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

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**Institutions:** National Research Council

**Published on:** 01 Jan 2005 - Studies in Surface Science and Catalysis (Elsevier)

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#### **Publisher's version / Version de l'éditeur:**

*Studies in Surface Science and Catalysis*, 156, pp. 343-348, 2005

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# 155

## 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 15,900m<sup>3</sup>/day (100,000 bbl/day) of synthetic crude oil requires the processing of 100,000 m<sup>3</sup>/day ore which results in a tailings stream consisting of 100,000 m<sup>3</sup> of coarse sand, 2,000 m<sup>3</sup> of coke, 100 m<sup>3</sup> of fly ash and 20,000 m<sup>3</sup> 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.



### 2.3.2. 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 AgNO<sub>3</sub> 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 SiO<sub>2</sub> 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

Table 2 lists physico-chemical properties of the clay fractions. The values for a commercial sample of bentonite from Aldrich have been included for comparison purposes. The successive treatments of the fly ash results in increased density of the resulting solids. The density of the acid leached samples ( $2.6 \pm 0.02$ ) is in the range for typical clay minerals such as kaolinite and bentonite [14, 15]. The specific surface area of these samples also increases considerably with each treatment. However, the surface area and grain size of the sample remains unaffected by the treatment of acid leached sample for surface modification. Relatively low cost and surface area higher than commercial bentonite render these materials as excellent candidates for potential applications in catalysis and/or catalyst support.

The particle size of the separated clay solids is significantly smaller than the original fly ash samples well as bentonite. Removal of unburnt carbon and water and acid soluble constituents of fly ash may have resulted in the deaggregation of mineral particles. This explains the particle size reduction of the separated clay solids. Smaller particle size in combination with large specific surface area render these clay solids as ideal candidates for applications as inorganic fillers for clay-reinforced polymer nanocomposites [16]. The surface modification of these solids was attempted to render them compatible with the hydrophobic polymers. These results will be reported at a latter date.

The value of silica to alumina ratios in these solids suggests higher silica content compared to bentonite or kaolinite clays.

Table 2. Physico-chemical characteristics of clay samples

Sample ID	Yield	Density (g/cm <sup>3</sup> )	Surface Area (m <sup>2</sup> /g)	Av. Pore Dia (nm)	Av. particle size (nm)	SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
Bentonite	100	2.7	31.4	4.8	1.4 μm	3.3
Untreated FA	100	2.1	9.7	6.7	11.6 μm	2.1
Ashed FA	18.4	2.3	20.6	6.3	1.1 μm	1.6
H <sub>2</sub> O insoluble FA	16.9	2.5	59.6	5.8	400	1.8
Acid leached FA	13.2	2.6	75.8	3.4	320	4.0
Acid leached ball milled FA	13.0	2.6	140.1	3.6	170	4.0
Modified FA	ND	2.6	72.5	4.9	330	6.0

ND= Not determined

### 3.2. X-Ray Diffraction

Fig. 1 compares the XRD profiles of the Syncrude fly ash samples after various treatments. There is considerable broadening of the peaks for untreated and ashed sample suggesting the presence of amorphous components [17]. However, after acid leaching only the crystalline material remains as suggested from the sharpness of peaks in the XRD pattern. The crystalline nature of the clay material does not change after surface modification. The X-ray diffraction pattern of the fly ash samples also suggests that quartz is the major component of this material with small amounts of kaolinite, mullite and TiO<sub>2</sub> [18].



### 3.3. Infra-red Spectroscopy

Fig. 2 compares the FTIR spectra of the samples. The spectra show symmetrical stretching of Si-O-Si in the region 470-800 cm<sup>-1</sup> due to the dissolved water compared with the band in this region [21]. The supported from a broad absorption bands due to siloxane groups for the surface modification.

### 3.4. Surface Analysis

The survey spectrum of all samples. Iron and vanadium provides information on the XPS and only in the untreated and untreated sample carbon adsorption from atmosphere.

### 3.5. Scanning electron microscope

Fig. 3 shows a scanning electron microscope image of the sample. It was found to be porous needle-like particles. The particles were prepared from the acid leached fly ash.

At higher magnification





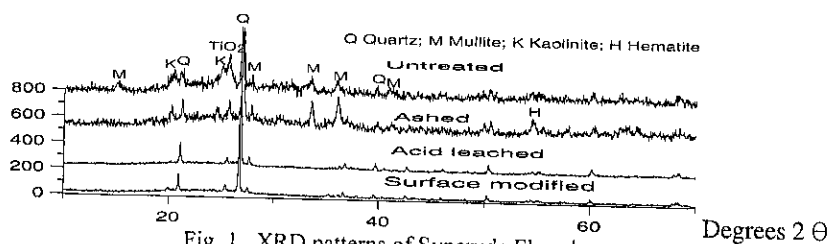


Fig. 1. XRD patterns of Syncrude Fly ash

### 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  $\sim 1100 \text{ cm}^{-1}$  attributed to the symmetrical stretching of siloxane groups [19]. The spectra of both samples show bands in the region  $470\text{--}800 \text{ cm}^{-1}$  due to Si-O-Si linkages [20]. The Strong absorption in the  $1500\text{--}1650 \text{ cm}^{-1}$  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  $3300 \text{ cm}^{-1}$  in its IR spectrum. The absorption bands due to silanol hydroxyl groups in the  $3650\text{--}3800 \text{ cm}^{-1}$  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.

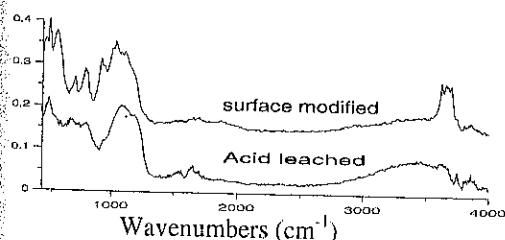


Fig. 2. PAS-FTIR spectra of Syncrude fly ash samples

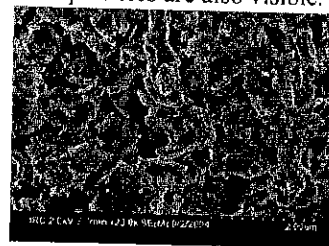


Fig. 3. SEM photograph of acid leached FA

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Av. particle size (nm)	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>
1.4 $\mu\text{m}$	3.3
11.6 $\mu\text{m}$	2.1
1.1 $\mu\text{m}$	1.6
400	1.8
320	4.0
170	4.0
330	6.0

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#### 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.

#### ACKNOWLEDGEMENT

The authors would like to express their appreciation to Dr. Farid Bensebaa and Dave Kingston for some technical assistance.

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Layered, porous, MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> systems formed by the variation of the synthesis parameters of a new procedure of synthesis.

#### 1. INTRODUCTION

Some zeolite synthesis (three dimensional) connect into the final zeolite structure. The synthesis of zeolite systems from two independent pillars throughout the structure of 0.7 μm and in similar synthesis may axis of broader peaks in benzene and 2,2-dimethyl transformation of the mesoporosity. The precursors intercalated with the separation. Calcination results inorganic pillars between the layers. TEOS, 5-5 nm and BET surface layers stay intact [10]. This can be pillared with other new modifications of Mg base properties [8,9]. Here Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> to prepare novel varieties application of a larger variety.