



Influence of humic acids on oil sand processing. Part I: Detection and quantification of humic acids in oil sand ores and their effect on bitumen wettability



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ABSTRACT

Eight oil sands ores were tested in order to quantify the levels of humic acids in these samples through the alkali extraction test originally developed to determine the oxidation of bituminous metallurgical coals. The test gives a concentration of humic acids released from ores, which in combination with the measurement of the total organic carbon (TOC) content in the alkali extracts provides a measure of ore/bitumen weathering. It was found that poor ores (low bitumen and high fines contents) exhibited the highest tendency to leach large amounts of humic acids per gram of bitumen in the samples. It was also shown that the absorbance at 520 nm obtained from the UV/visible spectra of the alkali extracted solutions correlated very well with the quality of the ores, with the highest absorbance obtained from the extracts produced by the poor ores. A comparison between the UV/Visible spectra of solutions obtained from the alkali-extraction tests and spectra of solutions of commercial humic acids also indicated that the total organic carbon content of the extracts of good ores primarily originated from compounds other than humic acids while the organic matter released by poor ores was dominated by humic acids.

The results of contact angle measurements on fresh and oxidized bitumen samples indicated that contact angles decreased and bitumen became more hydrophilic as pH increased. It was also shown that the hydrophobicity of bitumen drastically decreased when the sample was artificially oxidized, although the amount of humic acids generated in bitumen during the oxidation process was small. Additionally, the effect of added humic acids on the wettability of bitumen was also evaluated. It was found that the contact angle of bitumen significantly decreased in the presence of humic acids at pH 3, but the effect of humic acids was not significant at higher pH values (7 and 10). At pH 7 the effect of humic acids on bitumen wettability was minor compared to the effect of artificial oxidation of bitumen. These results suggest that humic acids make bitumen hydrophilic if they are part of internal/surface bitumen structure. However, if they are added as free chemicals their effect is minor, particularly under neutral and alkaline pH conditions, which also indicates that adsorption of humic acids from solution onto bitumen is low.

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1. Introduction

Oil sand ores are mixtures of bitumen, intrinsic water, and sand. A typical oil sand ore obtained from the Athabasca deposits in Alberta contains 4–14 wt.% bitumen, 80–85 wt.% mineral solids, and 2–15 wt.% of water (Takamura, 1982). Bitumen is a viscous organic mixture of high molecular weight hydrocarbons, containing low volatility components of a typical chemical composition of 83 wt.% carbon, 10.6 wt.% hydrogen, 0.4 wt.% nitrogen, and 4.8 wt.% sulfur (Basu et al., 1996). The sand fraction of oil sands is composed of quartz

(90–95 wt.%), and clays (5–10 wt.%), such as kaolinite, illite and minor amounts of montmorillonite (Mossop, 1980). For practical purposes, oil sand ores are defined as “good processing ores” when the bitumen content is higher than 10 wt.% and the fraction of sand particles finer than 44 μm is lower than 20 vol.%.

Many studies (Charrie-Duhaut et al., 2000; Majid et al., 2000a; Majid et al., 2000b; Majid and Sparks, 1996; Kotlyar et al., 1988; Kessick, 1979; Majid and Ripmeester, 1990; Majid et al., 1991; Majid et al., 1992; Ignasiak et al., 1985; Kotlyar et al., 1990; Kotlyar et al., 1985) isolated and characterized what is known as toluene/dichloromethane insoluble organic matter (IOM) present in oil sand ores. The IOM primarily consists of humic matter (Kotlyar et al., 1988), with minor amounts of organometallic compounds (Majid et al., 2000a). The presence of IOM was also directly related to the poor processability and degree of aging of oil sand ores (Ignasiak et al., 1985). It was proposed that oxygen

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functional groups were incorporated into the chemical structure of bitumen, converting hydrophobic hydrocarbons into more hydrophilic humic-like substances (Charrie-Duhaut et al., 2000).

Humic acids are the most widespread natural anionic polyelectrolytes in all terrestrial and aquatic environments (Terashimaa et al., 2004). They originate from degradation of plant polymers. An important characteristic of humic acids extracted from oil sands ores is their similarity to humic acids extracted from higher rank coals (Kotlyar et al., 1988; Majid and Ripmeester, 1990; Majid et al., 1991; Majid et al., 1992; Kotlyar et al., 1990).

Lowenhaupt and Gray (1980) developed the alkali-extraction test to assess the degree of oxidation/weathering of metallurgical coal. In this now standard test (ASTM-D5263-93), a given amount of pulverized coal is boiled in a concentrated solution of NaOH so that the weathered coal partly dissolves releasing humic matter into solution. Depending on the concentration of humic substances in the resulting alkali extract, which is proportional to the degree of coal oxidation and conversion to humic acids, the extracted solution acquires a yellow to dark brown color whose intensity is measured spectrophotometrically at a wavelength of 520 nm. Thus, the degree of oxidation of the treated sample can be quantified.

In Part I of this paper, the response of different types of oil sand ores to the alkali extraction test is investigated in order to detect and quantify the amount of humic acids in oil sand ores. Additional work was also done in order to demonstrate the effect of humic acids on the wettability of bitumen.

2. Material and methods

2.1. Samples and reagents

Eight oil sand ores of varying quality were supplied by Canadian Natural Resources Ltd. Table 1 shows the composition of the ores in terms of bitumen, water, solids and fines contents (Dean–Stark analysis—Bulmer and Starr, 1979). As can be seen from the wide range of bitumen concentrations and fines contents covered by these samples, the quality of these ores varies widely, including good and poor processing ores. All the oil sand ores were stored in freezers at approximately -4°C to minimize any effects of weathering.

The particle size distribution of the solids from the ores, and the content of fines in the solids, was determined with the use of a Malvern Mastersizer 2000, a laser scattering system. The data reported in Table 1 show that ores 6, 7 and 8 have bitumen contents lower than 8 wt.% and high concentrations of fines ($<44\ \mu\text{m}$) in the sand fraction. Consequently low bitumen recovery values are expected from these types of ores. Although ores 2, 3, 4, and 5 display bitumen contents above 9 wt.%, the concentration of fines in the sand fraction is for all of them larger than 20 vol.% (cut off value for defining an ore as poor or good), so average-low bitumen recovery values are expected from these ores.

Sodium hydroxide (NaOH) was used to prepare 1 M NaOH solutions for the alkali extraction tests. A sodium salt of humic acid obtained from Aldrich Chemicals was used to prepare humic acid solutions of varying

concentrations. Vermeer (1996) reported the elemental composition of Aldrich humic acids (Aldrich HA) as: 55.8% C, 38.9% O, 4.6% H; 0.6% N, and an average molecular weight of 21,000 Da. For contact angle measurements, bitumen samples were obtained from ore 1 by repeated extraction (flotation) using warm water at natural pH so no sodium hydroxide or other reagents were added.

2.2. Procedures

Alkali extraction tests were done on all eight oil sands ores, adapting the procedure developed by Lowenhaupt and Gray (1980) for bituminous coal. The procedure involved mixing a given amount of ore sample with 100 mL of 1 M NaOH solution in a 250 mL beaker. The amounts of ore samples used in the tests were chosen such that the amount of bitumen in the samples was always 1 g. The beaker was placed on a hot plate and heated until boiling. The suspension was kept under boiling conditions for 3 min, and then the beaker was removed from the hot plate and allowed to cool for 0.5 h under a fume hood. The mass of water that was evaporated during the test was accounted for by weighing the beaker with the slurry before and after the test. This mass difference was made up with fresh water in order to maintain the same volume of solution in all the tests. The resulting mixtures were centrifuged and filtered to obtain clear solutions containing the alkali-extracted components released from the samples. The extracts were analyzed in a Cary 50 Scan UV–Visible (Varian) spectrophotometer using a cell with a 1-cm optical path length to collect UV–Visible spectra from which the absorbance at 520 nm (Abs520) could be obtained. All the solutions were also analyzed for the total organic carbon content (TOC) in a Shimadzu TOC-V_{CPH} Total Organic Carbon Analyzer. TOC measurements required some additional precautions. All the samples were first diluted to reduce the concentration of residual NaOH, and afterwards acidified to pH 2 so that the inorganic carbon present in these samples (primarily as carbonates) was driven off as carbon dioxide before TOC analysis.

Contact angle measurements were performed on bitumen samples using the captive bubble technique in a FTA 1000 Drop Shape Instrument. The procedure started by attaching an air bubble with a volume of 5 μL to a layer of bitumen coated on a glass slide. Coating of glass slides with bitumen was carried out using a SCS 6800 spin coater rotating at 2000 rpm. In order to produce a smooth coating, pure bitumen was first heated to reduce viscosity, and then spread on the glass slide which was then rotated at high speeds in the spin coater. After attaching the small bubble to bitumen, images of the variation of the bubble shape with time were recorded for a period of 7 min. Then the contact angles were analyzed using the FTA software. The baseline along the contact line between the air bubble and bitumen, and the curvature of the air bubble are first defined. Then, the software computes the contact angle as the angle between the line tangent to the bubble curvature at the point of three-phase contact.

Fourier transform infrared spectroscopy (FTIR) spectra were collected for all eight oil sands ores, as well as on samples of bitumen prepared under different conditions. These measurements were done in a Perkin-Elmer Spectrum 100 FTIR (Fourier Transform Infrared) Spectrometer using a diamond-coated KRS5 crystal operated in the Attenuated Total Reflection (ATR) mode.

3. Results and discussion

3.1. Applicability of the alkali extraction tests to oil sand ores

The alkali extraction test relies on the fact that oxidation of bituminous coal leads to a gradual enrichment of the coal surfaces in humic matter containing various types of oxygen functional groups, most of which are of acidic nature (carboxylic, phenolic, etc.). When exposed to strong alkaline solutions, these products of oxidation dissolve in solution giving it a characteristic yellow-brown color. The intensity of

Table 1
Characterization of the tested oil sand ores.

	Bitumen (wt.%)	Water (wt.%)	Solids (wt.%)	Solids	
				$<44\ \mu\text{m}$ (vol.%)	$<3\ \mu\text{m}$ (vol.%)
Ore 1	15.0	1.0	84.0	7.0	1.3
Ore 2	10.7	3.6	84.8	26.4	5.6
Ore 3	10.6	3.0	85.7	41.5	7.9
Ore 4	9.2	4.6	86.2	58.3	14.8
Ore 5	9.4	3.9	86.1	35.1	6.3
Ore 6	6.4	4.3	89.3	32.6	6.9
Ore 7	5.9	4.7	88.9	55.2	8.7
Ore 8	3.6	8.2	88.2	69.2	12.7

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