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Powder X-ray Diffraction Determination of Phyllosilicate Mass and Area versus Particle Thickness Distributions for Clays from the Athabasca Oil Sands

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Abstract: Bitumen recovery from Athabasca oil sands is known to be affected by the clay component. This effect increases dramatically with decreasing particle sizes of the constituent clay minerals. The present work comprises a mineralogical study of distinct size-fractions of clays from the Athabasca oil sands. Mass and area versus thickness distributions per unit weight of phyllosilicate-mineral component are obtained by Bertaut analysis of measured XRD peak profiles for the first 00 ℓ reflection. Distributions for both kaolinite and illite components from distinct size-fractions correlate with particle size. The powder pattern for the smallest size-fraction (<0.1 μm) is shown to correspond to delaminated illite particles.

Keywords: Athabasca oil sands, illite, kaolinite, oil sands bitumen recovery, particle thickness distributions, phyllosilicate clays, powder x-ray diffraction

INTRODUCTION

The Alberta oil sands deposits are the largest source of bitumen in the world, and about 10% is accessible by surface mining techniques. The resource is highly variable with respect to the sand-clay matrix and the distribution of bitumen within it. This variability makes it difficult to determine the effect that any individual component in the oil sands may have on bitumen extraction from the mined ore.

Natural oil sands are a complex mixture of sand, silt, clay, water, and bitumen. The water contained is largely present at the surface of mineral

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particles comprising the bulk ore phase. This water wetted condition allows bitumen to be extracted using water based separation processes, usually the conventional Hot Water Extrusion Process. The bitumen and the fines ($<44\ \mu\text{m}$ size fraction) contents have traditionally been used as primary measures of oil sands processability. Unfortunately, these indicators are not reliable in a significant number of cases. Recently, it has become clear that the clay-mineral component may affect the bitumen separation process (see Tu et al., 2005).

During processing of mined oil sands, mechanical dispersion forces cause mobilization, or liberation, of clays into the process water. If the concentrations of clays and flocculating cations in the primary separation vessel (PSV) reach a critical level, the clay flocs begin to interact with each other to form a structured system that exhibits non-segregating settling (Kotlyar et al., 1996, 1998a; Tu et al., 2005). Under these circumstances, PSV gelation (sludging) may occur; coarser mineral particles and bitumen are entrapped in the gel structure, and no bitumen froth is produced. The clay concentration required to reach this state decreases dramatically with clay particle size. Sludging phenomenon is also known to be the primary contributor to fine tails formation (Kotlyar et al., 1992; Ripmeester et al., 1993). As a result of this problem, large sedimentation ponds are needed to provide enough recycled water and fine tailings storage capacity. The toxicity, loss of bitumen, diluent naphtha, and process water are among the most serious problems associated with the buildup of these clay sludges (Camp, 1977).

The work presented here comprises a detailed study of the mineralogical characteristics of distinct particle size fractions of clays from the Athabasca oil sands. This knowledge is of great importance with respect to its link to the mechanism of gelation. An understanding of this mechanism should help proposing technical strategies for solving oil sand processing problems related to the presence of clays.

EXPERIMENTAL

Materials

Synchrude Canada Ltd. (Edmonton, Alberta) provided the barren oil sands (waste unit) sample studied. For the purpose of comparisons, a commercial kaolinite (Sigma Chemical Co., USA) sample was also analyzed.

Separation

To separate oil sand solids based on particle size, the procedure described in detail elsewhere (Tu et al., 2004) was used. The following five sam-

Table 1. Specific areas obtained from Bertaut analysis of kaolinite-001 and illite-002 XRD profiles for distinct size-fractions

Size-fraction	Mean particle sizes, ^a μm	Specific areas, m^2/g	
		Kaolinite	Illite
A	4.01	138	103
C	1.50	204	156
E	0.26	302	169
F	0.14	336	230
H	<0.1 ^b	—	~687 ^c

^aMean particle sizes were determined using an Horiba LA-920 Particle Size Distribution Analyzer (USA) based on Mie scattering.

^bThe particle size for this size-fraction was assessed by TEM.

^cSpecific area calculated assuming a fully-delaminated illite structure, as described in the text.

ples were obtained: A (125 g/1 min), C (450 g/25 min), E (450 g/1 hr), F (25,000 g/30 min), H (250,000 g/1 hr). The information in parentheses denotes the centrifugation conditions. All separations were performed at room temperature.

Particle Size Measurements

A Horiba LA-920 laser diffractometer particle size analyzer system was used to measure mean particle sizes for samples A, C, E, and F; in the case of sample H, the particle size was assessed by transmission electron microscopy (TEM) using a Philips model CM20 200 kV instrument (Netherlands) (see Table 1).

Powder X-ray Diffraction

X-ray powder patterns were collected for all samples with an automated Bruker AXS D8 system θ - θ powder diffractometer (Karlsruhe, Germany) equipped with parallel beam, double Göbel mirror optics, using $\text{CuK}\alpha$ radiation with a scintillation detector. Samples were deposited in a flat-surfaced semi-infinite filled-trough machined in a low-background single-crystal silicon wafer holder. The powder samples were deposited into the trough and gently pressed flat using a glass slide. Diffractograms were collected in a step-scanning mode from $5^\circ 2\theta$ to $100^\circ 2\theta$, with a step of $0.02^\circ 2\theta$, and a counting time of 12 sec per step. The sample holder was rotated at 10 RPM during data collection for all experiments.

METHODS

Bertaut Analysis of XRD Debye-Scherrer Reflection Profiles

Bertaut (1949, 1950) calls $h(m)$ the scaled Fourier transform of a given powder-diffraction peak profile in reciprocal units with origin at the center of the peak. The scaling simply ensures that $h(0) = 100$. He shows that $h(m)$ relates the relative diffracting mass, h , and the extension, m , of crystallites projected onto the diffraction vector. More precisely, $h(m)$ is the percent mass of crystallites with projected extension longer than m . With application to mostly metals and alloys with random crystallite shapes in mind, m is not a constant characterizing a given crystallite but one among a number of statistical descriptors of the crystallite shapes in the sample. In this perspective, Bertaut (1949, 1950) shows that various statistical descriptors of the crystallite size distribution can be extracted from $h(m)$ and its successive derivatives.

Derivation of Phyllosilicate Particle Thickness Distributions from 00ℓ Reflections

Bertaut's approach, merged with Warren and Averbach's (1950) approach, aimed at the extraction of strain in cold-worked alloys, has been applied to phyllosilicate clays before in the form of the "BWA technique" by, e.g., Drits, Eberl, and Środoń (1998) and references therein. The complex equations manipulated are mostly those of Warren and Averbach (1950) that aim at recovering a strain component from the profile, in addition to a mean thickness and thickness distribution. The BWA technique works wonders on artificial data and oriented patterns from well-characterized phyllosilicate samples, but is unnecessarily complex for the crude engineering problem at hand here.

In fact, Bertaut's $h(m)$ function is particularly simple to interpret and straightforward to implement in the case of 00ℓ reflections for phyllosilicate clays (Figure 1). Phyllosilicate clays have relatively easy cleavages in between their composite layers such that, practically, their thicknesses can only be integer multiples, k , of that composite-layer building block of thickness, t . In the case of 00ℓ reflections, the diffraction vector is perpendicular to the plane of such layers. The projection of crystallites onto the diffraction vector is then the thickness, $k \cdot t$, of such crystallites. In other words, the only values that Bertaut's m variable can now take are such $k \cdot t$ thicknesses. According to Bertaut's explanation, $h(k \cdot t)$ is the mass percentage of crystallites with thickness greater than $k \cdot t$. It follows that, in the case of phyllosilicate clays, the quantity $Q(k) = h(k \cdot t) - h([k + 1] \cdot t)$ is the mass percentage of crystallites made of exactly k composite layers. This result is algebraically straightforward to derive and simple to understand.

(a)

(b)

Figure 1. Side views showing the crystal structures of (a) kaolinite (Young and Hewat, 1988) and (b) illite (Gualtieri, 2000). The various symbols that are shown are described in the text.

With Cu $K\alpha$ radiation, the 00ℓ reflection corresponding to a single composite-layer thickness occurs for reciprocal length $R = 1/t$. For the structure of kaolinite (Figure 1a; Young and Hewat, 1988), where the composite layers comprise a tetrahedral sheet stacked over an octahedral sheet (1:1 layers), this peak is 001 and occurs at $\sim 12.34^\circ 2\theta$. In the illite structure (Figure 1b; Gualtieri, 2000), the crystallographic, c , repeat encompasses two composite layers, each made of an octahedral sheet sandwiched between two tetrahedral sheets (2:1 layers). The peak corresponding to a single 2:1 layer thickness is then 002 and happens around $9^\circ 2\theta$. Those two 2θ values are fortunately sufficiently separated to allow thickness assessment of both kaolinite and illite on a same sample, without overlap from non- 00ℓ reflections, all of which happen at larger 2θ angles.

Practically, the analysis then consists in the application of the Lorentz-polarization correction for the powder instrument to the measured diffraction profile and then transformation of 2θ angles to reciprocal lengths, R , via the relationship $R = 2 \cdot \sin(\theta)/\lambda$, where λ is the wavelength of the radiation being used. Deconvolution of the low-angle peak for the $K\alpha 1$ - $K\alpha 2$ wavelength separation was not deemed to be meaningful in view of the scan step used and actual peak width observed, and was accordingly not performed. After that, tail limits and peak center are interactively and graphically ascribed to the peak. Straight Fourier transformation of corrected intensities with origin at the peak center for values of m equal to multiples, k , of the composite-layer thickness, t , then gives $h(k \cdot t)$ after scaling to $h(0) = 100$. As explained above, the mass percentage of phyllosilicate crystallites made of exactly k layers is then $Q(k) = h(k \cdot t) - h([k + 1] \cdot t)$.

Derivation of Area versus Thickness Plots and of the Specific Area of the Sample

Derivation of the area versus thickness distribution is straightforward from the fact that, in first approximation, the area of phyllosilicate crystallites results from their extension perpendicular to c^* (Figure 1). The mass of a crystallite is the product of this area by the thickness, $k \cdot t$, and the density, ρ , of the material. As we know the mass versus k distribution, $Q(k)$, it follows that the unscaled area versus k distribution is then $A(k) \sim Q(k)/k$. The scaling of that plot can be derived from $A(1)$, the area of a known weight of a single composite layer of phyllosilicate clay mineral with known molecular weight. In the case of kaolinite (Figure 1a) with formula $\text{Al}_4(\text{OH})_8\text{Si}_4\text{O}_{10}$, with $Z = 1$ in a $P1$ cell with $a = 5.1490(0)$, $b = 8.9335(1)$, $c = 7.3844(1) \text{ \AA}$, $\alpha = 91.930(1)$, $\beta = 105.042(1)$, $\gamma = 89.791(1)^\circ$ (Young and Hewat, 1988), this means that a formula weight of 516.32 g/mol corresponds to an $a \times b$ mesh area of $46.00 \text{ \AA}^2$. Considering that the layer has two faces, further multiplication by Avogadro's number value of 6.022×10^{23} atoms/mole indicates that this formula weight has an

area of 554,000 m². This is 1,073 m²/g. For a C2/c illite with formula KAl₄Si₂O₁₀(OH)₂, $Z = 4$ in a monoclinic cell with $a = 5.2226(12)$, $b = 9.0183(23)$, $c = 20.143(5)$ Å, $\beta = 95.665(21)^\circ$ (Gualtieri, 2000), with two 2:1 layers along c (Figure 1b), this is 687 m²/g. Further extraction of the specific area of an individual phyllosilicate-mineral component is then obtained by specific area per unit mass of component = sum of scaled areas/sum of masses = $\sum_{k=1}^{k_{\max}} A(k) / \sum_{k=1}^{k_{\max}} Q(k) = \sum_{k=1}^{k_{\max}} A(k) / h(0)$ even in the presence of other constituents in the powder pattern.

We developed an interactive and graphical Windows software program called *ThickMud* that performs the above corrections to the profile and then the Bertaut analysis of the 00 ℓ peak profile corresponding to a single component, producing a Microsoft Excel file for $h(k \cdot t)$, $Q(k)$, and $A(k)$, as well as the specific area per unit mass of the given constituent in m²/g.

Interpretation of the XRD Pattern from Size-fraction H Using Debye Formula

Superficial comparison of the XRD pattern from fraction H with those from other size-fractions indicates that whatever the H material is, its powder pattern is present in the other fractions and is increasingly recognizable from fraction A to fraction H. By electron-microscopy methods, we previously showed that similarly ultra-centrifuged Athabasca oil sand clay samples, extracted either from mature fine tailings (Kotlyar et al. 1998a) or from bitumen (Kotlyar et al. 1998b), consisted of a phyllosilicate with 1-nm thickness and particle diameters in the range of 5–200 nm. With the 2:1 layer thickness of illites being 10 Å (Figure 1b), this corresponds to fully delaminated illite. We here attempted to verify this conclusion by calculating the x-ray scattering patterns of delaminated kaolinite and illite. Standard crystallographic structure-factor calculations are not easily amenable to calculation of the diffraction pattern of a material with periodicity in two directions and no periodicity at all in the third direction. We then employed Debye's formula for exact calculation of the x-ray scattering by a molecule (Debye, 1915), i.e., in simple terms, the Debye-Scherrer pattern of a finite, non-periodical object, as implemented in *Materials Toolkit* (Le Page and Rodgers 2005; <http://www.tothcanada.com/>). Figure 2 shows both the experimental powder pattern for size-fraction H and the delaminated illite and kaolinite patterns calculated, as indicated above with Debye's formula.

RESULTS AND DISCUSSION

Mineral Phase Constituents

Figures 3a–3f are logarithmic scale experimental intensity powder profiles from the four centrifuged samples on which we performed a Bertaut analysis.

Figure 2. Logarithmic scale experimental intensity powder profile measured for size-fraction H compared to the delaminated illite and kaolinite patterns calculated with Debye's formula. The calculations assumed a particle with 6-nm diameter and a thickness, t , comprising one composite layer.

Figure 3. Logarithmic scale experimental intensity powder profiles from the four centrifuged samples (size-fractions A, C, E, and F) on which we performed a Bertaut analysis.

Figure 3k is from a commercial kaolinite sample described above. Apart from the kaolinite and illite components that are seen all the way from size-fraction A to at least size-fraction F, sample A is dominated by the strong reflections of a quartz component that is seen in lesser quantity in fraction C, but turns out to be absent from fractions E, F, and H. We ascribed the minor peak at $14.1^\circ 2\theta$ in sample A to a small quantity of lepidocrocite that is also seen in C and a little bit in E, but is absent from fractions F and H. A small intensity peak attributed to a minor amount of K-feldspar was also noted at $27.4^\circ 2\theta$. The elimination of those phases after the first stages of centrifugation is consistent with their relatively isodimensional expected habit. We did not notice any other phases in substantial amounts; all observed peaks in any of the diffractograms measured for the different size-fractions could be indexed to belong either to quartz, kaolinite, or illite.

Mass versus Particle Thickness Distributions for Kaolinite and Illite

Figures 4a–4f are the mass versus particle thickness distributions for size-fractions with corresponding labels. The more-or-less sinusoidal behavior superposed with a smooth curve is a well-known artifact due to the necessary truncation of peak tails (Bertaut, 1952) because of overlap with either small peaks from other phases or with a strong tail due to greater abundance of other phyllosilicate-mineral components. In spite of the different location within the oil sands, the analogy with mean thickness assessed by transmission electron microscopy (Kotlyar et al. 1998a) is as good as could be expected. New and particularly striking information is the high mass abundance of very thin particles, even in samples with little centrifugation. If scaled in terms of crystallite frequencies, the thin particles that also have smaller diameters from electron microscopy would then overwhelm the countings.

Area versus Thickness Distributions for Kaolinite and Illite

As indicated by the formula $A(k) \sim Q(k)/k$, the distributions of areas versus thickness (Figure 5) for both illite and kaolinite in the sample stresses the outstanding contribution of ultrafines to the sample specific area with respect to thicker crystallites. The specific area of the constituent phyllosilicate mineral in the sample is reported in m^2/g in Table 1. It is quite high, even for samples with little centrifugation.

Identification of Nano-particulate Delaminated Illite Particles

The synchronism of ups-and-downs of the experimental and computed curves on Figure 2 leave little doubt about the correctness of the interpretation of this pattern as that of delaminated illite. The fit of the pattern with that of

Figure 4. Mass versus particle thickness distributions for size-fractions with corresponding labels. LHS = kaolinite; RHS = illite.

Figure 5. Area versus particle thickness distributions for size-fractions with corresponding labels. LHS = kaolinite; RHS = illite.

delaminated kaolinite had some features in common, like the sharp raise at $20^\circ 2\theta$, but other features were in clear departure from the experimental results. The fit with illite is reasonable but not fully perfect. We attribute this to the exact atomic structure at the surface of the crystallite. The simple model we used for calculations assumed full occupancy of all potassium sites on each side of the aluminosilicate 2:1 layer. This model is not entirely sensible, even for dry material. It is in fact quite possible that not all potassium atoms are present, or that oxygen atoms from water and hydroxyls cap the exterior surfaces of the particles in an attempt to compensate electrostatically for the missing next layer. A full structural study of this phase is outside the scope of the present contribution and was not attempted here.

Implications for the Bitumen Recovery Process

A clear distinction should of course be made between specific areas extracted above from Debye-Scherrer powder diffraction profiles, and specific areas obtained by, e.g., the BET gas adsorption technique (Brunauer et al., 1938). Diffraction methods are about Bragg domains while the BET method is about areas that can be reached by the adsorbing gas. There would be reasons why the two would differ. However, the method presented here is relatively straightforward to implement and rather unique in terms of the amazing wealth of statistical descriptors of the physical state of the component phyllosilicate clays it supplies from just a peak profile analysis. Differences with results from gas adsorption methods are of course expected, but it is worth pursuing this avenue in view of its greater simplicity.

In spite of the above cautionary statements, it is clear that, combined with the information from Figure 2 in Kotlyar et al. (1998b), the above thickness and specific area measurements (Figures 4–5, Table 1) stress the economic importance of the control of ultrafines for a fuller recovery of bitumen from the Athabasca oil sands.

CONCLUSIONS

We have shown above that the application of Bertaut's $h(m)$ function to the particular case of phyllosilicate clay particles from oil sands leads directly to a simple-to-grasp-and-implement approach that supplies quantitative mass versus thickness and area versus thickness distributions for the individual phyllosilicate-mineral components. From those, a value of the specific area in m^2/g can be derived for each phyllosilicate-mineral component comprised in the sample. We do not expect a numerical fit with physicochemical characterizations of the sample, but the simple existence of parallel trends between (1) bitumen recovery rates and (2) illite/kaolinite mass versus thickness and area versus thickness distributions, and resulting component specific areas

would be of extreme economic significance in the exploitation of Athabasca oil sands. Given the opportunity, we intend to extend the present study with a search for such trends.

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REFERENCES

- Bertaut, E. F. (1949). X-ray study of the distribution of crystallite dimensions in a crystalline powder [in French]. *Comptes Rendus Acad. Sci. Paris* 228:492–494.
- Bertaut, E. F. (1950). Debye-Scherrer lines and distributions of Bragg Domains in polycrystalline powders [in French]. *Acta Crystallogr.* 3:14–18.
- Bertaut, E. F. (1952). On the correction of the Fourier transform of a Debye-Scherrer line in the measurement of crystallite dimensions [in French]. *Acta Crystallogr.* 5:117–121.
- Brunauer, S., Emmett, P. H., and Teller, J. (1938). Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60:309–319.
- Camp, F. W. (1977). Processing Athabasca tar sand: Tailings disposal. Paper 9a, *Proceedings of the 26th Canadian Chemical Engineering Conference, Symposium on Tar Sand*, Toronto.,
- Debye, P. (1915). Scattering of X-rays and Quantum Theory [in German]. *Ann. Phys. (Leipzig)* 46:809–823.
- Drits, V. A., Eberl, D. D., and Srodon, J. (1998). XRD measurement of mean thickness, thickness distribution and strain for illite and illite-smectite crystallites by the Bertaut-Warren-Averbach technique. *Clays and Clay Minerals* 46:38–50.
- Gualtieri, A. F. (2000). Accuracy of XRPD QPA using the combined Rietveld-RIR method. *J. Appl. Crystallogr.* 33:267–278.
- Kotlyar, L., Sparks, B., and Schutte, R. (1996). Effect of salt concentration on the flocculation behavior of nano particles in oil sands fine tailings. *Clays and Clay Minerals* 44:121–131.
- Kotlyar, L. S., Sparks, B. D., and Capes, C. E. (1992). Gel forming attributes of colloidal solids from fine tails formed during extraction of bitumen from Athabasca oil sands by the hot water process. *AOSTRA J. Res.* 8:55–61.
- Kotlyar, L. S., Sparks, B. D., Le Page, Y., and Woods, J. R. (1998a). Effect of particle size on the flocculation behavior of ultra-fine clays in salt solutions. *Clay Minerals* 33:103–107.
- Kotlyar, L. S., Sparks, B. D., Woods, J. R., Raymond, S., Le Page, Y., and Shelfantook, W. (1998b). Distribution and types of solids associated with bitumen. *Pet. Sci. Technol.* 16:1–19.

- Le Page, Y., and Rodgers, J. R. (2005). Quantum software interfaced with crystal-structure databases: Tools, results and perspectives. *J. Appl. Crystallogr.* 38:697–705.
- Ripmeester, J. A., Kotlyar, L. S., and Sparks, B. D. (1993). ²H NMR and the sol-gel transition in suspensions of colloidal clays. *Coll. Surf. A: Physicochem. Eng. Aspects* 78:57–63.
- Tu, Y., Li, Z., Pleizier, G., Ng, S., and Chung, K. (2004). Separation and characterization of problematic solids from Athabasca oil sands and waste unit samples. *Can. J. Chem. Eng.* 82:678–686.
- Tu, Y., O'Carrol, J. B., Kotlyar, L. S., Sparks, B. D., Ng, S., Chung, K. H., and Cuddy, G. (2005). Recovery of bitumen from oil sands: Gelation of ultra-fine clay in the primary vessel. *Fuel* 84:653–660.
- Warren, B. E., and Averbach, B. L. (1950). The effect of cold-work distortion on x-ray patterns. *J. Appl. Phys.* 21:595–599.
- Young, R. A., and Hewat, A. W. (1988). Verification of the triclinic crystal structure of kaolinite. *Clays and Clay Minerals* 36:225–232.