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Majid, Abdul; Argue, Steve; Kargina, Irina; Boyko, Victor; Pleizier, Gerry; Tunney, Jim

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Isolation and characterization of amorphous solids from oil sands fine tailings

Abdul Majid, Steve Argue, Irina Kargina, Victor Boyko, Gerry Pleizier and Jim Tunney

Institute for Chemical Process and Environmental Chemistry, National Research Council of Canada,
Ottawa, Ontario K1A 0R9, Canada

The hot water process used by Suncor and Syncrude to extract bitumen from the Athabasca oil sands produces tailings with about 35 % more volume than that occupied by the bituminous sands before mining. This increase is largely the result of water hold-up in the fines fraction from the tailings, arising primarily from the 'middlings' treatment circuit. Our recent work suggests that approximately 50% of these fines consist of amorphous clays. In this investigation we have developed fractionation methodology to separate amorphous solids from Syncrude fine tailings. This fraction has been characterized by elemental analysis, X-ray diffraction, XPS, SEM, infrared spectroscopy, and surface area measurement.

1. INTRODUCTION

Oil from Alberta oil sands is currently being separated using the Clark Hot Water Process. This results in the production of large volumes of fluid wastes called fine tailings [1,2]. Fine tailings are made up of a complex system of clays, minerals, and organics. They show little tendency to dewater, even when subjected to mechanical dewatering procedures [3]. These clay tailings are acutely toxic to aquatic organisms and are currently being stored in large tailings ponds. The buildup of these partially settled clay tailings presents not only an environment problem but also a significant repository for non-recyclable water which eventually must be reclaimed.

The reason for the intractability of the clay tailings has been a subject of considerable study [4-7]. Based on the results of published work it is generally believed that a combination of residual organics and fine clay particles contribute to the stability of fine tailings. The high water holding capacity of fine tailings has been attributed to the presence of amorphous minerals such as iron oxide and clays [8].

Our group at NRC has been actively involved in research dealing with various aspects of fine tailings [5-7, 9-15]. As a result we have developed a number of fractionation schemes to separate fine tailings into various components. In this investigation we have developed a fractionation methodology to separate amorphous solids from Syncrude fine tailings. This fraction has been characterized by elemental analysis, X-ray diffraction, XPS, infrared spectroscopy, and surface area measurement.

2. MATERIALS AND METHODS

2.1. Materials

Aqueous tailings samples, used in this investigation were obtained from the 17 m level of the Syncrude tailings pond. The physicochemical properties and handling procedures for these samples have been reported previously [7]. The recovery of amorphous solids was carried out from a fine tailings

sample as received, a clean sample of fine tailings after removing bitumen and hydrophobic solids and a sample of suspension fraction from clean fine tailings.

Tiron (4,5-dihydroxy-1,3-benzene-disulphonic acid disodium salt) was obtained from Sigma Chemicals Inc. It was used as 0.1 M-aqueous solution containing 5.3 g of anhydrous sodium carbonate. The final pH of the solution was adjusted to 10.5 with sodium hydroxide. The solution was kept in a polypropylene bottle and stored in a refrigerator for a maximum of one month. The solution pH dropped during storage and was adjusted to 10.5 before use.

All other reagents were obtained from Aldrich and used as received.

2.2. Measurements

PAS-FTIR (photoacoustic Fourier Transform Infrared Spectroscopy) spectra were collected using a MTEC Model 300 photoacoustic detector combined to a Bruker IFS 66/S FTIR spectrometer. 500 scans were collected at a resolution of 8 cm^{-1} in the rapid scan mode. 64 scans of Carbon black were used as reference and helium was the purge gas.

XPS was performed with a Physical Electronics (Perkin Elmer, Eden Prairie, MN, USA) model 550 instrument. Monochromatic Al K α radiation was used. The dry samples were pressed into indium foil for analysis. Survey spectra were collected using pass energies of 188 eV, while high resolution spectra were recorded with a 22 eV pass energy. An electron flood gun was used to neutralize the charge during the experiment. Binding energies were referenced to the carbon-carbon bond, which was assigned a binding energy of 284.6 eV. Atomic compositions were estimated using a standard program provided with the instrument. During analysis, the pressure inside the instrument was always below 5×10^{-9} torr ($<0.7\text{ }\mu\text{Pa}$).

Specific surface areas, pore volumes and pore size distributions were determined using a Micromeritics Gemini III 2375 apparatus. The density of the materials was determined by a pycnometry measurement with helium using Micromeritics Accupyc 1330 apparatus. Heavy metals were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

Cation exchange capacity (CEC) was measured using the BaCl_2 method [16].

X-ray powder diffraction data were collected between $2\theta = 5^\circ - 100^\circ$ with a scan rate of $2^\circ/\text{min}$ at room temperature on Scintag XDS 2000 with a theta-theta geometry and a copper X-ray tube. The diffractometer had a pyrolytic graphite monochromator in front of the detector. The samples were mounted on a zero background sample holder made of an oriented silicon wafer.

2.3. Procedures

Removal of residual bitumen and hydrophobic solids from fine tailings was carried out using a procedure reported previously [7]. For the separation of amorphous solids a typical procedure involved mixing an aqueous sample of fine tailings or centrifuged suspension (300g) with 0.1 M-alkaline Tiron solution (100 mL) in a 500 mL polypropylene bottle. The contents were agitated in an end-over-end fashion for seven days at 30 ± 2 rpm. The treated sample was centrifuged at 500 G for 15 minutes to separate a clear dark black solution from the coarser solids. The sediment was mixed with deionized water (100 mL) and centrifuged again to separate residual Tiron extract adsorbed on the surface of the coarser solids. The washing of the coarser solids was repeated two more times in order to obtain cleaner solids. All washings were combined with the Tiron extract from the first step.

The separation of amorphous solids from Tiron extract was carried out by precipitation with a mineral acid (HCl). A typical treatment involved acidification of the extract to pH ~1, when the amorphous solids precipitated as a gel, releasing free water. The contents were centrifuged and the wet sediment washed several times with distilled water. Finally, the wet cake containing the amorphous solids was dried at 80 °C under vacuum.

3. RESULTS AND DISCUSSION

The high water holding capacity of fine tailings has been attributed to the presence of clays and amorphous minerals of silicon, aluminum and iron [8]. The amorphous oxides may be cementing the clay particles. The removal of this coating by treatment with alkaline Tiron solution has been attempted. This treatment is known to remove the finely divided amorphous oxides of iron, aluminum and silicon [17].

Table 1 lists sample description, yield and carbon content of various samples of amorphous solids separated in this investigation. Compared with the sample of bulk fine tailings, Tiron extracted the highest amount of solids from the suspension fraction. Approximately 50 percent of the colloidal solids suspended in the suspension fraction appear to be amorphous. This supports Yong and Sethi's assertion [8] that fine amorphous colloidal solids contribute significantly to the stability of fine tailings. High levels of organic carbon indicate that there is a very important interaction between the organic and inorganic materials in these systems. Hydrous oxides are known to provide more sites for organic matter adsorption in soils than the surfaces of micaceous clay minerals [18]. Amorphous oxides are exceptionally stable in the presence of humified organic matter [19].

Table 1. Sample description and yield for tiron extracts

Fraction	Description	Yield (w/w% of solids)*	LOI at 500°C (w/w%)	Organic carbon (w/w%)
1	Tiron extract from tailings as received	3.6 (26.5)	29.8	16.3
2	Tiron extract from clean tailings	3.9 (34.0)	20.5	14.4
3	Tiron extract from suspension	52 (8.2)	34.5	16.8
4	Tiron extracted residual solids	91 (34.0)	4.1	1.5

* Amount of total solids in the feed is shown in parenthesis, LOI=Loss on ignition

Table 2. Physico-chemical characteristics of tiron extracts

Fraction	Density (g/cm ³)	Surface Area (m ² /g)	CEC Cmol[+]/Kg ⁻¹	Average pore size (Å)	Elemental Analysis (w/w%)			SiO ₂ :Al ₂ O ₃ Ratio
					Si	Al	Fe	
1	2.61	98	16.1	6.6	28	17	2.8	1.6
2	2.60	105	17.9	6.2	26	16	4.8	1.6
3	2.58	103	19.3	5.7	25	16	3.9	1.5
4	2.83	10.6	7.4	70	35	9.4	1.1	2.0

CEC= Cation Exchange Capacity

Table 2 lists elemental analyses and physico-chemical properties of the solid fractions. The three samples of Tiron extracts had remarkably similar characteristics indicating a homogeneous nature of these materials in the fine tailings. The density of the Tiron extracts (2.6 ± 0.02) is in the range for kaolinite, halloysite, quartz, allophanes and imogolite [20, 21]. This suggests that these solids may have a structural arrangement comparable with these materials. Surface area and pore size determine the accessibility to active sites and this is often related to catalytic activity and selectivity in catalyzed reactions. These materials have high specific surface areas that approach the values reported for silica-alumina gels [22]. Cation exchange capacity (CEC) values of the amorphous solids are higher than those reported for kaolinite minerals but within the range for halloysites [23]. Relatively low cost and micropores of the amorphous solids separated from fine tailings render these materials as excellent candidates for potential applications in heterogeneous catalysis [24]. Micropores control shape selectivity and molecular exclusion which contribute most extensively to the total surface area and often host the majority of active sites. Elemental content of these solids suggests the presence of 3-5% iron supporting Yong and Sethi's hypothesis regarding the role of iron in the stability of fine tailings [8]. The value of silica to alumina ratios in these solids supports the presence of high silica allophanes [25].

The residual solids after Tiron extraction had considerably lower surface area and CEC, but higher density and pore sizes. These solids had higher silica content and lower amounts of aluminum and iron. Silica to alumina ratio of 2 for these solids suggests structural similarity with kaolinite.

3.1. X-Ray Diffraction

The X-ray diffraction pattern of the Tiron extracts contained very broad peaks indicating the amorphous nature of the solids. Table 3 lists d-spacings and tentative assignments based on the comparison with the XRD patterns of the standards. The strongest peak overlaps with pattern for allophanes, amorphous silica, halloysites and muscovite suggesting that these materials may consist of a mixture of several components present in different proportions. Other peaks correspond to the standard X-ray diffraction patterns of halloysite and muscovite. Thus XRD pattern for the Tiron extracts indicates the presence of halloysites, muscovite and possibly allophanes and amorphous silica.

The X-ray diffraction pattern of the residual solids after Tiron extraction contained sharp peaks which is consistent with the presence of crystalline materials. The comparison of the XRD pattern for these solids with the standards suggests the presence of quartz as a major mineral. Minor amounts of other minerals identified from XRD include: kaolinite, muscovite, corundum and calcite. These results suggest that the treatment of oil sands fine tailings with alkaline Tiron solution can effectively separate amorphous components from crystalline components.

Table 3. XRD data (d spacings, Å) for tiron extracts and some standards*

Tiron Extracts	Halloysite	Muscovite	Allophane	Amorphous silica
9.93 (58)	10 (100)	9.97 (100)	-	-
5.0 (38)	-	5.0 (65)	-	-
4.42 (69)	4.46 (70)	-	-	-
3.36 (100)	3.35 (40)	3.31 (100)	3.30 (100)	3.52 (100)
2.54 (55)	2.54 (35)	-	-	-
1.98 (28)	-	2.0 (45)	-	-
1.43 (37)	1.48 (30)	-	-	-

* Relative intensities in parenthesis

3.2. Infra-red Spectroscopy

Many difficulties arise in the determination of the physical and chemical characteristics of amorphous materials. By their very nature amorphous substances are difficult to detect and estimate, and frequently their presence is determined by implication rather than by direct measurement. The principal forms of amorphous inorganic materials which occur in soils are the oxides, or more usually, the hydrous oxides of iron, aluminum, manganese, or silicon, either separately or combined. X-ray diffraction data has suggested the presence of allophanes, amorphous silica, halloysites and muscovite. Identification of these minerals from infrared spectrum is difficult because of other overlapping absorptions.

The Infrared spectra of Tiron extracts contained a very broad and strong absorption in the OH region centered around 3400 cm^{-1} . Absorption in this region is characteristic of amorphous aluminosilicate like allophane and amorphous oxides [26]. The presence of an amorphous silicious component is indicated by the silicate stretching area between 1110 and 900 cm^{-1} , where a strong and broad absorption is present in the infrared spectrum of Tiron extract [27]. Muscovite and halloysites also absorb in this region but cannot be distinguished from silicious materials.

The infrared spectra of the residual solids after Tiron extraction contained characteristic absorptions for kaolinite, quartz and calcite which is consistent with XRD results [28].

3.3. Surface Analysis

Table 4 lists a summary of XPS data for both Tiron extracts and the Tiron extracted residual solids. XPS provides information on the top 10 nm of the surface. Silicon, aluminum and carbon were detected on the surface of both solids suggesting that these elements may be an integral part of the mineral structure. The presence of significant amounts of carbon in this environment could be an indication for the existence of clay-organic complexes in these materials. Tiron extracts appear to contain a thin layer of iron strengthening the Yong and Sethi's concept regarding the association of amorphous aluminosilicates with iron oxide which acts as a cementing agent. The Tiron extracted residual solids did not show any iron on the surface.

Table 4. Elemental Concentrations by XPS

Element	Concentrations (atomic %)	
	Tiron Extract	Tiron Extracted Solids
Si	18	14
Al	12	9
Fe	1	-
C	24	20
Si:Al ratio	1.5	1.6

4. CONCLUSION

Nano-particles of clay present in oil sands fine tailings are coated with a matrix consisting of natural organic matter and hydrous metal oxides of iron, aluminum and silicon. This coating can be effectively removed by dissolution in alkaline Tiron solution. Tiron solution also dissolves substantial amounts of allophanes and micas with trace amounts of crystalline clays such as kaolinite and quartz. These findings support the Yong and Sethi theory regarding the stability of fine tailings.

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