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Isolation, characterization and modification of clay solids from oil sand wastes

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For the past several years, we have been exploring the possibility of using oil sand industry wastes, such as: coke, fly ash and fine tailings as resource materials for several potentially marketable products. In this investigation we have developed a technically feasible fractionation methodology to separate clay solids from oil sands coke fly ash for potential use as polymer reinforcements after surface modification. The separated clay fraction has been characterized by elemental analysis, X-ray diffraction, XPS, SEM, infrared spectroscopy, and surface area measurements.

1. INTRODUCTION

The production of refinery grade oil from the Alberta oil sands deposits as currently practiced by Syncrude and Suncor, generates a substantial amount of waste including, coke, fly ash, coarse sand and fine tailings [1]. Under current production conditions, a plant producing 15,900 m³/day (100,000 bbl/day) of synthetic crude oil requires the processing of 100,000 m³/day ore which results in a tailings stream consisting of 100,000 m³ of coarse sand, 2,000 m³ of coke, 100 m³ of fly ash and 20,000 m³ of Mature Fine Tailings (30% solids) [2]. As a result, large inventories of process-affected materials are accumulating. The major concern regarding these wastes is a question of the volumes involved. The reduction in the volume of the produced wastes by recycling would be economically and environmentally desirable.

For the past several years, we have been developing separation techniques for the recovery of by-products from oil sands industry wastes [3-10]. The principal objective of this work has been to develop technically feasible separation techniques for potentially marketable products. In this investigation we have developed a fractionation methodology to separate clay solids from oil sands coke fly ash for potential use as polymer reinforcements after surface modification. The separated clay fraction has been characterized by elemental analysis, X-ray diffraction, XPS, SEM, infrared spectroscopy, and surface area measurement.

2. MATERIALS AND METHODS

2.1. Materials

A sample of coke fly ash, used in this investigation was from Syncrude and had been characterized previously [11]. 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 [10].

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 ($<0.66\text{ }\mu\text{Pa}$).

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 pycnometry measurement with helium using Micromeritics Accupyc 1330 apparatus. Heavy metals were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

X-ray powder diffraction data were collected between $2\theta = 10^\circ - 70^\circ$ 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.

Scanning electron micrographs were recorded for clay thin films deposited on silicon substrate by dip coating technique using a Hitachi Field Emission Scanning Electron Microscope (SEM) Model S-4800 fitted with an Oxford Inca Energy Dispersive Spectrometer (EDS) used for elemental analysis. It was operated at 1.2keV electron volts and a current of 10 μA . The working distance was 8 mm. Before coating, the substrate was cleaned and dried as follows: Si wafers were sonicated in CCl_4 for 15 minutes and rinsed with 2-propanol and water. They were then sonicated in a hot piranha solution of conc. H_2SO_4 and 30% H_2O_2 (3:1) for 30 min to remove any organic matter, and rinsed with copious amount of water followed by cleaning ultrasonically in acetone for 5 min and then in methanol for 10 min prior to coating [12].

Particle size determination was carried out using Malvern Zetasizer Model 3000HS. The samples were dispersed in 1% aqueous solution of Na_3PO_4 .

2.3. Procedures

2.3.1. Removal of carbonaceous material

A low temperature ashing procedure developed previously [13] was used to remove carbonaceous material from fly ash. The fly ash sample ($\sim 100\text{ g}$) was weighed into a pre-weighed porcelain dish and placed in a well ventilated muffle furnace at $400 \pm 10^\circ\text{C}$. The sample was removed from the furnace after 24 hrs and allowed to cool to room temperature. It was then weighed. The procedure was repeated until the weight did not change. This took approximately five days. This sample was designated as ashed FA.

2.3.2. Removal of water soluble

A sample of ashed FA was sonicated for one hour in water to separate water soluble material. The procedure was repeated until no more material was designated as water in.

2.3.3. Leaching of heavy metals

In general, 10 grams of ashed FA was leached with 100 mL of 0.1 M HCl while still in the 1000 x g centrifuge. The supernatant was designated as acid leachate. On completion of leaching, the residue was designated as acid residue. The hydrochloric acid leachate and subsequent acid residue was designated as acid residue.

2.3.4. Surface modification

A sample of ashed FA was leached with 100 mL of 0.1 M HCl and centrifuged. The residue was designated as acid residue. The acid residue was then treated with 100 mL of 0.1 M HCl for 24 hrs using a 1000 x g centrifuge. The supernatant was designated as acid leachate. The residue was designated as acid residue. The acid residue was then treated with 100 mL of 0.1 M HCl for 24 hrs using a 1000 x g centrifuge. The supernatant was designated as acid leachate. The residue was designated as acid residue. The acid residue was then treated with 100 mL of 0.1 M HCl for 24 hrs using a 1000 x g centrifuge. The supernatant was designated as acid leachate. The residue was designated as acid residue.

RESULTS AND DISCUSSION

Effectiveness of leaching

Table 1 lists analytical results for the acid leachate and acid residue. Both SiO_2 and Al_2O_3 were detected.

The effect of acid

Sample	Si
FA	13.1
ashed FA	17.9
acid leachate	
acid residue	

2.3.2. Removal of water solubles

A sample of ashed FA (20 g) was dispersed in 250 mL of deionized water and the contents sonicated for one hr. The contents from this treatment were centrifuged at 1000 x g for 30 min to separate water insoluble solids from solution. The residue was dried at 120°C and weighed. The procedure was repeated until the weight did not change. These solids were designated as water insoluble FA.

2.3.3. Leaching of heavy metals

In general, 10 grams of water insoluble FA were agitated at 70°C for two hrs with 250 mL of ~6 M HCl while stirring using a magnetic stirring bar. The contents were cooled and centrifuged at 1000 x g for 30 minutes to separate the solid residue. The residue was dispersed in warm deionized water and centrifuged. The washing procedure was repeated until the supernatant was free of chlorides (absence of white precipitate on the addition of AgNO₃ solution). On completion of the washing, the residue was transferred to the beaker and agitated with concentrated HCl to dryness. About 200 mL of warm deionized water was added to the hydrochloric acid treated sample and after proper mixing the procedure for centrifugation and subsequent washing of the residue as described above was repeated. The chloride free residue was finally washed with isopropanol and dried at 120°C under vacuum. This was designated as acid washed FA.

2.3.4. Surface modification of acid washed FA

A sample of acid washed FA (1g) was suspended in a 0.1 molar cetyltrimethylammonium bromide (CTAB) solution in ethanol and stirred at 70°C for 6 hrs. It was then centrifuged and washed twice with ethanol before drying at 120°C under vacuum. The dried residue was dispersed in 50 mL solution of tetraethoxy silane (TEOS) and methyltriethoxysilane (MTS) in a molar ratio of 0.47:0.53. The contents were agitated at 90°C for 24 hrs using a magnetic stirring bar. The suspension was then cooled to room temperature and centrifuged. The residue was dried under vacuum at 70°C. The dried residue was stirred in 0.1 M HCl in ethanol for 24 hrs at 70°C. It was cooled to room temperature followed by centrifugation. The residue was washed with water followed by ethanol and finally dried at 70°C under vacuum. The product was designated as modified FA.

3. RESULTS AND DISCUSSION

3.1. Effectiveness of leaching process

Table 1 lists analytical results for the fly ash samples before and after acid leaching. Acid treatment resulted in complete leaching of S and V and varying amounts of Al, Fe, Mg, Ca, and K. Both SiO₂ and Ti were enriched.

Table 1. The effect of acid leaching on elemental compositions

Sample	Elemental composition, w/w%									
	Si	Al	Fe	Mg	Ti	Ca	Na	K	S	V
Ashed FA	13.1	9.3	2.3	0.49	0.39	0.55	0.61	0.94	4.1	0.48
Acid washed FA	17.9	5.0	0.27	0.21	0.90	0.36	0.50	0.22	ND	ND

ND= Not detected

ions. The values for a
for comparison purposes
y of the resulting solids
for typical clay minerals
za of these samples also
area and grain size of the
for surface modification
ite render these materials
atalyst support.

smaller than the original
d water and acid soluble
mineral particles. This
Smaller particle size in
ls as ideal candidates for
ocomposites [16]. The
em compatible with the
sts higher silica content

Av. particle size (nm)	SiO ₂ -Al ₂ O ₃
1.4 μ m	3.3
11.6 μ m	2.1
1.1 μ m	1.6
400	1.8
320	4.0
170	4.0
330	6.0

sh samples after various
reated and ashed sample
, after acid leaching only
peaks in the XRD pattern
ace modification. The X-
z is the major component
3].

Fig. 1. XRD patterns of Syncrude Fly ash

3.3. Infra-red Spectroscopy

Fig. 2 compares the PAS-FTIR spectra of acid leached and surface modified fly ash samples. The spectra showed strong and broad bands at ~ 1100 cm^{-1} attributed to the symmetrical stretching of siloxane groups [19]. The spectra of both samples show bands in the region $470\text{--}800$ cm^{-1} due to Si-O-Si linkages [20]. The Strong absorption in the $1500\text{--}1650$ cm^{-1} region in the spectrum for acid leached samples suggests higher amounts of adsorbed water compared with the surface modified sample that had only a broad and weak band in this region [21]. The presence of adsorbed water in the acid leached sample is further supported from a broad absorption centered around 3300 cm^{-1} in its IR spectrum. The absorption bands due to silanol hydroxyl groups in the $3650\text{--}3800$ cm^{-1} range are much stronger for the surface modified sample compared with the acid leached sample.

3.4. Surface Analysis

The survey spectrum of fly ash samples showed Al, Si, K, Na, Mg, Ti, Ca, C and O in all samples. Iron and vanadium were only detected in the untreated and ashed samples. XPS provides information on the top 10 nm of the surface. Carbon was detected in all samples by XPS and only in the untreated sample by Leco combustion analyses. This suggests that other than untreated sample carbon is present only on the surface. This may have been because of the adsorption from atmosphere.

3.5. Scanning electron micrography

Fig. 3 shows a scanning electron micrograph (SEM) of acid leached Syncrude fly ash sample. It was found to be present as large clusters of irregular plates of varying sizes and a few needle like particles. The SEM clearly shows planar clay flake platelets aggregated in a layered form.

At higher magnification the agglomeration of individual particles are also visible.

Fig. 2. PAS-FTIR spectra of Syncrude fly ash samples

Fig. 3. SEM photograph of acid leached FA

4. CONCLUSION

A technically feasible fractionation scheme has been developed for the separation of clay minerals from oil sands coke fly ash. The separated clay solids have high surface area and are in the nanometer size range. SEM micrographs suggest these solids to be planar clay flakes platlets aggregated in a layered form. These characteristics make these solids as potential candidates for applications as polymer reinforcements after surface modification.

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