University of Alberta

CHARACTERIZATION OF THE DISSOLVED ORGANIC MATTER IN STEAM ASSISTED GRAVITY DRAINAGE BOILER BLOW-DOWN WATER

by

Subhayan Guha Thakurta

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Department of Mechanical Engineering

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Abstract

The presence of high concentrations of dissolved organic matter (DOM) and total dissolved solids (TDS) in the boiler blow-down water (BBD) causes severe equipment fouling during the SAGD operation. For effective BBD management, a detailed understanding of the BBD chemistry is important. In this work, BBD DOM was fractionated using ion-exchange resins into hydrophobic and hydrophilic acids, bases and neutral fractions. Fluorescence excitation emission contours established discerning signatures of the organic fractions. The molecular weight distribution of the DOM was determined through filtration of BBD using membranes of different molecular weight cut-offs (MWCO). The effect of acidification on the BBD DOM and the mechanism of silica-DOM co-precipitation in presence of high salt concentration was determined. The DOM consisted mostly of low molecular weight compounds. Hydrophobic acids present in the BBD were predominantly humic acids and not naphthenic acids as observed in oilsands process affected waters.

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Chapter 1

Introduction

1.1 Background and Overview

Steam assisted gravity drainage (SAGD) is a widely used process for *in-situ* bitumen extraction from oilsands. During SAGD bitumen extraction, medium pressure wet steam is injected into the production wells which causes a reduction in viscosity of the bitumen thermally and facilitates bitumen extraction. The steam condensate flows down the periphery of the steam chamber along with the bitumen under the effect of gravity. The water produced during the SAGD extraction of bitumen is known as SAGD produced water. It is a mixture of bitumen, clay and water. About 80 to 90 % of the produced water (PW) is recycled and treated to produce boiler feed water. Gravity based separation methods like free water knock out (FWKO) drums, followed by induced static flotation (ISF), are used to remove most of the separable oil from the produced water. Following these, walnut shell filters are used to remove traces of oil from the water, and the deoiled water is stored as produced water in tanks. Silica is removed from the de-oiled produced water through warm lime softening (WLS). After filters and weak-acid cationic exchange (WAC) are employed for removal of suspended solids and calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, respectively, before the water is fed into the steam generator. The induced static flotation, WLS and WAC treatment of the produced water is known as conventional produced water treatment. The schematic diagram of treatment procedure of SAGD produced water is illustrated in Figure 1.1

Once through steam generators (OTSGs) are used for steam generation in SAGD instead of the conventional drum boilers as the OTSGs are capable

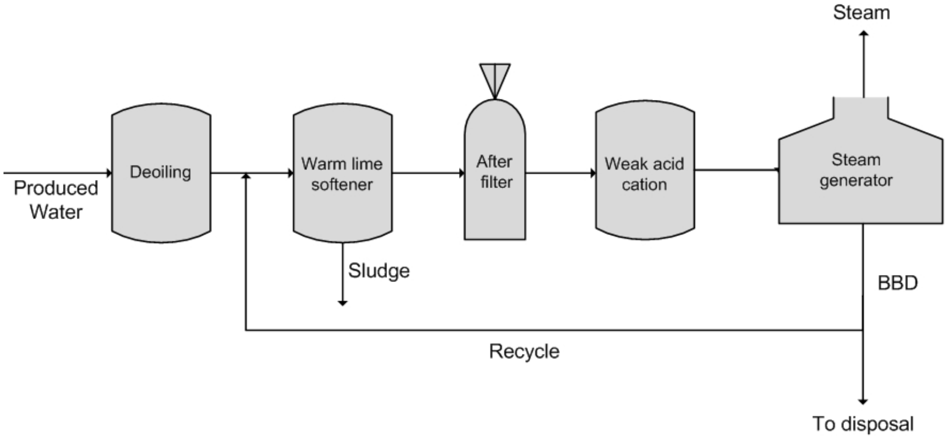

Figure 1.1 – Schematic Diagram of the treatment procedure for SAGD produced water.

of handling high total dissolved solids (TDS). The volume of the blow-down water obtained from OTSG is higher than that of the standard recirculation drum boilers. This is due to the high TDS concentration of the OTSG feed water. Currently, 20% of the volume of the boiler feed water is obtained as boiler blow-down (BBD) from the OTSGs. A portion of this BBD is recycled back to the WLS process and the rest is disposed through deep well injection.

The BBD water has high levels of dissolved organic matter (DOM) and total dissolved solids (TDS). Knowledge on the nature and effects of high DOM concentrations in SAGD application is limited. The high levels of DOM in SAGD produced water and OTSG blow-down have been implicated in numerous problems in the industrial processes, such as making highly sticky deposits with inorganic salts on economizer surfaces, irreversible fouling on downstream equipment surfaces, corrosion in pipelines, and clogging of injection wells [Wang et al., 2005, Jennings and Shaikh, 2007].

The disposal of highly alkaline waste like BBD into underground rock formation could potentially decrease the pH of the liquid [Roy et al., 1991]. The decrease in pH causes precipitation of silica [Iler, 1979]. The strong chemical interaction between siliceous and organic matter triggers silica-organic co-precipitation [Abramson et al., 2009]. Thus, deep well injection of BBD in the pH range of 8 to 9 may cause clogging of wells due to silica-organic co-precipitation. Other effects of disposal of a highly alkaline brine-like waste into underground rock formations is generation of precipitation products like $CaCO_3$, $Mg(OH)_2$ and sodium metasilicate due to interaction between BBD and underground mineral formations [Roy et al., 1991]. The detailed characterization of BBD is important is important to understand the causes of silica and organic co-precipitation.

Examining the chemical characteristics of deposits in the SAGD heat exchangers, it was observed that the deposits are predominantly organic acids and organic acid salts [Jennings and Shaikh, 2007]. High-resolution mass spectrometry analysis of these deposits identified several thousands of individual organic acids with broad distributions of molecular weight, heteroatom content, aromaticity, and carbon number [Schaub et al., 2007]. Analysis of the organic components in SAGD produced water showed the presence of a wide variety of organic compounds with carboxylic and phenolic functional groups [Petersen and Grade, 2011].

In the present scenario the treatment techniques used for SAGD wastewater is not capable of removal of organic matter from the water. The organic matter interacts with the dissolved silica and cause irreversible fouling in the equipment. A detailed understanding on silica and organic chemistry is essential for designing efficient plant equipment to mitigate the fouling issues in the SAGD process. However, a limited knowledge is available on the organic matter chemistry in SAGD wastewater. Thus, in this work the chemistry of the organic matter in the SAGD wastewater is explored to provide a qualitative understanding of chemical characteristics of the fouling organic matter which will be essential in designing effective treatment techniques for mitigating fouling in SAGD operations.

1.2 Problem Statement

BBD water is a complex mixture, having high alkalinity, high TDS, high levels of DOM and silica. Treatment of such a liquid to remove the contaminants and increase water recycle has been neglected in industrial practice because of the apparent lack of value of this wastewater. There is also a lack of scientific literature examining various treatment processes for such refractory water. In light of heightened interest in minimizing water disposal and make up water use in SAGD plants, treatment options for BBD are starting to get attention from the scientific community and industry.

Information regarding the nature and conventional water quality parameters of SAGD produced waters can be obtained from prior studies. However, knowledge of the chemical characteristics of SAGD DOM is limited. This is in contrast to the extensive literature available on the chemical character of Athabasca Oilsands process affected waters (OSPW) associated with the surface mining and extraction of bitumen, many of which conclude that the DOM of OSPW consists mainly of naphthenic acids [Kavanagh et al., 2009, Kim et al., 2011], although this conclusion is not universal [Barrow et al., 2010, Grewer et al., 2010].

From the above discussion, it is understood that the knowledge of the chemical composition of the DOM is necessary for designing adequate methods for mitigating the fouling in SAGD equipment. Despite its importance to SAGD water treatment processes, very little is known about the exact role each individual species in the SAGD DOM plays in the water treatment and equipment fouling processes. Understanding the organic matter chemistry in SAGD wastewater will facilitate designing efficient treatment techniques to mitigate fouling in SAGD process.

A fundamental framework for understanding the more general relationships between DOM and plant processes, needs to be developed using generalized DOM categorization techniques similar to those used in the study of natural organic matter (NOM) in natural waters.

NOM has been the subject of intense research over the last 40 years, primarily in relationship to drinking water treatment. This research has led to many well-developed techniques for characterizing NOM and relating its characteristics to the efficacy of various water treatment techniques [Matilainen et al., 2011]. Some of the pertinent questions on the SAGD DOM are;

1. How different is the SAGD DOM from the aquatic NOMs?

2. What effects do different process conditions have on the SAGD DOM?
3. What are the chemical nature of different organic compounds present in the DOM?
4. Understanding the BBD chemistry will pave the way for determining the efficacy of different waste water treatment techniques for SAGD water treatment.

1.3 Objectives and Scope

1.3.1 Objectives of the Present Study

The broad objective of this study is to provide a comprehensive understanding of the chemistry of BBD and to identify how this chemistry causes operational problems. The specific goals are:

1. Provide a detailed physico-chemical characterization of the SAGD blow-down water. Determine the concentration of inorganic and organic matter content.
2. Classify the dissolved organic matter in the SAGD blow-down water into different fractions based on thier hydrophobicity and hydrophilicity.
3. Establish a simple characterization method for identifying individual DOM fractions.
4. Determine the characteristic of each DOM fraction particularly during acidification or in presence of silica.
5. To provide insight regarding the influence of DOM on SAGD plant operations.

1.3.2 Scope of the Present Study

The scope of this thesis includes determination of the chemical nature of the organic matter present in the SAGD blow-down using spectrofluorescence technique. The qualitative fluorescence signature of the SAGD DOM is compared with the fluorescence signatures of various organic compounds present in the aquatic NOM, to provide an idea about the chemical nature of the DOM in

SAGD. Determination of exact chemical structure of the organic compounds present in the SAGD DOM are beyond the scope of this work. Though the knowledge gained from the characterization of the DOM will be eventually utilized in determining appropritate technology for SAGD water treatment, no technology evaluation is carried out in this work. This work focuses only on the characterization of SAGD blow-down water and providing qualitative information about the chemical nature of the organic matter present in the same.

1.4 Overview of the Thesis

In this study, the ion-exchange technique using DAX-8®, Duolite® and Dowex® resins is applied to separate different DOM fractions from the BBD. Specific UV absorbance (SUVA), fluorescence spectroscopy, Fourier transform infra-red spectroscopy (FTIR) and total organic carbon (TOC) analysis methods are used for characterizing the hydrophobic and hydrophilic fractions present in the BBD. The BBD is filtered through UF/NF membranes of different molecular weight cut-off (MWCO), in series, to obtain three molecular weight fractions in order to determine the molecular weight distribution of the DOM in BBD. The organic compounds retained on the membranes are analyzed using a ATR-FTIR technique. The spectrofluorescence signatures of the permeates obtained from the three membranes in sequential operation are also examined. The effect of pH on the SAGD DOM was analyzed by acidifying the BBD and preparing BBD solution at different pH. The characterization of the supernatant obtained at different pH (as the organic precipitates) identifies the organic fraction predominant in the precipitates.

This thesis consists of six chapters, each focussing on different aspects of characterization of the SAGD BBD.

In the present chapter, a brief overview of the SAGD process and organic fouling is presented followed by a problem statement and objectives of the present study. The scope of the work is also outlined in this chapter.

In Chapter 2, a review of the existing work on characterization of natural organic matter and SAGD water treatment is presented. This includes the details of spectrofluorescence technique employed for analysis of aquatic NOMs. Based on the intensity peaks obtained during fluorescence analysis, the aquatic NOM fluorophores are classified into different groups. The different aquatic fluorophores and thier respective peak intensity regions are presented in this chapter. The current work on the acidification of wastewater is also summarized. Details on other characterization techniques like Fourier transform infra-red (FTIR) spectroscopy, total organic carbon (TOC) analysis etc. are also presented.

Chapter 3 describes the experimental materials and methods used in characterizing the SAGD blow-down water. The ion-exchange fractionation is the principal experimental procedure in this study. This process is described in detail with respect to resin cleaning, experimental procedures and elution of organic fractions. Other characterization techniques like spectrofluorescence, acidification, TOC Analysis and FTIR are also described in this chapter.

In Chapter 4, the percentage distribution of the different organic matter fractions in the SAGD BBD is reported. The spectrofluorescence signatures of the organic fractions along with their molecular weight distribution are presented in this chapter. The fluorescence signatures of Oilsands process affected water and SAGD blow-down water are compared using this characterization method.

Chapter 5 presents a systematic study on the effect of pH on the SAGD DOM. Analysis of the spectrofluorescence signatures of the supernatant obtained after precipitation of organics identifies the predominant organic fraction in the precipitate.

Chapter 6 summarizes the major conclusions of this work and identifies the probable future work possible based on this study.

Chapter 2

Literature Review

2.1 Conventional and non-conventional produced water

The oily wastewater produced during oil and gas production from conventional and non-conventional sources is known as produced water. The physico-chemical properties of the produced water vary with the sources from which they are obtained [Alley et al., 2011]. Conventional produced waters are obtained during reclamation of oil and gas [Tellez et al., 2005, Johnson et al., 2008]. The co-produced waters are also obtained during oil and gas extraction from non-conventional sources like coal bed methane [Dahm et al., 2011] and oilsands. Oilsands process affected water (OSPW) is generated during bitumen extraction through mining [Kavanagh et al., 2009], whereas, the SAGD produced water is obtained during the *in situ* bitumen extraction using steam assisted gravity drainage (SAGD). Numerous studies are available delineating the physico-chemical characteristics of the OSPW [Kavanagh et al., 2009, Kim et al., 2011, Barrow et al., 2010, Grewer et al., 2010]. However, there is limited literature describing the properties of the SAGD produced waters. The properties of different conventional and non-conventional produced waters are summarized in Table 2.1.

During extraction of bitumen from oilsands using surface mining, hot water, caustic soda and diluent (naphtha) are mixed with the ore to form a slurry [Masliyah et al., 2004]. Bitumen is recovered from the slurry and alkaline extraction water is obtained as residue [Clemente and Fedorak, 2005]. In order to store this hazardous residue huge tailings ponds have been constructed. The

Table 2.1 – Comparision of chemical characteristics of oil-field produced water (OFPW) [Li et al., 2010, Mondal and Wickramasinghe, 2008, Alley et al., 2011, Lu et al., 2009, Benko and Drewes, 2008, Tellez et al., 2005], coal bed methane produced water (CBMPW) [Alley et al., 2011, Dahm et al., 2011], Oilsands process-affected water (OSPW) [Kavanagh et al., 2009, Kim et al., 2011, Holden et al., 2011, El-Din et al., 2011, Peng et al., 2004], SAGD produced water (SAGDPW). All units in mg/L except conductivity (μS/cm) and pH.

Chemical Characteristics	Source of produced water			
	OFPW	CBMPW	OSPW	SAGDPW
pH	5.18-8.9	6.56-9.87	8.6-9.12	7.11
Conductivity	838-1469	94.8-145000	2370-3459	1540
TDS	700-2000	150-6230	2477	1005
TSS	90-180	ND-24.8	97	-
TOC	76-140	0.45-2.35	48.3-83	232-500
Alkalinity	300-380	54.9-9450	490-690	120
Dissolved SiO_2 (Soluble)	7-14	-	2.77	102
Oil and Grease	~92	1-11	-	29.1

residual water at the surface of the tailings pond is known as oilsands process affected water (OSPW). OSPW is considered highly toxic and cannot be discharged directly to the open water systems [MacKinnon, 1986]. Treatment procedures for OSPW are of cardinal interest [Scott et al., 2008]. The OSPW contain sands, clay and mixture of different alicyclic carboxylic acid compounds collectively known as naphthenic acids [Lochte and Littmann, 1955, Clemente and Fedorak, 2005, Holowenko et al., 2002]. Of these constituents, naphthenic acids are highly toxic and impedes the disposal of the OSPW into environment [Rogers et al., 2002].

Steam assisted gravity drainage (SAGD) is thermally enhanced in situ oilsands extraction process. Steam is injected through the injector well into the oilsands layer to reduce the viscosity of bitumen. Heated oil is received on the surface from the producer wells [Butler, 1991]. A large fraction of steam condensate is obtained as residue in the wells. This residue is a mixture of free and emulsified oil, solids and water and is known as SAGD produced water (SAGDPW) [Petersen and Grade, 2011]. The SAGD produced water is treated and converted to boiler feed water which is used to generate steam for SAGD utilization. During steam generation about 20% of the feed is obtained as blow-down water. The boiler blow-down (BBD) obtained five to ten folds concentrated with DOM than the SAGDPW. The water is partly recycled and partly disposed through deep well injection. The presence of high concentration of dissolved organic in the BBD causes several problems like injection well clogging, economizer fouling etc. in the SAGD operations [Wang et al., 2005, Jennings and Shaikh, 2007]. Despite the importance of BBD in SAGD operation detailed characterization of the organic matter in the BBD are not obtained in literature.

The physico-chemical properties of different produced waters summarized in Table 2.1 show presence of similar components in these waters, irrespective of the source. However, the concentration of these components are discernibly different for the conventional and non-conventional produced waters. For example, the dissolved organic matter content in the SAGD produced water is much higher than that observed in other produced waters, like, OFPW and OSPW. The OSPW has a maximum of 100 mg/l of organic matter in dissolved condition whereas the SAGDPW contains $200-500$ mg/l of DOM. The nature of the SAGD DOM may be different from the OSPW DOM due to the difference in the mining and SAGD extraction techniques. SAGD extraction technique employs higher temperatures (150-300 °C) in comparision to moderate temperatures (70-90 °C) in the mining process. The BBD is a concentrated version of the SAGDPW and thus the nature of the organic compounds in BBD should be quite different from that of OSPW. However, the characteristics of the dissolved organic matter present in the BBD are not available in literature.

2.2 Characterization of dissolved organic matter in natural water

Dissolved organic matter (DOM) is a complex mixture of various types of organic compounds abundant in aquatic systems [Matilainen et al., 2011]. The characteristics of DOM play a critical role in determining the treatment techniques for aquatic systems [Matilainen et al., 2010]. The physico-chemical properties of the DOM vary with the sources from which they are obtained [Fabris et al., 2008, Wei et al., 2008].

It is evident from the discussion in the previous section that due to the difference in the extraction techniques the SAGD produced water and mining process affected water have different concentrations of dissolved organic matter. The characterization techniques available in literature has been applied to natural aquatic systems which has much lower organic matter concentration. In this study, the applicability of these techniques for systems containing high concentration of dissolved organic matter is determined.

In the following chapters the fractionation and analyses methods suitable for DOM characterization in thermally enhanced oilsands extraction produced waters will be discussed. The characteristics of the organic matter in the BBD in terms of hydrophobicity, hydrophilicity and molecular weight distribution will be determined. This study will help to understand the fouling behaviors of individual fractions of DOM in membrane separation process and aggregation behavior with foulants like silica, iron, magnesium etc. which are found in the SAGD produced waters.

2.2.1 Fractionation of DOM

The aquatic DOMs contain two distinct organic fractions, hydrophobic and hydrophilic. The hydrophilic fraction is composed of aliphatic lower molecular weight compounds whereas the hydrophobic fraction comprise of aromatic high molecular weight compounds [Sharp et al., 2006, Swietlik et al., 2004, Matilainen et al., 2011, 2010, Liu et al., 2007].

Qualitative and quantitative information on the DOM characteristics are important for determining appropriate treatment techniques to remove DOM from water [Matilainen et al., 2011, Hua and Reckhow, 2007]. Analytical methods like total organic carbon (TOC) analysis, UV absorbance and chemical oxygen demand (COD) measurement are useful for determination of the quantitative characteristics of the DOM in a sample [Matilainen et al., 2011]. Whereas, the qualitative characteristics of the DOM are determined through the techniques like spectrofluorescence [Coble, 1996, Marhaba et al., 2000], specific UV-absorbance [Edzwald and Tobiason, 1999, Weishaar et al., 2003] and Fourier transform infra-red spectroscopy [Rodriques and Nunez, 2011, Orgill et al., 1999].

DOM is composed of variety of organic molecules and in order to determine the characteristics of DOM accurately isolation of different fractions is necessary [Marhaba et al., 2003]. There are different ways of isolating fractions from DOM. Separation of hydrophobic and hydrophilic fractions using resin fractionation procedure is well established technique used in various DOM characterization studies [Kanokkantapong et al., 2006, Sharp et al., 2006, Marhaba et al., 2000]. The other fractionation technique is a membrane based procedure classifying the DOM into different molecular weight fractions [Hua and Reckhow, 2007].

Resin fractionation is a well-established technique for characterizing DOM. The DOM from any aquatic system can be fractionated into hydrophobic and hydrophilic acid/base/neutral fractions using an ion-exchange fractionation procedure as proposed by Leenheer [Leenheer, 1981]. The procedure proposed by Leenheer utilizes a series of non-ionic and ionic resins to fractionate DOM. Non-ionic resins like DAX-8 or XAD-8 are used to separate hydrophobic fractions from the DOM whereas, anionic and cationic resins are used to separate hydrophilic acids and hydrophilic bases, respectively [Leenheer, 1981, Marhaba et al., 2003]. XAD-8 is out of production for some time now and hence in recent studies DAX-8 has been used. Several modifications and procedural adjustments have been made to the Leenheer's procedure to make the method more effective for different organic matter samples [Marhaba et al., 2003, Aiken et al., 1992, Thurman and Malcolm, 1981, Malcolm and MacCarthy, 1992]. Aiken *et al.* used XAD-8 and XAD-4 resins in series ro remove the hydrophobic acids and hydrophilic acids [Aiken et al., 1992]. XAD-8 adsorbed the hydrophobic acid fraction whereas the hydrophilic acid fraction was removed by XAD-4 [Aiken et al., 1992]. Marhaba *et al.* used three DAX-8 columns instead of a single XAD-8 column for isolation of hydrophobic acid, base and neutral fractions and also suggested several changes in the method and reagents used for isolation of DOM Fractions [Marhaba et al., 2003]. The fractionation technique as proposed by Leenheer or the modified versions of it have been used to study the treatability of NOM fractions by various water treatment processes, like coagulation [Sharp et al., 2006] and membrane filtration [Her et al., 2008] and oxidation [Swietlik et al., 2004].

The ion-exchange fractionation method is applied for natural aquatic systems which contains a very low amount of dissolved organic matter. However, in SAGD BBD a high amount of organic matter is solubilized. The ion-exchange fractionation procedure proposed by Leenheer [Leenheer, 1981] was modified to fractionate SAGD BBD which contains a high concentration of dissolved organic matter. The modified procedure is described in Chapter 3 and Appendix A.2.4 of the thesis.

NOMs are also a mixture of organic compounds with different molar masses [Liu et al., 2007]. The molecular weight fractionation of DOM involves ultrafiltration (UF) and nanofiltration (NF) of the sample using membranes of different molecular weight cut-offs [Benner et al., 1992, Minor et al., 2002]. Sequential filtration of DOM with different MWCO samples generate DOM fractions of similar molecular size [Wu et al., 2003, Zhao et al., 2006]. Membrane based fractionation of organic matter in the natural water revealed that the higher molecular weight organic compounds are the major fraction in natural organic matter (NOM) [Hua and Reckhow, 2007].

2.2.2 SUVA

The optical density or absorbance of a sample is defined as the logarithm of the ratio of the intensity of light transmitted to the intensity of light absorbed, when light of a certain wavelength is passed through the sample. The concentration of an organic compound in a solution can be determined by measuring the absorbance of the sample [Matilainen et al., 2011]. An idea of the chemical characteristics of the organic compounds in the sample can also be obtained through absorbance studies. For example, absorbance at an ultra-violet wavelength of 254 nm is correlated to the aromaticity of the organic compounds in the sample [Korshin et al., 2009]. However, as the absorbance is dependent on the sample concentration the quantitative results are more reliable than qualitative estimations obtained from absorbance sprectroscopy.

Qualitative analysis of the samples can be performed by a normalized UV-absorbance technique called SUVA. Specific UV absorbance, commonly known as SUVA, is the ratio of UV absorbance of a given sample at 254 nm and the DOC concentration of the sample in mg/L multiplied by 100 [Weishaar et al., 2003]. This allows the aromatic biased UV absorbance at 254 nm measurement to be normalized over the overall organic load in the water. SUVA is a useful parameter for qualitative estimation of the dissolved aromatic carbon content in aqueous systems [Weishaar et al., 2003]. This parameter has been correlated to the chemical characteristics of NOM in the water in terms of hydrophobicity and hydrophilicity; a SUVA >4 indicates mainly hydrophobic and especially aromatic material, whilst a SUVA ≤ 2 illustrates mainly hydrophilic material [Edzwald and Tobiason, 1999]. Table 2.2 summarizes the correlation of SUVA value with the chemical characteristics of dissolved organic matter.

Table 2.2 – Interpretation for SUVA results [J.Edzwald, 1999]

SUVA value	Characteristics of DOM
> 4	Predominantly humic organic matter, highly hydrophobic and aromatic
$2 - 4$	A mixture of both humic and non-humic organic matter
≤ 2	Low hydrophobicity, predominantly aliphatic and non-humic

2.2.3 Fourier transform infra-red spectroscopy

Fourier transform infra-red (FTIR) spectroscopy is used to determine the inorganic and organic compounds present in the DOM [Kanokkantapong et al., 2006, Hay and Myneni, 2007]. During FTIR analysis infra-red light is passed through the sample under observation and the absorption spectra is recorded. The inorganic and organic compounds present in the DOM have different infrared absorption bands which serve as their characteristic signatures [Matilainen et al., 2011]. The absorption bands of various inorganic and organic compounds for FTIR analysis are summarized below in Table 2.3. However, the presence of a large number of organic compounds in the DOM causes overlapping of the spectral signatures which in turn makes the interpretaion of the FTIR results difficult [Chen et al., 2002].

The naphthenic acids in the OSPW have been analyzed using FTIR techniques [Jivraj et al., 1995]. The method followed for analysis is as follows; samples are filtered with 0.45 μm filter, acidifed to pH 2.5, evaporated and dried and FTIR analysis of the residue was performed [Jivraj et al., 1995, Holowenko, 2001]. The FTIR peaks of commercial naphthenic acids and the organic matter extracted from OSPW are obtained at bands of 1706 cm^{-1} and 1743 cm^{-1} [Holowenko, 2001]. The peak at 1743 cm^{-1} is assigned to carboxylic acid monomers whereas 1706 cm^{-1} is assigned to carboxylic acid dimers [Clemente and Fedorak, 2005]. Thus, it is evident that naphthenic acids are principal component in the OSPW DOM. FTIR analysis were also employed to analyze the organic matter content in the SAGD produced waters and peaks were obtained for carboxylic acids monomers and dimers and thus, presence of naphthenic acids in the SAGD produced waters were predicted [Scott et al., 2008].

2.2.4 Fluorescence excitation emission contours

When an organic molecule is excited with photons of a certain wavelength the electrons in the outermost shell move from a lower energy state to higher energy state. As the electrons lose energy and return to the original energy level fluorescence is observed. The wavelengths at which the absorption and emission is observed is different for different molecules [Lakowicz, 1999]. The

Table 2.3 – Absorption bands of various inorganic and organic functional groups in FTIR spectroscopy [Orgill et al., 1999, Rodriques and Nunez, 2011, Falcone et al., 2010, Falcone Jr. et al., 2010, Sarawade et al., 2011]

Functional Group	Absorption bands (cm^{-1})	Description
C-H stretching	2850-2931	CH_2 and symmetric and anti-symmetric CH_3
C=O stretching	1706-1767	Carboxylic acids
C=C stretching	1630-1646	Alkenes and Aromatic Rings
C-H bend	1451-1455	Antisymmetric CH_3 deformation
O-H bend	1410	Carboxylic groups
C-H bend	1379	Symmetric CH_3 deformation
C-O stretching	1120-1260	Carboxylic groups, phenols, aromatic and unsaturated ethers
Si-OH	968	Silica
Si-O-Si	1017-1098	Silica

organic compounds which absorbs light energy and re-emits it are known as fluorophores [Mopper et al., 1996, Coble et al., 1990]. The fluorescence emission intensity peaks of DOM are generally observed due to the presence of high aromaticity, hydroxyl and amine groups in the organic fluorophores [Liu et al., 2007, Wu et al., 2007, Hudson et al., 2007, Matilainen et al., 2011]. The aromatic organic compounds exhibit fluorescence due to the presence of unpaired electrons which can be easily excited through photon energy. The signatures of the fluorophores in the aquatic DOM when compared to certain laboratory standard fluorophores shows that the organic compounds in the aquatic DOM resembles the humic-like, fulvic-like, tryptophan-like and tyrosine-like signatures [Patel-Sorrentino et al., 2002, Hudson et al., 2007, Coble et al., 1990]. However, certain samples may have their own characteristic fluorescence signature which may resemble the signatures of one or more standard fluorophores [Marhaba et al., 2000, Mayer et al., 1999].

The fluorophores in aquatic systems can be classified into five major types: A, C, M, B and T [Coble, 1996]. These fluorophores are also assigned as α', α, β, γ, δ in other literature [Parlanti et al., 2000]. Another classification of the fluorophores in the DOM is done based on hydrophobicity and hydrophilicity [Marhaba et al., 2000]. Individual fluorophores have distinct excitation/emission wavelength region for thier respective intensity peaks. The excitation (Ex) and emission (Em) wavelength range of maximum fluorescence intensity for different aquatic fluorophores are presented in Table 2.4.

Excitation emission matrix spectroscopy (EEMS) is an analytical technique of spectrofluorescence widely used for organic matter characterization [Coble, 1996, Hudson et al., 2007, Matilainen et al., 2011]. In this method the fluorescence intensity over a range of excitation and emission wavelengths are observed. Data obtained from 3-D scanning of organic molecules over a range of excitation emission wavelengths used to generate contour plots which are known as the excitation emission matrix (EEM) [Coble, 1996]. The advantage of EEMS over single scanning fluorescence techniques is that the data processing is rapid [Baker, 2001], discerning a variety of fluorophores present in a complex mixture of DOM [Hudson et al., 2007] and large amount of data is available for processing [Spencer et al., 2007, Lombardi and Jardim, 1999]. However, the parameters like pH, temperature and dilution have pronounced effects on the fluorescence intensity [Larsson et al., 2007, Hautala et al., 2000, Westerhoff, 2001, Mobed et al., 1996, Baker, 2005].

The fluorescence intensity of any fluorophore is reduced by the interfering effects of other molecules present in the DOM [Larsson et al., 2007]. In presence of other organic molecules the fluorescence peak intensity of a certain fluorophore is either shifted to longer wavelength or to a shorter wavelength. The shift to the longer wavelength is known as red shift, whereas, the shift to

Table 2.4 – Fluorophores of different types and thier intensity peaks [Hudson et al., 2007]

Fluorophore Name			Chemical Nature of fluorophores	Ex/Em wavelength range of intensity peaks
Coble's Nomenclature [Coble et al., 1990]	Parlanti's Nomenclature [Parlanti et al., 2000]	Marhaba's Nomenclature [Marhaba et al., 2000]		
A	α'	HPoA	Humic-like	237-260/400-500
C	α		Humic-like	300-370/400-500
M	β		Marine Humic-like	312/380-420
B	γ	HPoN	Tyrosine-like	225-237/309-321 and 275/310
T	δ	HPoB HPiA HPiN	Typtophan-like	225-237/340-381 and 275/340
		HPiB		225-237/357-369[Marhaba et al., 2000]

a shorter wavelength is known as blue shift [Hudson et al., 2007]. The inner filtration effects are avoided if the sample is diluted to a TOC concentration of 1-20 mg/l [Westerhoff, 2001, Hautala et al., 2000, Hudson et al., 2007, Yang and Zhang, 1995, Vodacek and Philpot, 1987]. Dilution of the sample reduces the amount of fluorophores present in it and therefore, the amount of light absorbed by the surrounding molecules is less [Hudson et al., 2007]. Hence, the inner filtration effects are negated through dilution of samples.

The fluorescence intensity varies with changes in the pH of the sample [Vodacek and Philpot, 1987]. The fluorescence intensities of standard humic and fulvic acid solutions were different in the pH ranges of 2 to 12 [Patel-Sorrentino et al., 2002, Westerhoff, 2001, Vodacek and Philpot, 1987]. Increase in peak intensity was observed as the pH of the solution was increased [Patel-Sorrentino et al., 2002]. However, this change in peak intensity with the variation of pH was reversible [Patel-Sorrentino et al., 2002, Vodacek and Philpot, 1987]. As the pH of a solution is varied the structure of the organic fluorophores present in the solution also change. With a decrease in pH the fluorophore molecule coils and the fluorescence sites present in the molecules are eclipsed [Myneni et al., 1999]. This causes a reduction in the fluorescence intensity. However, when the pH of the sample is re-adjusted to the original value the fluorophores start exhibiting higher intensity peaks. The effect of temperatures on the other hand are irreversible. When a fluorophore is subjected to higher temperatures they suffer a permanent change in thier structure due to thermal decomposition [Vodacek and Philpot, 1987]. Hence, the fluorescence experiments must be performed at a constant temperature in order to prevent thermal decomposition of the fluorophores.

Fluorescence EEMS has been used for characterizing the DOM present in fresh waters, marine waters and different waste water systems. It was observed that the DOM in the marine waters are primarily constituted of humic acids of type C and tryptophan like fluorophores [Mayer et al., 1999, Parlanti et al., 2000]. Analysis of estuarine waters show the presence of tyrosine like molecules the sources of which are believed to be microbial activity [Mayer et al., 1999]. The freshwater DOM on the other hand is predominantly composed of humic acids of type A and C [Katsuyama and Ohte, 2002]. In addition to these fluorophores tryptophan like fluorophores of type T are also observed in the fresh waters [Baker and Spencer, 2004].

The naphthenic acids in the oil sands process affected water has been characterized using spectrofluorescence techniques [Kavanagh et al., 2009, Mohamed et al., 2008]. The fluorescence peaks for OSPW were obtained at the excitation wavelengths of 282 and around 340 nm using synchronous fluorescence spectroscopy [Kavanagh et al., 2009, Mohamed et al., 2008]. Classically, the naphthenic acids were not considered to be fluorescent [Grewer et al., 2010]. However, the naphthenic acids in the OSPW show fluorescence signatures. This feature is attributed to the presence of certain aromatic compounds along with naphthenic acids in the OSPW [Headley et al., 2009].

However, fluorescence signatures of the DOM in the SAGD produced water is unavailable in literature. Since the process conditions in the mining and SAGD is significantly different it is expected that the characteristics of the DOM in the SAGD prodiced water shall be different from the OSPW. Fluorescence EEMS can be utilized to obtain information about the chemical structure of the SAGD DOMs.

2.3 Summary

It is evident from literature review discussed in this chapter that the produced water characteristics vary significantly with the source. Though literature delineating physico-chemical properties of various produced waters is available, knowledge on the chemical characteristics of SAGD boiler blow down (BBD) water is lacking. Since the boiler blow down water plays an important role in the SAGD operation detailed characterization of the SAGD BBD is necessary. Various characterization techniques for aquatic DOM are available in literature. However, these techniques are tried and tested mostly on natural aquatic systems like sea and river, and not extensively on the SAGD produced waters. Furthermore, complete information on the aquatic DOM cannot be obtained from a single characterization technique. For example, characterization of OSPW, obtained from oil sands mining process, showed that naphthenic acid is the dominant fraction in the OSPW DOM but recent spectrofluorescence analysis indicated presence of aromatic and unsaturated organic compounds in the OSPW in addition to the naphthenic acids. The physico-chemical properties of the SAGD produced water available in literature is also quite different from the OSPW properties. This suggests that like the SAGD produced water, the BBD may also have some unique characteristics which are quite different from the other produced waters and in order to determine effective BBD management techniques, its characterization is extremely necessary. In light of the above the current study aims to characterize the DOM in SAGD blow down water to determine the chemical characteristics of various organic compounds present in the SAGD BBD. The experimental techniques used and procedures followed in characterization of BBD DOM is discussed in details in chapter 3.

Chapter 3

Experimental Methods

3.1 Introduction

In this Chapter the experimental techniques and materials used in this study are described. Two sets of experiments were performed in this research. First, the ion exchange fractionation of the DOM in SAGD BBD and the subsequent analyses of the different fractions was conducted. The second set of experiments was performed to determine the molecular weight distribution of the organic fractions and the effect of pH adjustment in SAGD BBD.

In the ion exchange fractionation experiments BBD samples obtained from a large Athabasca SAGD operation were classified into different organic fractions using non-ionic, cationic and anionic resins. Six organic fractions viz., hydrophobic base (HPoB), hydrophobic acid (HPoA), hydrophobic neutral (HPoN), hydrophilic base (HPiB), hydrophilic acids (HPiA) and hydrophilic neutral (HPiN) were isolated from the DOM present in the SAGD BBD. The fluorescence signatures of these individual fractions were determined by generating their fluorescence excitation-emission matrix. Spectrofluorescence technique was used to show that each individual organic fraction in the SAGD BBD has a discernible fluorescence signature from other fractions. The dissolved organic carbon concentration in the raw BBD and the organic fractions were determined using TOC analysis. The percentage distribution of individual fractions in the SAGD BBD was calculated. The samples were also analyzed using techniques like UV-Absorbance to determine the aromaticity and ATR-FTIR to identify the organic functional groups dominant in the organic fractions.

SAGD BBD was filtered through different molecular weight cut-off (MWCO) membranes using a stirred dead-end ultrafiltration cell to determine the molecular weight distribution of the DOM. The functional groups dominating in each molecular weight fraction was determined by diffused reflectance FTIR spectroscopy.

The pH of the BBD was adjusted through acid addition to observe the effect of pH change on the BBD DOMs. In order to observe appreciable peaks of the organic compounds present in the BBD DOMs the BBD was distilled to generate a BBD concentrate. Other methods of characterization of SAGD BBD used in this work are inductively coupled plasma mass spectrometry (ICP-MS) and potentiometric titration.

The details of these methods including thier principles, experimental procedures and data processing are documented in this chapter.

3.2 Samples

The water samples used for this study were the SAGD boiler blow-down (BBD), SAGD de-oiled produced water (SAGDPW) and Oilsands process affected water (OSPW). They were received from large Athabasca Oilsands SAGD operation. The samples were collected hot and kept under a nitrogen blanket until they were opened for sample analysis.

The raw BBD was passed through a 0.22 μm membrane (Cellulose Acetate, Millipore, USA) to remove the suspended matter. This enables us to use the total organic carbon (TOC) content in the water samples, interchangeably with the dissolved organic carbon (DOC) content.

De-ionized (DI) water (Purelab® Ultra) was used for diluting samples, rinsing, resin washing and the preparation of blank samples. The TOC of the DI water obtained from the water purification unit was measured to be less than 1 mg/L.

12 N HCl (Fisher Scientific, USA) was diluted in DI water to obtain acid solution of different strengths. Similarly, basic solution of NaOH were prepared by dssolving solid beads of NaOH (Fisher Scientific, USA) in DI water. 16 N ammonium hydroxide solution (Fisher Scientific, USA) was dissolved in different proportions in DI water to prepare NH_4OH solution of different strengths, which is required in the ion exchange experiments.

The commercial naphthenic acids (Sigma Aldrich, USA) were dissolved in de-ionized (DI) water to prepare a 500 ppm solution. The pH of this solution was set to 11 (a value close to the pH of BBD) using 1 (N) NaOH (Fisher Scientific, USA) solution.

Various resins were used for ion exchange fractionation of the DOM. Nonionic macroporous DAX-8® resin (Supelco™, Sigma Aldrich, USA) for separation of hydrophobic fractions, cationic DOWEX 50W X8® (Sigma aldrich, USA) and anionic DUOLITE® (Sigma Aldrich, USA) for the separation of the hydrophilic fractions.

Methanol (Fisher Scientific, USA), Acetonitrile (Fisher Scientific, USA), Di-ethyl ether (Fisher Scientific, USA), and Acetone (Fisher Scientific, USA) were used for resin conditioning.

The conditioning of resin with the organic solvents were performed in a Soxhlet Apparatus (Sigma Aldrich, USA). This apparatus is made of three parts; flask, thimble and condenser. The resin is taken in a porous bag prepared from a nylon membrane (Fisher Scientific, USA). This bag is placed in the thimble while the organic solvent is taken in the flask. The condenser is then placed on the top of the thimble. The solvent is then heated and the solvent vapor moves upwards through the distillation arm and gets condensed in the condenser. The desired organic material gets dissolved in the condensate. The condensate is siphoned back to the flask through the siphon arm as the thimble becomes flooded with condensate. After the Soxhlet extraction is over the organic solvent is evaporated in a rotary evaporator to obtain the desired organic material.

Three different membranes of molecular weight cut-offs 10 kDa, 3 kDa and

0.5 kDa were used to determine the molecular weight distribution of the DOM in the SAGD BBD. The 10 kDa (PLGC, Millipore, USA) and 3 kDa (PLBC, Millipore, USA) membranes were made of regenerated cellulose whereas the 0.5 kDa membrane (YC05, Millipore, USA) was made of cellulose acetate.

3.3 Ion exchange fractionation of dissolved organic matter

The dissolved organic matter present in the SAGD boiler blow-down water was divided into different chemical fractions of acid, base and neutral components based on their hydrophobicity and hydrophilicity using ion exchange fractionation. The sample water was passed through a sequence of non-ionic, cationic and anionic resin and different organic fractions were collected through elution with suitable elutants. The ion exchange columns of different sizes were prepared from drying tubes (Fisher Scientific, USA) capped at both ends.

DAX-8®, a non-ionic, macroporous resin was used for separating the hydrophobic acids, bases and neutrals from boiler blow-down. DOWEX® 50W X8, a cationic resin was used for obtaining hydrophilic base fraction. Hydrophilic acid fraction was obtained through the anionic resin DUOLITE®. Hydrophilic neutral was the final fraction remaining in the water after removal of all the other fractions. The method used in this work was a modified version of Leenheer's method of NOM fractionation [Leenheer, 1981]. The flow diagram of the isolation procedure is shown in Figure 3.1.

3.3.1 DAX-8 conditioning

The cleaning and conditioning of the resin is an important step before performing the fractionation experiment. The resin was cleaned in order to prevent DOC bleeding, which may lead to erroneous DOC measurement.

DAX-8 resin was washed using 0.1 N NaOH, and the fines were decanted off. The resin was further washed with DI water and methanol. The resin was packed in a nylon bag and was conditioned in a Soxhlet apparatus for 24

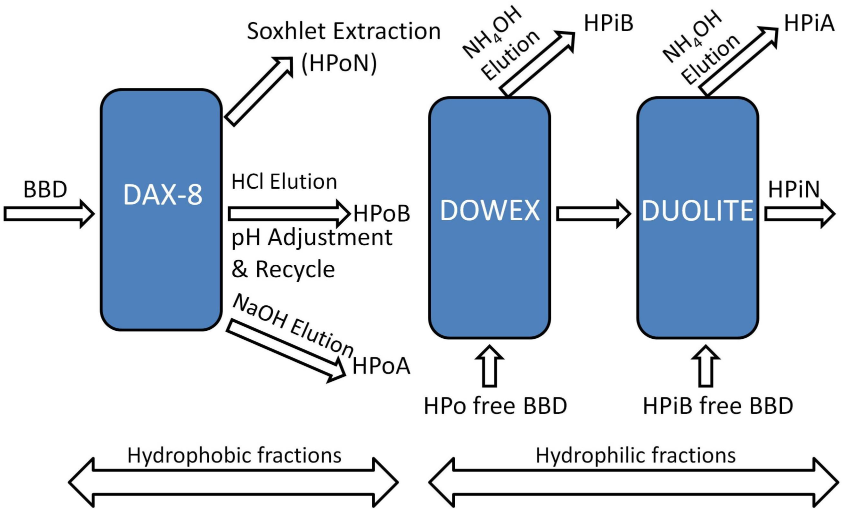

Figure 3.1 – Schematic diagram of the ion exchange fractionation method for isolation of hydrophobic and hydrophilic organic fractions from the dissolved organic matter in SAGD boiler blow-down water.

hours with methanol. Then, it was cleaned with acetonitrile, di-ethyl ether and methanol in a cycle of 24 hours.

The cleaned DAX-8 resin was taken in a resin column prepared by cutting drying tubes 1.6 cm I.D. X 15 cm long. The organic content in the resin was removed by pumping DI water through the resin. The TOC value of the effluent was measured and cleaning was continued until the effluent TOC was less than 1 mg/L. The resin was cleaned with 0.1 N NaOH and 0.1 N HCl followed by DI water just before the sample was passed through it.

3.3.2 Dowex conditioning

The organic impurities in the Dowex resin were Soxhlet extracted with methanol for 24 hours. The cleaned resin was mixed with water and stored. 3 N NH_4OH was pumped through the resin column until the breakthrough of the ammonia was reached. 2 N HCl was passed through the Dowex column after the NH_4OH cleaning. Finally, DI water was pumped through the column until the conductivity in the effluent from the column becomes less than 10 μS/cm.

3.3.3 Duolite conditioning

The organic impurities in the Duolite resin was removed through Soxhlet extraction with acetone. The resin was then cleaned by pumping 1 N HCl and 3 N NH_4OH through the resin column. Finally, DI water was pumped through the column until the conductivity in the effluent from the column becomes less than 10 μS/cm.

The step by step cleaning procedure along with the information of the amount of acid, base and water used for cleaning, amount of organic solvents required for conditioning and the pump speed maintained during the conditioning process is reported in A.2.4.

3.3.4 Isolation of organic fractions

The boiler blow-down water is filtered through a 0.22 μm filter (Whatman, Millipore, USA) to remove the suspended particulate matter. A sample solution of total organic carbon (TOC) concentration of 70 mg/L was prepared mixing the filtered boiler blow-down and de-ionized (DI) water.

300 ml of the sample solution was pumped through the DAX-8 resin column using a peristaltic pump. The column was then back eluted with 0.1 N HCl and 0.01 N HCl to isolate the hydrophobic base (HPoB) fraction. After separation of the HPoB fraction the pH of the effluent of the DAX-8 column was adjusted to 2. A part of the DOM in SAGD BBD precipitated when the pH of the solution was adjusted. This precipitated organics were filtered using a 0.22 μm filter and the filtrate was pumped back to the DAX-8 column. The HPoA fraction was isolated through back-elution using 0.1 N NaOH and DI water. After the separation of hydrophobic acid (HPoA) fraction the resin was unpacked and left to dry on aluminum foil for 10 hours. The dried resin was Soxhlet extracted with methanol for 24 hours. The methanol was evaporated using a rotary evaporator to yield the hydrophobic neutral (HPoN) fraction.

The final effluent from the DAX-8 column was sent through the cationic Dowex column and anionic Duolite column in series. The hydrophilic base (HPiB) fraction was isolated through forward elution by 3 N NH_4OH from the Dowex column and the hydrophilic acid (HPiA) fraction was recovered through back-elution with 3 N NH_4OH. The water remaining that has passed through all the columns contain hydrophilic neutral (HPiN) fraction as the HPiN fraction cannot be adsorbed by any of these resins.

The amount of resins to be used for fractionation was determined based on available literature data. The amount of DAX-8 resin to be used was based on a curve-fit equation developed based on a chart provided by Malcom *et al.* [Thurman and Malcolm, 1981] whereas a conductivity based correlation was used for Dowex and Duolite resins [Leenheer, 1981]. The flow diagram of the procedure is delineated in Figure 3.2

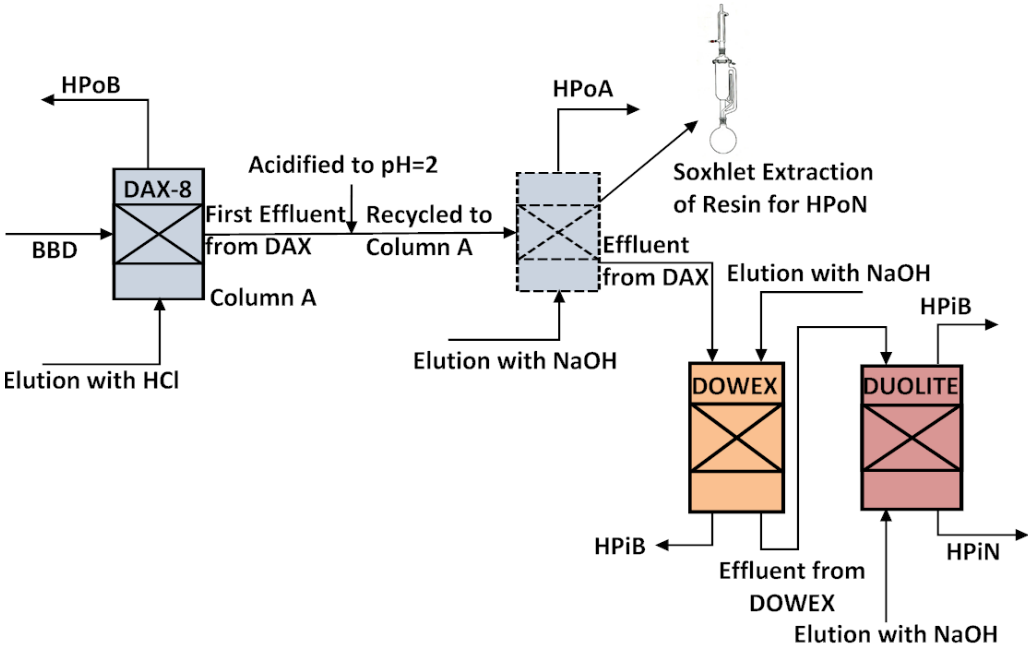

Figure 3.2 – Flow diagram of the ion exchange fractionation technique used to fractionate the dissolved organic matter in BBD DOM.

3.4 Spectrofluorescence

Spectrofluorescence technique was employed to determine the signatures of individual fluorophores present in the BBD DOM. The samples were analyzed using a fluorescence spectrophotometer (Varian, Cary Eclipse, USA).

3.4.1 Sample preparation

1 ml of the sample was taken in a test tube and adequate amount of DI water was added to adjust the TOC of the solution to a range of 20-30 mg/L to minimize the inner filtration (or quenching) effects.

3.4.2 Excitation emission matrix

Fluorescence excitation emission contour maps for water samples were generated by collecting the emission scans against different excitation wavelengths. DI water was used as blank. The samples were taken in an open top quartz cell (Varian, USA) and placed in the fluorescence spectrophotometer for analysis. The scan speed maintained was 600 nm/min with a response time of 0.1 s. The excitation and emission slit were 5 nm.

The excitation emission matrix (EEM) for each sample were formed by plotting the intensity contours over an excitation wavelength range of 200 to 500 nm at an interval of 5 nm and emission wavelength range of 200 to 500 nm at an interval of 10 nm. The EEM of de-ionized (DI) water was obtained and subtracted from the EEM of the samples in order to remove most of the Raman peaks. The pH of the samples were adjusted to the value of 11 (pH of the raw BBD) to mitigate the pH effects on fluorescence.

3.5 Molecular weight based fractionation

The molecular weight distribution of organic matter in the SAGD BBD were determined by filtering the BBD in a stirred cell batch filtration (Amicon, Millipore, USA). The particulate matter free BBD was passed through three different types of membranes of molecular weight cut-offs(MWCO) of 10 kDa, 3kDa, and 0.5 kDa, sequentially.

3.5.1 Apparatus description

The stirred cell for batch filtration consists of a cap assembly with a pressure relief valve, a stirrer assembly, filter body for holding the sample solution and a membrane holder accompanied by O-ring and elastomeric tubings. The membranes are placed in the membrane holder and the O-rings are placed on top of the membrane so that it sits evenly on the bottom of the holder. The stirrer assembly is placed in the cell body and the sample is poured in the cell for filtration experiments. The gas pressure is applied directly to the batch cell and the pressure relief valve is closed to keep the system in a pressurized condition. Nitrogen gas is used for the cell pressurization as using compressed air can cause large pH shifts due to dissolution of carbon dioxide. The cell is inserted in the retaining stand and placed on a magnetic stirring table to maintain a fixed rpm during filtration.

3.5.2 Fractionation procedure

200 ml of the raw BBD sample filtered through 0.22μm filter, was taken in the stirred batch cell. A schematic diagram of the membrane based fractionation procedure is presented in Figure 3.3. The operating trans-membrane pressure and stirring rate in the cell were set to 30 psi and 300 rpm respectively. At first the 10 kDa MWCO membrane was placed inside the cell. The permeate flux was measured after every 5 ml of volume was collected and the flux versus time plot showed no flux decline upto a volume of 120 ml. Then, the permeate obtained from the 10 kDa membrane was passed through the membrane of 3 kDa MWCO. 50 ml of the permeate was collected, and the collection was stopped before any observable decline of flux. Finally, 50 ml of the permeate of 3 kDa was passed through the membrane of 0.5 kDa MWCO. Since a low volume was passed through 0.5 kDa membrane concentration polarization effect was not prominent.

3.6 Fourier transform infra-red spectroscopy

FTIR analysis was performed on the samples to obtain information about the silica and organic matter present in the SAGD DOM. Two types of FTIR tech-

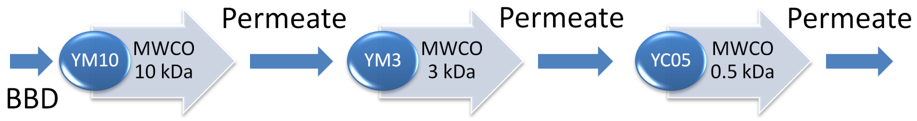

Figure 3.3 – Schematic diagram of the membrane based fractionation method used for classifying the dissolved organic matter in SAGD boiler blow-down water in molecular weight based fractions.

niques were used in this work. The diffused reflectance technique was employed to analyze the organic matter deposited on the solid membrane surfaces. The attenuated total reflectance (ATR) technique was employed to analyze the liquid samples.

3.6.1 Diffused reflectance FTIR

The foulants deposited on the surface of the 10 kDa, 3 kDa and 0.5 kDa membranes were examined using Diffused reflectance FTIR (Thermo Nicolet, Nexus 670 FTIR, USA). Since polymer membranes were used, spectra of the clean membrane was recorded as backgrounds. The spectra of fouled membrane were subtracted from the spectra of the clean membranes to obtain the FTIR signature of the organic matter deposited on the membranes. 20 scans at 4 cm^{-1} resolution were taken for each sample.

3.6.2 Attenuated Total Reflectance FTIR

The water samples were analyzed using FTIR (Thermo Nicolet, Nexus 670 FTIR, USA) spectroscope with an attenuated total reflectance (ATR) accessory. In ATR-FTIR analysis, 600 scans for each sample were collected at a resolution of 4 cm^{-1}. The BBD and the fractionated samples were analyzed with DI water as the background. The samples were scanned in the region of 600-3000 cm^{-1} to avoid interference as water has a very strong IR absorbance in the region of 3000-3600 cm^{-1}

3.7 Specific UV absorbance

Absorbance of the samples was measured at a wavelength of 254 nm using UV-visible spectrophotometer (Varian, Model: Cary 50, USA). DI water was used as blank. The samples were diluted to obtain absorbance in the range of 0 to 1.2. The $SUVA_{254}$ of samples were calculated using the corresponding DOC value.

3.8 TOC analysis

The sum total of the suspended and dissolved organic carbon present in a water sample is defined as the total organic carbon (TOC) of the sample. The TOC concentration of the filtrate, obtained by filtering a solution through 0.45 μm filter is earmarked as its dissolved organic carbon (DOC) concentration [Danielsson, 1982].

The total dissolved organic carbon (DOC) was measured using a TOC analyzer (Shimadzu, Model: TOC-L CPH/CPN) after filtering through a 0.22 μm membrane filter (Cellulose acetate, Millipore, USA). The organic concentration in BBD is measured as TOC after filtering through a 0.22 μm filter. Thus, the organic concentration reported in BBD is solely due to dissolved organic compounds, as oil and grease is filtered [Kocherginsky et al., 2003].

3.8.1 Preparation of total carbon (TC) standard solution

2.125 g of potassium hydrogen phthalate was accurately weighed and taken in a 1 L volumetric flask. DI water was added upto the 1 L mark and the solution was stirred. The potassium hydrogen phthalate solution prepared has a concentration equivalent to 1000 ppm carbon concentration was prepared. This solution was used as a standard for total (TC) analysis.

3.8.2 Preparation of inorganic carbon (IC) standard solution

3.497 g of reagent grade sodium bi-carbonate and 4.412 g of sodium carbonate was accurately weighed and taken in a 1 L volumetric flask. DI water was added to the flask upto the 1 L mark and the flask was shaken well. In this manner a liquid solution equivalent to 1000 ppm carbon concentration was prepared. This solution was used as standard for inorganic carbon (IC) analysis.

3.8.3 Analysis of dissolved organic matter

The samples were collected in 40 ml vials for TOC analysis. The sample vials were capped in order to prevent the volatilization and contamination of the TOC components in the samples. A calibration curve was generated by analyzing various concentrations of the total carbon (TC) and inorganic carbon (IC) standard solutions. The TC value of the samples were determined by heating the samples at a temperature of 680 °C over a high sensitivity oxidation catalyst. Samples were injected to the IC reaction vessel equipped with TOC-L IC reactor kit to measure the IC content in the sample. TOC is measured as the difference between the TC and IC analysis values.

3.9 Analysis of inorganics and ions

The metallic ion concentrations in the BBD was determined through quadrupole-inductively coupled plasma mass spectrometry (Perkin Elmer, Elan 6000 Quadrupole ICP-MS, USA).

3.10 Measurement of pH, conductivity, COD

pH and conductivity were measured using pH/ion/conductivity meter (AR50, Fisher Scientific Accumet Research, USA). This instrument was also used to measure total dissolved solids (TDS) based on ionic conductivity. The chemical oxygen demand (COD) of water samples was measured by international standard ISO 6060 (ISO, 1990) method.

3.11 Measurement of total suspended solids (TSS) and total dissolved solids (TDS)

The samples were filtered through glass fiber filters of known weight. The residue on the filter was dried in an oven at 103-105 °C until a constant weight is attained. The increase in weight of the filter was used to calculate TSS.

Known volume of sample was filtered through glass fiber filter. The filtrate was collected in a beaker of known weight and dried in an oven at 180 °C until a constant weight is attained. The increment observed in the beaker weight was used to calculate TDS.

3.12 Acidification of BBD

In the ion-exchange fractionation experiment it was observed that the DOM in the SAGD BBD precipitates at pH 2. The following set of experiments were performed to analyze the effects of pH on the DOM.

3.12.1 Potentiometric titration of raw BBD and concentrate

BBD was titrated in a potentiometric titration system (PCM QC-Titrate, Mandel Scientific, Canada) with standardized 0.12 (M) HCl solution. The titration was stopped at different pH values for BBD and resultant solutions were collected in test tubes. The test tubes were allowed to stand alone for 24 hours. The supernatants and precipates obtained at different pHs were observed.

3.12.2 pH adjustment of SAGD BBD

A series of pH-adjusted BBD samples were prepared by adding increasing amounts of concentrated hydrochloric acid dropwise to sample aliquots of 15 ml volume under continuous stirring. The pH of the solutions prepared varied within the range of 2 to 12. The solutions were allowed to settle for 24 hours. DOM precipitation was observed during acidification. The supernatant were analyzed after filtering through 0.22 μ-m filter.

3.13 Summary

The experimental methods used for characterizing the DOM in the SAGD blow-down water were documented in this chapter. The materials used and the procedures followed in the sample preparation for different analysis were discussed in details. This chapter also delineates the instruments used and operating conditions maintained in different experiments. Ion exchange fractionation procedure isolated the hydrophobic and hydrophilic organic fractions present in the BBD DOM. The spectrofluorescence techniques were employed to determine the excitation emission signatures of the fluorophores present in different fractions. The molecular weight distribution in the DOM was determined by filtering the BBD with membranes of 10 kDa, 3 kDa and 0.5 kDa molecular weight cut-offs. The boiler blow-down was acidified to see the effect of change of pH in the organic matter present in the SAGD BBD. Other characterization experiments performed were FTIR spectroscopy, UV-absorbance, TOC-Analysis to obtain informations about the organic functional groups, aromaticity and the organic matter concentration in the water samples. Information regarding the inorganics and ions present in the SAGD BBD was obtained from the inductively coupled plasma mass spectrometry.

Chapter 4

Characterization of the dissolved organic matter in the SAGD boiler blow-down water [1]

4.1 Introduction

Boiler blow-down (BBD) is the final concentrated waste water stream in a SAGD plant that is often disposed off by injecting into deep wells. A portion of the BBD can be treated and recycled back to the process as make-up water. Due to strict disposal regulations, efficient and economic treatment techniques need to be designed for BBD [Matilainen et al., 2011, Wade, 2004, Schooley, 2004]. In order to develop efficient techniques for BBD treatment a detailed understanding of the physico-chemical characteristics of BBD is necessary. The DOM present in the BBD cause several problems in the SAGD operation such as equipment fouling and clogging of injection wells due to silica-organic co-precipitation.

A detailed understanding of the organic matter present in the BBD is necessary for efficient DOM removal. Chararacterization of aquatic natural organic matter (NOM) is challenging owing to the presence of a plethora of organic compounds. In order to characterize the NOM accurately, different organic fractions of NOM are isolated before performing analysis [Matilainen et al., 2011]. Similarly, SAGD DOM is fractionated in this work into hydrophobic and hydrophilic fractions for analysis. Resin fractionation is a widely

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[1] Parts of this chapter have been submitted to *Environmental Science & Technology*, July 2012.

used technique for isolation of DOM fractions. The DOM from any aquatic system can be fractionated into hydrophobic and hydrophilic acid/base/neutral fractions using an ion-exchange fractionation procedure [Leenheer, 1981]. The organic compounds in the DOM can be classified into different molecular weight fractions by sequential filtration through different molecular weight cut-off membranes [Huguet et al., 2010]. Fractionation of NOM using ultrafiltration(UF)/nanofiltration(NF) membranes show that the higher molecular weight organic compounds are the major fraction in natural water [Hua and Reckhow, 2007].

Quantitative and qualitative information on DOMs can be obtained through a number of analytical methods. For example, measurement of dissolved organic carbon and absorption of UV-light (at 254 nm) helps determining the amount of organic matter present in a sample, whereas, spectrofluorescence and FTIR analysis determines the chemical nature of the compounds present in the DOM [Matilainen et al., 2011].

In this chapter, the physico-chemical properties of SAGD blow-down water are presented. To determine the chemical nature of the BBD DOM accurately, the BBD was fractionated into hydrophobic and hydrophilic fractions and spectrofluorescence signatures of the organic fractions were determined. The molecular weight distribution of the organic matter was determined through fractionation using 10 kDa, 3 kDa and 0.5 kDa membranes. The fluorescence signatures were compared with signatures of naphthenic acid which is considered as the principal DOM component in the Oilsands process affected water (OSPW) produced during mining based extraction. The fluorescence intensity peaks were analyzed and compared with literature data available for the fluorophores present in natural organic matter as discussed in the Chapter 2.

4.2 Physico-chemical characteristics of SAGD BBD

The physico-chemical characteristics, like TDS, TSS, pH, conductivity, total dissolved organic carbon and the ionic concentration of different metals in SAGD blow-down water (BBD) are presented in Table 4.1. It is evident that the characteristic parameters of BBD is quite different from the corresponding parametric values of other produced waters. Of note, SAGD BBD has a distinctly higher dissolved organic matter in presence of high silica unlike the other produced waters. The DOM content in the produced water is higher than oil-field produced water (OFPW) and oilsands process affected water (OSPW) due to the high temperature and pressure employed during extraction process. In the current industrial practice DOM is not removed from the produced water during treatment. Furthermore, during steam generation from treated produced water in OTSG, the residual water obtained as BBD is five to ten times concentrated with DOM (refer Table 2.1 and 4.1).

The alkalinity in the BBD is mainly due to the carbonate ions formed during the warm lime softening of BBD. Due to presence of organic matter in BBD the TDS concentration obtained through gravimetric analysis is always higher than the TDS concentration obtained from conductivity measurement. The divalent cations (Ca^{+2} and Mg^{+2}) concentration in BBD is negligible, as a major portion of these ions are removed during the weak acid cation exchange operation. ICP-MS analysis of the BBD showed the presence of high concentrations of dissolved silica in the SAGD BBD.

From Tables 2.1 and 4.1 it is evident that SAGD BBD has a higher TDS, TOC and SiO_2 than other produced waters. The dissolved organic matter content in the OSPW is about 100 mg/l whereas about 2400 mg/l of organic matter is obtained in dissolved condition in the SAGD BBD. Presence of such a high amount of dissolved organic matter in a produced water obtained from conventional or non-conventional sources is unprecedented. The difference in solubility of organic matter may be due to difference in nature of the SAGD DOM and OSPW DOM which is caused by the difference in mining and SAGD extraction tchniques. SAGD extraction technique employs higher temperatures (150-300 °C) in comparision to moderate temperatures (70-90 °C) in the mining process. In the following section OSPW and SAGD BBD are analyzed using FTIR spectroscopy to identify the differences in organic compounds present in both.

Table 4.1 – Physico-chemical properties of the SAGD blow-down water. All the properties are in mg/L unless otherwise stated.

Chemical Properties	BBD
pH	10.5-12.33
Conductivity (μS/cm)	3870-18090
TDS	4026-17200
TSS	$\sim$ 65
COD	1400-4400
TOC	695-2482
Alkalinity	1040-2700
Na^+	819-5199
Ca^+2	4.25-4.8
Mg^+2	0.08-0.68
Iron(Total)	2.06-3.3
B	47.7-187
Ba^+2	0.02-0.102
Al^+3	0.016-0.43
SiO_2(soluble)	65-238
Cl^-	494-6715

4.2.1 ATR-FTIR signature of BBD

In order to obtain information about the chemical characteristics of the DOM present in the SAGD BBD, it was analyzed using ATR-FTIR spectroscopy. Figure 4.1 shows the ATR-FTIR spectra for the raw BBD. The band obtained at 968.7 cm^{-1} is due to Si-OH bond stretching. The bands of 1017 and 1098 cm^{-1} are obtained due to Si-O-Si bonds stretching [Falcone et al., 2010, Falcone Jr. et al., 2010, Sarawade et al., 2011]. This confirms the presence of silica in the SAGD BBD.

The band of 1412 cm^{-1} shows the presence of carboxylic groups and 1548 cm^{-1} is for N-H structures [Rodriques and Nunez, 2011]. The 1660 cm^{-1} are assigned to aliphatic and aromatic C=C bond stretching and the bands of 2870 and 2931 cm^{-1} are due to C-H bond stretching [Orgill et al., 1999]. Thus, the BBD is composed of aromatic carboxylic acids.

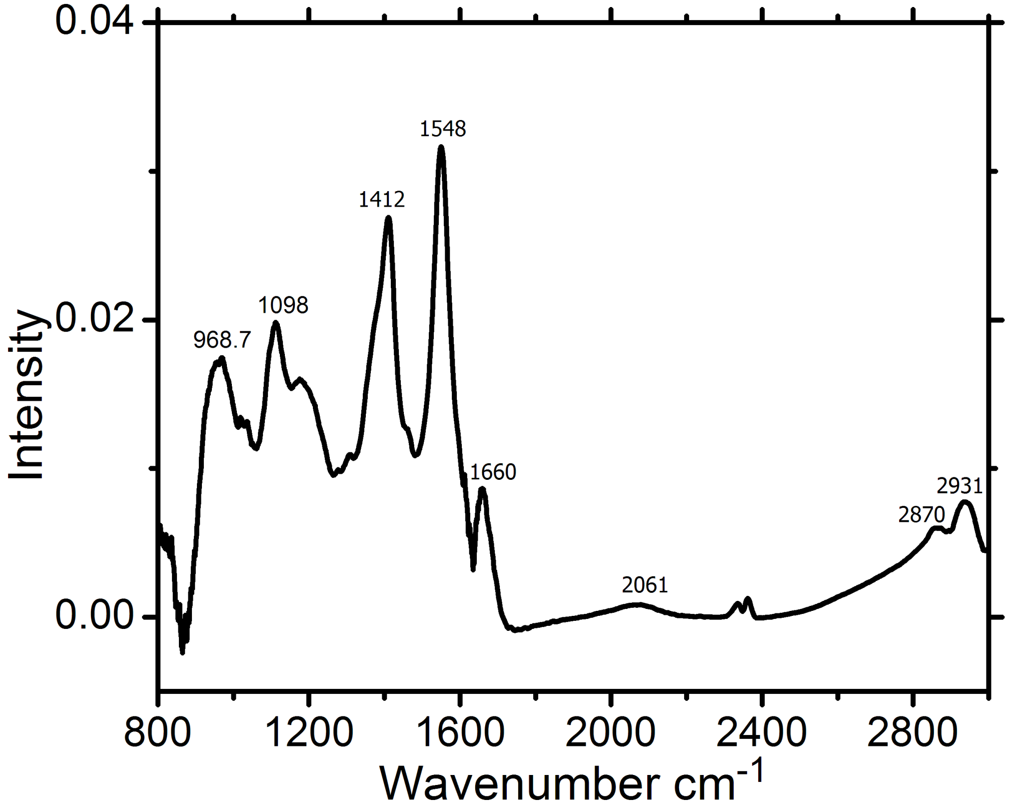

Figure 4.1 – The ATR-FTIR signatures of the DOM present in the SAGD BBD

The peaks obtained in the oilsands process affected water are shown in Figure 4.2. Signatures of Si-O-Si bond stretching is obtained at 1035 and 1105 cm^{-1} [Falcone et al., 2010]. Presence of C-H type bonds are indicated by the peaks at 2853 and 2922 cm^{-1} [Orgill et al., 1999]. The band of 1361 cm^{-1} is due to the presence of a C-H bend whereas the band of 1614 cm^{-1} is attributed to the C=C stretching.

It is clear that the peaks for carboxylic groups and N-H structures are absent in the oilsands process affected water (OSPW). This shows that SAGD BBD contains certain organic compounds which are not present in the OSPW. Bitumen extraction in SAGD and mining processes are carried out in different operating conditions. In SAGD BBD about 2400 mg/l of organic matter is obtained in dissolved condition whereas in the OSPW as best as 100 mg/l of dissolved organics are obtained. This may be the cause that the organic matter obtained in OSPW and SAGD BBD are different from one another. The difference in the FTIR signatures of OSPW and SAGD BBD indicates that a different class of organic compounds constitute the SAGD BBD. These compounds are characterized in the next few sections.

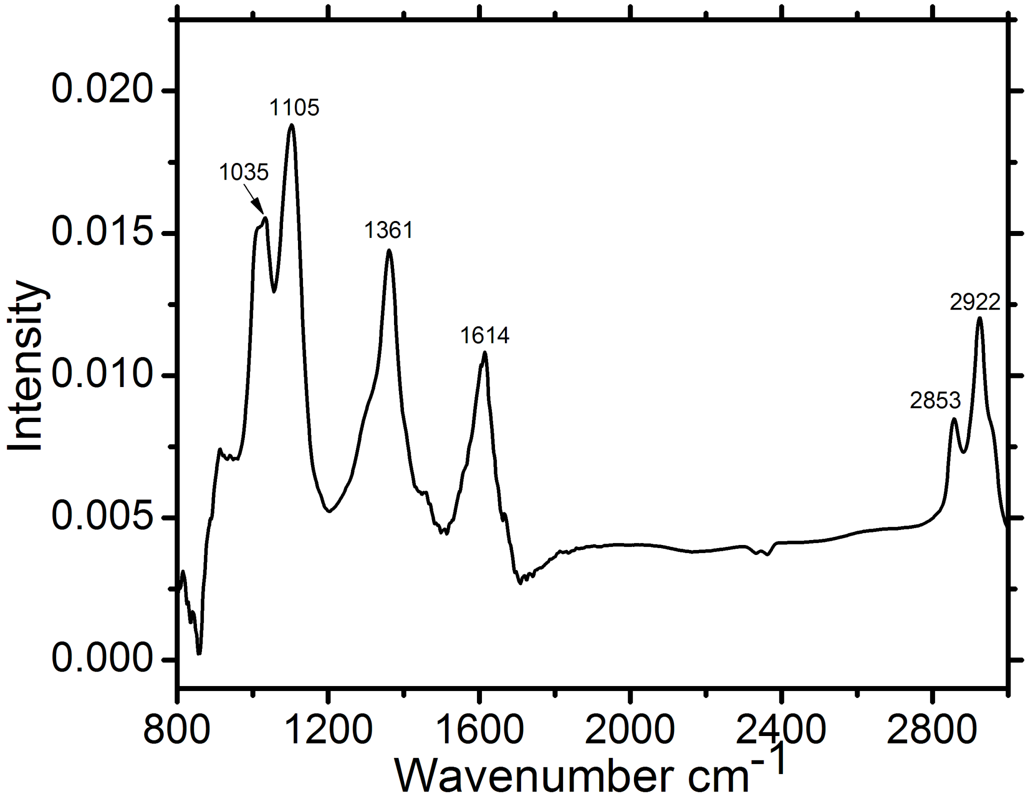

Figure 4.2 – ATR-FTIR peaks of the Oilsands process affected water (OSPW).

4.3 Fractionation of DOM based on chemical nature

Hydrophobic and hydrophilic fractions of acid, base and neutral organic compounds were isolated from the dissolved organic matter (DOM) present in the SAGD blow-down water (BBD). The fractionation procedure was described in Chapter 3. Figure 4.3 depicts the percentages of different organic matter fractions in the BBD.

Ion exchange fractionation of the DOM in the BBD shows that the hydrophobic acid (HPoA) fraction is the major component constituting 39% of the total DOM. The hydrophilic neutral (HPiN) fraction is 28.4%. The hydrophobic neutral (HPoN) fraction is comprises 14% of the organic matter. The hydrophilic acid (HPiA), base (HPiB), and hydrophobic base (HPoB) fractions constitute 9.4%, 5.4% and 2.7% of the organic matter, respectively.

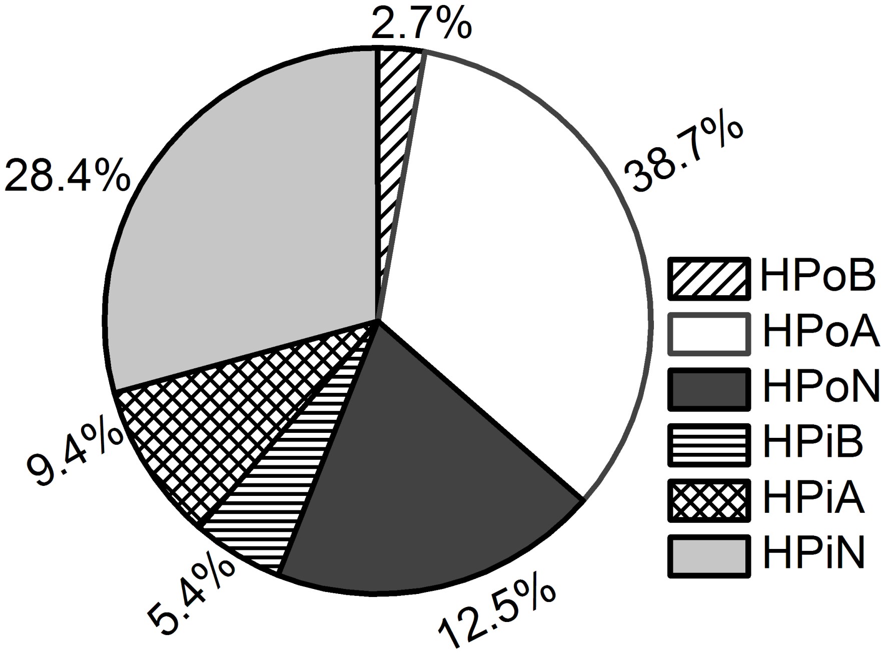

Figure 4.3 – Pie chart showing the percentage of dissolved organic matter fractions in the boiler blow-down.

4.4 Fluorescence excitation emission matrix of BBD and DOM fractions

The signatures of the BBD DOM and different DOM fractions were determined using fluorescence excitation emission matrix spectroscopy (EEMs). The fluoroscence intensity peaks for the individual organic fractions were compared to the data reported in the literature for NOM [Hudson et al., 2007, Coble, 1996, Parlanti et al., 2000, Marhaba et al., 2000, Chen et al., 2003]. The data from these studies are shown in Table 2.4 for comparative purposes.

4.4.1 Comparision of EEM contours of raw BBD, OSPW and commercial naphthenic acids

As seen in Figure 4.4, the fluorescence response for BBD occurs over a wide range of wavelengths, with two dominant peaks at Excitation/Emission wavelength ranges of 225-250/375-425 and 300-340/400-425. EEMs contour maps were also produced for commercial naphthenic acids and for actual OSPW shown in Figure 4.5 and 4.6, respectively. There is a considerable difference in the Ex/Em signatures of raw BBD and those from commercial NAs or oil sands process affected water (OSPW) obtained in mining based oil sands extraction. As seen in the 4.6 the naphthenic acids (NAs) fluorescence peaks were obtained in the Ex/Em wavelength (nm) range of 215-230/350-375. This does not correspond to the overall fluorescence signatures of the BBD. However, the EEMS of NAs and OSPW appear to have considerable similarities to each other as depicted in 4.5. The results of naphthenic acid fluorescence reveal that the NAs are not a major component of the BBD DOM whereas they are major component in the OSPW Kavanagh et al. [2009], Kim et al. [2011], Edge et al. [2010], Holowenko et al. [2002], Peng et al. [2004], He et al. [2011], Rowland et al. [2011], Wang and Kasperski [2010].

4.4.2 EEM contours of DOM fractions obtained from ion-exchange fractionation

The fluorescence peaks for BBD occurs in a Ex/Em wavelength (nm) range of 325-480 and 375-480. 2.4 shows that the peaks for fluorophore type C and A are in the same Ex/Em wavelength range, leading to the conclusion that

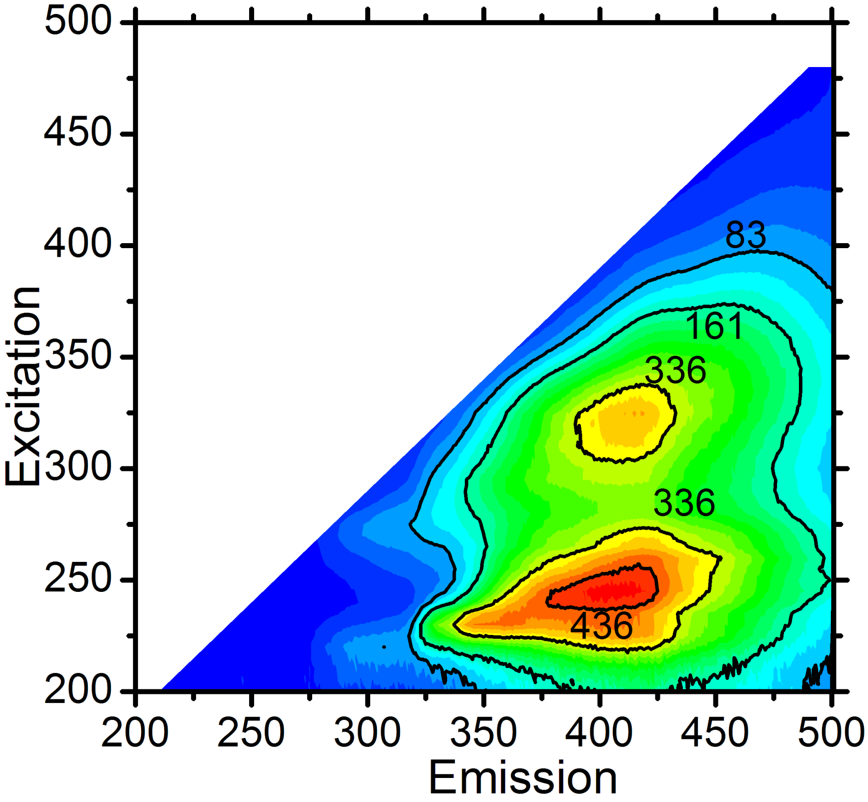

Figure 4.4 – Excitation emission matrix (EEM) contour map of the dissolved organic matter in SAGD BBD. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

the humic like hydrophobic acids are the dominant fraction in the BBD. This result is validated by the dominance of the HPoA fraction in BBD based on resin fractionation shown in Figure 4.3. The intensity peak region for raw BBD, commercial naphthenic acids, OSPW and the isolated DOM fractions are reported in Table 4.2.

HPoA and HPiA

The fluorescence EEM contour of the HPoA fraction is shown in the Figure 4.7. The maximum fluorescence intensity for the HPoA fraction is obtained in the Ex/Em wavelength range of 310-340/400-500, which is same as the range for the type C (or α) humic acids. The hydrophilic acids (HPiA) exhibit Ex/Em

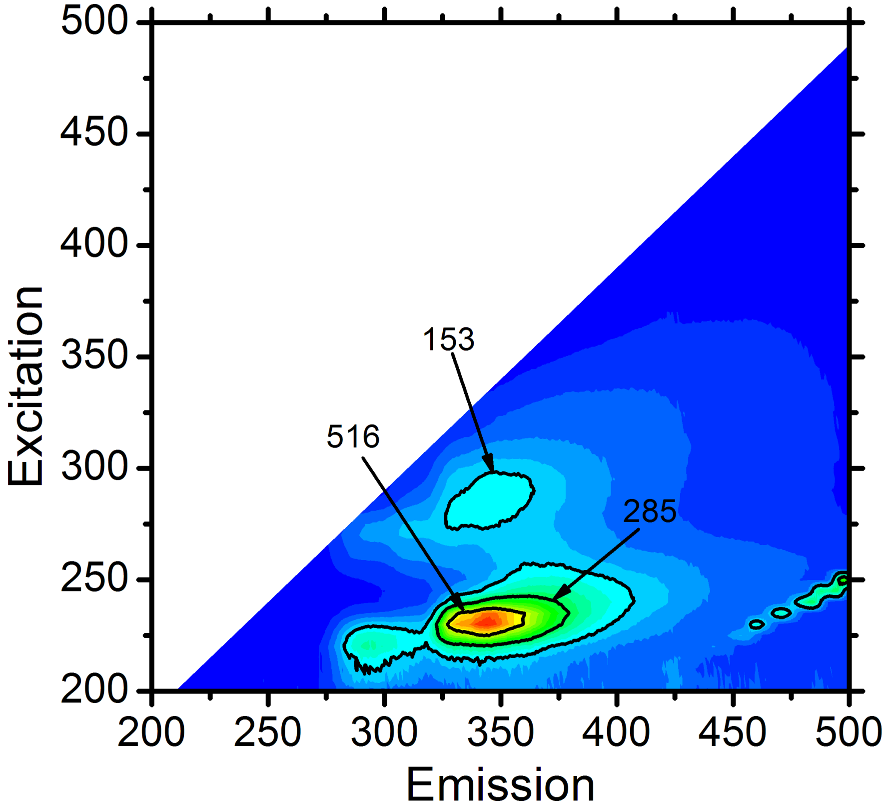

Figure 4.5 – Excitation emission matrix (EEM) contour map of the dissolved organic matter in Oilsands process affected water. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

peaks in the range 300-400/375-475 as shown in the Figure 4.8.

This Ex/Em range for the BBD water soluble organic acids is vastly different from the EEMS signatures of commercial NAs or OSPW soluble organics. Literature attributes the signatures of these organic acid fractions to type C/α or type M/β humic acids or marine humics for the hydrophobes, and type T/δ (tryptophan like fluorophores) for the hydrophilic moieties.

HPoB and HPiB

The fluorescence contour maps for HPoB and HPiB fraction are presented in Figure 4.9 and 4.10, respectively. The HPiB fraction has a peak intensity region at Ex/Em wavelength (nm) 210-225/275-310 and 325-400. Marhaba

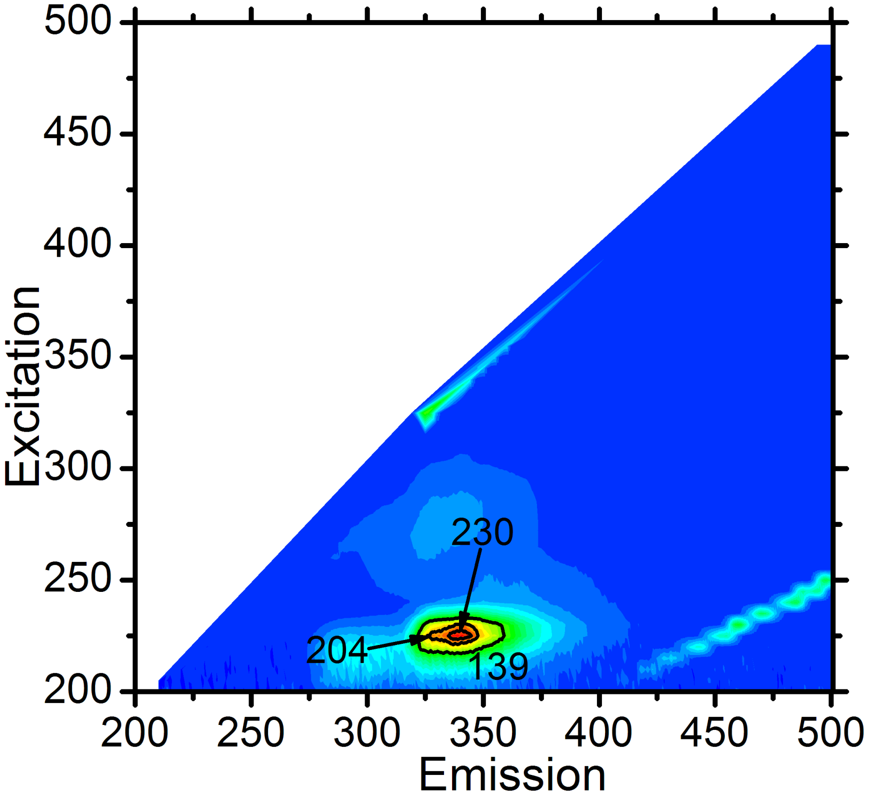

Figure 4.6 – Excitation emission matrix (EEM) contour map of the dissolved organic matter in commercial naphthenic acids. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

and Lippincott Marhaba et al. [2000] assigned the peak intensity region for the HPiB fractions in NOM in the Ex/Em range of 225-237/357-369 nm. The result shows that the HPiB fraction in the SAGD DOM is similar to the HPiB fractions obtained from organic matter in natural systems like rivers. However, the HPoB fraction has a fluorescence peak intensity at the Ex/Em wavelength range of 260-290/280-320 which is different from the data reported in literature which is 225-237/340-381 and 275/340. This difference is best explained through the phenomena of low Stokes shift Cook and Le [2006], Penzkofer et al. [2011]. The Stokes shift is increased in the presence of π-configuration framework in the fluorophore Xie et al. [2011], that is, with an increase in aromaticity, there may be an increase in the Stokes shift. On the contrary, with little aromaticity, lower Stokes shifts may be observed in the

Table 4.2 – Fluorescence peak intensity region for BBD, OSPW, commercial naphthenic acid and DOM fractions

Sample	Ex/Em range for fluorescence peaks
BBD	225-250/375-425 and 300-340/400-425
OSPW	220-230/325-355
Commercial Naphthenic Acids	215-230/325-350
HPoA	310-340/400-500
HPoB	260-290/280-320
HPoN	225-250/325-380
HPiA	320-375/375-500
HPiB	210-225/275-310
HPiN	250-275/280-320

fluorophores. In the subsequent section the aromaticity of the organic fractions are determined using UV absorbance analysis.

HPoN and HPiN

The fluorescence EEM contour of the HPoN fraction is shown in the Figure 4.11. The fluorophores of type T, which are tryptophan like molecules, are noticed in the unfractionated BBD. However, the fluorophore B assigned as HPoN is not observed in the contour maps for unfractionated BBD although it is observed in the HPoN fraction from the resin fractionation experiment. This absence of intensity peak for HPoN in the raw BBD is best explained by the quenching effect [Larsson et al., 2007] which occurs due to presence of

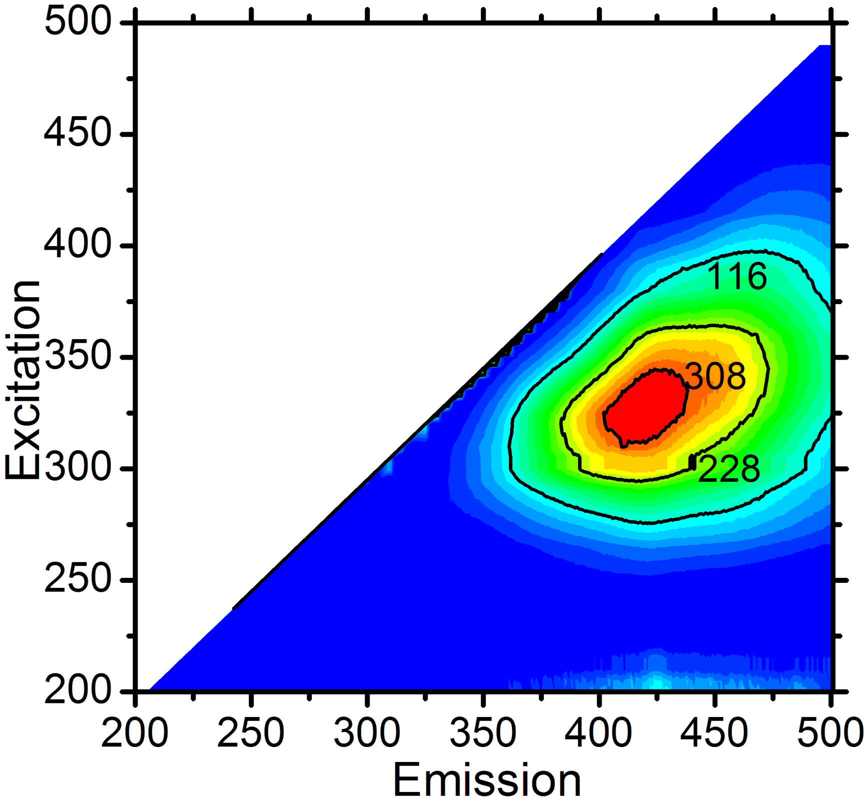

Figure 4.7 – Excitation emission matrix (EEM) contour map of hydrophobic acid (HPoA) fraction BBD DOM. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

other strong fluorophores in heterogeneous solutions. The fluorescence intensity peaks for the HPiN fraction is obtained in the Ex/Em wavelength range of 210-225 and 250-275/280-320 as shown in Figure 4.12. Thus, the fluorophores can be classified as type T Coble [1996] or type δ Parlanti et al. [2000] fluorophores.

4.4.3 SUVA

For SUVA of 4 or greater, NOM composition is dominated by humic substances; high hydrophobic and aromatic character. For SUVA of 2 to 4, the water contains a mixture of humic and non-humic substances; mixture of aromatic and aliphatic substances. For SUVA ¡ 2, high fraction of nonhumic

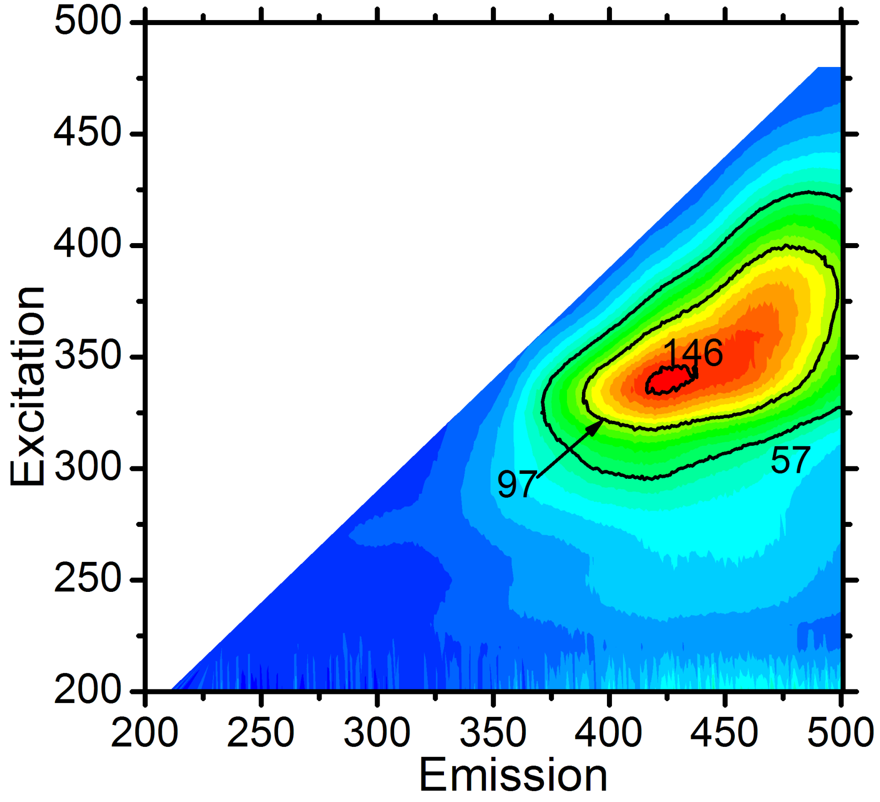

Figure 4.8 – Excitation emission matrix (EEM) contour map of hydrophilic acid (HPiA) fraction of the BBD DOM. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

substances; high aliphatic and low hydrophobic character [Edzwald and Tobiason, 1999]. SUVA has also been shown to be strongly correlated with percent aromaticity for NOM [Weishaar et al., 2003]. The value of SUVA for raw BBD is 4.17 L mg^{-1} m^{-1}. This shows that the humic-like hydrophobic fractions are dominant in the SAGD BBD. A high SUVA value also depicts the presence of higher aromatic content in the BBD DOM.

The SUVA values of different fractions obtained from ion-exchange fractionation were measured. The SUVA results for different DOM fractions are presented in 4.3. It is observed that the SUVA values for HPoB and HPiN are 0.6066 and 0.1781 L mg^{-1} m^{-1}, respectively. The lower SUVA values for both these fractions show that very little aromatic organic matter is present in these

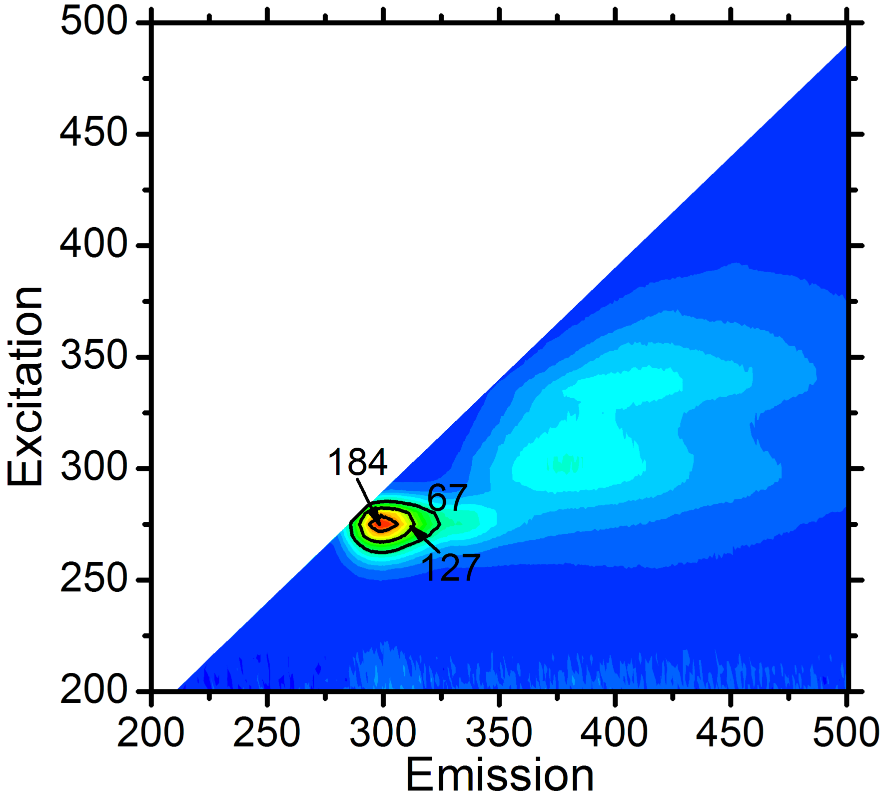

Figure 4.9 – Excitation emission matrix (EEM) contour map of hydrophobic base (HPoB) fraction of the BBD DOM. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

two fractions. This also explains the low Stokes shift observed in these two fractions. Hence, we can conclude that the organic nature of these fractions is different from the NOM fractions in natural aquatic systems. The HPiA has a SUVA value of 2.02 L mg^{-1} m^{-1} which corroborates the fluorescence results that hydrophilic acids are not humic acid-like but tryptophan like molecules. The HPoA and HPoN have SUVA values greater than 3 indicating the presence of aromatic content in these organic fractions. From the SUVA values in 4.3, it can be observed that amongst all the DOM fractions, only the hydrophobic acid and neutral are rich in aromatic content.

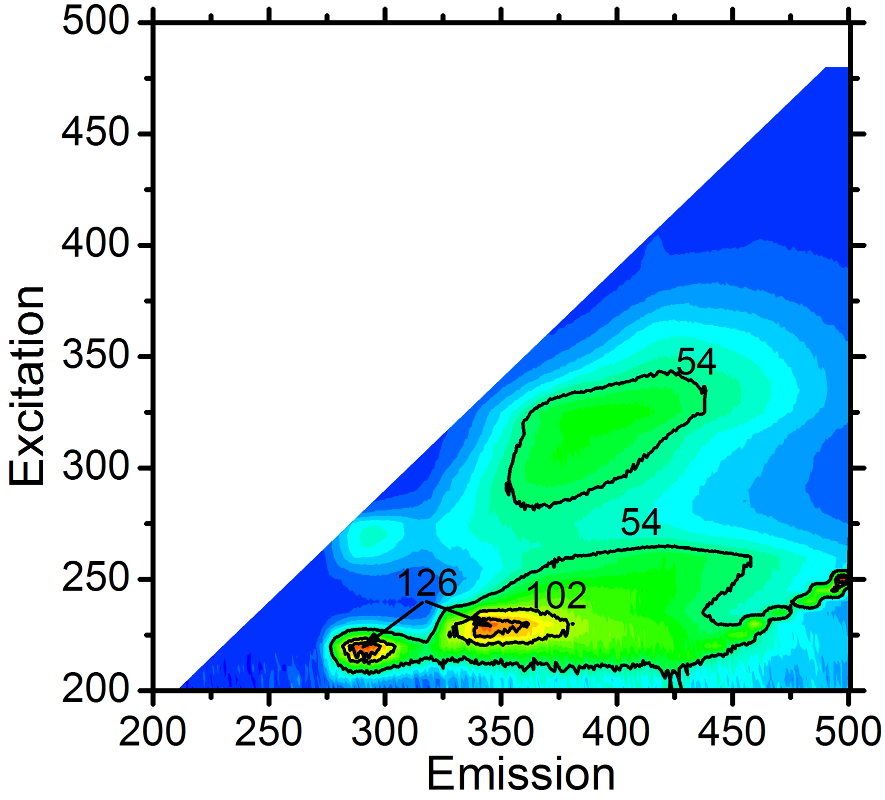

Figure 4.10 – Excitation emission matrix (EEM) contour map of hydrophilic base (HPiB) fraction of the BBD DOM. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

Table 4.3 – DOC concentration and SUVA of different DOM fractions

Sample Name	DOC (mg/L)	SUVA
Raw BBD	695	4.1
Hydrophobic Acid	256.85	3.6
Hydrophobic Base	21.59	0.61
Hydrophobic Neutral	31.56	3.95
Hydrophilic Acid	126.5	2.02
Hydrophilic Base	54.46	1.11
Hydrophilic Neutral	19.72	0.18

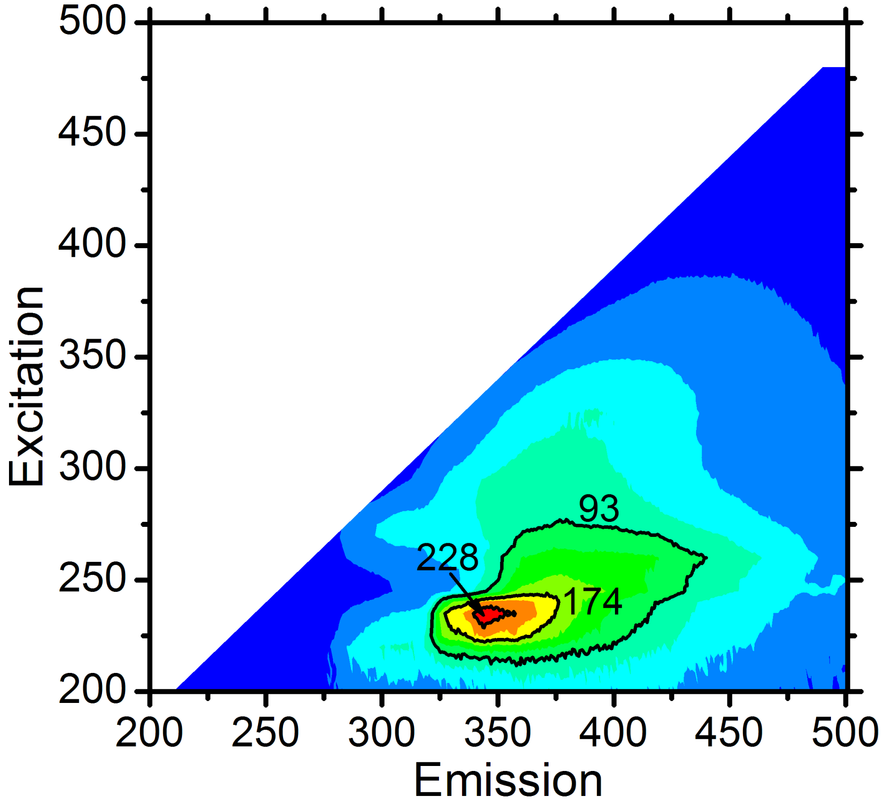

Figure 4.11 – Excitation emission matrix (EEM) contour map of hydrophobic neutral (HPoN) fraction of the BBD DOM. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

4.4.4 Fractionation of DOM based on molecular weight

The BBD sample was filtered through 10 kDa, 3 kDa and 0.5 kDa membranes in series in order to determine the molecular weight distribution of the organic fractions. The BBD has a DOC value of 695 mg/L as shown in Table 4.4. The permeate obtained from the 10 kDa membrane has a DOC of 641 mg/L showing a reduction of only 8% of the organic matter. The DOC of the permeate from the 3 kDa membrane indicates that almost 75% of the organic matter has a molecular weight less than 3 kDa. The DOC value of the permeate of the 0.5 kDa membrane is 269 mg/L,indicating that about 40% of the organic fraction in the BBD is of molecular weight less than 0.5 kDa. The SUVA value of the permeates from 10 kDa, 3 kDa and 0.5 kDa are 2.1779, 1.7111 and 1.0641

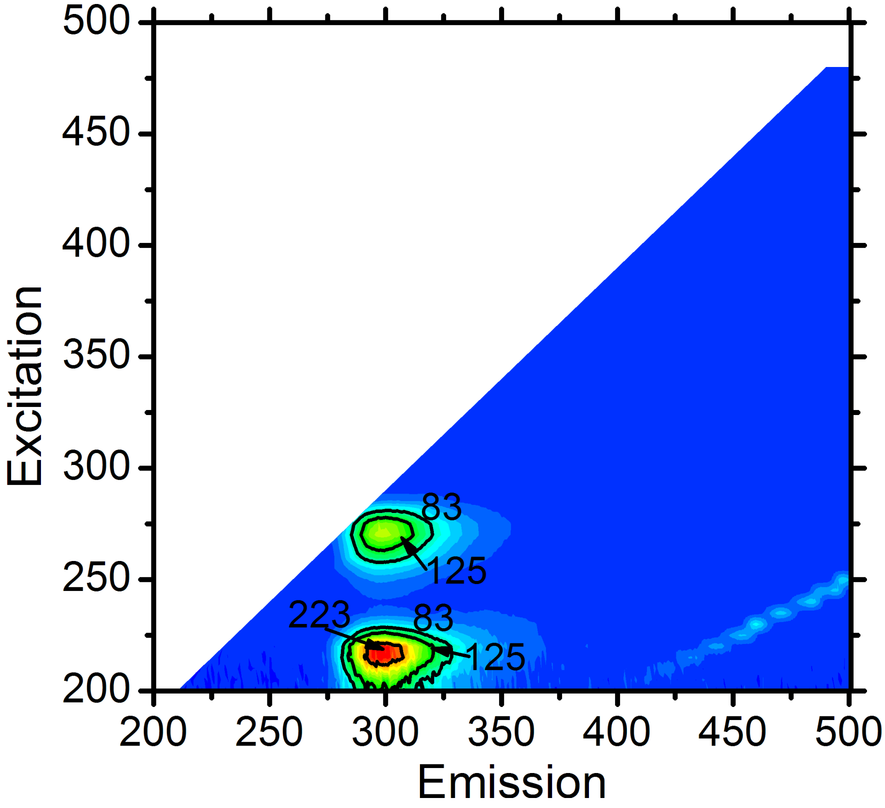

Figure 4.12 – Excitation emission matrix (EEM) contour map of hydrophilic neutral (HPiN) fraction of the BBD DOM. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

L mg^{-1} m^{-1}, respectively, indicating the reduction of aromatics as molecular weight decreases. The molecular weight distribution of the DOM also shows that about 19% and 33% of the DOM are in the ranges of 3 kDa < MW < 10 kDa and 0.5 kDa < MW < 3 kDa, respectively.

4.4.5 Diffused reflectance FTIR of the DOM absorbed by the membranes

The organic matter and silica, from BBD, deposited on the membranes are observed in the diffused reflectance FTIR scan results presented in Figure 4.13. The silica peaks observed in the band of 1030-1040 cm^{-1} are prominent in

Table 4.4 – Molecular weight distribution of the DOM in SAGD BBD

Molecular Weight (MW) Range	Percentage of DOM
MW > 10 kDa	8%
3 kDa < MW < 10 kDa	19%
0.5 kDa < MW < 3 kDa	33%
MW < 0.5 kDa	40%

the material deposited on the 10 kDa membrane. The peaks of the material deposited on the 0.5 kDa membrane are observed in the bands of 1094, 1163, 1272, 1386, 1761 and 2870 cm^{-1} of which the band of 2870 cm^{-1} is due to C-H bond stretching [Orgill et al., 1999], and the rest are for different types of aliphatic and aromatic C=O and C-O bond stretching [Orgill et al., 1999]. About 19% of the DOM is deposited on the 3 kDa membrane which is corroborated by the diffused reflectance FTIR scan of the organic matter adsorbed onto the membranes. The intensity of the peaks for the 3 kDa membrane is weaker than that of the peaks for the 0.5 kDa membranes, since about 60% of the DOM is removed by the latter.

4.4.6 Fluorescence excitation emission matrix of molecular weight fractions

The EEMs contour maps of different molecular weight fractions obtained when BBD was filtered through 10 kDa, 3 kDa and 0.5 kDa membranes are shown in Figure 4.14, 4.15, 4.16, respectively. The contour maps of the permeates all have similar signatures. Thus, each class of fluorophore in the BBD has a wide range of molecular weight distribution.

The characterization of DOM based on its chemical nature may be used to select the appropriate DOM removal technique for boiler blow-down water. For example, since the BBD has a high amount of humic-like hydrophobic acid, microbial treatment of this type of waste may not be suitable for DOM removal[Klapper et al., 2002, Park et al., 2009]. This is because humic substances are generally resistant to microbial degradation under anaerobic conditions [Klapper et al., 2002]. Membrane filtration processes like microfiltration, ultrafiltration and nanofiltration have been used for removing dissolved

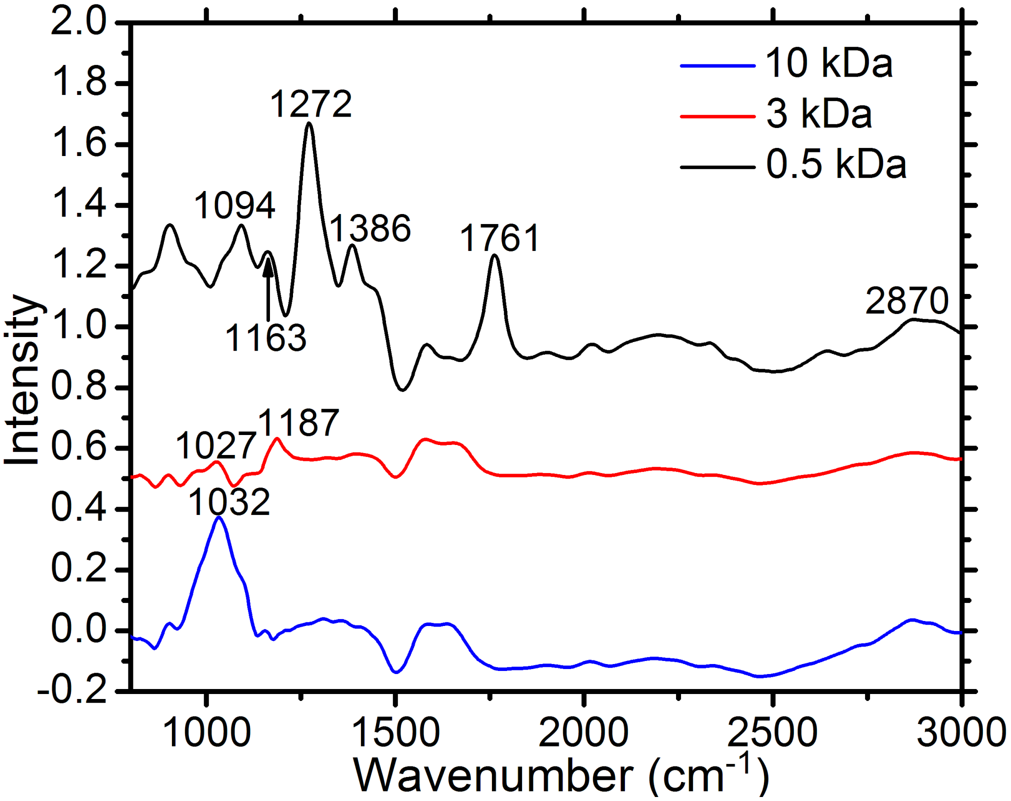

Figure 4.13 – FTIR spectra of the dissolved organic matter deposited on the 10 kDa, 3 kDa and 0.5 kDa membrane. The blue line represents the DOM deposited on the 10 kDa membrane. The red line is for the DOM on 3 kDa membrane. The black line represents the FTIR signatures of organic matter on 0.5 kDa membrane.

components from various aqueous systems [Li and Lee, 2009, Liu et al., 2008, Deriszadeh et al., 2010, Ciputra et al., 2010]. A fouling resistant ultrafiltration membrane was reported to remove 45% of the organics from a conventional oil field produced water [Asatekin and Mayes, 2009].

In this study, it is observed that only 7% and 27% of the DOM are removed by the 10 kDa and 3 kDa membranes, respectively. Hence micro and ultrafiltration cannot be used effectively for DOM removal from BBD unless the DOM is first converted to a solid phase through precipitation or co-precipitation with a coagulant. The 0.5 kDa nanofiltration membrane was able to remove 40% of the DOM. Further, due to the wide molecular weight distribution of different fluorophores as observed in Figure 4.14, 4.15 and 4.16, the organic fractions in the BBD cannot be separated based on their chemical nature using nanofiltration. The chemical nature based fractionation of DOM in BBD and the fluorescence signature of the organic fractions shown in suggests that the humic acid fraction is dominant in the BBD. Humics adsorb readily on fresh granular activated carbon (GAC), but the capacity of the GAC reduces rapidly [Velten et al., 2011]. Further, the lower molecular weight compounds and the hydrophilic fraction are not usually removed effectively by the coagulation process[Matilainen et al., 2010], whereas hydrophobic and high molecular weight compounds are effectively removed by the same. Since the majority of the fraction in the DOM is hydrophobic, inspite of the fact that 40% of the DOM in BBD is of lower molecular weight, the enhanced coagulation process may be more effective for the removal of DOM from the BBD.

4.5 Summary

The DOM in the SAGD BBD can be classified into six different fractions of hydrophobic and hydrophilic acids, bases and neutrals. The hydrophobic acid and hydrophilic neutral are the major fractions in the SAGD DOM consisting of more than 60% of the total organic content in the BBD. The fluorescence excitation emission mapping of the organic fractions clearly show the differences between the fluorescence signatures of the various fractions. For the filtration experiments, the DOC analysis of the permeate shows that the 10 kDa and 3 kDa membranes can separate only 5% and 20% of the total organic matter, respectively, whereas the 0.5 kDa membrane removes as much as 60% of the DOC. The fluorescence excitation emission maps for different membrane permeate samples show that the membranes fail to resolve the signatures of all the fractions originally present in the BBD water.

The fluorescence excitation emission mapping of the hydrophobic acid fraction clearly shows that they are mainly humic acids. The fluorescence signature of the OSPW obtained from the Athabasca Oil sands operation shows that the principal component of the OSPW is naphthenic acids. The fluorescence signature of the BBD shows that significant amounts of naphthenic acids are not present in the SAGD BBD.

The results presented above indicate that most of the DOM in SAGD BBD

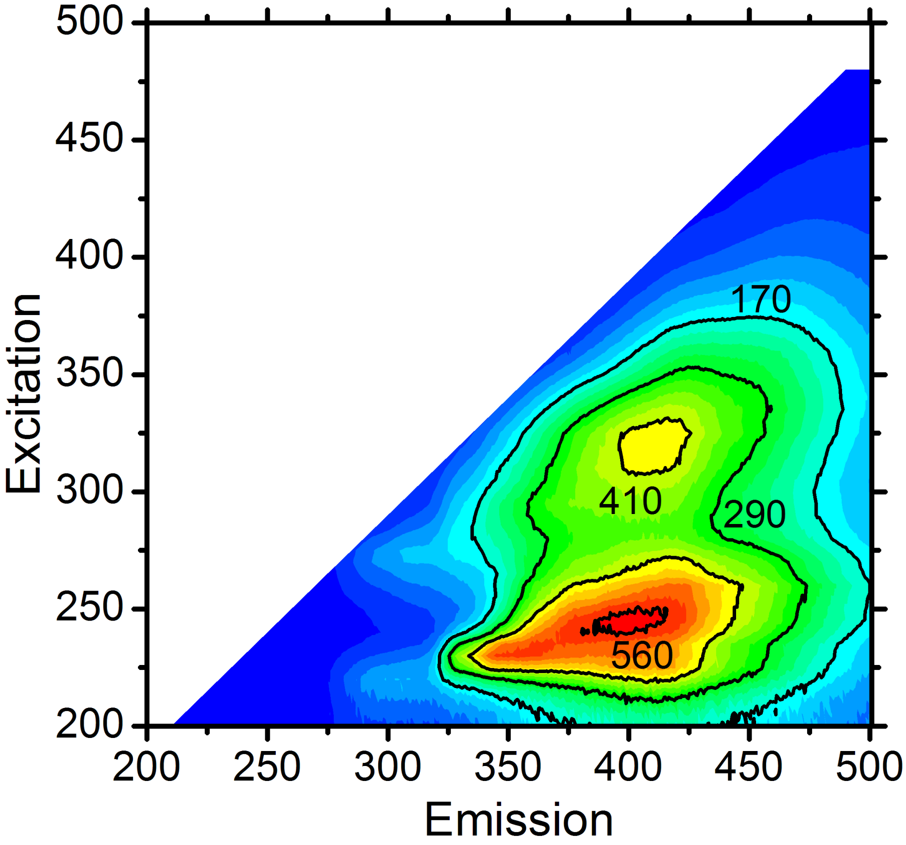

Figure 4.14 – Excitation emission matrix (EEM) contour map of the dissolved organic matter in the permeate of 10 kDa membrane during filtration of BBD. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

consists of low molecular weight compounds, with hydrophobic acids and hydrophilic neutral compounds representing the predominant fractions. However, filtration using tight ultrafiltration, or loose nanofiltration membranes does not preferentially remove any of these fractions. Processes like coagulation or adsorption/ion-exchange techniques targeting the removal of specific organic matter fractions might be more suitable for the removal of organic matter in SAGD BBD water compared to filtration based processes.

Finally, we note that in thermal EOR, such as SAGD, a significant amount of organic matter from petroleum becomes soluble in water. Since this is not

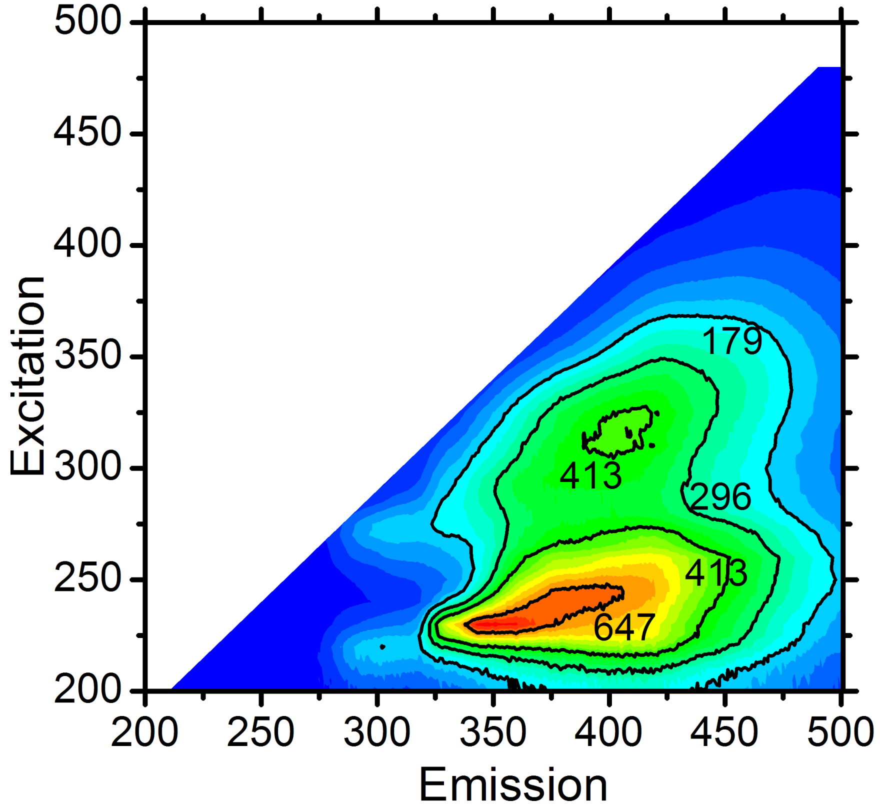

Figure 4.15 – Excitation emission matrix (EEM) contour map of the dissolved organic matter in the permeate of 3 kDa membrane during filtration of BBD. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

observed in mining, we speculate that the thermal history of the produced fluid causes this enhanced solubilization. From the filtration experiments it is discernible that these water soluble class of compounds do not have a molecular weight or size based behavior, but are more representative of solubility class behavior of other petroleum fractions like asphaltenes and maltenes, which is commonly used for petroleum fractionation through SARA analysis. Our study indicates the presence of a significant amount of additional water soluble class of petroleum organic matter, which needs to be accounted for when dealing with produced water during thermal EOR and enhanced temperature based oil recovery.

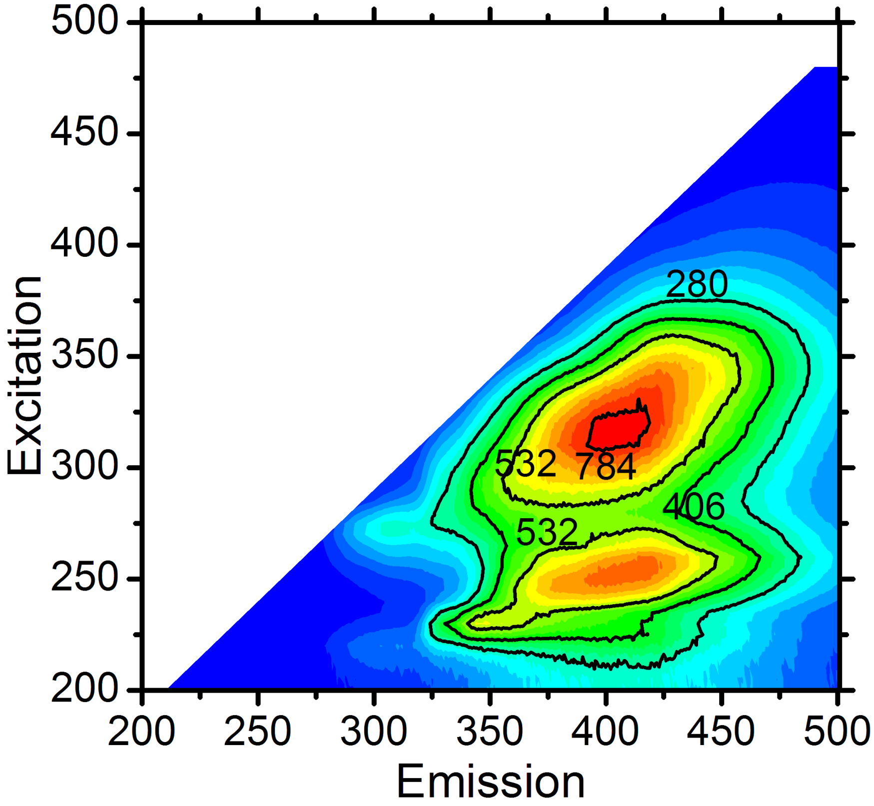

Figure 4.16 – Excitation emission matrix (EEM) contour map of the dissolved organic matter in the permeate of the 0.5 kDa membrane during filtration of BBD. Fluorescence excitation wavelengths at 5 nm intervals from 200 to 500 nm and corresponding emission wavelength data collected between 200 to 500 nm are plotted along Y and X axis, respectively. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

Chapter 5

Removal of dissolved organic matter from SAGD boiler blow-down water [1]

5.1 Introduction

The objective of the work presented here is to demonstrate the removal of DOM from BBD by co-precipitation with silica as a function of pH. At pH ca. 11 the silica remains dissolved in aqueous medium as negatively charged dissolved silicate [Nordstrom et al., 2011, Tognonvi, 2011, Gorrepati et al., 2010, Iler, 1979]. When the pH is reduced less than 9.5 aggregation of silica particles are observed. This is due to reduction in electrostatic double layer repulsion between negatively charged silica particles [Gorrepati et al., 2010, Iler, 1979, Merrill and Spencer, 1950].

Silica polycondensation (gelation) starts at alkaline pH range 10.5 to 8.0 and the polymerization rate is highest below pH 5.5 [Iler, 1979]. The precipitation of polymerized products occurs due to charge neutralization by added H^+ ions, and the rate of precipitation increases with increase in ionic strength of the solution, which decreases the electrostatic repulsion among the negatively charged silica species [Icopini, 2005, Masliyah, 2006]. The long chain polymerized silica species interact with organic matter present in the water via hydrogen bonding and van der Waals attraction [Parida et al., 2006]. Thus, it is highly possible that hydrogen bonding could occur between the hydrogen of Si-OH and oxygen and nitrogen of different functional groups in the DOM

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[1] Parts of this chapter have been submitted to *Energy & Fuels*, July 2012.

of BBD.

Dissolved organic matter is adsorbed on the silica surface [Alagha et al., 2011, Louguet et al., 2011, Liu et al., 2010, Samiey and Toosi, 2010, Su, 2006, Parida et al., 2006] owing to a strong chemical interaction between siliceous and organic components [Abramson et al., 2009]. This triggers silica organic co-precipitation. Precipitation was observed while performing the ion-exchange fractionation of the SAGD DOM as the sample pH was adjusted to 2. Therefore, it was decided to systematically explore solution pH adjustment as a possible technique to remove organic matter from the boiler blow down water.

One of the major concerns in the water treatment industries is the silica fouling. Silica is often deposited on the walls of boilers, economizers and other process equipments causing irreversible fouling. The presence of calcium, magnesium, aluminum, iron etc. increase the silica precipitation through formation of silicates. In SAGD, the metal ions are removed through processes like warm lime softening and weak acid cation-exchange to prevent silica precipitation. The SAGD operation is carried out at a highly alkaline pH such that the silica remains in the dissolved condition. However, the SAGD operation handles high concentrations of dissolved organic matter (DOM). Due to strong interaction between silica and DOM, silica-organic co-precipitation is observed in the SAGD equipments resulting in irreversible fouling [Jennings and Shaikh, 2007]. However, there has been no systematic study of how these entities interact with each other, and lead to aggregation, precipitation, scaling, etc. In order to develop management strategies for large volumes of these wastewaters a knowledge on the interaction mechanisms of silica and organics is essential. It is also known from the discussion in previous chapters that there are altogether six classes of organic compounds in the SAGD BBD. It is important to know which of these classes of compounds have higher affinity towards silica in order to develop efficient treatment techniques for silica and organic removal.

In this Chapter, the effect of acidification on the DOM removal in SAGD BBD is reported. The mechanism of silica and organic interaction are also studied in this Chapter. The BBD was acidified using concentrated hydrochloric acid to generate BBD solutions at different pH. The organic removal at different pH was studied using TOC analysis and UV absorbance techniques. The supernatant obtained after precipitation of DOM at different pH was analyzed through FTIR and fluorescence spectroscopy. The fluorescence and FTIR signatures of the organic fractions present in the SAGD DOM were compared to the signatures of the supernatants obtained at different pH to identify the organic fraction that precipitates at lower pH ranges. This Chapter presents the probable interaction mechanism of silica and organic matter. A quantitative analysis of amount of silica and organic removed through acidification is also depicted. Finally, the organic fractions having higher affinity towards silica to form aggregates are identified in this Chapter.

5.2 Potentiometric titration of BBD

The raw BBD sample was subjected to titration with 0.12 (M) HCl solution using potentiometric auto-titrator. Figure 5.1 depicts the titration curve and first derivative of pH plot for the BBD water. The titration curve has pH plotted along the Y-axis and mol of HCl added per L of BBD along X-axis. The first derivative of pH plot has dpH/dV along the Y-axis and mol of HCl added per L of BBD along X-axis. BBD titration was stopped at pHs, viz., 1.99, 2.84, 3.64 and 6.11. The first derivative of pH plot shows that two main inflection points, at 7.29 and 3.32, and a small inflection point at 10.2 are obtained for BBD during titration over the pH range of 11.0 - 2.0. These end points indicate the pH at which the carboxylates convert to carboxylic acids through protonation mechanism which will be discussed in Section 5.4.

The resultant solutions after the above titrations were left standing in different test tubes. The photographs of these solutions are shown in Figure 5.2. At pH of 9.8, no precipitation was observed in the BBD water. However, as the pH was adjusted below 7, a dark brown precipitate was observed. From the photographic evidence in Figure 5.2 it is concluded that a considerable amount of precipitation of dissolved organic matter is observed at pH value range of 2 - 3. This is corroborated from the analysis of the supernatants obtained from acidification of BBD which will be discussed in the subsequent sections.

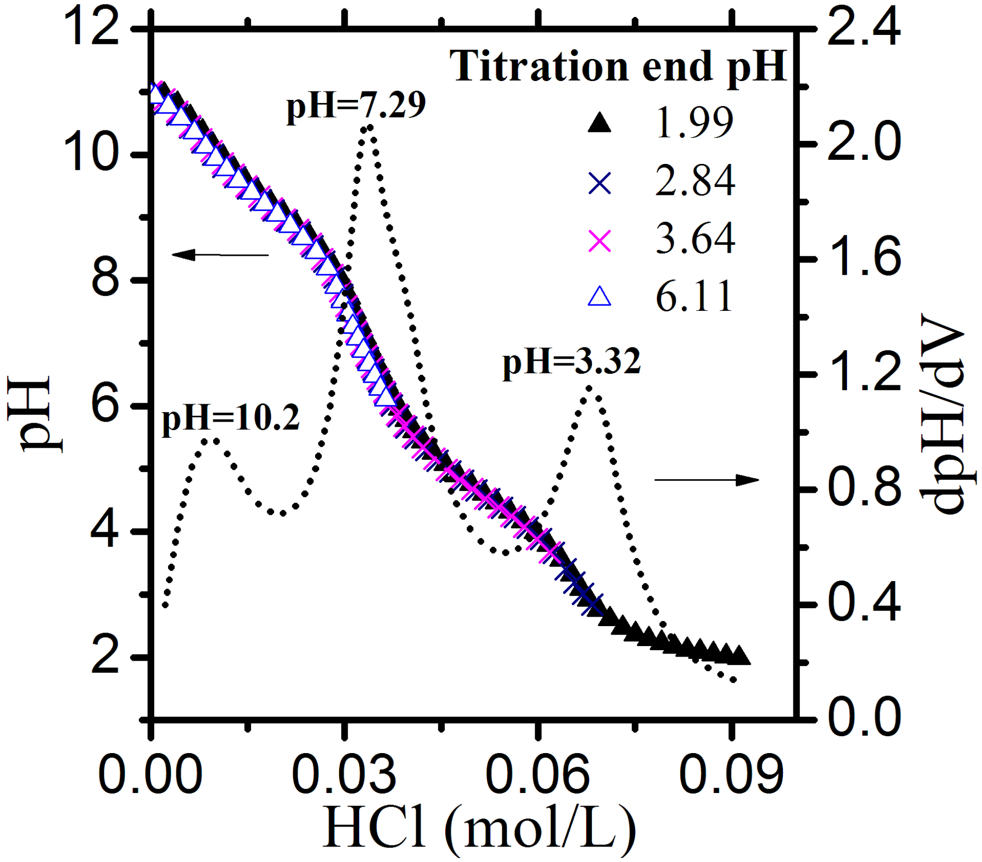

Figure 5.1 – Potentiometric titration curve of BBD, titrations stopped at pHs 6.1, 3.6, 2.8 and 1.99 presented as titration curves, with pH along Y-axis and mol of HCl per L of BBD along X-axis, using different symbols as indicated on the graph. The short dot curve represents the first derivative of pH plot with dpH/dV along Y-axis and mol of HCl per L along X-axis

5.3 Acidification of BBD

The BBD was acidified using 1 (M) HCl and solutions at different pH were prepared as shown in Figure 5.3. The BBD when acidified to basic pH ranges (> 7), no distinct changes in the color is observed. However, as the pH is shifted towards the acidic range precipitation accompanied by a change in the color of the supernatant is observed. This corroborates that organics are precipitated at these pH ranges since potentiometric titration indicates neutralization at similar values.

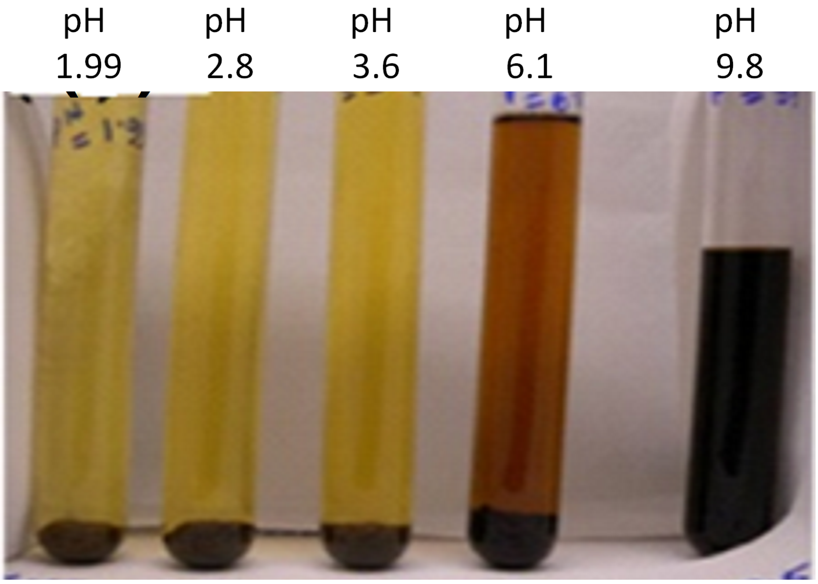

Figure 5.2 – Photographic representation of solutions obtained at different pHs (1.99, 2.8, 3.6, 6.1, and 9.8) during potentiometric titration of BBD

5.3.1 Removal of DOM and silica

Figure 5.4 shows the decrease in TOC concentration in the supernatants obtained from the acidified BBD. At pH values of 9.48, 8.19 and 7.48, which lie in the basic pH range, the TOC reduction was about 10 % only. As the pH is further lowered the DOC removal is increased. At a pH close to 7 about 15 % of DOC removal is observed.

In accordance with the potentiometric titration results, the TOC removal increased in the acidic pH ranges. At pH 5.9 and 4.9, the DOC concentration was reduced by 22 % and 34 %, respectively. The maximum DOC removal is observed at the pH value of 2 and 3. At pH 3.06 the TOC reduction is 42 %, whereas lowering the pH to 2 removes 45 % of the organic content. Thus, almost half the organic matter present in the BBD DOM can be removed by acidifying the BBD to pH 2.

ICP-MS analysis showed that at about 84 % of the silica originally present in the BBD precipitated at the pH 2. Thus, the removal of DOM can be explained through the polymerization (precipitation) of silica at different solution pHs. Above pH 10.6, silica exists as dissolved silicate, and silica particles are

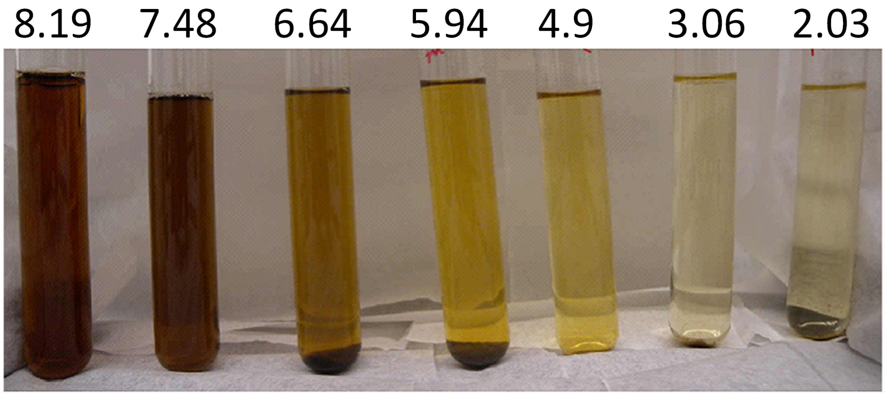

Figure 5.3 – Photographic representation of acidified BBD solutions at different pHs (2.03, 3.06, 4.9, 5.94, 6.64, 7.48 and 8.19).

negatively charged, thereby strongly repelling each other [Nordstrom et al., 2011, Tognonvi, 2011, Gorrepati et al., 2010, Iler, 1979]. In the presence of higher ionic strength of 0.2 - 0.3 M and upon acidification, the range of the electrostatic double layer repulsion is considerably reduced and aggregation (polymerization) occurs [Gorrepati et al., 2010, Merrill and Spencer, 1950].

5.3.2 SUVA_{254} analysis of the supernatants

SUVA_{254} values of the supernatant obtained from BBD solutions at different pH is presented in Figure 5.5. The SUVA_{254} of BBD at pH 12 is 4.1 L $\text{mg}^{-1}\text{m}^{-1}$. As discussed in chapter 2 and 4, SUVA_{254} value greater than 4 signifies presence of hydrophobic, humic-like substances and high aromaticity [Edzwald and Tobiason, 1999, Weishaar et al., 2003].

At basic pH ranges like 9.48, 8.19, 7.48 the SUVA_{254} value of the BBD samples were 3.04, 2.89, 2.58, respectively. The SUVA_{254} value reduction corroborates the DOC removal from the BBD with the change of pH. Initially, at pH 12, the SUVA_{254} value is greater than 4 indicating presence of aromatic carboxylic acids (humic acids). The reduction of SUVA_{254} value with the reduction of pH indicates that the aromatic carboxylic groups precipitate with the change of pH.

The SUVA_{254} value of the BBD sample at pH of 5.94 and 4.9 is still greater than 2, indicating that though the aromatic components are reduced, the sam-

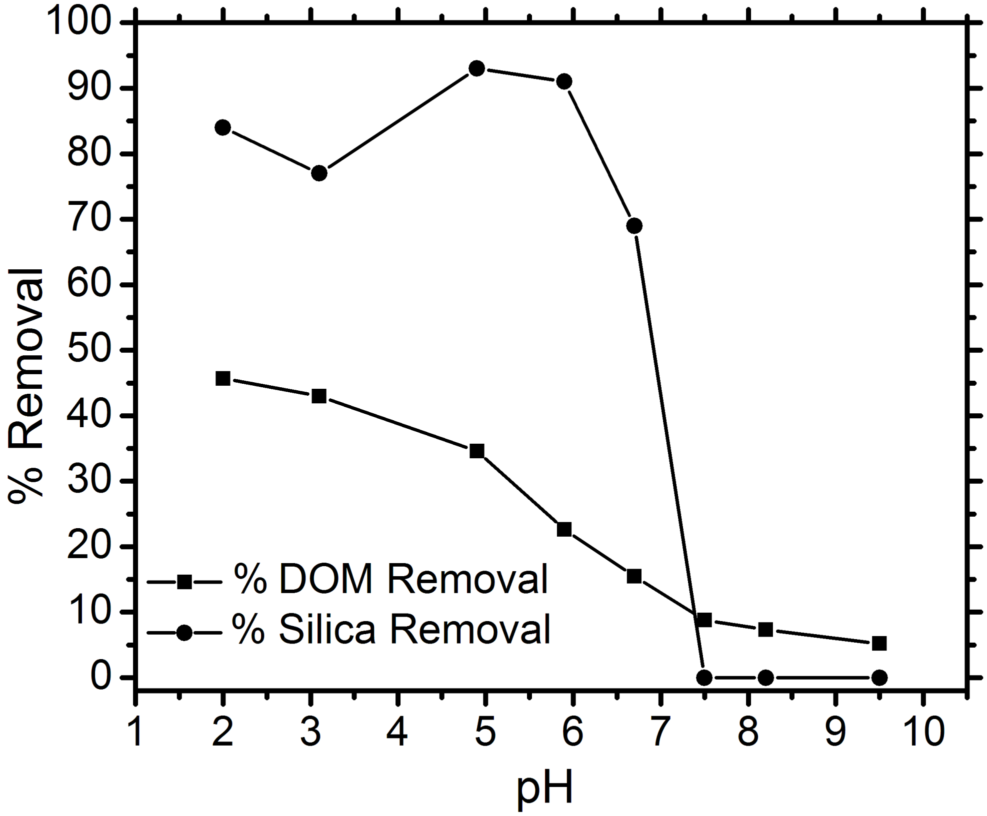

Figure 5.4 – The percentage reduction of dissolved organic matter and silica in the supernatants obtained from BBD samples at different pH after precipitation of DOM

ple still contains a mixture of humic and non humic, aliphatic and aromatic substances.

At pH 2.03 and 3.06, the SUVA$_{254}$ value becomes less than 2, indicating that humic like substances are removed from the BBD through precipitation. This result is confirmed through the spectrofluorescence analysis which also shows the removal of hydrophobic humic like fraction at the same pH values.

5.4 Silica-organic co-precipitation mechanism

When H$^+$ ion is added to an aqueous alkaline solution polycondensation reaction occurs among the silicate species at a pH between 10.5 to 8 [Tognonvi,

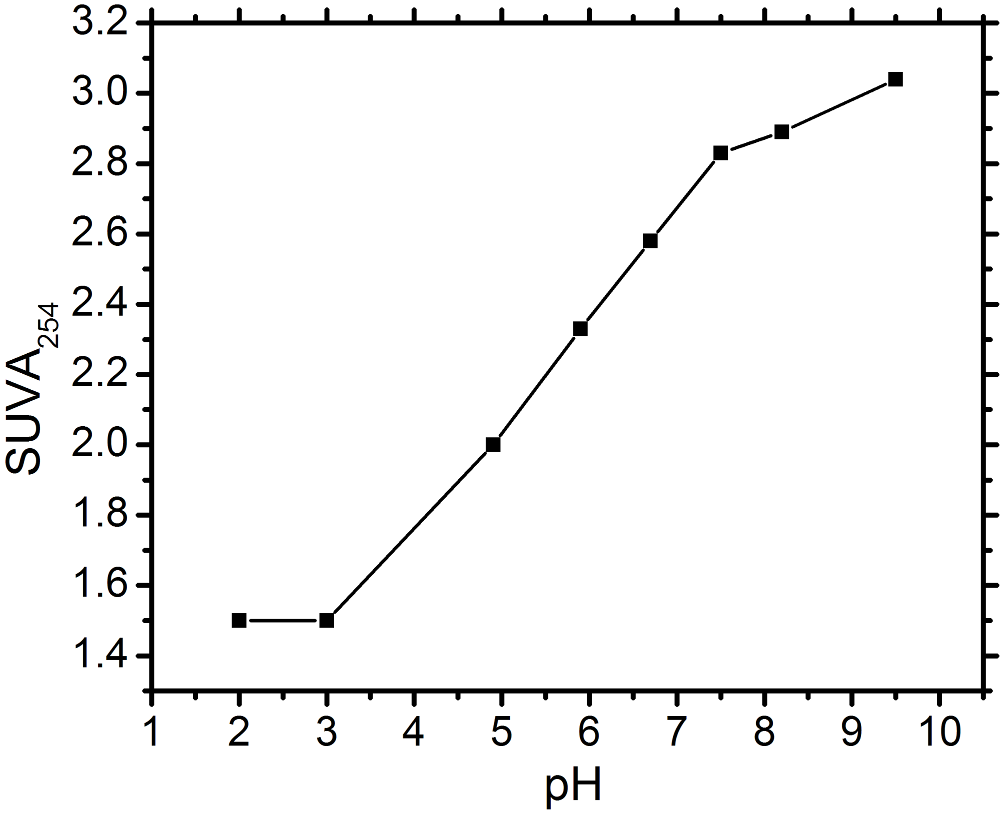

Figure 5.5 – $SUVA_{254}$ values of the supernatants obtained from BBD at different pH after the precipitation of DOM

2011, Gorrepati et al., 2010, Jesionowski, 2009, Iler, 1979]. With reduction of pH, due to charge neutralization by added H^+ ions, the electrostatic repulsion among the negatively charged silica species is reduced and silica aggregates [Icopini, 2005, Masliyah, 2006]. Organic matter is adsorbed on the long chain polymerized silica molecules through hydrogen bonding and van der Waals attraction [Parida et al., 2006]. Thus, silica and organic form an aggregate and precipitate out of the solution with the change in pH.

The carboxylic acids in the BBD DOM exist as sodium carboxylates at high pH. On acidification the Na^+ ion is replaced by H^+ ion resulting in formation of carboxylic acids. Since the carboxylic acids are insoluble in aqueous medis precipitation of organic compounds are observed on acidification. It is to be noted that in the alkaline pH ranges silica removal was not observed and the organic removal was very less. However, in the acidic pH ranges more precipitation of silica and organic were observed (refer Figure 5.4. This shows that on acidification the DOM starts precipitating through the mechanism of protonation but the major fraction of organic is precipitated through silica organic interactions.

The spectrofluorescence and FTIR analysis of the SAGD DOM shows presence of aromatic hydrocarbons containing carbon and nitrogen bearing functional groups in the BBD. Thus, it is highly probable that strong hydrogen bonding occurs between hydrogens of Si-OH and oxygen and nitrogen of different functional groups in the DOM of BBD water. Highly surface-active silica adsorbs DOM and the later co-precipitates with silica resulting into DOC reduction with decrease in pH. The precipitation of organic matter through metal complexation during acidification of BBD can be ruled out due to low concentration di- or multi-valent metal ions in BBD as seen in Table 4.

5.5 FTIR analysis of the supernatant and precipitate

The SUVA analysis showed that, most likely, it is the HPoA fraction, which is hydrophobic and humic-like, precipitating on acidification of BBD. ATR-FTIR analysis of the supernatant and precipitate were performed and compared with the HPoA fraction of the BBD to validate the SUVA results.

The FTIR peaks for the precipitate at pH 2 were obtained at the bands of 950, 1026, 1280, 1416, 1620, 1707, 2870 and 2932 cm^{-1}. The 950 cm^{-1} band indicate Si-OH bonds whereas, the peak at 1026 cm^{-1} is due to Si-O-Si bond stretching [Falcone et al., 2010, Falcone Jr. et al., 2010, Sarawade et al., 2011]. The band of 1280 cm^{-1} is attributed to C-O stretching, whereas the 1416 cm^{-1} is due to presence of carboxylic OH groups [Rodriques and Nunez, 2011]. The band of 1620 cm^{-1} represent the C=C stretching whereas, 1707 cm^{-1} represent aromatic carboxylic acids [Rodriques and Nunez, 2011]. Finally, presence of C-H stretching is confirmed through the bands of 2870 and 2932 cm^{-1} [Orgill et al., 1999].

The FTIR peaks obtained for the supernatant showed no traces of silica either in Si-OH or in Si-O-Si bands. This proves that the organic matter co-precipitated with silica due to strong chemical interaction.

Comparing the FTIR signature of HPoA fraction with the BBD precipitate at pH 2 we see the presence of C-H stretching at 2849 and 2916 cm^{-1}. Presence of aromatic carboxylic acids are confirmed through the presence of C=C stretching, aromatic C=O ring and O-H bend at 1682, 1709 and 1406 cm^{-1}, respectively. The HPoA also shows the presence of N-H bend at 1534 cm^{-1}. The 1045 cm^{-1} represents C-O stretching.

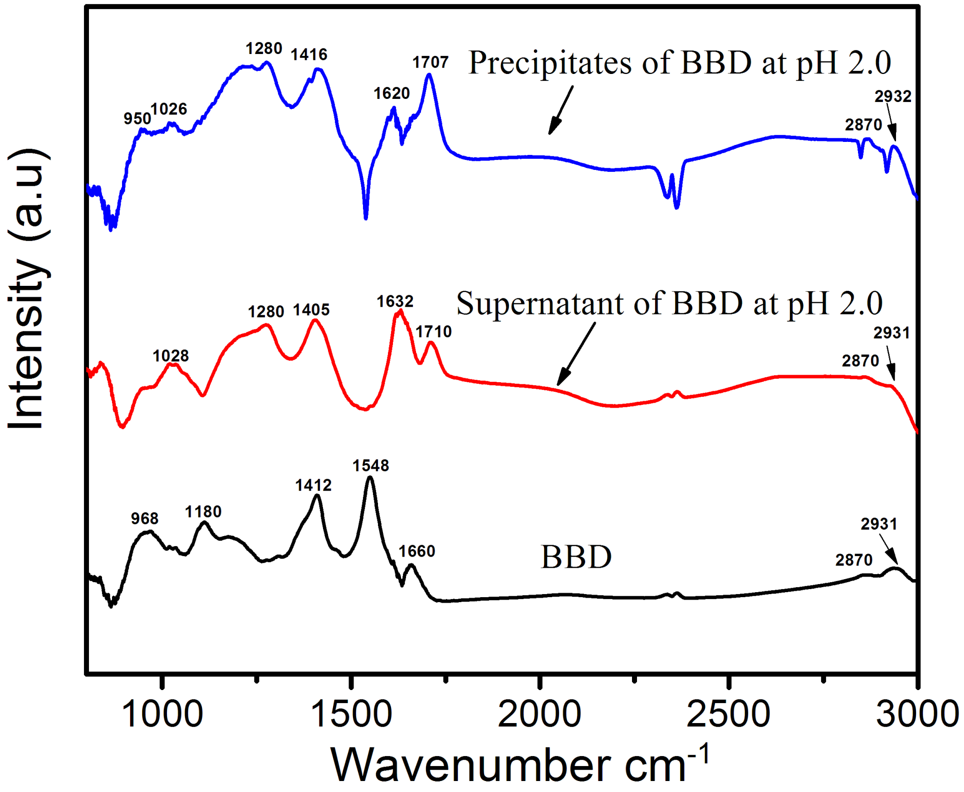

Figure 5.6 – ATR-FTIR spectra of the dissolved organic matter present in the supernatant and precipitate obtained from BBD at pH 2. The blue line represents the DOM in the precipitate. The red line is for the DOM in the supernatant. The black line represents the FTIR signatures of organic matter in raw BBD at pH 12.

Since the organic signatures of the HPoA fraction closely match with the organic signatures of the BBD precipitate at pH 2 it can be concluded that aromatic carboxylic acids are present in the precipitate obtained from acidification of BBD. The SUVA analysis also predicts that the humic like hydrophobic fractions precipitate at pH 2. EEM contours of the BBD samples at different pH discussed in the following section validates the same.

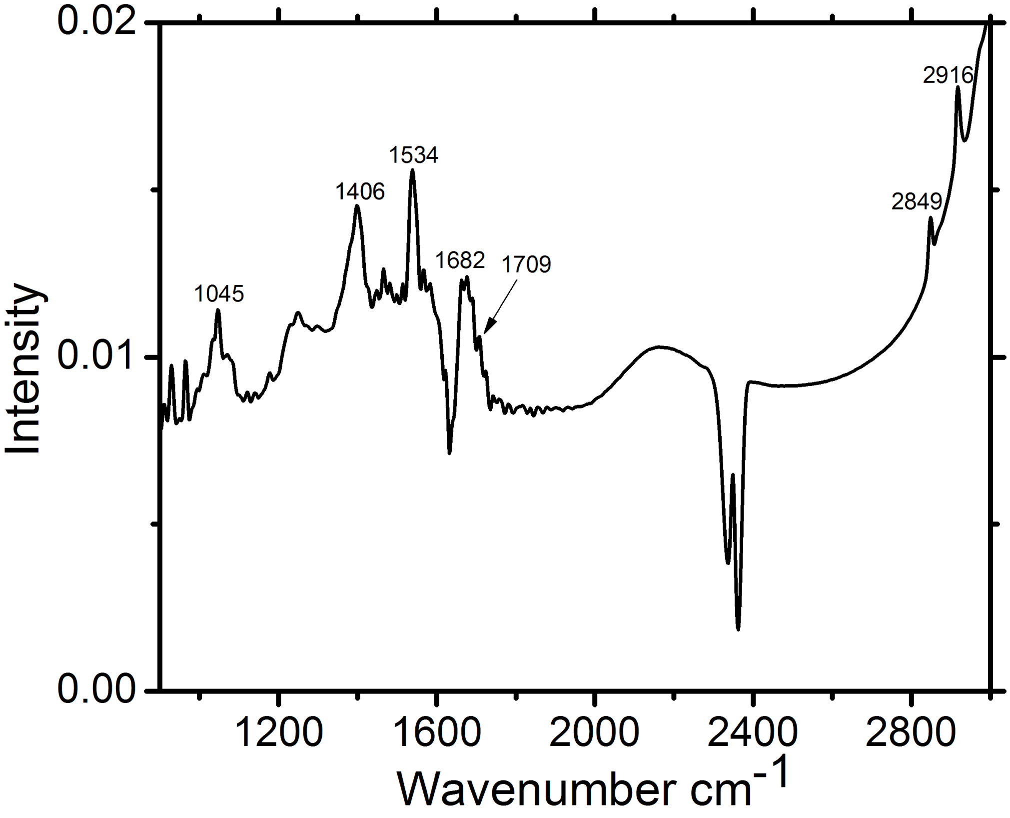

Figure 5.7 – The ATR-FTIR peaks of the hydrophobic acid fraction obtained from SAGD DOM

5.6 Spectrofluorescence analysis of the BBD water at different pH

The fluorescence EEM contours for raw BBD at a pH of 12.33 is presented in the Figure 4.4 in Chapter 4. The intensity peaks are obtained in the region with Ex/Em wavelength of 225-250/375-450 and 300-340/400-425. The BBD was acidified to generate BBD solutions at different pH. Precipitation was observed as the pH of the BBD was decreased. The supernatant obtained, after filtering the precipitated organic matter from the solution, was analyzed using spectrofluorescence technique.

As the pH of the BBD is decreased to a pH value of 9, the intensity of fluorescence in the EX/Em range of 310-340/400-425 is reduced. The spectrofluorescence contour of the supernatant obtained after acidifying the BBD to a pH of 9 is presented in Figure 5.8. However, the peak intensity in the region of Ex/Em 225-240/375-450 does not change appreciably with the change of pH. Table 4.2 shows that the fluorescence intensity peak of the HPoA fraction in the BBD is observed over the region of Ex/Em wavelength 310-340/400-500. Comparing the intensity peak regions of HPoA and the supernatants of acidified BBD, it is evident that mostly the hydrophobic acid fraction precipitates with the change of pH.

Figure 5.9 represents the spectrofluorescence analysis of the supernatants obtained at pH 7.48 and 8.19. The EEM of the supernatants show a reduction in peak intensity in the Ex/Em wavelength of 310-340/400-425 also. However, the comparision of intensity peak values show that the reduction is nominal. This is best explained in Figure 5.4 which shows that only about 10 % of DOC reduction is observed in the basic pH range. Since silica removal at this pH is also nominal it can be concluded that organic matter in these pH ranges precipitate through the mechanism of protonation. It is also observed that the hydrophobic acids which are humic acid-like molecules are precipitating.

Potentiometric titration of the BBD shows that maximum DOC removal is expected in the pH range of 2 - 3. Figure 5.4 also shows that about 45 % of the organic carbon can be removed on acidification of BBD to pH 2. Humic-like organic matter precipitates at pH 2 [Harvey et al., 1983, Leenheer, 1981, Malcolm, 1991, Thurman and Malcolm, 1981]. Since, HPoA are primarily humic-like (refer Table 2.4 and 4.2) it is highly probable that they precipitate as the solution is rendered acidic with decrease in pH.

Figure 5.10 shows the fluorescence contour of BBD supernatants at pH 5.94 and 4.9. An appreciable reduction in the intensity of the Ex/Em region of 310-340/400-425 in comparision to the basic pH ranges is observed. This is corroborated by Figure 5.4 which shows that almost 22 % of the TOC is

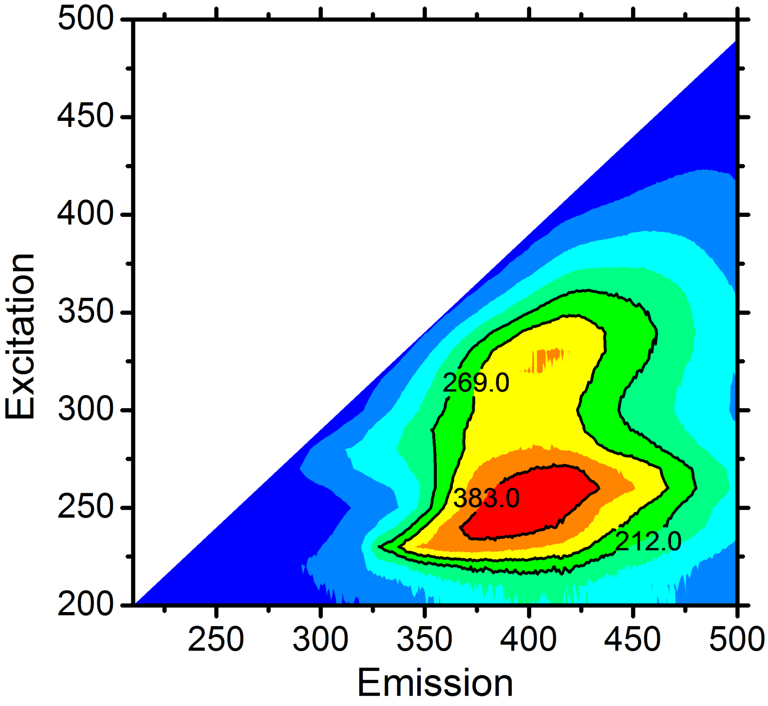

Figure 5.8 – Excitation emission matrix (EEM) contour map of supernatant obtained during acidification of BBD to pH 9.48. The samples were allowed to settle for 24 hours. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

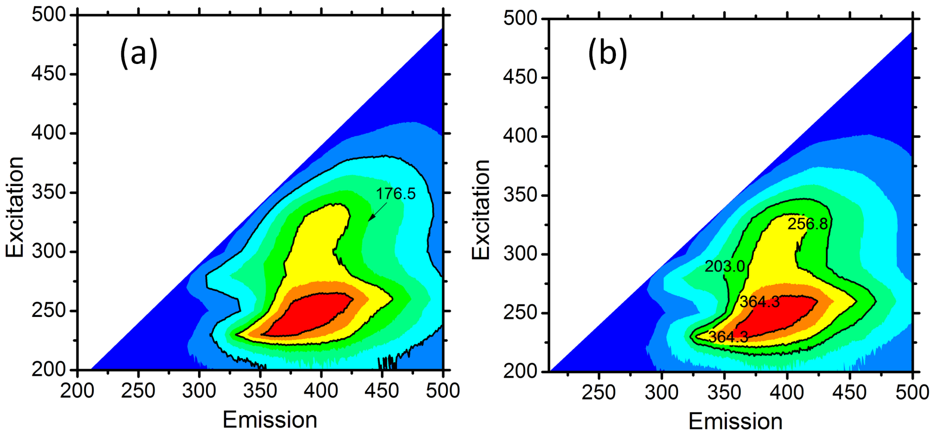

Figure 5.9 – Excitation emission matrix (EEM) contour map of supernatant obtained during acidification of BBD to pH (a) 7.48 and (b) 8.19. The samples were allowed to settle for 24 hours. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

removed from the BBD at this pH.

Finally, at pH values 3.07 and 2.06 the fluorescence intensity in the EEM contour of the BBD supernatant is very low in the region representing HPoA fraction. Since the maximum DOC removal is observed in this pH range it is concluded that HPoA fraction is the major component of the precipitate. The fluorescence EEM contours corroborate the ATR-FTIR results which predicted that humic-like aromatic carboxylic acids are the major components in the precipitate obtained from BBD at pH 2. Comparision of the fluorescence signatures in Table 2.4 and 4.2 shows that the HPoA are humic-like organic compounds. The spectrofluorescence analysis of the supernatants strengthens the argument that the major organic compounds in BBD are humic acids unlike the OSPW where the naphthenic acids are the major components.

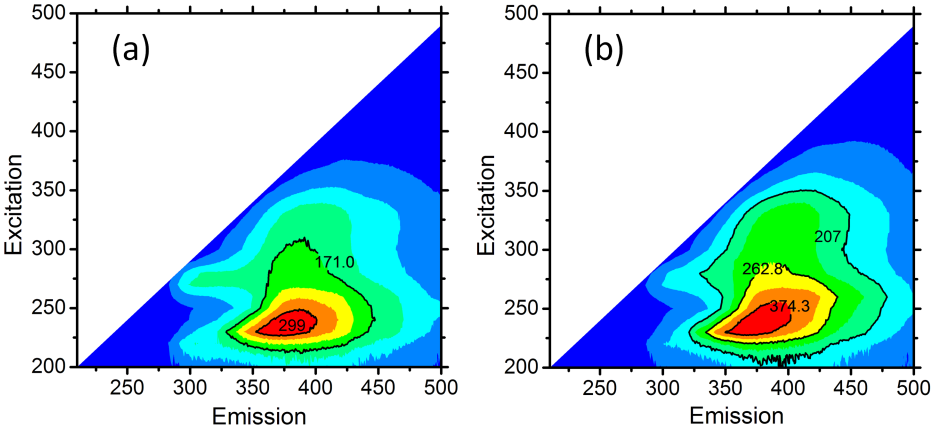

Figure 5.10 – Excitation emission matrix (EEM) contour map of supernatant obtained during acidification of BBD to pH (a) 4.9 and (b) 5.9. The samples were allowed to settle for 24 hours. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

In Figure 5.11(a), signatures of the HPoB fraction in the BBD are observed in the EX/Em wavelength of 260-290/280-320. HPoB is a minor fraction in the BBD DOM. Fluorescence signatures of these fractions were not observed in the EEM contour maps of the raw BBD. The strong fluorescence of the hydrophobic acid fluorophores masked the fluorescence signatures of the HPoB. On removal of the HPoA fractions the EEM contours manifest the presence of

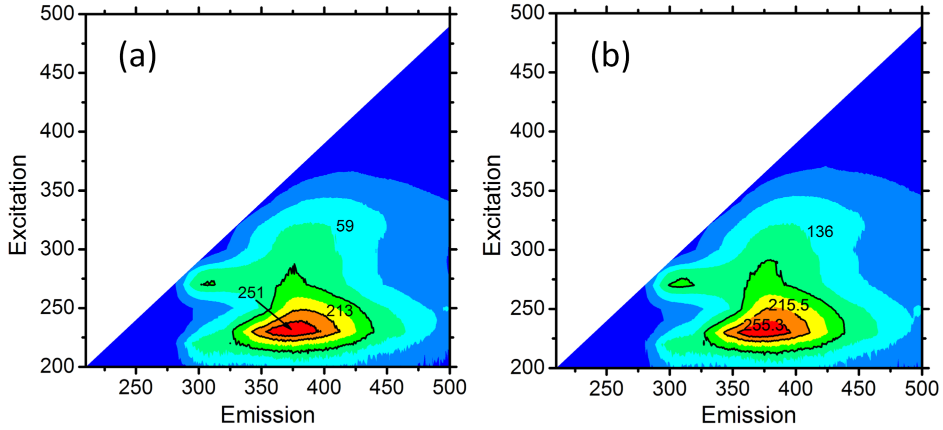

Figure 5.11 – Excitation emission matrix (EEM) contour map of supernatant obtained during acidification of BBD to pH (a) 2.06 and (b) 3.07. The samples were allowed to settle for 24 hours. The region of fluorescence intensity peaks are marked in the contour map. The region with the highest intensity is marked in red.

HPoB in the BBD. Thus, isolation of organic fractions are necessary to provide accurate qualitative information about BBD DOM through spectrofluorescence.

From the results obtained in the previous sections it is observed that silica-organic co-precipitation is maximum in the acidic pH ranges. During disposal of BBD into underground rock formations through deep well injection the pH of the solution decreases owing to formation of metasilicates and carbonates [Roy et al., 1991]. As the pH of the solution is reduced the organic silica co-precipitation is observed in the injection wells resulting in clogging. The FTIR signatures showed presence of carboxylic and NH- functional groups in the BBD DOM. The interaction of silica and organic occurs between hydrogen of Si-OH and oxygen and nitrogen of organic compounds in BBD. Among the six fractions of organic matter obtained from the SAGD DOM the hydrophobic acid fraction is major foulant. It interacts with silica triggering silica-organic co-precipitation causing irreversible fouling in the economizers, injection wells and other SAGD process equipments.

5.7 Summary

The DOM in the SAGD BBD precipitates out on acidification. Potentiometric titration of the BBD shows that the maximum removal of the organic matter can be obtained in the acidic pH range of 2 - 3. At a pH value around 2 about 45 % reduction in TOC concentration of the BBD is observed. This corroborates the results obtained from the potentiometric titration and confirms that acidification is a potential mechanism for organic matter removal from SAGD BBD.

This study also shows that fractionation of DOM into distinct fractions are necessary for spectrofluorescence analysis. As the BBD was acidified and the humic-like fractions precipitated, signatures of the minor components like HPoB are observed in the EEM contours of BBD. These signatures were earlier masked by the presence of the hydrophobic acid fraction. Thus, in order to analyze the BBD accurately using standard characterization techniques used for NOM, isolation of different organic fractions from the DOM is necessary. Thus, in order to characterize the dissolved organic matter in the SAGD BBD the first step should be isolation of DOM fractions using the fractionation procedure described in Chapter 3 and Appendix A.2.4.

The silica removal from BBD is also very high (above 80%) in the acidic pH region. The silica remains in dissolved condition in the basic pH ranges which prevail in the SAGD BBD. As the pH shifts towards acidic region the silica tends to precipitate out. Due to strong chemical interactions between the silica nad organic matter the DOM in the BBD co-precipitate along with silica during acidification. In the injection wells the pH is reduced due to the formation of carbonates, silicates and hydroxides [Roy et al., 1991]. This reduces the pH of the system and silica tends to precipitate along with the organic matter causing clogging in injection wells. Characterization of the precipitates obtained during acidification of BBD shows that the humic like aromatic carboxylic acids constitute the major portion of the precipitates obtained from the BBD. Hence, removal of the total DOM is not necessary to prevent the injection well clogging. The removal of hydrophobic acid fraction alone is sufficient to prevent the injection well clogging.

Chapter 6

Conclusions and Future Work

6.1 Concluding Remarks

In this study, detailed characterization of SAGD boiler blow-down (BBD) water was explored. Ion exchange fractionation was employed to isolate different organic fractions from the DOM in the SAGD BBD. Qualitative information about the chemical nature of different DOM fractions was obtained using standard analytical techniques like TOC analysis, spectrofluorescence, UV absorbance and FTIR spectroscopy. The pH effect on dissolution of organics in the SAGD BBD was examined. This work provides an insight into the silica and organic matter co-precipitation in BBD. Based on the experiments performed during this work the following conclusions can be drawn.

1. Ion-exchange fractionation of DOM in SAGD blow-down (BBD) shows that hydrophobic acids, hydrophilic neutrals and hydrophobic neutrals are the principal DOM fractions in SAGD BBD.
2. The fluorescence EEM contour of the hydrophobic acid fraction clearly shows that they are mainly humic acid-like.
3. The fluorescence signature of the commercial naphthenic acids and OSPW obtained from the Athabasca Oil sands mining operation shows that the principal component of the OSPW have signatures corroborating presence of naphthenic acids. The fluorescence signature of the BBD on the other hand, does not reveal naphthenic acids.
4. The DOC analysis of the permeates of 10 kDa and 3 kDa membranes show that they can separate only 8% and 19% of the total organic matter

in BBD, respectively, whereas the 0.5 kDa membrane removes as much as 60% of the DOC. This indicates the organic matter present in the SAGD BBD are predominantly of lower molecular weight.

5. The fluorescence excitation emission contours for different membrane permeate samples show that the membranes fail to resolve the signatures of all the fractions originally present in the BBD water showing a wide molecular weight distribution in all the fluorophore types in BBD.
6. About 46% of the organic matter present in the BBD precipitates out at pH 2 showing that a large fraction of organic matter can be removed from BBD water through acidification.
7. FTIR analysis of the precipitate and EEM contours of the supernatant obtained during acidification shows a high probability of precipitation of hydrophobic acid fractions at pH 2.

6.2 Future Work

Experimental analysis in this work shows that the hydrophobic acid fraction precipitates at lower pH and may be responsible for the organic fouling observed in deep well injection and SAGD downstream equipments. Thus, the removing the hydrophobic acid fraction can alleviate the organic fouling problems in SAGD. However, the analysis performed in this work is qualitative and does not provide information on the percentage contribution of the other organic fractions in fouling.

In the light of the above discussion the following future work are suggested.

1. Evaluation of coagulation as a organic removal technique. Identification or development of an effective coagulant and determination of the optimum dosage and process conditions for DOM removal.
2. Qualitative analysis performed in this work suggests that the hydrophobic acid fraction in the SAGD DOM is the principal cause of the organic fouling. However, the quantitative contribution of the different organic fractions in the SAGD equipment fouling needs to be determined.

3. An alternative method for production of boiler feed water from SAGD produced water is through evaporation. Effect of evaporation on the chemical characteristics of the SAGD DOM needs to be studied.

4. The signatures of DOM fractions obtained through spectrofluorescence analysis were compared with signatures of aquatic fluorophores obtained in literature. The possible chemical nature of the organic compounds were predicted with aquatic fluorophores as baseline. Further information about the chemical nature of the organic fractions can be obtained through more precise analytical techniques like nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry etc.

5. The probable mechanism of organic precipitation with the change of pH was cited as silica-organic co-precipitation through hydrogen bonding. Detailed study on different mechanisms of silica-organic interactions in BBD like systems will be of extreme importance for SAGD process optimization.

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Appendix A

Standard operating procedure of Ion-exchange experiments

A.1 Amount of resins required

A.1.1 Amount of DAX-8® required for fractionation

The amount of DAX-8 required for the fractionation depends on the DOC value of the sample. Table A.1 shows a relationship between the DOC value of the sample and the breakthrough volume, which is the maximum sample volume that can be passed through 1 ml of the resin for complete organic matter adsorption [Thurman and Malcolm, 1981]. So, if the TOC of the sample is 50 mg/L then maximum 25 ml of the sample can pass through 1 ml of the resin for a complete hydrophobic fraction adsorption.

Table A.1 – Amount of DAX-8 resin required for the fractionation [Thurman and Malcolm, 1981]

DOC (mg/L)	Breakthrough volume
5	50
25	30
50	25
100	15
200	10
500	5

A.1.2 Amount of DOWEX 50W X8® and DUOLITE® required

The amount of DOWEX 50W X8® and DUOLITE® used for the fractionation is related to the exchange capacities of the resins and the specific conductance of the water fed to these resins by the Equations A.1 and A.2.

$$C = 12.5 * \sigma \tag{A.1}$$

where, C is the salt concentration in the sample in mequiv/L and σ is the specific conductance of the sample in mS/cm.

$$V_{resin} = \frac{V_{sample} * C}{\eta} \tag{A.2}$$

where, V_{resin} is the volume of the resin required in ml, V_{sample} is the volume of the sample to be passed through the resin in L, C is the salt concentration in mequiv/ml and η is the exchange capacity of the resin in mequiv/ml.

The exchange capacity of DOWEX 50W X8® and DUOLITE® resin is 1.7 mequiv/ml and 2.1 mequiv/ml, respectively.

A.2 Standard operating procedure

A.2.1 DAX-8® cleaning

1. Take required amount of DAX-8® resin in a glass beaker
2. Wash the resin with 0.1 N NaOH and decant the fines. Wash with DI water and then with methanol
3. Soxhlet extract the resin using 125-150 ml of methanol for 24 hours
4. Repeat steps 3 and 4 with acetonitrile, diethyl ether and methanol
5. Store the resin in methanol and keep it in a refrigerator

A.2.2 DOWEX 50W X8® cleaning

1. Take required amount of DOWEX 50W X8® resin in a glass beaker
2. Wash the resin with DI water
3. Soxhlet extract the resin using 125-150 ml of methanol for 24 hours
4. Store the resin in water and keep it in a refrigerator

A.2.3 DUOLITE® cleaning

1. Take required amount of DUOLITE® resin in a glass beaker
2. Wash the resin with DI water and decant the fines
3. Soxhlet extract the resin using 125-150 ml of acetone for 24 hours
4. Store the resin in water and keep it in a refrigerator

A.2.4 Fractionation of DOM

The resins must be conditioned just before the sample is being passed. The procedure for resin conditioning is as follows;

DAX-8® conditioning

1. Pump DI water through the DAX-8® column until the DOC of the effluent is less than 1 mg/L
2. Pump 10 bed volumes of 0.1 N NaOH and the 0.1 N HCl through the column
3. Pump 60 bed volumes of DI water through the column

DOWEX 50W X8® conditioning

1. Pump 3 N NH_4OH through the DOWEX 50W X8® column until the breakthrough of ammonia is reached in the column
2. Pump 4 bed volumes 2 N HCl through the column
3. Pump DI water through the column until the conductivity of the effluent water becomes 10 μS/cm

DUOLITE® conditioning

1. Pump 5 bed volumes of 1 N HCl through the DUOLITE® column
2. Pump 25 bed volumes of 3 N NH_4OH through the resin column
3. Pump DI water through the column until the conductivity of the effluent water becomes 10 μS/cm

Fractionation

1. Pump the sample water through the DAX-8 column
2. Pump 2.5 bed volumes of DI water through the column and mix the water back with the sample
3. Back elute HPoB fraction by pumping 0.25 bed volume of 0.1 N HCl followed by 1.5 bed volume of 0.01 N HCl
4. Acidify the effluent of DAX-8® column to pH 2
5. Filter the acidified sample through 0.22 μ-m filter
6. Pump the filtrate through the DAX-8® column again
7. Pump 1 bed volume of 0.01 N HCl to displace the non-sorbed portion of the sample and allow to mix it back to the effluent
8. Back elute HPoA fraction by pumping 0.25 bed volume of 0.1 N NaOH followed by 1.5 bed volume of DI water
9. Unpack the resin on an aluminium pan and leave it open for drying for 10 hours
10. Forward elute HPiB by pumping 3 N NH_4OH through the DOWEX 50W X8® column
11. Back elute HPiA by pumping 2 bed volume of DI water followed by 3 bed volumes of 3 N NH_4OH through the DOWEX 50W X8® column

Note: All the pump flow rates must be maintained at less than 15 bed volumes per hour.