase of the asphaltenes content. However, this hypothesis was not further investigated.

5.4.6 Simulated distillation (SimDis) of organic emulsion phase

The variations observed in the simulated distillation were related mainly to the water content of the organic emulsion. **Figure 5.5** shows the simulated distillation for the Athabasca bitumen and the organic emulsion obtained from experiments 1-3. The weight of the organic emulsion phase samples was corrected considering the water content determined in **Table 5.7**. The corrected simulated distillations are shown in **Figure 5.6**, it can be observed that the distillation profiles after water correction showed no significant difference between the organic emulsion phase samples and the raw bitumen, therefore it can be inferred that the water washing had no effect on this property.

5.4.7 Fourier Transform Infrared Spectroscopy

FTIR analysis was performed on the organic emulsion samples (**Figure 5.7**). The region between 3600 – 3200 cm^{-1} corresponds to the O-H stretching for free liquid water, however it was observed a high percentage of transmittance which seems not to be corresponding to the water content in the samples determined by Karl Fisher titration (**Table 5.7**). Some studies refer that the presence of certain anions can destroy or weaken the hydrogen-bonded network of water (Uchida et al., 2015). This might explain the absence of strong absorbance related to free water. On the other hand, the C-H stretching at 3032 cm^{-1} as well as the C-C stretching at 1506 cm^{-1} corresponding to aromatic ring were not observed in the different collected spectra. However, at 728 cm^{-1} it could be observed a slight decrease of the transmittance, indicating the presence of toluene. It can be considered that after the toluene removal through evaporation in the Rotavap, no significant amount of this solvent can be detected through this analysis.

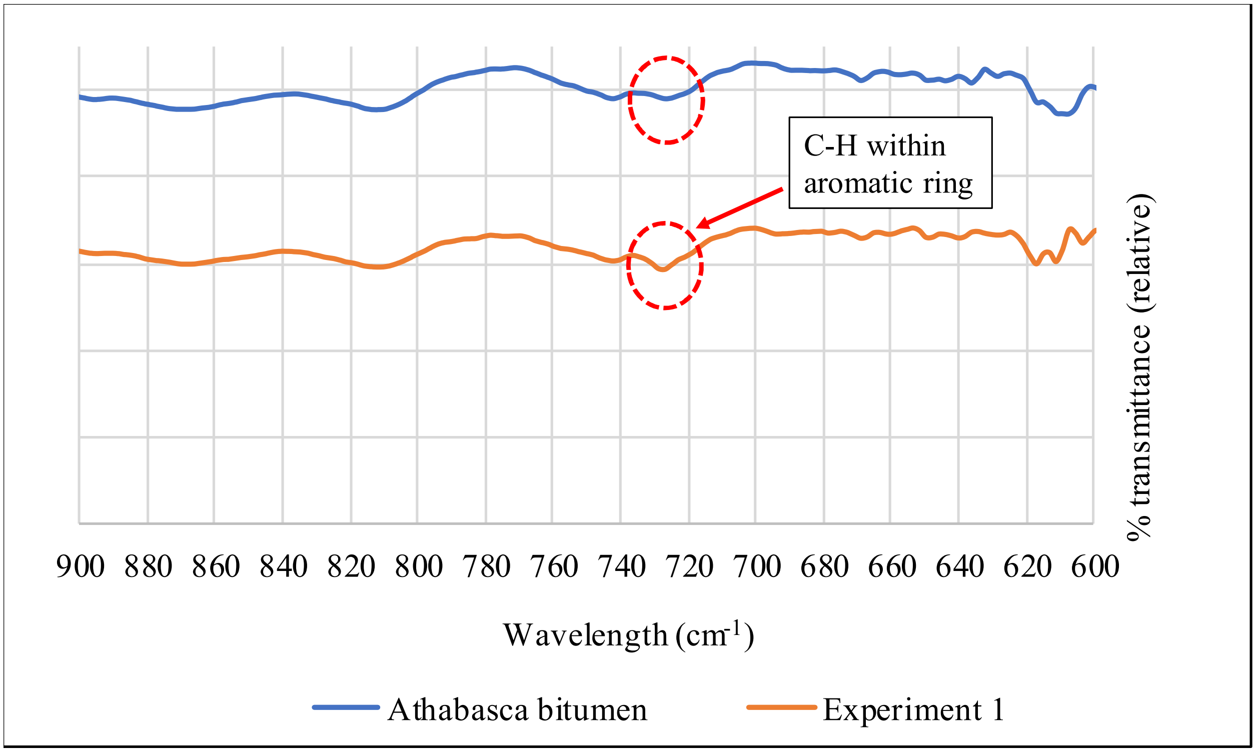

Figure 5.12 Fourier Transform Infrared Spectroscopy for Athabasca bitumen and experiment 1 within the range of 900-600 cm^{-1}

Differences observed in the region of 2400 and 2200 cm^{-1} can be attributed to background CO_2. Regarding the range of 1780-1740 cm^{-1} (C=O interactions), even when it was observed a lower percentage of transmittance for the Athabasca bitumen compared to the recovered bitumen from experiment 1, a pathlength correction was not made for these analyses; therefore, the difference between the intensities in both cases could be related to differences in the pathlength.

5.5 Conclusions

The main purpose of this chapter was to determine if the water washing was able to remove some ions from the Athabasca bitumen. Anion and cation determination in both aqueous and organic emulsion phase was fundamental to answer this question. Other complementary analysis allowed to study if the water washing could affect some bitumen properties. The main findings are:

- The water washing as described in this study, produced two main phases: an aqueous phase, and an organic emulsion containing up to 27% w/w of water. The water content determination was fundamental to correctly interpret the results. Also, homogenization of the sample was required to express more accurately the effect of water content on the organic emulsion phase.

- Water washing was able to remove Cl^- and SO_4^{2-}. Further evaluation of the HPLC chromatogram led to the identification of HCO_3^-/CO_3^{2-} that were also removed. HPO_4^{2-} was also removed in a much lower proportion.

- Most of the cations were not significantly removed from the bitumen. Higher removal was observed in cations of elements such as Al, Ca, Fe, Na, K and Si.

- Other cations of elements such as Ni, Ti and V were barely removed through the water washing performed on Athabasca bitumen, and the percentage of difference between the quantification of these elements in the raw bitumen and the sum of both the aqueous and organic phases was found to be lower than 10% w/w in average.

- The removal of ions was linked to the Athabasca bitumen and not to the connate water. This was verified by building projection curves of ion concentration in the existent water and comparing it to the actual concentrations obtained experimentally.

- Other characteristics such as pH and conductivity of the aqueous phase were in agreement with the results observed of anion and cation removal. Additionally, the aqueous phases changed from alkaline to acidic as the washing progressed through the four equilibrium stages.

- The asphaltenes content increased around 2% w/w after washing the bitumen. It was speculated that the ion removal after the washing procedure led to some additional bonding between the asphaltenes and other bitumen structures, however, this hypothesis was not further investigated.

- Other bitumen properties (simulated distillation and Fourier Transform Infrared Spectroscopy) showed little variations in the organic emulsion after water washing. The presence of remaining toluene could be observed in the Fourier Transform Infrared spectra; on the other hand, the influence of the high water content was observed on the simulated distillation profiles.

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6. CONCLUSIONS

The goals of this study were the investigation of the effect of water chemistry on the bitumen, specifically in the removal of ions and its impact on some bitumen properties. Different strategies were explored to evaluate how the water in contact with bitumen can influence the bitumen. The following are the most important conclusions of this study:

Chapter 3 - Washing of bitumen with neutral and acid aqueous solutions, at different salt concentrations:

In this chapter, it was of interest to determine if the dissolved salts in the water used to process bitumen industrially had an impact on its properties. This question was based on the observations pointed in previous work about the effect of acid washing on bitumen (Gonzalez, 2015). The conclusions related to this section can be summarized as:

- The increase of salt content in neutral solutions increased the viscosity of the bitumen after washing. **Figure 6.1** corresponding to the washing of Cold Lake at neutral pH illustrates this finding.

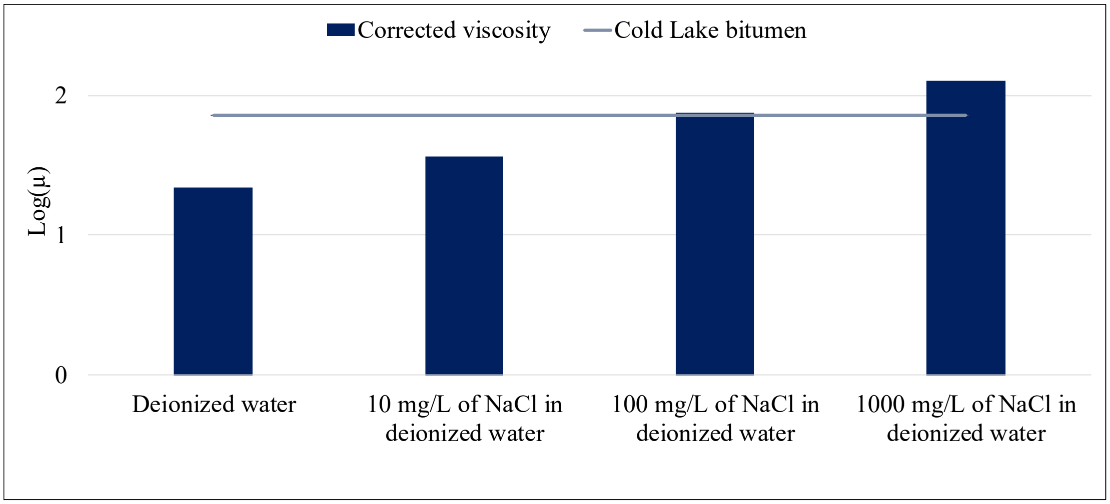


Figure 6.1 Impact of salt content on viscosity at neutral pH

- The increase of salt content in acid solutions decreased the viscosity of the bitumen after washing. **Figure 6.2** corresponding to the washing of Cold Lake bitumen at acid pH shows this trend.

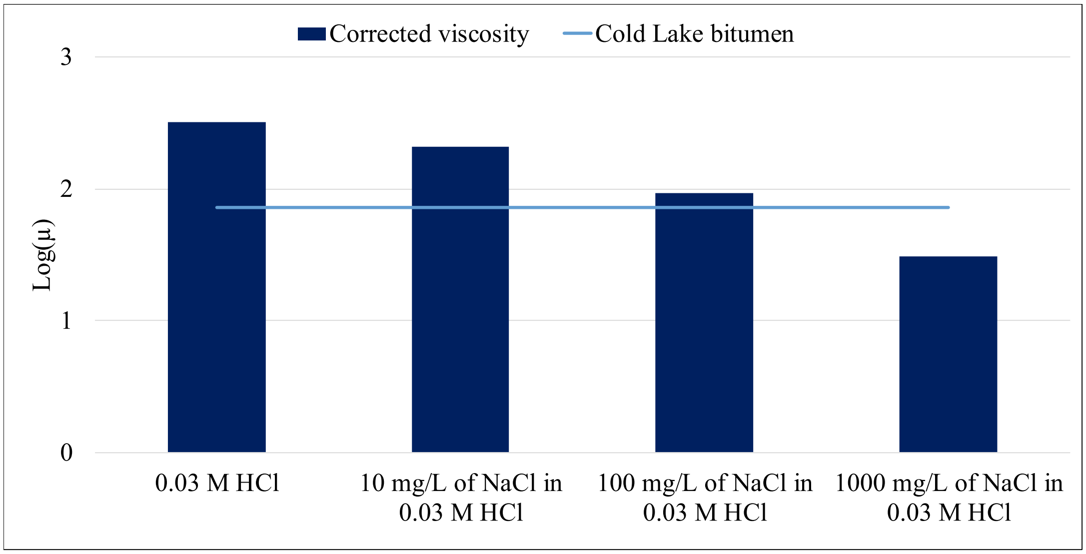


Figure 6.2 Impact of salt content on viscosity at acid pH

Chapter 4 - Washing of Cold Lake bitumen with deionized water, at several equilibrium separation stages:

In this section, four-step washing of Cold Lake bitumen with deionized water was performed. It was of interest to investigate if the removal of ions observed in Chapter 3 was linked to connate water, as well as to determine if this washing could improve the removal of these ions. The following are the main findings:

- Based on ion concentration, removal of ions can be explained to come from the connate water. However, the experimental results suggested that the salts were retained in some way by the organic phase. Using the removal of cations of Na as example, the **Figure 6.3** shows that, there is a gap between the removal of cations of Na after each washing step, and the theoretical dilution based on the Na concentration in the connate water.

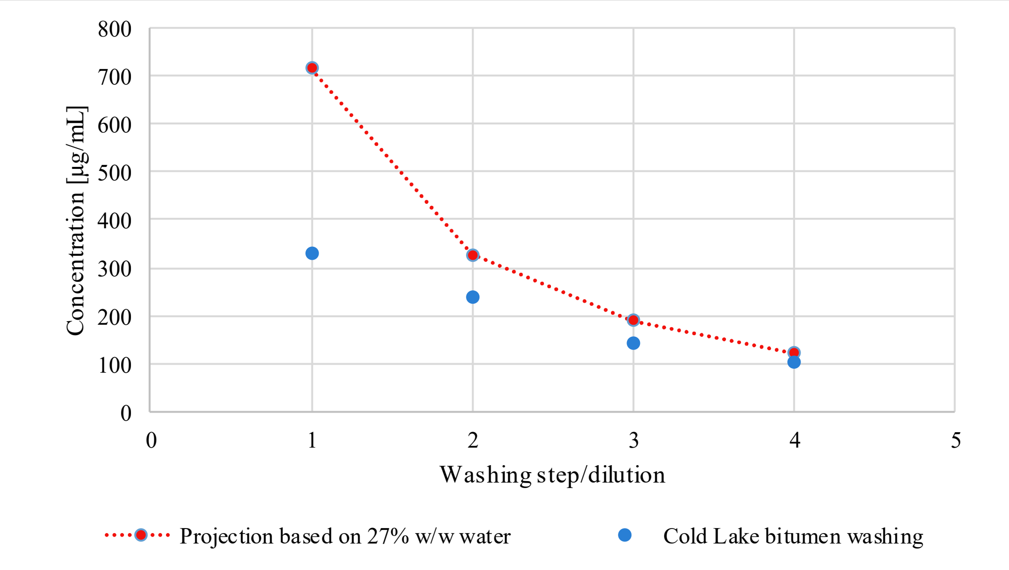
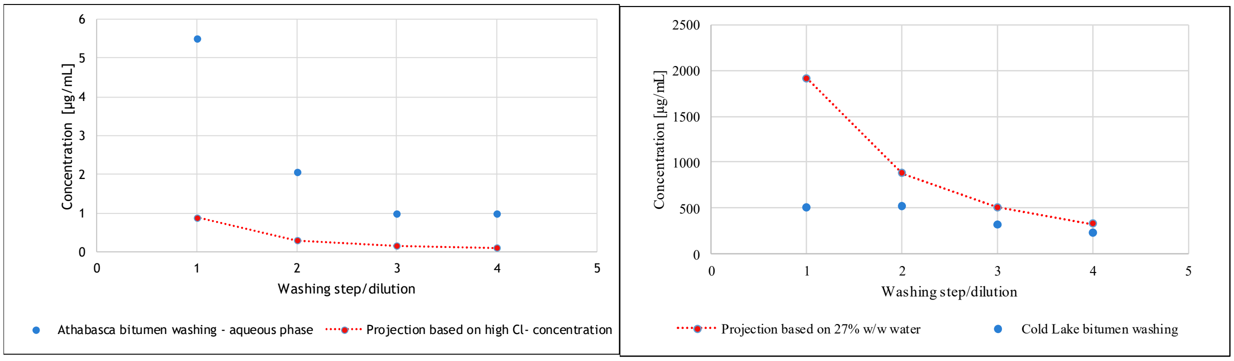


Figure 6.3 Na concentration in aqueous phase vs theoretical Na concentration from dilution of connate water.

Chapter 5 - Washing of Athabasca bitumen with deionized water

In this section, the washing of Athabasca bitumen was performed by the same procedure applied in **Chapter 4**. The main objective was to determine if using a bitumen with low water content, the removal of ions could still be explained in terms of connate water, or whether some ions were removed from the bitumen. The findings of this section can be summarized as:

- The removal of ions from the Athabasca bitumen washing was linked to the bitumen. This is demonstrated in **Figure 6.4** by using the Cl^- removal as example. The experimental concentration of Cl^- exceeded the theoretical dilution of the connate water. Additionally, the comparison of the washing of a low-water content bitumen, and the washing of a high-water content bitumen, showed that there is an important difference in the order of magnitude when washing when high-water content is present in the bitumen. Additionally, the use of a low-water content bitumen demonstrated that ions linked to the bitumen were removed and detected in the aqueous phase.



(A) **(B)**

Figure 6.4 Comparison of Cl^- concentration in aqueous phase vs theoretical Cl^- concentration for A: Athabasca bitumen washing, B: Cold Lake bitumen washing.

Recommendations

- Washing was performed using two different bitumen feeds. The water content of the raw bitumen highly influenced the results. Determining in a precise way the water content is fundamental, and the selection of bitumen with low water content is suggested to avoid the misinterpretation of the results.

- The remaining solvent in the bitumen had an important influence on properties such as the viscosity. The addition of controlled amounts of solvent in the recovered bitumen to make this remaining content equal for all the samples, would equilibrate the contribution of the solvent in all the samples.

- The asphaltenes content was determined for the recovered emulsions on a wet basis. Then, the water content was discounted from the original weight to calculate the asphaltenes content on a basis free of water. In a future work, it is recommended to evaporate the water from the samples at low temperatures (up to 150°C), before determining the asphaltenes content. This could avoid inaccuracies and misinterpretation of the results.

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Appendix 3.1 WATER CONTENT DETERMINATION – COLD LAKE BITUMEN

In this section, the procedures that were developed to determine the water content in the Cold Lake bitumen used in the experiments of **Chapter 3** and **Chapter 5** are described. Additionally, it is described the procedure used to separate the water contained in this bitumen, as well as the results of the analysis of this water by ICP-OES and HPLC.

A.3.1.1 Equipment and procedure

Water content in the bitumen was determined by Karl Fisher titration (**Chapter 3, Section 3.2.3.4**). For the Cold Lake bitumen, the results were cross-checked using the following procedure:

Samples of 10 and 20 g of bitumen were placed in a 100-mL Fisherbrand® wide-form porcelain crucible. The dish was previously dried at 150ºC in a Carbolite CWF1100 oven for 30 minutes and then weighed. Weighing was performed using a Mettler Toledo ML-3002E/03 balance (capacity 3.2 kg, readability 0.1 g).

The bitumen was placed at 150ºC for 8 hours, checking the weight until it remained constant. The water content was then determined by:

$$\%_{water\ by\ weight,bitumen} = \frac{Mass_{bitumen,initial} - Mass_{bitumen,final}}{Mass_{bitumen,initial}} * 100 \qquad \textbf{Equation A3.1}$$

Where

$\%_{water\ by\ weight,bitumen}$: Percentage of water by weight in the bitumen [%] w/w
$Mass_{bitumen,initial}$: Initial mass of bitumen [g]
$Mass_{bitumen,final}$: Final mass of bitumen, after drying in the oven [g]

In the case of obtaining high percentage of water in the bitumen (>3% w/w), it was of interest to characterize the connate water; therefore, the following procedure was applied (**Figure A3.1**):

100 g of bitumen were diluted in 400 mL of toluene in a 1000 mL-beaker. To ensure the dissolution of the bitumen, the beaker was stirred for one hour at 400 rpm, using a 5 cm octagonal magnetic bar and a Heidolph MR Hei – Standard hot plate. Then, the mixture was left for two hours in a 1000-mL separation funnel. After this, the bottom layer (water-in-oil emulsion) was transferred to 30 mL centrifuge vials, until completely transfer this layer. The vials were centrifuged at 7830 rpm for 20 minutes, using Eppendorf 5430 centrifuge. The top layer was removed using a 9 inches glass pipette. Then, the bottom layer was weighed, and diluted by 100 with deionized water.

The vials were sonicated for 5 minutes in a BRANSON 2800 sonicator. The top layer (organic) was removed using a 9 inches glass pipette, and then the bottom layer (aqueous) was filtered using a Sep-Pak® filter to remove any organic traces. Anion and cation content was analyzed by HPLC and ICP-OES. The analysis and calibration for the anion and cation determination were described in **Chapter 3,** Sections, **3.2.3.1**, **3.2.3.2**, **3.2.4.2**, **3.2.4.3**.

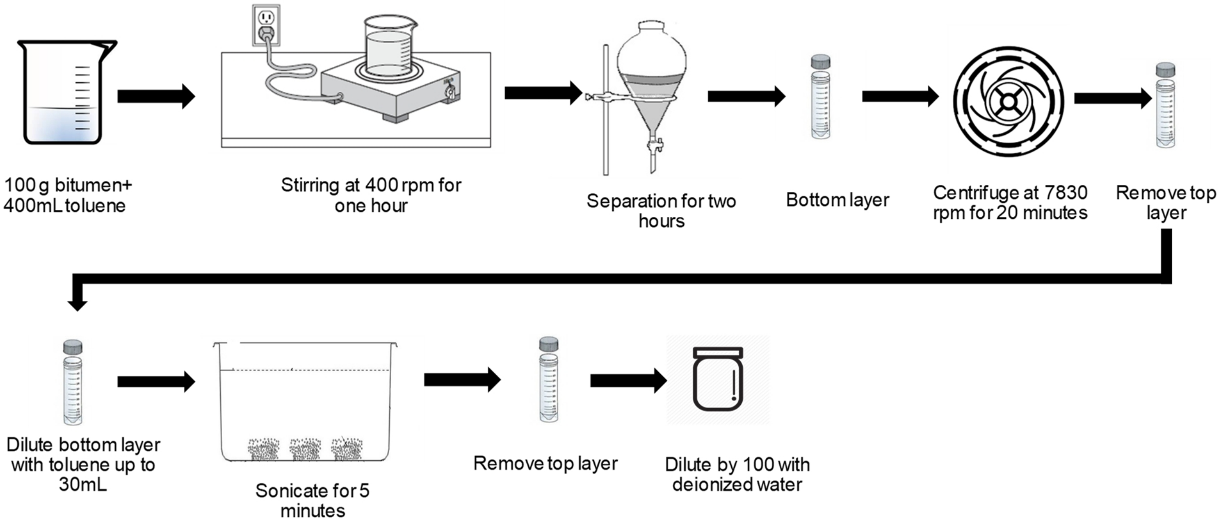

Figure A3.1.1 Experimental procedure - Water removal from Cold Lake bitumen

A.3.1.2 Results

The water content determined by drying the Cold Lake bitumen, can be found in the **Table A3.1.1**. It can be noticed that the water content was 27.1 ± 1.9 % w/w. It can be noticed that the water content was found to be higher than the water content determined by Karl Fisher. As it was discussed in **Chapter 5**, the small amount of sample used to determine the water content by this method (0.500 g) could lead to these differences when comparing to the drying of 20 g of bitumen.

Table A3.1.1 Water content in Cold Lake bitumen by drying at 150ºC

Sample	Cold Lake bitumen							
	SimDis recovery at 187°C [%] w/w^{a}=0.5 %							
	1	2	3	4	5	6	Average samples 1-3	Average samples 4-6
$Mass_{bitumen,initial}$ [g]	20.0	20.1	20.6	10.0	10.0	10.0	20.2 ± 0.3	10.0 ± 0.0
$Mass_{bitumen,1\ hour}$ [g]	15.6	15.4	15.6	7.9	7.7	7.6	15.5 ± 0.1	7.7 ± 0.2
$Mass_{bitumen,10\ hour}$ [g]	14.3	14.5	14.8	7.7	7.3	7.2	14.5 ± 0.3	7.4 ± 0.2
$Mass_{bitumen,final}$ [g]	14.3	14.5	14.8	7.7	7.3	7.2	14.5 ± 0.3	7.4 ± 0.2
$\%_{water\ by\ weight,bitumen}$	28.5	27.9	28.2	23.3	27.0	27.8	27.1 ± 1.9	

[a]: Simulated distillation reported in **Chapter 5**, **Figure 5.9**

On the other hand, since the water content was found to be high, the separation of water and its analysis was performed as described in **Figure A3.1.1**. After the mixture was left for two hours in the separation funnel, it was observed a top and bottom layer (**Figure A.3.1.2**). The bottom layer consisted of an water-in-oil emulsion, and it was obtained around 60 to 100 mL of emulsion from the separation funnel. After centrifuging the sample, it was observed that the phase separation was improved (**Figure A3.1.3**).

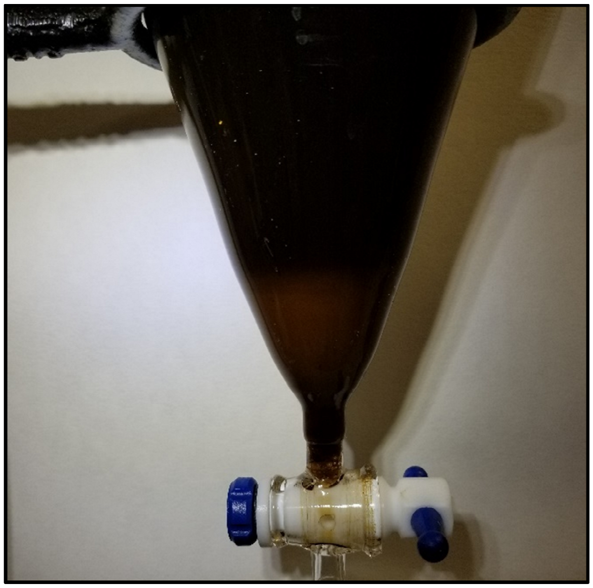

Figure A3.1.2 Mixture of Cold Lake bitumen and toluene after two hours in the separation funnel

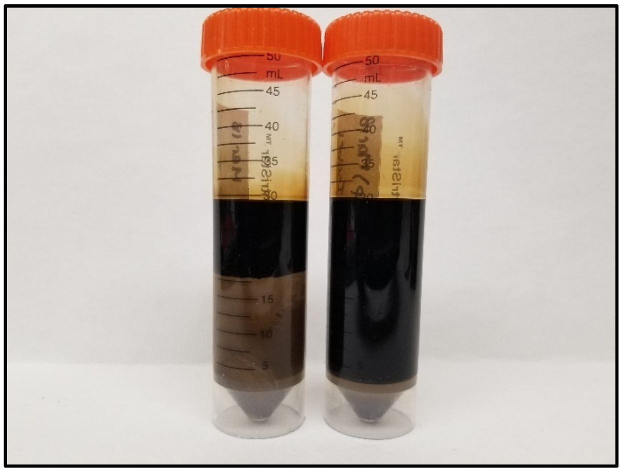

Figure A3.1.3 Vials after centrifuging to improve separation. To the left, the lower bottom portion taken from the separation funnel. To the right, the higher bottom portion taken from the separation funnel

After sonicating the sample, it was recovered 3 ± 2 g of free water (**Figure A.3.1.4**). After removing the top layer, the aqueous phase was diluted by 100 times with deionized water.

Figure A3.1.4 Aqueous phase separation after dilution with toluene and sonication

It was observed that the top layer consisted of an emulsion. This was confirmed by filtering it with a Sep-Pak® filter. **Figure A.3.15** and **Figure A.3.1.6** shows that effectively the top layer retained more water that could not be separated by sonication.

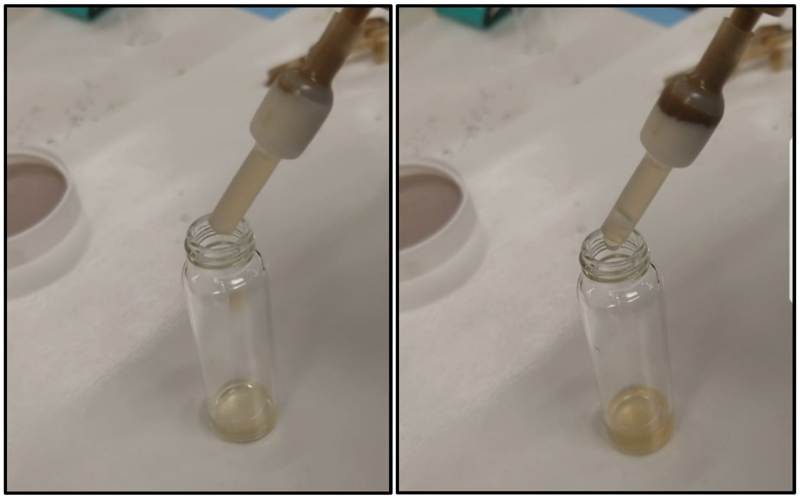

Figure A.3.1.5 Filtration of top emulsion after sonication. To the left, it can be observed that water is filtered at the beginning of the filtration. To the right, the filter rapidly saturates with organics.

The anion and cation content were determined by HPLC and ICP-OES respectively. Results are reported in the **Table A3.1.2** and **Table A3.1.3**. It was quantified the presence of Cl^-, and it was detected the presence of SO_4^{2-}, but the concentration was too low that it could not be quantified. The concentrations of Cl^- was found to be higher than 4800 mg/L; however, due to the low amount of water that it could be separated from the bitumen, when calculating the amount of Cl^- per mass of bitumen, it was determined 240 ± 37 μg/g bitumen.

Table A3.1.2 Anion determination in water separated from the Cold Lake bitumen

Sample	**Water recovered from Cold Lake bitumen**							
	1		**2**		**3**		**Average**	
Recovered aqueous solution M_{aq} [g]	5		2		2		3 ± 2	
Initial bitumen [g]	100		100		100		100	
Anion	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass Mx,aq [µg/g bitumen]**
F^-	nd	-	nd	-	nd	-	nd	-
CO_3^{2-}	nd	-	nd	-	nd	-	nd	-
Cl^-	4835	242	11977	275	10120	202	8977 ± 3706	240 ± 37
NO_2^-	nd	-	nd	-	nd	-	nd	-
Br^-	nd	-	nd	-	nd	-	nd	-
NO_3^-	nd	-	nd	-	nd	-	nd	-
HPO_4^{2-}	nd	-	nd	-	nd	-	nd	-
SO_4^{2-}	nq	-	nq	-	nq	-	nq	-

nd: not detected, nq: not quantified, -: not calculated

Regarding the cation determination, it was determined that the highest concentration corresponded to the cations of Na (3361 ± 1351 mg/L), and the amount of this cation per mass of bitumen was calculated in 95 ± 6 µg/g bitumen. However, it is important to mention that not all the water could be separated from the bitumen due to the formation of highly stable emulsions. Cations of other elements such as B, Ca, K, Li and Mg were found in lower concentration in the aqueous phase.

Table A3.1.3 Cation determination in water separated from the Cold Lake bitumen

Sample	Water recovered from Cold Lake bitumen							
	1		2		3		Average	
Recovered aqueous solution M_{aq} [g]	5		2		2		3 ± 2	
Initial bitumen [g]	100		100		100		100	
Cation of element	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass $M_{x,aq}$ [µg/g bitumen]**	**Concentration $C_{x,aq}$ [mg/L]**	**Total mass Mx,aq [µg/g bitumen]**
Al	nd	-	nd	-	nd	-	nd	-
As	nd	-	nd	-	nd	-	nd	-
B	77	4	155	4	137	3	123 ± 41	4
Ba	nd	-	nd	-	nd	-	nd	-
Ca	42	2	78	2	68	2	63 ± 19	2
Cd	nd	-	nd	-	nd	-	nd	-
Co	nd	-	nd	-	nd	-	nd	-
Cr	nd	-	nd	-	nd	-	nd	-
Cu	nd	-	nd	-	nd	-	nd	-
Fe	1	<1	1	<1	1	<1	<1	<1
K	71	4	166	4	138	3	125 ± 49	4
Li	2	<1	6	<1	5	<1	4 ± 2	<1
Mg	7	<1	12	<1	10	<1	10 ± 3	<1
Mn	nd	-	nd	-	nd	-	nd	-
Mo	1	<1	2	<1	2	<1	2 ± 1	<1
Na	1853	93	4459	103	3772	91	3361 ± 1351	95 ± 6
Ni	nd	-	nd	-	nd	-	nd	-
P	nd	-	nd	-	nd	-	nd	-
Pb	nd	-	nd	-	nd	-	nd	-
Sb	nd	-	nd	-	nd	-	nd	-
Se	nd	-	nd	-	nd	-	nd	-
Si	84	4	136	3	123	3	114 ± 27	3 ± 1
Ti	nd	-	nd	-	nd	-	nd	-
V	nd	-	nd	-	nd	-	nd	-
Zn	nd	-	nd	-	nd	-	nd	-

nd: not detected, nq: not quantified, -: not calculated

Appendix 4.1 MATERIAL BALANCE – COLD LAKE BITUMEN WASHING

The material balance corresponding to experiment 1-6 are shown in this Appendix. It is shown for each washing step the initial mass of bitumen/organic emulsion, added deionized water, added toluene. In the recovery stage it is shown the mass of: recovered organic emulsion, recovered aqueous phase, and recovered toluene. Lastly, the losses are expressed in mass and percentage also. The material balance for experiment 1 is shown in **Table A4.1.1**, it can be observed that the organic emulsion after the evaporation of toluene contained a high amount of water, comparing the initial mass of bitumen (100.50 g) and the mass of the final organic emulsion (218.06 g). The losses in this experiment were up to 4.6%.

Table A4.1.1 Material balance for experiment 1

Stage	Compound	Unit	Washing step				Rotavap
			1	2	3	4	
Initial	Bitumen (M_{bit})	[g]	100.50	-	-	-	-
	Organic emulsion	[g]	-	253.90	313.23	311.39	347.21
	Toluene	[g]	100.49	-	-	-	-
	Deionized (MilliQ) water	[g]	100.48	100.14	100.00	99.71	-
	Total	[g]	301.47	354.04	413.23	411.10	347.21
Recoverec	Aqueous phase ($M_{aq,n}$)	[g]	43.94	40.50	89.13	62.31	30.61
	Organic emulsion	[g]	255.55	314.58	322.65	348.63	218.06
	Toluene	[g]	-	-	-	-	82.67
	Total	[g]	299.49	355.08	411.78	410.94	331.34
	Losses	[%]	0.7	-0.3	0.4	0.0	4.6

The material balance of experiment 2 (**Table A4.1.2**), showed a toluene recovery of 85 g approximately, and a high water retention in the organic emulsion (192 g of emulsion). The losses were found to be lower than 1% for this experiment.

Table A4.1.2 Material balance for experiment 2

Stage	Compound	Unit	Washing step 1	2	3	4	Rotavap
Initial	Bitumen	[g]	100.73	-	-	-	-
	Organic emulsion	[g]	-	268.18	302.28	318.31	338.47
	Toluene	[g]	100.70	-	-	-	-
	Deionized (MilliQ) water	[g]	100.87	100.00	100.24	100.18	-
	Total	[g]	302.30	368.18	402.52	418.49	338.47
Recovered	Aqueous	[g]	29.46	63.96	94.10	81.54	27.67
	Organic emulsion	[g]	268.53	302.28	309.44	338.47	192.04
	Toluene	[g]	-	-	-	-	85.79
	Total	[g]	299.92	368.32	404.42	421.49	339.90
	Losses	[%]	0.8	0.0	-0.5	-0.7	-0.2

Table A4.1.3 summarizes the material balance of experiment 3, and **Table A4.1.4** the material balance of experiment 4.

Table A4.1.3 Material balance for experiment 3

Stage	Compound	Unit	Washing step				Rotavap
			1	2	3	4	
Initial	Bitumen (M_{bit})	[g]	100.28	-	-	-	-
	Organic emulsion	[g]	-	281.15	251.76	292.10	295.94
	Toluene	[g]	100.32	-	-	-	-
	Deionized (MilliQ) water	[g]	100.20	100.12	100.22	100.05	-
	Total	[g]	300.80	381.27	351.98	392.15	295.94
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	13.61	128.85	58.47	94.73	0.00
	Organic emulsion	[g]	281.47	251.76	291.25	295.94	160.26
	Toluene	[g]	-	-	-	-	89.97
	Total	[g]	296.68	381.93	350.75	392.78	290.33
	Losses	[%]	1.4	-0.2	0.3	-0.2	0.1

Table A4.1.4 Material balance for experiment 4

Stage	Compound	Unit	Washing step				Rotavap
			1	2	3	4	
Initial	Bitumen (M_{bit})	[g]	100.75	-	-	-	-
	Organic emulsion	[g]	-	287.42	288.92	376.65	429.36
	Toluene	[g]	100.04	-	-	-	-
	Deionized (MilliQ) water	[g]	100.02	100.28	99.93	100.27	-
	Total	[g]	300.81	387.70	388.85	476.92	429.36
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	10.68	95.92	9.90	30.24	95.11
	Organic emulsion	[g]	289.22	289.85	376.65	446.23	253.02
	Toluene	[g]	-	-	-	-	80.34
	Total	[g]	299.90	385.77	386.55	476.47	428.47
	Losses	[%]	0.3	0.5	0.6	0.1	0.2

Table A4.1.5 and **Table A4.1.6** shows the material balance for the experiments 5 and 6 respectively. Lower recovery of toluene was observed for these two experiments compared to experiments 1-4.

Table A4.1.5 Material balance for experiment 5

Stage	Compound	Unit	Washing step				Rotavap
			1	2	3	4	
Initial	Bitumen (M_{bit})	[g]	100.51	-	-	-	-
	Organic emulsion	[g]	-	263.00	314.17	376.09	304.58
	Toluene	[g]	100.44	-	-	-	-
	Deionized (MilliQ) water	[g]	100.01	100.16	100.05	100.49	-
	Total	[g]	300.96	363.16	414.22	476.58	304.58
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	37.35	47.82	20.04	165.58	9.22
	Organic emulsion	[g]	264.25	314.17	376.09	308.75	211.48
	Toluene	[g]	-	-	-	-	77.84
	Total	[g]	301.60	361.99	396.13	474.33	298.54
	Losses	[%]	2.1	1.7	1.5	0.3	0.3

Table A4.1.6 Material balance for experiment 6

Stage	Compound	Unit	Washing step				Rotavap
			1	2	3	4	
Initial	Bitumen (M_{bit})	[g]	100.28	-	-	-	-
	Organic emulsion	[g]	-	276.57	290.53	374.26	313.06
	Toluene	[g]	100.20	-	-	-	-
	Deionized (MilliQ) water	[g]	100.41	100.59	100.48	99.56	-
	Total	[g]	300.89	377.16	391.01	473.82	313.06
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	22.73	82.27	16.20	151.52	4.63
	Organic emulsion	[g]	276.57	290.53	374.26	319.77	239.03
	Toluene	[g]	-	-	-	-	67.41
	Total	[g]	299.30	372.80	390.46	471.29	311.07
	Losses	[%]	0.5	1.2	0.1	0.5	0.6

Appendix 4.2 ANION DETERMINATION ON AQUEOUS AND ORGANIC PHASE – COLD LAKE BITUMEN WASHING

This section shows the anions that were found through HPLC analysis for experiments 2-6. As it was pointed in **Chapter 4**, Cl^- was removed from the bitumen in considerable concentrations. Also, it was detected low concentrations of HCO_3^-/CO_3^{2-}. Anions such as SO_4^{2-} and HPO_4^- were detected in some samples, in such low concentrations that it could not be quantified. Other anions such as F^-, NO_2^-, NO_3^- and Br- were not detected.

Table A4.2.1 Anion determination on aqueous and organic phase for experiment 2

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	
Recovered aqueous solution M_{aq} [g]	**29**	**64**	**94**	**82**	**28**	**Removed from bitumen**
Initial bitumen [g]			**100**			
Anion	**$C_{x,aq\ 1}$ [mg/L]**	**$C_{x,aq\ 2}$ [mg/L]**	**$C_{x,aq\ 3}$ [mg/L]**	**$C_{x,aq\ 4}$ [mg/L]**	**$C_{x,aq\ rot}$ [mg/L]**	**[µg/g bitumen]**
F^-	nd	nd	nd	nd	nd	-
CO_3^{2-}	<1	nd	<1	<1	nd	<1
Cl^-	517	636	332	185	nd	1022
NO_2^-	nd	nd	nd	nd	nd	-
Br^-	nd	nd	nd	nd	nd	-
NO_3^-	nd	nd	nd	nd	nd	-
HPO_4^{2-}	nq	nq	nq	nq	nd	-
SO_4^{2-}	nd	nq	nq	nq	nd	-

nq: not quantified; nd: not detected element, -: not calculated

Table A42.2 Anion determination on aqueous and organic phase for experiment 3

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	
Recovered aqueous solution M_{aq} [g]	**14**	**129**	**58**	**95**	**0**	**Removed from bitumen**
Initial bitumen [g]			**100**			
Anion	**$C_{x,aq\ 1}$ [mg/L]**	**$C_{x,aq\ 2}$ [mg/L]**	**$C_{x,aq\ 3}$ [mg/L]**	**$C_{x,aq\ 4}$ [mg/L]**	**$C_{x,aq\ rot}$ [mg/L]**	**[µg/g bitumen]**
F^-	nd	nd	nd	nd	-	-
CO_3^{2-}	<1	nq	<1	nq	-	<1
Cl^-	743	640	402	240	-	1386
NO_2^-	nd	nd	nd	nd	-	-
Br^-	nd	nd	nd	nd	-	-
NO_3^-	nd	nd	nd	nd	-	-
HPO_4^{2-}	nq	nd	nq	nq	-	-
SO_4^{2-}	nd	nq	nq	nq	-	-

nq: not quantified; nd: not detected element, -: not calculated

Table A4.2.3 Anion determination on aqueous and organic phase for experiment 4

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	
Recovered aqueous solution M_{aq} [g]	**44**	**22**	**63**	**38**	**95**	**Removed from bitumen**
Initial bitumen [g]			**100**			
Anion	**$C_{x,aq\ 1}$ [mg/L]**	**$C_{x,aq\ 2}$ [mg/L]**	**$C_{x,aq\ 3}$ [mg/L]**	**$C_{x,aq\ 4}$ [mg/L]**	**$C_{x,aq\ rot}$ [mg/L]**	**[µg/g bitumen]**
F^-	nd	nd	nd	nd	nd	-
CO_3^{2-}	<1	nd	<1	nq	nd	<1
Cl^-	517	665	381	289	123	840
NO_2^-	nd	nd	nd	nd	nd	-
Br^-	nd	nd	nd	nd	nd	-
NO_3^-	nd	nd	nd	nd	nd	-
HPO_4^{2-}	nq	nq	nq	nq	nq	-
SO_4^{2-}	nq	nq	nq	nq	nq	-

nq: not quantified; nd: not detected element, -: not calculated

Table A4.2.4 Anion determination on aqueous and organic phase for experiment 5

Washing step	1	2	3	4	Rotavap	
Recovered aqueous solution M_{aq} [g]	53	7	36	99	9	Removed from bitumen
Initial bitumen [g]			100			
Anion	$C_{x,aq\,1}$ [mg/L]	$C_{x,aq\,2}$ [mg/L]	$C_{x,aq\,3}$ [mg/L]	$C_{x,aq\,4}$ [mg/L]	$C_{x,aq\,rot}$ [mg/L]	[µg/g bitumen]
F^-	nd	nd	nd	nd	nd	-
CO_3^{2-}	1	nd	nq	nd	1	<1
Cl^-	455	638	404	302	nd	723
NO_2^-	nd	nd	nd	nd	nd	-
Br^-	nd	nd	nd	nd	nd	-
NO_3^-	nd	nd	nd	nd	nd	-
HPO_4^{2-}	nq	nq	nq	nq	nd	-
SO_4^{2-}	nq	nq	nq	nq	nd	-

nq: not quantified; nd: not detected element, -: not calculated

Table A4.2.5 Anion determination on aqueous and organic phase for experiment 6

Washing step	1	2	3	4	Rotavap	
Recovered aqueous solution M_{aq} [g]	71	11	18	183	5	Removed from bitumen
Initial bitumen [g]			100			
Anion	$C_{x,aq\,1}$ [mg/L]	$C_{x,aq\,2}$ [mg/L]	$C_{x,aq\,3}$ [mg/L]	$C_{x,aq\,4}$ [mg/L]	$C_{x,aq\,rot}$ [mg/L]	[µg/g bitumen]
F^-	nd	nd	nd	nd	nd	-
CO_3^{2-}	<1	nd	<1	<1	nd	<1
Cl^-	592	580	365	282	0	1061
NO_2^-	nd	nd	nd	nd	nd	-
Br^-	nd	nd	nd	nd	nd	-
NO_3^-	nd	nd	nd	nd	nd	-
HPO_4^{2-}	nq	nq	nq	nq	nq	-
SO_4^{2-}	nq	nq	nq	nq	nq	-

nq: not quantified; nd: not detected element, -: not calculated

Appendix 4.3 CATION DETERMINATION ON AQUEOUS AND ORGANIC PHASE – COLD LAKE BITUMEN WASHING

The cation determination through ICP-OES was discussed in **Chapter 4, Section 4.3.3**. Detailed information of the cations found in 2-6 is reported in this Appendix. As it was mentioned in the referred section, high percentage of difference between the mass in the raw bitumen, and the mass in the recovered aqueous and organic phases for cations of elements such as Si, B, Ca, Na was encountered. Cations of elements such as Ni, Ti, V and Zn were not removed through the performed washing procedure.

Table A4.3.1 Cation determination on aqueous and organic phase for experiment 2

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen** ($M_{x\ aq,total}$)	**Organic phase** ($M_{x,org}$)	**Total** ($M_{x\ aq,total}$ + $M_{x,org}$)	**Cold Lake bitumen** ($M_{x,bit}$)	*% difference*	*% removal*
Recovered aqueous solution M_{aq} **[g]**	29	64	94	82	28						
Cation of element	$C_{x,aq\ 1}$ **[mg/L]**	$C_{x,aq\ 2}$ **[mg/L]**	$C_{x,aq\ 3}$ **[mg/L]**	$C_{x,aq\ 4}$ **[mg/L]**	$C_{x,aq\ rot}$ **[mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**	**[%]**
Al	<1	<1	<1	<1	<1	<1	1	1	2 ± 2	50	*
As	nq	nq	nq	nq	nq	nq	nq	nq	nq	NA	NA
B	12	6	3	2	<1	12	<1	12	<1	>-1100	-
Ba	<1	<1	<1	<1	nd	<1	<1	<1	1 ± <1	*	*
Ca	4	5	4	2	1	10	24	34	27 ± 11	-26	37
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Co	nd	nd	nd	nd	nd	nd	<1	<1	<1	*	*
Cr	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Cu	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Fe	<1	<1	<1	nd	nd	<1	7	7	9 ± <1	22	*
K	11	9	5	3	<1	16	17	33	34 ± 4	3	47
Li	<1	<1	<1	<1	nd	<1	1	2	2 ± <1	0	*
Mg	<1	<1	<1	<1	<1	1	3	4	4 ± 1	0	25
Mn	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Mo	<1	<1	<1	<1	<1	1	3	4	6 ± 1	33	17
Na	270	215	117	66	4	381	214	596	664 ± 89	10	57
Ni	nq	nd	nd	nd	nd	nd	43	43	50 ± 4	14	0
P	<1	<1	<1	<1	nd	<1	<1	<1	<1	*	*
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Sb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Si	17	13	14	8	<1	33	4	37	11 ± 2	-236	300
Ti	nd	nd	nd	nd	nd	nd	<1	<1	1 ± <1	*	*
V	<1	<1	<1	<1	<1	<1	101	101	124 ± 22	19	*
Zn	nq	nq	nq	nq	nq	nq	1	1	1 ± <1	0	0

nd: not detected, nq: not quantified, -: not calculated, *: too low to be calculated, NA: not applicable

Table A4.3.2 Cation determination on aqueous and organic phase for experiment 3

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen ($M_{x\ aq,total}$)**	**Organic phase ($M_{x,org}$)**	**Total ($M_{x\ aq,total}$ + $M_{x,org}$)**	**Cold Lake bitumen ($M_{x,bit}$)**	**% *difference***	**% *removal***
Recovered aqueous solution M_{aq} [g]	14	129	58	95	0						
Cation of element	**$C_{x,aq\ 1}$ [mg/L]**	**$C_{x,aq\ 2}$ [mg/L]**	**$C_{x,aq\ 3}$ [mg/L]**	**$C_{x,aq\ 4}$ [mg/L]**	**$C_{x,aq\ rot}$ [mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**	**[%]**
Al	<1	<1	<1	<1	-	<1	2	2	2 ± 2	0	*
As	nq	nq	nq	nq	-	nq	nq	nq	nq	NA	NA
B	12	6	3	2	-	13	<1	13	<1	>-1200	-
Ba	0.1	0.04	0.04	0.02	-	0.11	0.31	0.42	1 ± <1	58	11
Ca	10	5	4	3	-	13	16	29	27 ± 11	-7	49
Cd	nd	nd	nd	nd	-	nd	nd	nd	nd	NA	NA
Co	nd	nd	nd	nd	-	nd	<1	<1	<1	*	*
Cr	nq	nq	nq	nq	-	nq	<1	<1	<1	*	*
Cu	nq	nq	nq	nq	-	nq	<1	<1	<1	*	*
Fe	<1	<1	<1	nd	-	<1	6	6	9 ± <1	33	*
K	18	9	6	3	-	21	8	29	34 ± 4	15	62
Li	<1	<1	<1	<1	-	1	<1	1	2 ± <1	50	50
Mg	1	1	1	<1	-	2	2	4	4 ± 1	0	50
Mn	nq	nq	nq	nq	-	nq	<1	<1	<1	*	*
Mo	<1	<1	<1	<1	-	1	3	4	6 ± 1	33	17
Na	401	212	134	83	-	484	94	578	664 ± 89	13	73
Ni	nq	nd	nd	nd	-	nd	32	32	50 ± 4	36	0
P	<1	<1	<1	<1	-	<1	<1	<1	<1	*	*
Pb	nd	nd	nd	nd	-	nd	nd	nd	nd	NA	NA
Sb	nd	nd	nd	nd	-	nd	nd	nd	nd	NA	NA
Se	nd	nd	nd	nd	-	nd	nd	nd	nd	NA	NA
Si	27	14	10	8	-	35	55	90	11 ± 2	-718	318
Ti	nd	nd	nd	nd	-	nd	<1	<1	1 ± <1	*	*
V	<1	<1	<1	<1	-	<1	90	90	124 ± 22	27	*
Zn	nq	nq	nq	nq	-	nq	1	1	1 ± <1	0	0

nd: not detected, nq: not quantified, -: not calculated/sample not enough to perform analysis, *: too low to be calculated, NA: not applicable

Table A4.3.3 Cation determination on aqueous and organic phase for experiment 4

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen ($M_{x\ aq,total}$)**	**Organic phase ($M_{x,org}$)**	**Total ($M_{x\ aq,total}$ + $M_{x,org}$)**	**Cold Lake bitumen ($M_{x,bit}$)**	**$\%_{difference}$**	**$\%_{removal}$**
Recovered aqueous solution M_{aq} [g]	44	22	63	38	95						
Cation of element	**$C_{x,aq\ 1}$ [mg/L]**	**$C_{x,aq\ 2}$ [mg/L]**	**$C_{x,aq\ 3}$ [mg/L]**	**$C_{x,aq\ 4}$ [mg/L]**	**$C_{x,aq\ rot}$ [mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**	**[%]**
Al	<1	<1	<1	<1	<1	<1	3	3	2 ± 2	-50	*
As	nq	nq	nq	nq	nq	nq	nq	nq	nq	NA	NA
B	11	7	4	3	1	11	<1	11	<1	>-1000	-
Ba	<1	<1	<1	<1	nd	<1	1	1	1 ± <1	0	*
Ca	8	6	5	4	2	12	31	43	27 ± 11	-59	44
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Co	nd	nd	nd	nd	nd	nd	<1	<1	<1	*	0
Cr	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	0
Cu	nq	nq	nq	nq	<1	<1	1	1	<1	*	*
Fe	<1	nd	nd	nd	<1	<1	11	11	9 ± <1	-22	*
K	17	11	6	5	<1	15	18	34	34 ± 4	1	45
Li	<1	<1	<1	<1	nd	1	1	2	2 ± <1	0	50
Mg	1	1	1	<1	<1	1	3	4	4 ± 1	0	25
Mn	nq	nq	nq	nq	nq	nq	nq	nq	<1	*	*
Mo	<1	<1	<1	<1	<1	1	5	6	6 ± 1	0	17
Na	377	278	167	123	4	383	327	710	664 ± 89	-7	58
Ni	nq	nd	nd	nd	nd	nd	52	52	50 ± 4	-4	0
P	<1	nd	<1	nd	<1	<1	<1	<1	<1	*	*
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Sb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Si	21	7	6	3	1	17	62	79	11 ± 2	-618	155
Ti	nd	nd	nd	nd	nd	nd	2	2	1 ± <1	-100	0
V	<1	<1	<1	<1	<1	<1	150	150	124 ± 22	-21	*
Zn	nq	nq	nq	nq	<1	<1	1	1	1 ± <1	0	*

nd: not detected, nq: not quantified, -: not calculated, *: too low to be calculated, NA: not applicable

Table A4.3.4 Cation determination on aqueous and organic phase for experiment 5

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen ($M_{x\ aq,total}$)**	**Organic phase ($M_{x,org}$)**	**Total ($M_{x\ aq,total}$ + $M_{x,org}$)**	**Cold Lake bitumen ($M_{x,bit}$)**	**% *difference***	**% *removal***
Recovered aqueous solution M_{aq} [g]	53	7	36	99	9						
Cation of element	**$C_{x,aq\ 1}$ [mg/L]**	**$C_{x,aq\ 2}$ [mg/L]**	**$C_{x,aq\ 3}$ [mg/L]**	**$C_{x,aq\ 4}$ [mg/L]**	**$C_{x,aq\ rot}$ [mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**	**[%]**
Al	<1	<1	<1	<1	<1	<1	5	5	2 ± 2	-150	*
As	nq	nq	nq	nq	nq	nq	nq	nq	nq	NA	NA
B	12	6	3	2	<1	10	<1	10	<1	>-900	-
Ba	<1	<1	<1	<1	nd	<1	<1	<1	1 ± <1	*	*
Ca	4	6	5	4	1	8	18	26	27 ± 11	4	30
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Co	nd	nd	nd	nd	nd	nd	<1	<1	<1	*	*
Cr	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Cu	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Fe	<1	nd	nd	nd	nd	<1	9	9	9 ± <1	0	*
K	12	10	6	5	<1	14	10	24	34 ± 4	29	41
Li	<1	<1	<1	<1	nd	<1	<1	1	2 ± <1	50	*
Mg	<1	<1	<1	<1	<1	1	3	4	4 ± 1	0	25
Mn	nq	nq	nq	nq	nq	nq	nq	nq	<1	-	-
Mo	<1	<1	<1	<1	<1	<1	4	5	6 ± 1	17	*
Na	285	259	170	125	4	351	151	503	664 ± 89	24	53
Ni	nq	nd	nd	nd	nd	nd	42	42	50 ± 4	16	0
P	<1	nd	nd	nd	nd	<1	<1	<1	<1	*	*
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Sb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Si	15	7	6	3	1	13	65	79	11 ± 2	-618	118
Ti	nd	nd	nd	nd	nd	nd	1	1	1 ± <1	0	0
V	<1	<1	<1	<1	nd	<1	124	124	124 ± 22	0	*
Zn	nq	nq	nq	nq	nq	nq	1	1	1 ± <1	0	0

nd: not detected, nq: not quantified, -: not calculated, *: too low to be calculated, NA: not applicable

Table A4.3.5 Cation determination on aqueous and organic phase for experiment 6

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen ($M_{x\ aq,total}$)**	**Organic phase ($M_{x,org}$)**	**Total ($M_{x\ aq,total}$ + $M_{x,org}$)**	**Cold Lake bitumen ($M_{x,bit}$)**	**% difference**	**% removal**
Recovered aqueous solution M_{aq} [g]	**71**	**11**	**18**	**183**	**5**						
Cation of element	**$C_{x,aq\ 1}$ [mg/L]**	**$C_{x,aq\ 2}$ [mg/L]**	**$C_{x,aq\ 3}$ [mg/L]**	**$C_{x,aq\ 4}$ [mg/L]**	**$C_{x,aq\ rot}$ [mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**	**[%]**
Al	<1	<1	<1	<1	-	<1	3	3	2 ± 2	-50	*
As	nq	nq	nq	nq	-	nq	nq	nq	nq	NA	NA
B	11	7	4	2	-	13	<1	14	<1	>-1300	-
Ba	<1	<1	<1	<1	-	<1	<1	1.00	1 ± <1	0	*
Ca	6	5	4	4	-	12	16	28	27 ± 11	-4	44
Cd	nd	nd	nd	nd	-	nd	nd	nd	nd	NA	NA
Co	nd	nd	nd	nd	-	nd	<1	<1	<1	*	*
Cr	nq	nq	nq	nq	-	nq	<1	<1	<1	*	*
Cu	nq	nq	nq	nq	-	nq	1	1	<1	*	*
Fe	<1	nd	nd	nd	-	<1	8	8	9 ± <1	11	*
K	15	9	6	5	-	21	12	32	34 ± 4	6	62
Li	<1	<1	<1	<1	-	1	1	2	2 ± <1	0	50
Mg	<1	<1	<1	<1	-	1	2	3	4 ± 1	25	25
Mn	nq	nq	nq	nq	-	nq	nd	nd	<1	*	*
Mo	<1	<1	<1	<1	-	1	4	5	6 ± 1	17	17
Na	339	239	159	118	-	510	146	657	664 ± 89	1	77
Ni	nq	nd	nd	nd	-	nd	36	36	50 ± 4	28	0
P	<1	nd	nd	nd		<1	<1	<1	<1	*	*
Pb	nd	nd	nd	nd	-	nd	nd	nd	nd	NA	NA
Sb	nd	nd	nd	nd	-	nd	nd	nd	nd	NA	NA
Se	nd	nd	nd	nd	-	nd	nd	nd	nd	NA	NA
Si	17	7	5	3		18	48	66	11 ± 2	-500	164
Ti	nd	nd	nd	nd	-	nd	1	1	1 ± <1	0	0
V	<1	<1	<1	<1	-	<1	106	106	124 ± 22	15	*
Zn	nq	nq	nq	nq	-	nq	1	1	1 ± <1	0	0

nd: not detected, nq: not quantified, -: not calculated/sample not enough to perform analysis, *: too low to be calculated, NA: not applicable

Appendix 4.4 FTIR SPECTRA – COLD LAKE BITUMEN WASHING

FTIR spectra of experiments 2 and 3 are shown in **Figure A4.4.1** and **Figure A4.4.2**, as well as the spectrum of the raw bitumen. As it was pointed in **Chapter 4**, the main differences observed are related to the CO_2 (background) and remaining toluene in the organic emulsion samples.

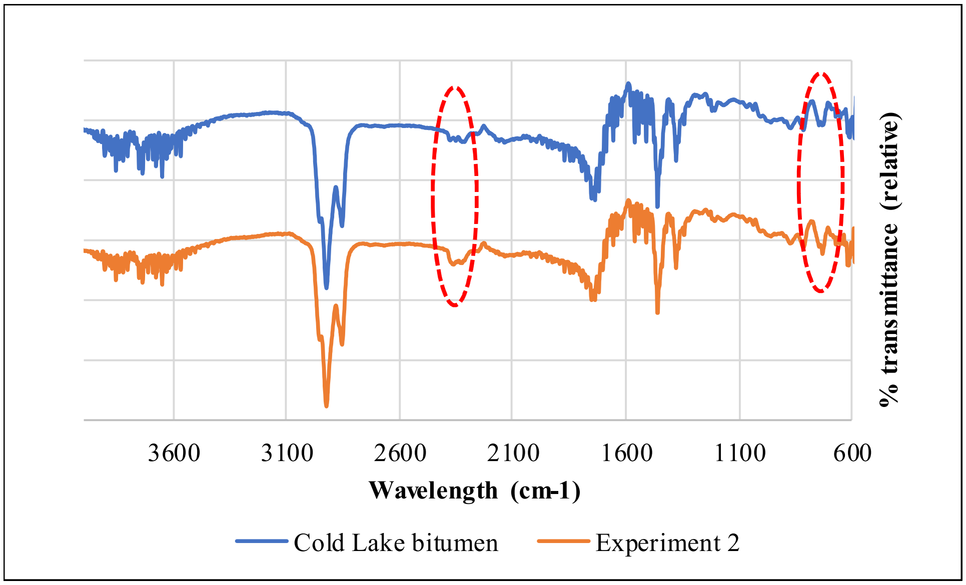

Figure A4.4.1 Fourier Transform Infrared Spectroscopy for experiment 2

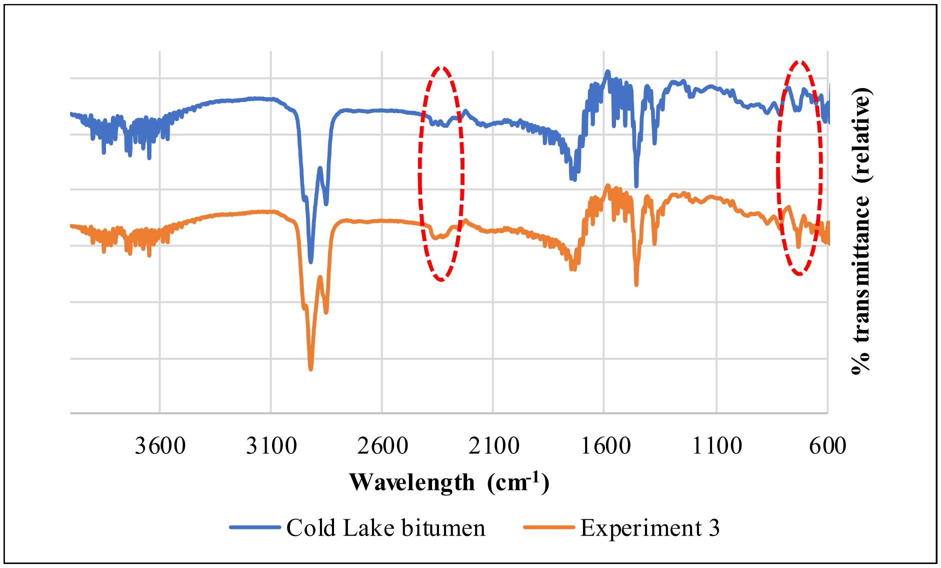

Figure A4.4.2 Fourier Transform Infrared Spectroscopy for experiment 3

Appendix 4.5 LEACHING DETERMINATION FROM GLASSWARE

The leaching of cations of elements such as B, Ca, Na and Si was investigated in this section, with the purpose of determine if the concentrations of cations of B and Si quantified in the aqueous phase after washing the bitumen could be attributed to this effect.

A.4.5 Equipment and procedure

200 g of deionized water/0.03 M HCl were heated up to 75oC using a a Heidolph MR Hei – Standard hot plate for 15 minutes in a 500 mL beaker. Then the sample was transferred to a 300 mL glass jar and stored in a dark place. The concentration of cations of B, Ca, Na and Si was determined by ICP-OES **(Chapter 3**, **Section 3.2.3.2**), from 2 days to 16 days of storage. The experiments were performed in triplicate, as well as the analysis of the cations.

A.4.5.2 Results

Table A4.5.1 shows the cation concentration of the samples at the different storage time. For the deionized water, it can be observed that no cations of B were detected. The rest of the analyzed cations (Ca, Na, Si) exhibited an increase of the concentration as the storage time progressed. However, the observed increase was lower than the quantified in the aqueous samples after the washing of bitumen was performed. Regarding the 0.03 M HCl samples, higher concentrations of the cations compared to the deionized water samples was obtained; however, the determined values were lower than the obtained in the aqueous phase after the washing of bitumen.

Table A4.5.1 Cation determination of aqueous samples stored in glassware

Sample	Storage time [days]	Cation of element B [mg/L]	Ca [mg/L]	Na [mg/L]	Si [mg/L]
Deionized water	2	nd	0.08 ± 0.01	0.45 ± 0.01	0.08 ± 0.03
	4	nd	0.09 ± 0.01	0.44 ± 0.01	0.07 ± 0.01
	7	nd	0.10 ± 0.01	0.50 ± 0.02	0.11 ± 0.02
	16	nd	0.12 ± 0.01	0.61 ± 0.00	0.09 ± 0.01
0.03 M HCl	2	0.01 ± 0.01	0.16 ± 0.07	0.51 ± 0.04	0.21 ± 0.04
	4	0.03 ± 0.03	0.17 ± 0.07	0.50 ± 0.03	0.26 ± 0.04
	7	0.03 ± 0.03	0.17 ± 0.06	0.56 ± 0.04	0.51 ± 0.12
	16	0.03 ± 0.03	0.19 ± 0.06	0.73 ± 0.15	1.08 ± 0.25

Appendix 5.1 MATERIAL BALANCE – ATHABASCA BITUMEN WASHING

The material balance corresponding to experiment 1 is shown in **Table A4.1.1**. As it can be observed, the mass losses through each washing step and the evaporation in the Rotavap was lower than 2%. The toluene recovered after evaporation in the Rotavap was 69 g of 100 g added. This means that an important amount of toluene was even evaporated during the washing procedure, the storage time between each washing step, or was kept in the organic emulsion phase.

Table A5.1.1 Material balance for experiment 1

Stage	Compound	Unit	Washing step				Rotavap
			1	2	3	4	
Initial	Bitumen (M_{bit})	[g]	100.16	-	-	-	-
	Organic emulsion	[g]	-	286.47	356.39	415.57	465.70
	Toluene	[g]	108.81	-	-	-	-
	Deionized (MilliQ) water	[g]	100.15	99.88	100.12	100.04	-
	Total	[g]	309.12	386.35	456.51	515.61	465.70
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	17.83	23.87	30.33	39.61	241.14
	Organic emulsion	[g]	286.47	356.39	416.47	466.09	165.88
	Toluene	[g]	-	-	-	-	68.37
	Total	[g]	304.30	380.26	446.80	505.70	475.39
	Losses	[%]	1.56	1.58	2.13	1.92	-2.08

s: sample standard deviation, -: not calculated

The material balance of experiment 2 can be seen in **Table A.5.1.2**. As experiment 1, the mass losses were found to be up to 2% in the second washing step. Also, it can be observed that the water retained in the water in oil emulsion seems not to follow a pattern, i.e. the water retained in the organic emulsion during the experiment 2 was higher than that retained for experiment 2. Regarding the toluene recovery, almost all the toluene was recovered in experiment 2.

Table A5.1.2 Material balance for experiment 2

Stage	Compound	Unit	Washing step 1	2	3	4	Rotavap
Initial	Bitumen (M_{bit})	[g]	100.30	-	-	-	-
	Organic emulsion	[g]	-	256.15	343.04	374.68	420.91
	Toluene	[g]	108.83	-	-	-	-
	Deionized (MilliQ) water	[g]	100.30	99.91	99.88	100.02	-
	Total	[g]	309.43	356.06	442.92	474.70	420.91
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	49.79	6.10	57.72	54.42	229.22
	Organic emulsion	[g]	256.15	343.04	374.68	419.64	96.40
	Toluene	[g]	-	-	-	-	99.75
	Total	[g]	305.94	349.14	432.40	474.06	425.37
	Losses	[%]	1.13	1.94	2.38	0.13	-1.06

s: sample standard deviation, -: not calculated

The information corresponding to the material balance for experiment 3 is reported in **Table A.5.1.3**. As mentioned for experiment 2, the water retention did not follow a trend, in this case it was lower than the amount retained by the organic emulsions of experiments 1 and 2. The mass losses were calculated to be up to 4% for the fourth washing step. Similarly, in experiment 4 (**Table A.51.4**) the mass losses were found to be up to 2%.

Table A5.1.3 Material balance for experiment 3

Stage	Compound	Unit	Washing step 1	2	3	4	Rotavap
Initial	Bitumen (M_{bit})	[g]	100.25	-	-	-	-
	Organic emulsion	[g]	-	239.10	306.70	358.03	395.88
	Toluene	[g]	108.71	-	-	-	-
	Deionized (MilliQ) water	[g]	100.25	100.21	99.82	99.76	-
	Total	[g]	309.21	339.31	406.52	457.79	395.88
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	67.35	27.03	44.72	45.73	170.62
	Organic emulsion	[g]	239.10	306.70	358.03	395.27	135.64
	Toluene	[g]	-	-	-	-	96.92
	Total	[g]	306.45	333.73	402.75	441.00	403.18
	Losses	[%]	0.89	1.64	0.93	3.67	-1.84

s: sample standard deviation, -: not calculated

Table A5.1.4 Material balance for experiment 4

Stage	Compound	Unit	Washing step 1	2	3	4	Rotavap
Initial	Bitumen (M_{bit})	[g]	100.19	-	-	-	-
	Organic emulsion	[g]	-	253.76	325.20	357.57	412.84
	Toluene	[g]	100.19	-	-	-	-
	Deionized (MilliQ) water	[g]	99.53	100.09	100.10	100.46	-
	Total	[g]	299.91	353.85	425.30	458.03	412.84
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	44.35	22.02	63.05	37.77	175.19
	Organic emulsion	[g]	253.76	325.20	357.57	416.40	144.37
	Toluene	[g]	-	-	-	-	85.8
	Total	[g]	298.11	347.22	420.62	454.17	405.36
	Losses	[%]	0.60	1.87	1.10	0.84	1.81

s: sample standard deviation, -: not calculated

Table A.5.15 and **Table A.5.1.6** shows the material balance for the experiments 5 and 6 respectively. Mass losses for experiment 5 were up to 5%, with a recovery of 80 g of toluene, while for experiment 6, mass losses were below 2% and toluene recovery was found to be 87 g of 100 g added. Again, high variation of water content in the final organic emulsion was found.

Table A5.1.5 Material balance for experiment 5

Stage	Compound	Unit	Washing step 1	2	3	4	Rotavap
Initial	Bitumen (M_{bit})	[g]	100.06	-	-	-	-
	Organic emulsion	[g]	-	241.09	328.74	386.34	381.90
	Toluene	[g]	100.06	-	-	-	-
	Deionized (MilliQ) water	[g]	100.10	99.87	100.10	99.95	-
	Total	[g]	300.22	340.96	428.84	486.29	381.90
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	52.85	6.51	35.88	98.61	159.09
	Organic emulsion	[g]	241.09	328.74	386.34	386.02	122.75
	Toluene	[g]	-	-	-	-	80.1
	Total	[g]	293.94	335.25	422.22	484.63	361.94
	Losses	[%]	2.09	1.67	1.54	0.34	5.23

s: sample standard deviation, -: not calculated

Table A5.1.6 Material balance for experiment 6

Stage	Compound	Unit	Washing step 1	2	3	4	Rotavap
Initial	Bitumen (M_{bit})	[g]	100.15	-	-	-	-
	Organic emulsion	[g]	-	222.82	306.52	383.05	293.40
	Toluene	[g]	100.16	-	-	-	-
	MiliQ water	[g]	100.18	99.89	100.04	100.09	-
	Total	[g]	300.49	322.71	406.56	483.14	293.40
Recovered	Aqueous phase ($M_{aq,n}$)	[g]	70.67	11.01	17.56	183.09	93.85
	Organic emulsion	[g]	222.82	306.52	383.05	296.78	108.04
	Toluene	[g]	-	-	-	-	87.87
	Total	[g]	293.49	317.53	400.61	479.87	289.76
	Losses	[%]	2.33	1.61	1.46	0.68	1.24

s: sample standard deviation, -: not calculated

Appendix 5.2 ANION DETERMINATION ON AQUEOUS PHASE – ATHABASCA BITUMEN WASHING

This section shows the anions that were found through HPLC analysis for experiments 2-6. As it can be observed, CO_3^{2-}, SO_4^{2-} and Cl^- exhibited higher concentration for each washing step. It can be also noticed that the concentration of these anions decreased after each washing step. Also, low concentrations of HPO_4^{2-} were found, this anion also followed the decreasing trend after each washing step. Other anions such as F^-, NO_2^-, NO_3^- and Br- were not detected.

Table A5.2.1 Anion determination by HPLC for aqueous phase of experiment 2- Athabasca bitumen washing

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	
Recovered aqueous solution M_{aq} [g]	50	6	58	54	229	**Removed from bitumen**
Initial bitumen [g]			100			
Anion	**$C_{x,aq\ 1}$ [ppm]**	**$C_{x,aq\ 2}$ [ppm]**	**$C_{x,aq\ 3}$ [ppm]**	**$C_{x,aq\ 4}$ [ppm]**	**$C_{x,aq\ rot}$ [ppm]**	**$(M_{x\ aq,total})$ [µg/g bitumen]**
F^-	nd	nd	nd	nd	nd	-
CO_3^{2-}	38	46	18	12	9	58
Cl^-	5	2	1	<1	nd	3
NO_2^-	nd	nd	nd	nd	nd	-
Br^-	nd	nd	nd	nd	nd	-
NO_3^-	nd	nd	nq	nq	nd	-
HPO_4^{2-}	<1	<1	nd	nd	<1	1
SO_4^{2-}	15	13	11	12	14	53

nd: not detected, nq: not quantified, -: not calculated

Table A5.2.2 Anion determination by HPLC for aqueous phase of experiment 3- Athabasca bitumen washing

Washing step	1	2	3	4	Rotavap	
Recovered aqueous solution M_{aq} [g]	67	27	45	46	171	Removed from bitumen
Initial bitumen [g]			100			
Anion	$C_{x,aq\ 1}$ [ppm]	$C_{x,aq\ 2}$ [ppm]	$C_{x,aq\ 3}$ [ppm]	$C_{x,aq\ 4}$ [ppm]	$C_{x,aq\ rot}$ [ppm]	($M_{x\ aq,total}$) [µg/g bitumen]
F^-	nd	nd	nd	nd	nd	-
CO_3^{2-}	28	26	27	8	13	63
Cl^-	6	1	2	1	nd	5
NO_2^-	nd	nd	nd	nd	nd	-
Br^-	nd	nd	nd	nd	nd	-
NO_3^-	nd	nd	nq	nq	nd	-
HPO_4^{2-}	<1	<1	nd	<1	nd	<1
SO_4^{2-}	14	12	13	14	8	38

nd: not detected, nq: not quantified, -: not calculated

Table A5.2.3 Anion determination by HPLC for aqueous phase of experiment 4 - Athabasca bitumen washing

Washing step	1	2	3	4	Rotavap	
Recovered aqueous solution M_{aq} [g]	44	22	63	38	175	Removed from bitumen
Initial bitumen [g]			100			
Anion	$C_{x,aq\ 1}$ [ppm]	$C_{x,aq\ 2}$ [ppm]	$C_{x,aq\ 3}$ [ppm]	$C_{x,aq\ 4}$ [ppm]	$C_{x,aq\ rot}$ [ppm]	($M_{x\ aq,total}$) [µg/g bitumen]
F^-	nd	nd	nd	nd	nd	nd
CO_3^{2-}	30	15	19	31	9	55
Cl^-	6	2	1	<1	nd	4
NO_2^-	nd	nd	nd	nd	nd	nd
Br^-	nd	nd	nd	nd	nd	nd
NO_3^-	nd	nd	nd	nd	nd	nd
HPO_4^{2-}	<1	<1	<1	<1	nd	<1
SO_4^{2-}	12	17	14	12	8	37

nd: not detected, nq: not quantified, -: not calculated

Table A5.2.4 Anion determination by HPLC for aqueous phase of experiment 5 - Athabasca bitumen washing

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	
Recovered aqueous solution M_{aq} [g]	53	7	36	99	159	**Removed from bitumen**
Initial bitumen [g]			100			
Anion	**$C_{x,aq\ 1}$ [ppm]**	**$C_{x,aq\ 2}$ [ppm]**	**$C_{x,aq\ 3}$ [ppm]**	**$C_{x,aq\ 4}$ [ppm]**	**$C_{x,aq\ rot}$ [ppm]**	**($M_{x\ aq,total}$) [µg/g bitumen]**
F^-	nd	nd	nd	nd	nd	nd
CO_3^{2-}	16	17	17	18	13	54
Cl^-	5	4	1	<1	1	5
NO_2^-	nd	nd	nd	nd	nd	nd
Br^-	nd	nd	nd	nd	nd	nd
NO_3^-	nd	nq	nd	nq	nd	nd
HPO_4^{2-}	<1	<1	nd	nq	<1	<1
SO_4^{2-}	13	16	14	12	10	40

nd: not detected, nq: not quantified, -: not calculated

Table A5.2.5 Anion determination by HPLC for aqueous phase of experiment 6 - Athabasca bitumen washing

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	
Recovered aqueous solution M_{aq} [g]	71	11	18	183	94	**Removed from bitumen**
Initial bitumen [g]			100			
Anion	**$C_{x,aq\ 1}$ [ppm]**	**$C_{x,aq\ 2}$ [ppm]**	**$C_{x,aq\ 3}$ [ppm]**	**$C_{x,aq\ 4}$ [ppm]**	**$C_{x,aq\ rot}$ [ppm]**	**($M_{x\ aq,total}$) [µg/g bitumen]**
F^-	nd	nd	nd	nd	nd	nd
CO_3^{2-}	31	14	18	3	14	46
Cl^-	5	1	<1	nd	nd	4
NO_2^-	nd	nd	nd	nd	nd	nd
Br^-	nd	nd	nd	nd	nd	nd
NO_3^-	nq	nd	nd	nd	nd	nd
HPO_4^{2-}	<1	<1	nq	nq	nd	<1
SO_4^{2-}	11	17	14	13	9	44

nd: not detected, nq: not quantified, -: not calculated

Appendix 5.3 CATION DETERMINATION ON AQUEOUS AND ORGANIC PHASE – ATHABASCA BITUMEN WASHING

The cation determination through ICP-OES for the experiments 2-6 is reported in this section. It can be observed that due to the high variation in the amount of aqueous phase recovered in each washing step, the mass of cations removed from bitumen exhibited also variations between each experiment. Differences between the mass in the raw bitumen, and the mass in the recovered aqueous and organic phase for cations of elements such as B, Si, Ca, Na was found.

Table A5.3.1 Cation determination on aqueous and organic phase for experiment 2

Washing step	1	2	3	4	Rotavap	Removed from bitumen ($M_{x\ aq,total}$)	Organic phase ($M_{x,org}$)	Total ($M_{x\ aq,total}$ + $M_{x,org}$)	Athabasca bitumen ($M_{x,bit}$)	% difference	% removal
Recovered aqueous solution M_{aq} [g]	50	0	58	54	229						
Cation of element	$C_{x,aq\ 1}$ [mg/L]	$C_{x,aq\ 2}$ [mg/L]	$C_{x,aq\ 3}$ [mg/L]	$C_{x,aq\ 4}$ [mg/L]	$C_{x,aq\ rot}$ [mg/L]	[µg/g bitumen]	[µg/g bitumen]	[µg/g bitumen]	[µg/g bitumen]	[%]	[%]
Al	<1	-	<1	<1	<1	<1	3	3	2 ± 1	-69	<33
As	nq		nq	nq	nq	nq	nq	nq	nq	-	-
B	<1	-	<1	<1	<1	1	4	5	1 ± 1	-376	*
Ba	nd	-	nd	nd	nd	nd	<1	<1	<1	*	*
Ca	<1	-	<1	<1	<1	3	19	21	8 ± 7	-163	38
Cd	nd	-	nd	nd	nd	nd	nd	nd	nd	NA	NA
Co	nd	-	<1	<1	<1	<1	<1	<1	<1	*	*
Cr	nq	-	nq	nq	nq	nq	<1	<1	<1	*	*
Cu	<1	-	<1	<1	<1	<1	5	5	1 ± 2	-400	*
Fe	<1	-	<1	<1	<1	<1	3	3	3	0	<33
K	2	-	<1	<1	<1	2	4	6	3 ± 1	-100	67
Li	<1	-	nd	<1	<1	<1	<1	<1	<1	*	*
Mg	<1	-	<1	<1	<1	1	1	2	1 ± <1	-100	*
Mn	nd	-	<1	<1	<1	<1	<1	<1	<1	*	*
Mo	<1	-	nd	nd	<1	<1	8	8	9 ± 1	11	<11
Na	13	-	4	3	3	18	19	37	16 ± 6	-131	113
Ni	nd	-	<1	<1	<1	1	65	66	68 ± 7	3	<2
P	<1	-	<1	<1	<1	<1	<1	<1	<1	*	*
Pb	nd	-	nd	nd	nd	nd	nd	nd	nd	NA	NA
Sb	nd	-	nd	nd	nd	nd	nd	nd	nd	NA	NA
Se	nd	-	nd	nd	nd	nd	nd	nd	nd	NA	NA
Si	<1	-	<1	<1	<1	1	3	3	10 ± 2	70	<10
Ti	nd	-	nd	nd	nd	nd	2	2	2	0	0
V	<1	-	<1	<1	<1	<1	192	192	186 ± 31	-3	0
Zn	nd	-	<1	<1	<1	<1	1	1	1 ± 1	0	*

nd: not detected, nq: not quantified, NA; not applicable, -: not calculated, *: not calculated due to the low concentration

Table A5.3.2 Cation determination on aqueous and organic phase for experiment 3

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen** ($M_{x\ aq,total}$)	**Organic phase** ($M_{x,org}$)	**Total** ($M_{x\ aq,total}$ + $M_{x,org}$)	**Athabasca bitumen** ($M_{x,bit}$)	% *difference*	% *removal*
Recovered aqueous solution M_{aq} **[g]**	**67**	**27**	**45**	**46**	**171**						
Cation of element	$C_{x,aq\ 1}$ **[mg/L]**	$C_{x,aq\ 2}$ **[mg/L]**	$C_{x,aq\ 3}$ **[mg/L]**	$C_{x,aq\ 4}$ **[mg/L]**	$C_{x,aq\ rot}$ **[mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**	**[%]**
Al	<1	<1	<1	<1	<1	<1	2	2	2 ± 1	-17	<50
As	nq	nq	nq	nq	nq	nq	nq	nq	nq	-	-
B	<1	<1	<1	<1	<1	1	1	2	1 ± 1	-100	100
Ba	nd	nd	nd	nd	nd	nd	<1	<1	<1	*	*
Ca	<1	1	1	1	1	4	5	9	8 ± 7	-13	50
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Co	nd	<1	<1	<1	<1	<1	<1	<1	<1	*	*
Cr	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Cu	nd	<1	<1	<1	<1	<1	1	1	1 ± 2	*	*
Fe	<1	nd	nd	nd	nd	nd	3	3	3	15	<33
K	1	<1	1	<1	<1	2	3	5	3 ± 1	-67	67
Li	<1	<1	nd	nd	nd	<1	<1	<1	<1	*	*
Mg	<1	<1	<1	<1	<1	<1	1	1	1 ± <1	*	*
Mn	nd	<1	<1	<1	<1	<1	nd	<1	<1	*	*
Mo	<1	nd	nd	nd	nd	<1	7	7	9 ± 1	22	<11
Na	12	6	5	3	2	16	12	28	16 ± 6	-75	100
Ni	nd	<1	<1	<1	<1	<1	63	64	68 ± 7	6	<2
P	<1	<1	<1	<1	<1	<1	<1	<1	<1	*	*
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Sb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Si	<1	<1	<1	<1	<1	1	1	2	10 ± 2	80	<10
Ti	nd	nd	nd	nd	nd	nd	2	2	2	0	0
V	<1	<1	nd	nd	nd	<1	187	187	186 ± 31	-1	0
Zn	nd	<1	<1	<1	<1	<1	1	1	1 ± 1	0	*

nd: not detected, nq: not quantified, NA; not applicable, -: not calculated, *: not calculated due to the low concentration

Table A5.3.3 Cation determination on aqueous and organic phase for experiment 4

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen ($M_{x\ aq,total}$)**	**Organic phase ($M_{x,org}$)**	**Total ($M_{x\ aq,total}$ + $M_{x,org}$)**	**Athabasca bitumen ($M_{x,bit}$)**	**% difference**	**% removal**
Recovered aqueous solution M_{aq} [g]	**44**	**22**	**63**	**38**	**175**						
Cation of element	**$C_{x,aq\ 1}$ [mg/L]**	**$C_{x,aq\ 2}$ [mg/L]**	**$C_{x,aq\ 3}$ [mg/L]**	**$C_{x,aq\ 4}$ [mg/L]**	**$C_{x,aq\ rot}$ [mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**	**[%]**
Al	<1	<1	<1	<1	<1	<1	3	3	2 ± 1	-50	<50
As	nq	nq	nq	nq	nq	nq	nq	nq	nq	-	-
B	<1	<1	<1	<1	<1	<1	<1	<1	1 ± 1	*	*
Ba	nd	nd	nd	nd	nd	nd	<1	<1	<1	*	*
Ca	<1	<1	<1	<1	<1	2	11	12	8 ± 7	-50	25
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Co	nd	<1	<1	<1	<1	<1	1	1	<1	*	*
Cr	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Cu	nd	nd	<1	<1	<1	<1	<1	1	1 ± 2	0	*
Fe	nd	nd	nd	nd	<1	<1	3	3	3	0	<33
K	1	<1	<1	<1	<1	1	3	4	3 ± 1	-33	35
Li	<1	<1	<1	<1	<1	<1	<1	<1	<1	*	*
Mg	<1	<1	<1	<1	<1	<1	1	2	1 ± <1	-100	*
Mn	<1	<1	<1	<1	<1	<1	<1	<1	<1	*	*
Mo	<1	0	0	0	0	<1	<1	1	9 ± 1	89	<11
Na	13	1	4	4	3	14	14	29	16 ± 6	-81	88
Ni	<1	<1	<1	<1	<1	<1	55	56	68 ± 7	18	<2
P	<1	<1	<1	<1	<1	<1	1	1	<1	*	*
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Sb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Si	<1	<1	<1	<1	2	4	4	8	10 ± 2	20	40
Ti	nd	nd	nd	nd	nd	nd	2	2	2	0	0
V	<1	nd	nd	nd	nd	nd	162	162	186 ± 31	13	0
Zn	<1	<1	<1	<1	<1	<1	<1	1	1 ± 1	*	*

nd: not detected, nq: not quantified, NA; not applicable, -: not calculated, *: not calculated due to the low concentration

Table A5.3.4 Cation determination on aqueous and organic phase for experiment 5

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen** ($M_{x\,aq,total}$)	**Organic phase** ($M_{x,org}$)	**Total** ($M_{x\,aq,total}$ + $M_{x,org}$)	**Athabasca bitumen** ($M_{x,bit}$)	% *difference*	% *removal*
Recovered aqueous solution M_{aq} **[g]**	**53**	**7**	**36**	**99**	**159**						
Cation of element	$C_{x,aq\,1}$ **[mg/L]**	$C_{x,aq\,2}$ **[mg/L]**	$C_{x,aq\,3}$ **[mg/L]**	$C_{x,aq\,4}$ **[mg/L]**	$C_{x,aq\,rot}$ **[mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**	**[%]**
Al	<1	<1	<1	<1	<1	<1	3	3	2 ± 1	-50	<50
As	nq	nq	nq	nq	nq	nq	nq	nq	nq	-	-
B	<1	<1	<1	<1	<1	1	1	1	1 ± 1	*	*
Ba	nd	nd	nd	nd	<1	<1	<1	<1	<1	*	*
Ca	<1	nd	1	<1	<1	2	7	9	8 ± 7	-13	25
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Co	nd	nd	<1	<1	<1	<1	<1	<1	<1	*	*
Cr	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Cu	nd	nd	<1	<1	<1	<1	<1	1	1 ± 2	0	*
Fe	nd	nd	nd	nd	<1	<1	3	3	3	-9	<33
K	1	<1	<1	<1	<1	1	3	4	3 ± 1	-33	33
Li	<1	<1	<1	<1	<1	<1	<1	<1	<1	*	*
Mg	<1	nd	<1	<1	<1	<1	<1	1	1 ± <1	*	*
Mn	<1	nd	<1	<1	<1	<1	nd	<1	<1	*	*
Mo	<1	nd	nd	nd	<1	<1	7	8	9 ± 1	11	<11
Na	13	1	5	2	3	15	9	25	16 ± 6	-56	94
Ni	nq	<1	<1	<1	<1	<1	64	65	68 ± 7	4	<2
P	<1	nd	<1	<1	<1	<1	<1	<1	<1	*	*
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Sb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Si	<1	<1	<1	<1	7	12	7	19	10 ± 2	-90	120
Ti	nd	nd	nd	nd	nd	nd	2	2	2	0	0
V	<1	nd	nd	nd	nd	<1	192	192	186 ± 31	-3	<1
Zn	nd	nd	<1	<1	<1	<1	<1	<1	1 ± 1	*	*

nd: not detected, nq: not quantified, NA; not applicable, -: not calculated, *: not calculated due to the low concentration

Table A5.3.5 Cation determination on aqueous and organic phase for experiment 6

Washing step	**1**	**2**	**3**	**4**	**Rotavap**	**Removed from bitumen ($M_{x\ aq,total}$)**	**Organic phase ($M_{x,org}$)**	**Total ($M_{x\ aq,total}$ + $M_{x,org}$)**	**Athabasca bitumen ($M_{x,bit}$)**	*% difference*	*% removal*
Recovered aqueous solution M_{aq} [g]	**71**	**11**	**18**	**183**	**94**						
Cation of element	$C_{x,aq\ 1}$ **[mg/L]**	$C_{x,aq\ 2}$ **[mg/L]**	$C_{x,aq\ 3}$ **[mg/L]**	$C_{x,aq\ 4}$ **[mg/L]**	$C_{x,aq\ rot}$ **[mg/L]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[µg/g bitumen]**	**[%]**	**[%]**
Al	<1	nd	<1	<1	<1	<1	3	3	2 ± 1	-50	<50
As	nq	nq	nq	nq	nq	nq	nq	nq	nq	-	-
B	<1	<1	<1	<1	<1	1	<1	1	1 ± 1	*	100
Ba	nd	nd	nd	nd	nd	nd	<1	<1	<1	*	*
Ca	<1	<1	1	<1	<1	2	5	7	8 ± 7	13	25
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Co	nd	nd	<1	<1	<1	<1	<1	<1	<1	*	*
Cr	nq	nq	nq	nq	nq	nq	<1	<1	<1	*	*
Cu	nq	nq	<1	<1	<1	<1	1	1	1 ± 2	0	*
Fe	nd	nd	nd	nd	<1	<1	3	3	3	0	<33
K	1	<1	<1	<1	<1	1	2	3	3 ± 1	0	33
Li	<1	<1	<1	<1	<1	<1	<1	<1	<1	*	*
Mg	<1	<1	<1	<1	<1	<1	1	1	1 ± <1	0	*
Mn	nd	nd	<1	<1	<1	<1	<1	<1	<1	*	*
Mo	<1	nd	nd	nd	nd	<1	8	8	9 ± 1	11	<11
Na	12	<1	6	2	3	16	6	22	16 ± 6	-38	100
Ni	nd	<1	<1	<1	<1	<1	69	69	68 ± 7	-1	<2
P	<1	nd	<1	<1	<1	<1	<1	<1	<1	*	*
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Sb	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Si	<1	<1	<1	<1	3	4	4	8	10 ± 2	20	40
Ti	nd	nd	nd	nd	nd	nd	2	2	2	0	0
V	<1	nd	nd	nd	nd	<1	206	206	186 ± 31	-11	<1
Zn	nd	nd	<1	<1	<1	<1	<1	1	1 ± 1	0	*

nd: not detected, nq: not quantified, NA; not applicable, -: not calculated, *: not calculated due to the low concentration

Appendix 5.4 FTIR SPECTRA - ATHABASCA BITUMEN WASHING

The spectra of experiments 2-3 is compared with the one for the Athabasca bitumen in **Figure A5.4.1** and **Figure A5.4.2**. As it was mentioned in **Chapter 5, Section 5.3.8** for experiment 1, the main differences that were observed are related to the CO2 (background at 2400-2200 cm^{-1}) and remaining toluene (at 728 cm^{-1}). Also, differences in the range of 1780-1740 cm^{-1} were observed (C=O interactions) between the Athabasca bitumen and the organic emulsion phase recovered in experiments 2 and 3.

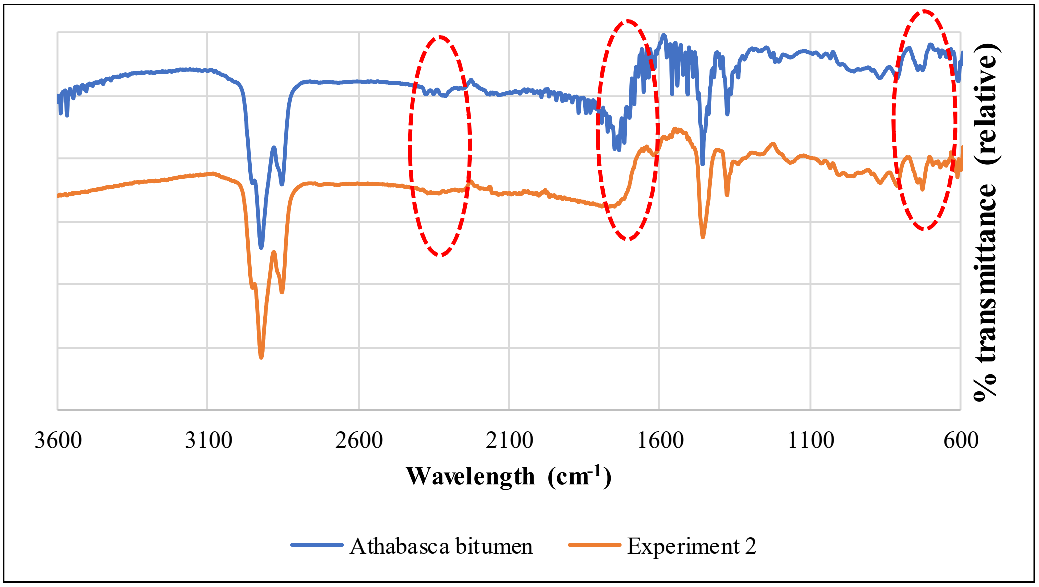

Figure A4.5.1 Fourier Transform Infrared Spectroscopy for experiment 2

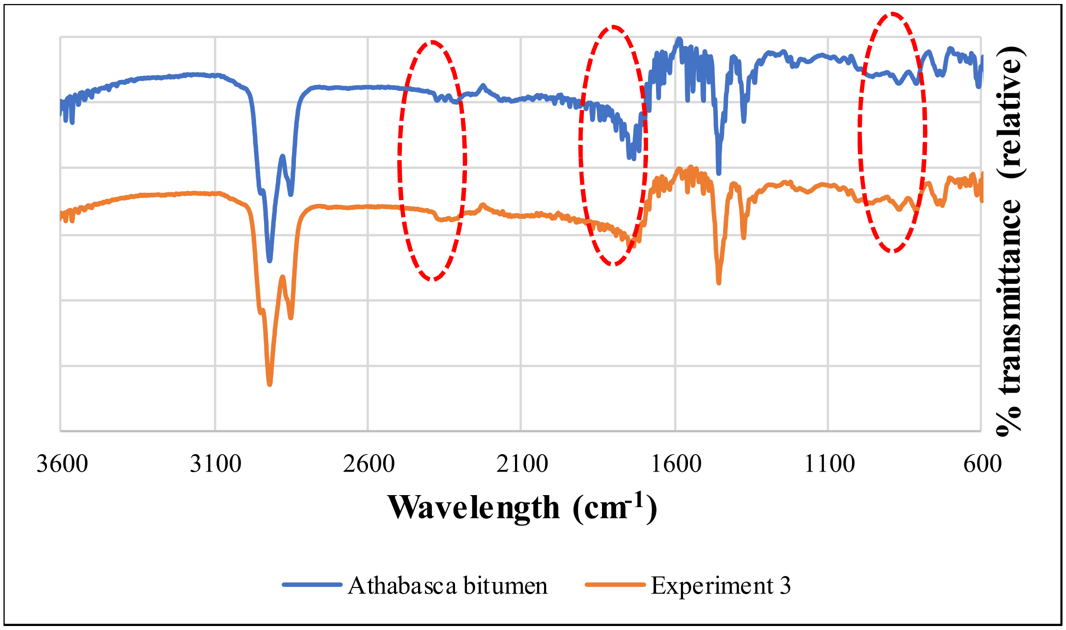

Figure A4.5.2 Fourier Transform Infrared Spectroscopy for experiment 3