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SLURRY TANK CONDITIONING OF OIL SANDS:

TAILINGS BEHAVIOUR

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EXECUTIVE SUMMARY

Slurry tank conditioning as an oil sands process step prior to extraction can be expected to produce a tailings material significantly different from conventional Clark hot water process tailings. Recycle water pond design and operation will depend upon the settling and consolidation properties of the fine tailings stream, and these properties in turn depend upon the chemical and physical conditions to which the oil sands are exposed in the extraction process. Slurry tank conditioning occurs at 50°C and without the addition of any process aides. The release of bitumen from the sand matrix is accomplished using mechanical agitation (stirring) in a tank, prior to desanding and flotation using conventional oil sands separation processes. This is in contrast to the Clark process which conditions the oil sand using tumblers, heat (80°C), and an alkaline water chemistry. The alkaline water chemistry serves to disperse the fine clays, as well as enhance the release of natural surfactants in the bitumen. Both of these effects result in rapid release of bitumen from the sand, allowing for very short residence times (5 to 10 min) in the tumblers.

The non-alkaline water chemistry, and (longer residence time) mechanical conditioning in the slurry tank process results in a reduction in dispersion of the fine clays, as well as an increase in the flocculation and settling rate, compared to the Clark process tailings. The rapid flocculation and settling of the fine clays results in a fine tailings stream that begins settling without any induction time and that has a solids free release water. The slurry tank process tailings have an order of magnitude higher permeability than Clark hot water process tailings and they have a significantly improved capacity to support a sand surcharge which will provide a stress to further enhance dewatering, relative to the Clark tailings. The improved capacity to support a sand surcharge indicates that a lower calcium addition would be needed to create CT (relative to Clark tailings). Because of the similar water chemistry, slurry tank and OSLO tailings behaviour will be similar, with the additional potential benefit of tailoring the degree of mechanical conditioning in the slurry tank to maximize bitumen recovery, but minimize clay dispersion.

The beneficial fine tailings properties result from both the water chemistry, as well as the more controlled mechanical conditioning in the slurry tank. Depending upon the connate water chemistry of the oil sands, maintaining a non-alkaline environment after many years of recycle may require chemical treatment of the recycled water. For the lease 13 oil sands tested here, chemical treatment is not likely to be required to control the water chemistry.

Toxicity of the release water is significantly lower for the slurry tank conditioned oil sands than for the Clark tailings, although it has some level of toxicity. This means that in any treat and release scenario, the slurry tank conditioned tailings will require less treatment than conventional Clark tailings.

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INTRODUCTION

The nature and behaviour of the fine clays in oil sands extraction tailings define a number of operationally important factors ranging from the size of the recycle water storage area to the degree of chemical intervention required to maintain extraction efficiency. The recognition throughout the industry that it is undesirable to store fluid fine tailings has resulted in the development of a number of tailings reclamation options that will result in a solid landscape. The most recently developed options include the consolidated tailings (CT) process and paste technology. Both of these involve counteracting the clay dispersion which results during the Clark hot water process.

The advantages of an extraction process which does not disperse the clays has long been recognised. The OSLO extraction process utilising coal flotation reagents, but with a non caustic water chemistry produces a tailings with superior settling and permeability characteristics relative to Clark process tailings. The BITMIN process is another non-caustic extraction method which, with a thickener and a filtration step produced a solid tailings. These two applications of conventional mineral processing technology to oil sands extraction, along with the development of hydrotransport or pipeline conditioning of oil sands lead to the concept of slurry tank storage of oil sands. This in turn leads to the substitution of mechanical energy (stirring) for the heat and chemical conditioning of oil sands which occurs in the Clark hot water process.

Slurry tank conditioning, which utilises no process aides, will result in a rapidly flocculating fine clay tailings which should be analogous to the tailings produced from other non-caustic extraction processes. A series of index tests developed at CANMET help to quantify the extent of any tailings property improvements relative to the Clark or OSLO processes. The most important of these properties are the settling rate and the permeability. The settling rate is defined by the degree of dispersion of the clays in the tailings (the particle size distribution) and establishes the minimum recycle water pond size required to provide clear water back to the extraction process. The permeability determines the rate at which the mature fine tailings will undergo further consolidation.

Another important property is the strength of the flocculated fine clays which determines the mature fine tailings' ability to support a sand surcharge or a stress which would enhance dewatering. In addition, since the solid landscape reclamation options involve chemical treatment to overcome the clay dispersion, an extraction process which minimises clay dispersion in the first place will require less chemical treatment to achieve the same result.

Settling behaviour is often quantified by simply observing the rate at which an interface drops under standard conditions in a graduated vessel. The solids content of the feed slurry and the resulting settled material is then used to predict behaviour on a larger scale. This approach leads to problems with the dual nature (combined sand and clay) of oil sands tailings. Sand material settles very quickly and does not contribute to the production of mature fine tailings (or sludge). Only the clay component contributes to "sludge make" and it is the behaviour of this fraction of the tailings stream that is important. Mature fine tailings (MFT) from Syncrude and Suncor have C:W ratios of 0.2 to 0.3. It takes 3 to 5 years for the Clark fine tailings to reach a C:W ratio of about 0.2, after which further consolidation is extremely slow due the low permeability of the MFT. Build up of the MFT with time then requires increases in recycle water pond capacity in order to store the resulting MFT. With OSLO tailings, the settling rate is much faster, but the final C:W ratio is not significantly different. This results in a much smaller initial recycle water facility, but with a similar long term MFT storage requirement. Since slurry tank conditioning is also a non-caustic process, there is an expectation that the fine tailings behaviour will be similar to that observed for the OSLO tailings.

EXPERIMENTAL

The CANMET index tests for characterizing and quantifying tailings behaviour have been discussed elsewhere (1,2) and will only briefly be described here. Standard tests such as settling tests, methylene blue index, x-ray diffraction, hydrometer particle size distribution determinations, toxicity determinations and other tests commonly used in the oil sands industry will not be described. Settling rate, C:W ratios, clay mineralogy, permeability, and flocculated clay tailings strength have all been quantified and compared to Clark and OSLO equivalents.

MINERALOGY

Mineralogical characterization of four fine tailings and one froth solid samples were carried out on a Rigaku RU-200B rotating anode, automated powder diffractometer system. The tailings were sampled in: June 25/97 (Shell Lease 13), August 19/1997 (Suncor high grade), July 3/97 (Suncor low grade), July 28/97 (Suncor medium grade) and July 21/97 (non caustic froth). The x-ray diffractometer is equipped with a horizontal goniometer, a graphite crystal monochromator and a copper target. All the analyses were carried out at 40 kV and 150 mA. To reduce the instrumental broadening effect and enhance identification of trace minerals, 0.15° aperture receiving slit was used.

The tailings were washed with sodium hypochlorite to remove the organic components and then separated into ± 44 μm fractions. Only the fines (- 44 μm) were analyzed. The + 44 μm fraction is

mostly coarse sand. The - 44 μm fraction was separated into two parts, each saturated with 0.1 M calcium chloride and 1 M potassium chloride. Residual salt was removed by rinsing several times with de-ionized water. Hydrolysis was stopped by further rinsing with a 50/50 ethanol/water mixture. Sample preparation entails filtering each portion through a 0.5 μm filter for about 2 minutes and inverting on a glass slide. High degree of preferential orientation was achieved this way.

For each tailings sample, the Ca - saturated portions were pretreated in three ways and the K - saturated samples in four ways prior to x-ray diffraction analysis. The Ca – saturated samples were equilibrated at 54% relative humidity (Ca-RH), with ethylene glycol (Ca-EG) and glycerol (Ca-GY). The K – saturated samples were equilibrated at 0 relative humidity (K0) and 54% relative humidity (K1), 300°C (K2) and 550°C (K3). Talc was used as an internal standard for quantitative analysis.

For the froth sample, solids obtained from the Dean Stark procedure was ground in a mortar and pestle and spread on a glass slide with a thin layer of vaseline. No pretreatment was carried out prior to mineralogical analysis.

Crystallite size and surface area

The average crystallite size (which is comparable to the particle size at particle sizes < 100 nm) was determined by modeling the X- ray diffraction profile broadening due to crystallite size (τ) and strain ($\in$) (Klug and Alexander). This is stated in Equation 1.

$$\beta \cos\theta_k = \frac{57.2958\lambda}{\tau} + 57.2958 * 4 \in \sin\theta_k \qquad \dots.. 1$$

β = the integral-breadth of the specimen profile at $2\theta_k$

λ = primary radiation wavelength (CuKα1)

θ_k = the Bragg diffraction angle of the line.

The surface area of a specific mineral is calculated from the crystallite size. Contributions from non-clay minerals such as quartz, rutile, siderite, and feldspar that are sometimes present in the tailings are ignored, because of their minor contributions to the overall surface area.

X-ray microanalysis

A Noran Instrument energy dispersive x-ray spectrometer linked to a Hitachi S-2500 scanning electron microscope was used to obtain the elemental composition of the froth solid samples. Specimen preparation required the dried solid powders to be glued to a graphite sample holder. Characteristic x-rays were collected at 20 kV. Semi quantitative elemental analysis was accomplished using virtual standards (standardless quantification).

SPECIFIC RESISTANCE TO FILTRATION

Specific resistance to filtration measurement is conducted with a pressure filtration set-up (supplied by Micro Filtration Systems). It consists of a stainless steel cylinder with 200 cm^3 capacity and a control panel which permits a pressure of up to 700 kPa to be applied to the top of the sludge in the cylinder. The filter paper used for filtration media is "Whatman No. 17" with a filtration area of 12.5 cm^2. 100 grams of fine tailings is placed in the cylinder. After the pressure was applied, the filtrate (water) was drained out from the bottom of the cylinder and collected in a beaker placed on a balance (PM 2000, Fisher Scientific). The balance was interfaced to a micro computer which recorded the weight of the filtrate as a function of time (50-second time interval for the tailings). Each filtration test was done in 5000 seconds with a total of 100 data points collected. The viscosity of filtrate is measured using a capillary viscometer at the same temperature as the filtration temperature. The weight of the filtrate at time t is then converted to volume. If the density of the filtrate is unknown a separate measurement of the density is required. A graph of time/volume (t/v) versus volume (v) is plotted and a straight line will be obtained. The slope of this graph is then used in the calculation of specific resistance to filtration. All the pressure filtration experiments should be conducted at the same temperature.

The SRF is a parameter based on a theoretical model of the filtration. According to D'Arcy's law and assuming that the filter cake is incompressible and the resistance of the filter media (filter paper here) is negligible compared to that of cake, the following equation can be used to describe the constant pressure filtration behaviour:
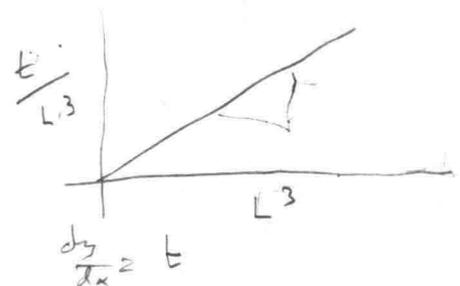
$$\frac{1}{A} \cdot \frac{dV}{dt} = \frac{A \Delta P}{\mu \, rcV}$$

$$\frac{1}{L^3} L^3 = \frac{L^2}{T}$$

In the above equation,

V = volume of filtrate (cm^3) at time t

A = filter area (cm^2)

ΔP = applied pressure differential (kPa)

m = filtrate viscosity (Pa.s)

c = solids content of sludge (g/cm^3) which should be determined separately.

r = specific resistance of cake to filtration, i.e., SRF (cm/g).

Integration of Equation 1 for a batch filtration leads to a mathematical expression of specific resistance to filtration. Where b is the slope of the graph of time/volume against volume in units of s/cm^6.

$$SRF = \frac{2\Delta PA^2 b}{c\mu}$$

what are the dimensions

RHEOLOGY

10^{-4} to 10^{5}

Rheological measurements were conducted on Bohlin VOR rheometer using a concentric cylinder sensor system (model C25) which has a viscosity range of 10-4-105 Pa(s. The gap spacing is 2.5 mm and the radius of the rotating cup is 27.5 mm. The C25 has a large sensing area and is the most sensitive of the standard concentric cylinder types available. A sample volume of 13 mL is required to cover the stationary bob which is 375 mm in height. Torsion bars of 11, 90, and 283 g.cm were used, depending on the volume fraction of pond tailings studied. The system was operated at 20.0±0.5°C. A Neslab RTE 110 circulatory bath was used to maintain stable temperatures.

The classical rheological tests used in this experimental study were steady-state viscometry; dynamic testing consisted of strain sweep and oscillatory sweep. Steady-state viscometry (shear stress versus shear rate) curves were obtained in 55 steps over a shear rate range of 5.8 x 10-3s-1 to 1.46 x 103s-1. Up/down curves were obtained to measure the degree of structural breakdown due to shearing.

In dynamic testing, a measure of the linear viscoelastic properties of the fine tails was obtained by determining the linear viscoelastic region using strain sweeps. Strain sweeps were performed at 1 Hz. Oscillatory sweeps in the linear viscoelastic region were performed at a strain of 0.008 in 12 steps ranging from 0.009 Hz. to 1.5 Hz.

RESULTS AND DISCUSSION

TAILINGS CHARACTERIZATION

Four ores were used in the pilot scale extraction studies with a range of fines and clay content. The ore properties are summarized in Table 1.

Table 1: Oil sands properties. The clay content is typically 40 to 50% of the fines content.

Process	Stream	Dean Stark (w/w)			< 325 mesh	
(Sample ID)		% oil	% Solids	% Water	% Fines	σ
Shell Lease 13	Oil sand	10.9%	84.9%	4.1%	12	1%
Suncor High Grade	Oil sand	11.2%	84.3%	4.3%	10	1%
Suncor Medium Grade	Oil sand	9.3%	85.8%	4.7%	29	3%
Suncor Low Grade	Oil sand	7.7%	84.6%	7.4%	27	2%

Mineralogy

Tailings were collected from the secondary flotation circuit during several extraction pilot plant runs. The clay content of the tailings solids was determined by methylene blue adsorption and by hydrometer testing and found to vary widely, due to variations in pilot plant operation. This is shown in Figures 1 to 4 (Table A-1 in Appendix A) which plot the clay content on the solids versus the per cent solids. The variation in clay content makes comparisons of settling rates difficult since any increase in sand content relative to the clay will result in both a fast settling rate and a high solids content. Using the concept of clay to water ratio avoids these problems and is really the only way to determine and/or compare tailings properties. This will be illustrated in the discussion that follows.

Relatioship between the % solids in Suncor high grade tailings versus the clay content of the solids
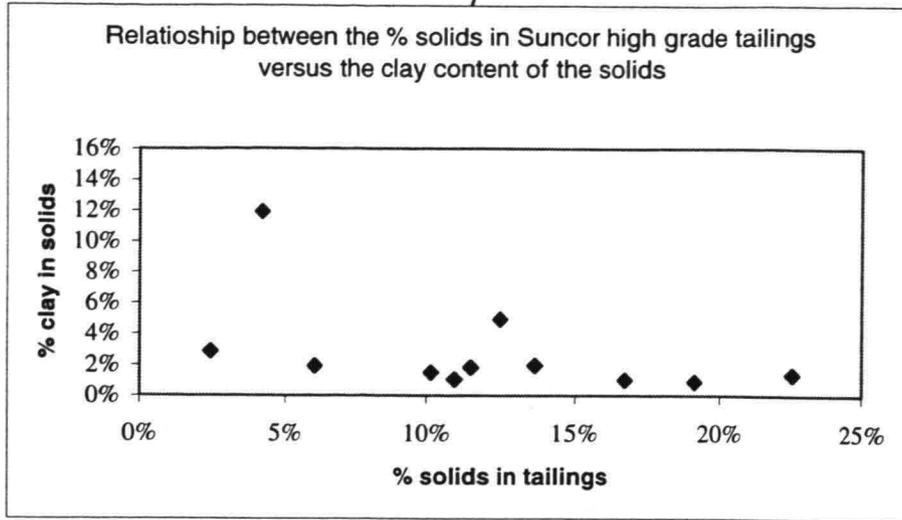
Figure 1: The relatively low but still quite variable clay content in tailings solids for the high grade ore.

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Relatioship between the % solids in Suncor low grade tailings versus the clay content of the solids
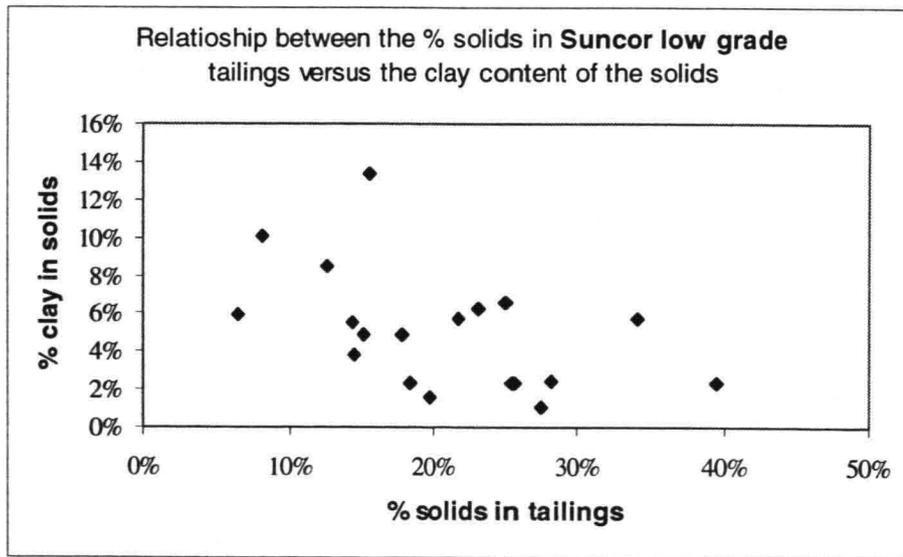
Figure 2: The relatively high and variable clay content in tailings solids for the low grade ore.
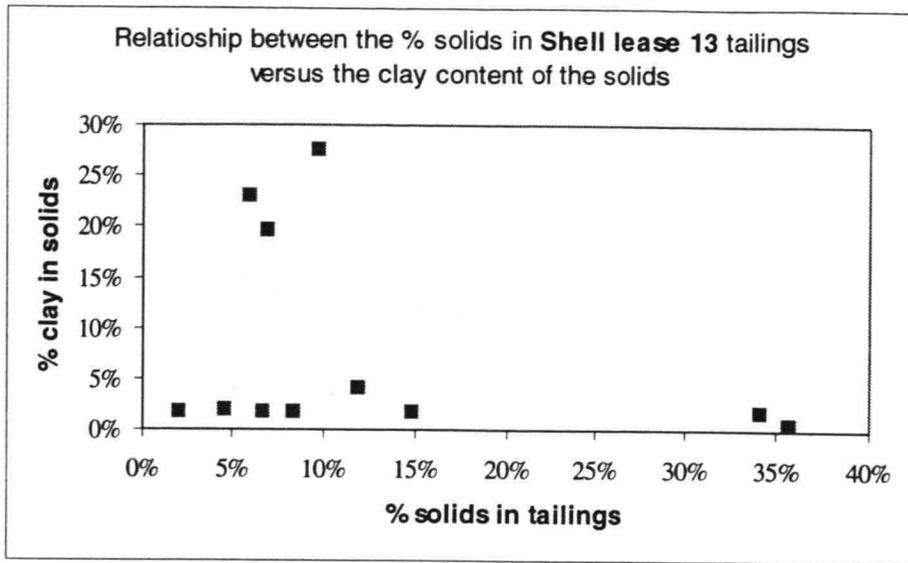
Figure 3: The low clay content in tailings solids for the lease 13 ore.

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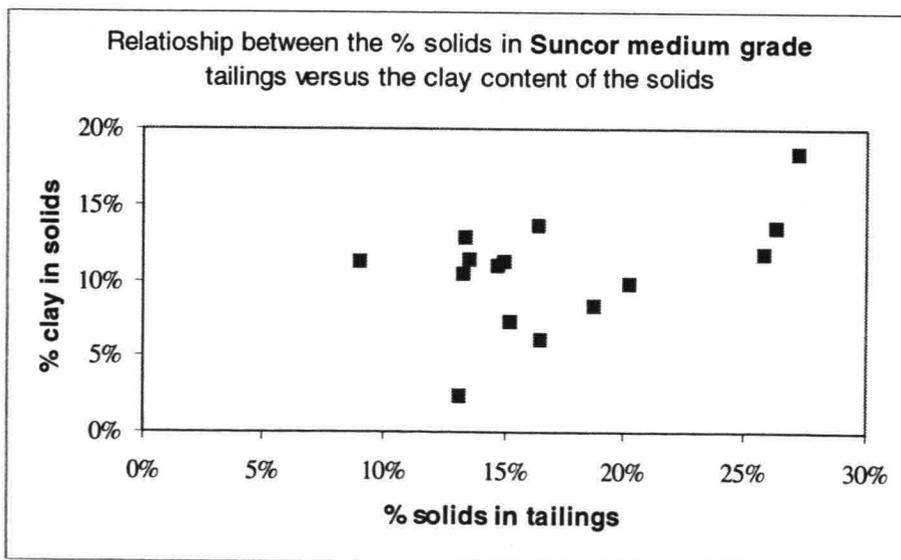
Figure 4: The high clay content in tailings solids for the medium grade ore.

Oil sand ores of various grades were used in the extraction pilot and they included Suncor low, medium, and high grades, as well as a sample of ore from Shell's lease 13. The mineralogy of all four ores was evaluated and determined to be the same (Table 3-5). This equality is not unexpected and it ensures that direct comparisons of settling rate via clay to water ratio can be made using fine tailings from any ore. The amount of clay in each ore would determine the total volume of MFT ultimately produced, but will not impact the MFT properties.

Figure 5 depicts the diffraction patterns of Lease 13 fine tailings (-44 μm) obtained for all the seven pretreatments. Smectities could not be identified. If present, they are in very minute quantities. Kaolin, illite and chlorite (possibly chamosite – high Fe- chlorite) are the identifiable clay minerals. Fine quartz, rutile and small amounts of siderite are present in the -44 μm fractions. All the other samples (Suncor high, medium and low grade fine tailings) show similar mineralogical composition to Shell Lease 13 tailings with minor variations in the apparent concentrations of the minerals. The diffraction patterns of the four samples (Ca- saturated – ethylene glycol solvated) are shown in Figure 6.

Table 2 shows the composition of the – 44 μm fractions. For this particular set of samples, the high grade ore (Suncor high grade) has the highest clay content (~ 74% $\pm$ 10%) and the Suncor low grade ore the lowest clay content (64% $\pm$ 10%). The relative amounts of clay types, however, are similar, confirming that these variations are due to coincidences in the sampling (see Figures 1-4). The amorphous FeO concentration was obtained from x-ray microanalyasis. This is highest in the Suncor medium grade oil sand tailings (~ 7 %).

Figure 7 shows the diffraction pattern of the froth solids. The quartz peak is pronounced because the particles were randomly oriented as opposed to the preferential orientation in the fine tailings patterns. Preferred orientation greatly enhances the diffraction of the orienting clay particles relative to the non – orientating quartz particles. Even though no quantitative analysis was carried out on the froth solid, it is apparent that it has more pyrite and siderite than the – 44 μm fractions of the fine tailings. This is typical since these hydrophobic minerals tend to associate with the organic phase during the extraction process.

Crystallite size and surface area

Table 3 shows the crystallites sizes and surface areas of the four fine tailings. For these particular samples, the average crystallite sizes of illite are consistently larger than those of kaolinite. The total surface area of the Suncor high grade ore is the highest primarily because of its higher clay

content. As can be seen in Figures 1-4, however, this is atypical and the low grade tailings usually have the higher clay content.

Elemental composition

The chemical compositions of the – 44 μm fractions are shown in Table 4 . There are no major differences in the elemental concentrations of all the samples analyzed. Most of the iron in all the samples is attributed to amorphous iron oxide. Some of the iron is associated with siderite. Some of the iron is also present in the chlorite and illite phases. The froth solid comprises significantly greater amounts of iron and sulphur than the tailings. These are manifested in the greater quantities of pyrite and siderite observed from x-ray diffraction. The similar silicon to aluminum ratio in the froth solids (~ 1.6) than the tailings solids (~1.7) indicates that both clays and very fine quartz are evenly partitioned between the froth and the tailings. The smaller potassium content of the froth solid than the tailings also indicates a smaller amount of illite in the froth solid.

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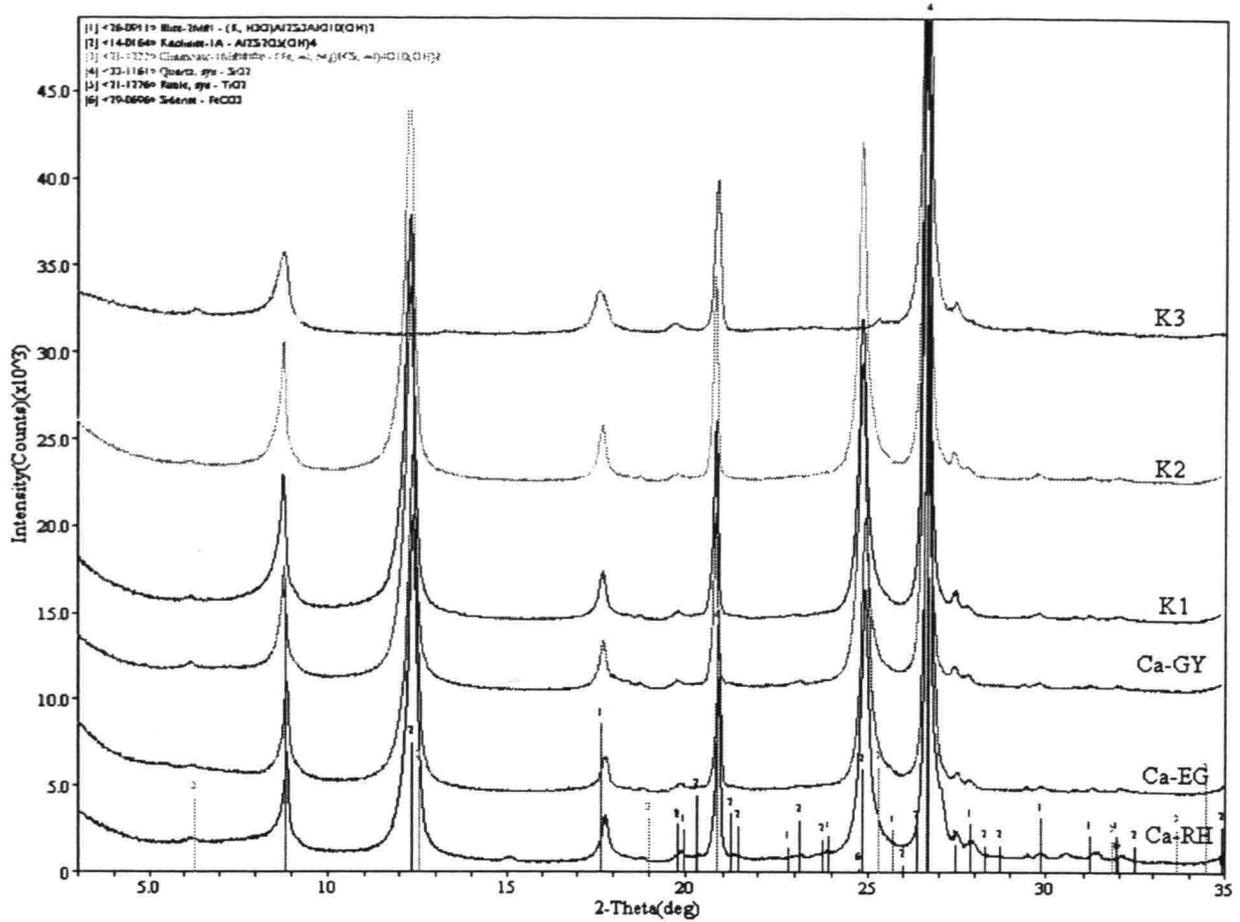
Figure 5: Lease 13 fine tailings (<325 mesh solids), subjected to various treatments to enhance identification of smectites and mixed layer clays. Quartz, kaolinite, and illite are the major phases. Rutile, chlorite, (chamosite) and siderite are present in small concentrations. No significant quantities of mixed layer or swelling clays could be identified.
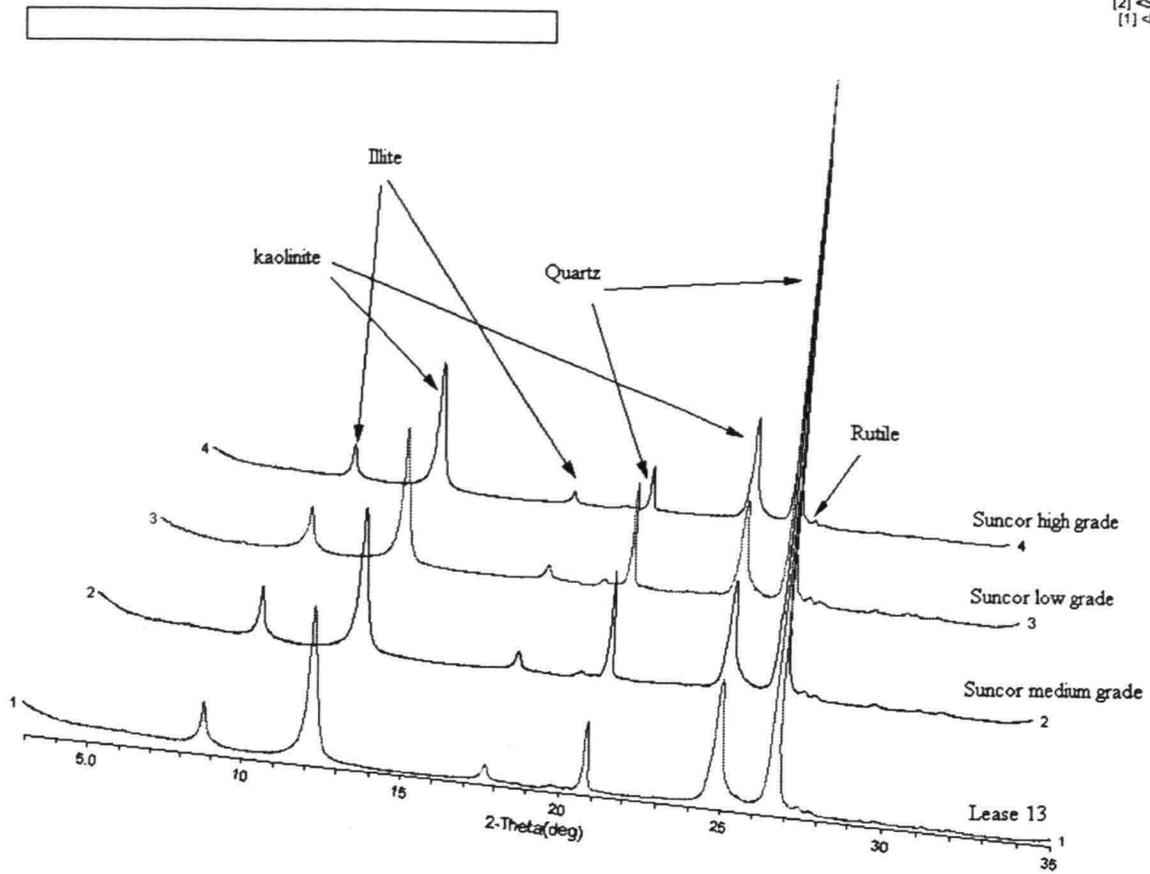
Figure 6: Ethylene glycol solvated samples of the four tailings solids samples. The mineralogy is essentially the same. Quartz, kaolinite, and illite are the major phases. Rutile, chlorite, (chamosite) and siderite are present in small concentrations.

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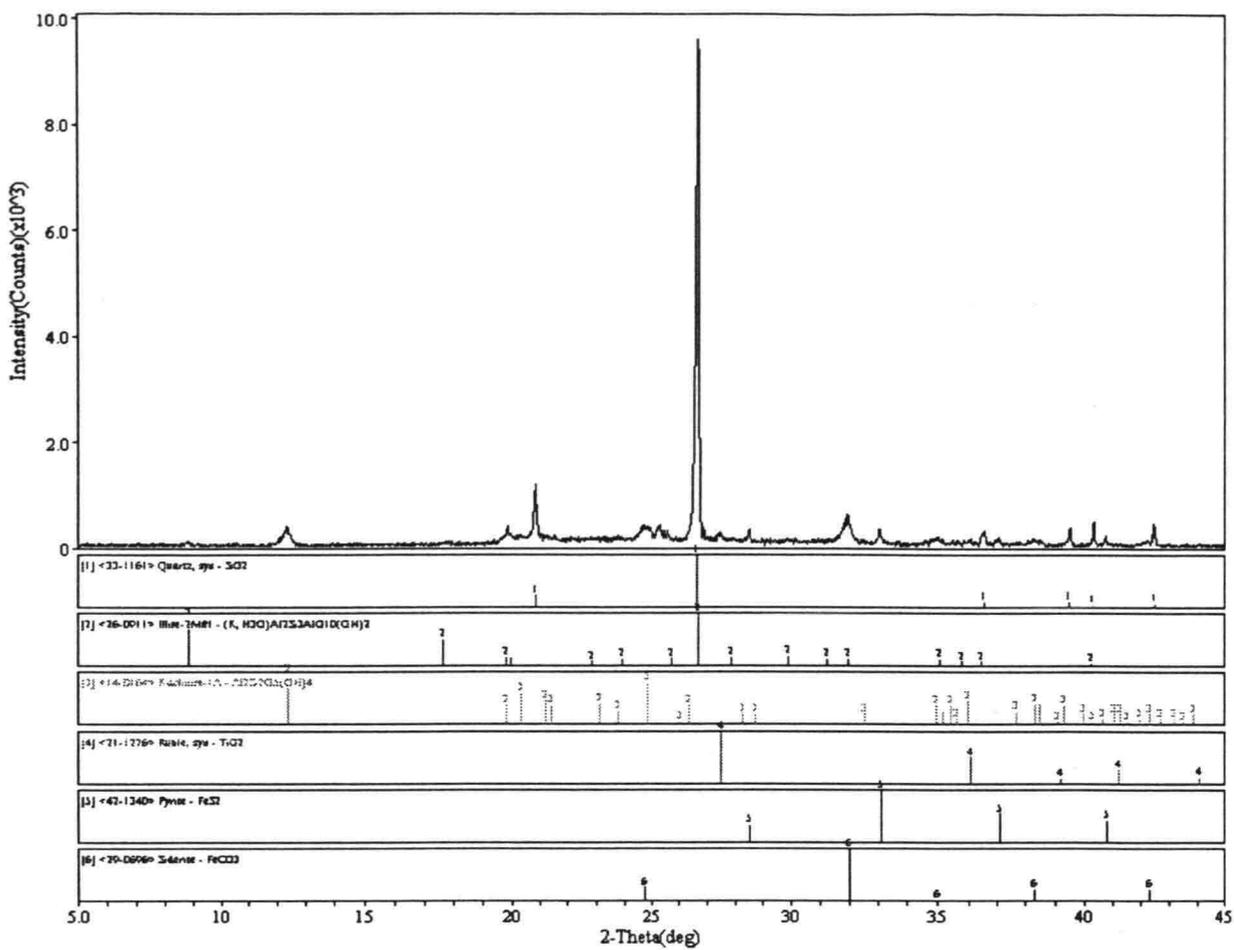
Figure 7: X-ray diffraction pattern of froth solids. Quartz, kaolinite and siderite peaks are most prominent. Illite and pyrite are also present in significant quantities.

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Table 2: Quantitative x-ray diffraction analysis of fine tailings (< 325 mesh) obtained from non - caustic extraction of different oil sands. The concentration of amorphous iron oxide was obtained from x-ray microanalysis. (XRD (wt %) sigma 10% < 325 mesh material)

Mineral	Low Grade	Medium Grade	High Grade	Shell Lease 13
Kaolin	32.3%	30.8%	40.8%	39.7%
Illite	28.5%	31.5%	30.9%	29.2%
Fe-chlorite (chamosite)	3.6%	2.8%	2.1%	3.2%
Quartz	31.8%	27.4%	20.3%	22.1%
Rutile	0.3%	0.4%	0.5%	0.2%
Amorphous FeO	3.5%	7.0%	5.6%	5.6%
Siderite	0.1%	0.1%	0.1%	0.1%

Table 3: Surface area of < 325 mesh fine tailings. The total surface area was calculated from the average crystallite thicknesses of illite and kaolinite, the most abundant clays in the fine tailings.

Mineral	Suncor Low Grade		Suncor medium Grade		Suncor High Grade		Shell Lease 13	
	Average	Surface area	Average	Surface area	Average	Surface area	Average	Surface area
	Crystallite size (nm)	(m^2/g)	Crystallite size (nm)	(m^2/g)	Crystallite size (nm)	(m^2/g)	Crystallite size (nm)	(m^2/g)
Kaolin	27.1	10.5	24.5	11.0	28.8	12.5	26.1	13.3
Illite	32.2	7.9	39.2	7.2	32.1	8.6	41.1	6.4

Table 4: X - ray microanalysis of fine tailings (< 325 mesh) from different oil sands and from the froth solids.

	Al	Fe	Mg	K	Si	Na	S	Ti
Suncor High Grade	16.5%	2.0%	0.3%	2.0%	28.8%	0.4%	0.1%	0.5%
Suncor Low Grade	16.0%	2.2%	0.5%	2.0%	28.5%	0.6%	0.4%	0.5%
Shell Lease 13	16.0%	2.3%	0.5%	2.2%	28.7%	0.6%	0.2%	0.4%
Suncor Medium Grade	15.5%	2.5%	0.3%	2.3%	29.0%	0.4%	0.3%	0.5%
Froth solids	13%	10%	1.3%	1.2%	21%	1%	4%	3%

Settling behaviour

Figure 8 shows a comparison of settling rate (expressed as recycle water released) for the slurry tank conditioned tailings and calcium treated Clark hot water tailings (3). Since these tailings have similar initial solids and clay content, this graph can be used to illustrate the improved settling rate of the non-caustic (relatively non-dispersed) slurry tank fine tailings. However, the use of solids content is not recommended for anything but comparative prediction of tailings properties since it is very sensitive to the sand content in the tailings and this can be variable.
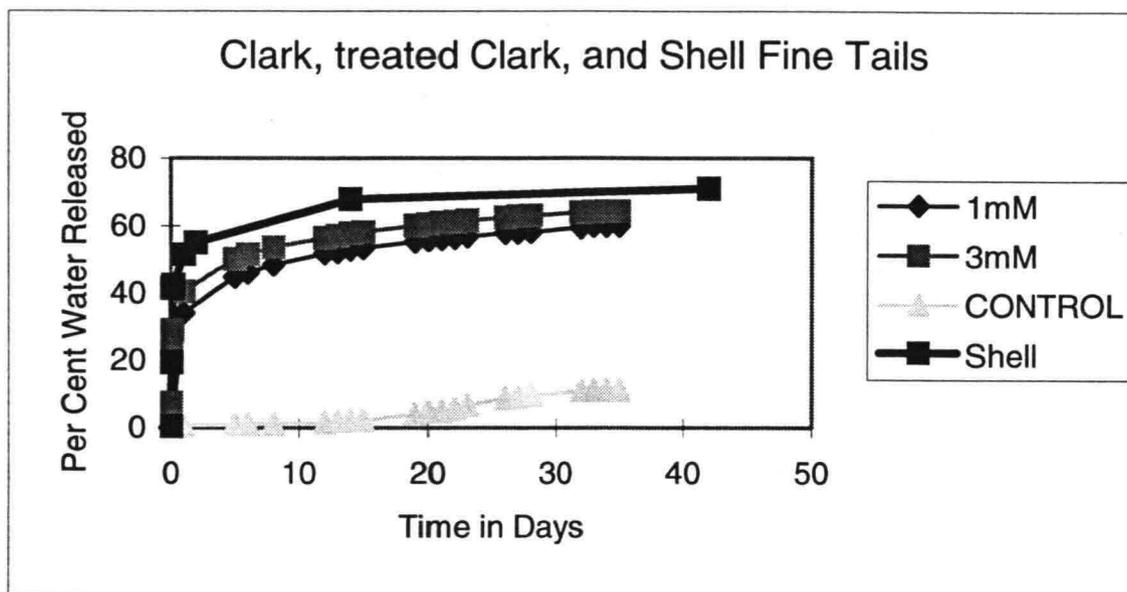
Figure 8: The water release rate from fine tailings from the Shell extraction process compared to Clark and gypsum treated Clark tailings. (1mM = 40 ppm Calcium).

Note that the settling rate, or water release rate is orders of magnitude higher than for untreated Clark tailings. At very long times (not illustrated here), however, the curves tend to converge, reflecting the fact that the final settled volume or sludge make will be similar. A combination of factors is responsible for this behaviour. The rapid flocculation of the fine tailings because of the water chemistry, and the lack of dispersion in the first place (due to the nature of the slurry tank conditioning), both contribute to the favourable properties of the slurry tank conditioned tailings.

Figure 9 shows the particle size distribution comparisons for comparable OSLO, Clark, and slurry tank conditioned fine tailings (determined using hydrometers (4, 5). When the OSLO and slurry tank tailings are dispersed using sodium hexametaphosphate, they have size distributions similar to the

Clark tailings. This means that the total clay content in the two types of tailings is similar, which will result in similar final settled volumes. However, the effective size of the clays is much greater in the non-dispersed, non-caustic tailings. This results in the short induction time and rapid settling rate observed for the slurry tank tailings relative to those from the Clark hot water process.
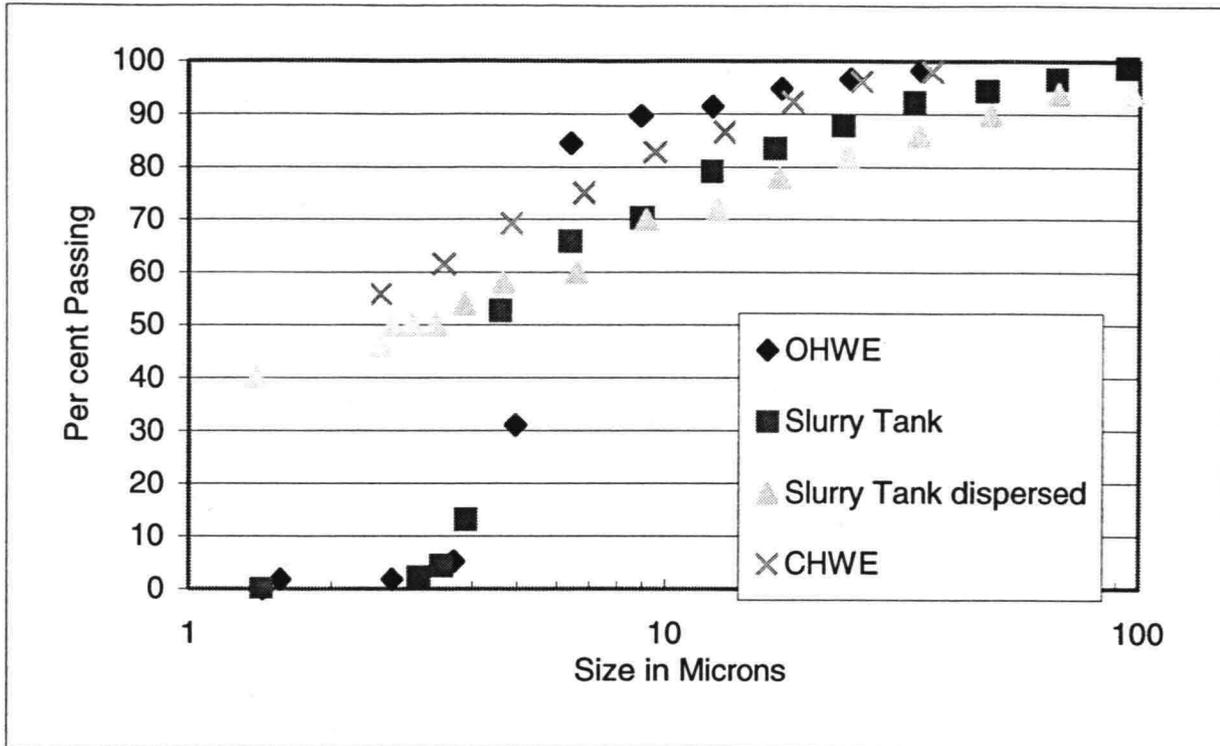
Figure 9: Particle size distributions for OSLO (OHWE) and Clark hot water extraction (CHWE) tailings, Slurry Tank tailings and for the dispersed slurry tank tailings. The absence of any significant amount of clay size material (-2µ) in the OSLO and Slurry Tank tailings is responsible for the rapid initial settling.

WATER CHEMISTRY

In determining the clay to water ratio, it is the dispersed percentage that is used since these represent the total clays in the feed that could potentially form sludge or mature fine tailings. The degree to which these clays behave as larger particles is determined by the water chemistry and the degree of dispersion which occurs in the conditioning step (6). As a result, laboratory based tests can only give relative comparisons of behaviour and it is critical that particle size distributions be determined in quantifiable and reproducible water chemistries. (Note the significant differences in settling rate with variations in calcium content shown in Figure 8). Figure 10 shows the clarity of the

supernatant in settling tests using slurry tank tailings. Clark tailings, even after a significant induction time, do not have such a solids free release water. In order to maintain release water clarity and the rapid initial settling rate, bicarbonate concentration must be kept low and calcium concentration must be maintained even after many years of recycle. Depending upon the nature of the oil sands ore, acidification of the tailings release water (extraction recycle water) may be required.
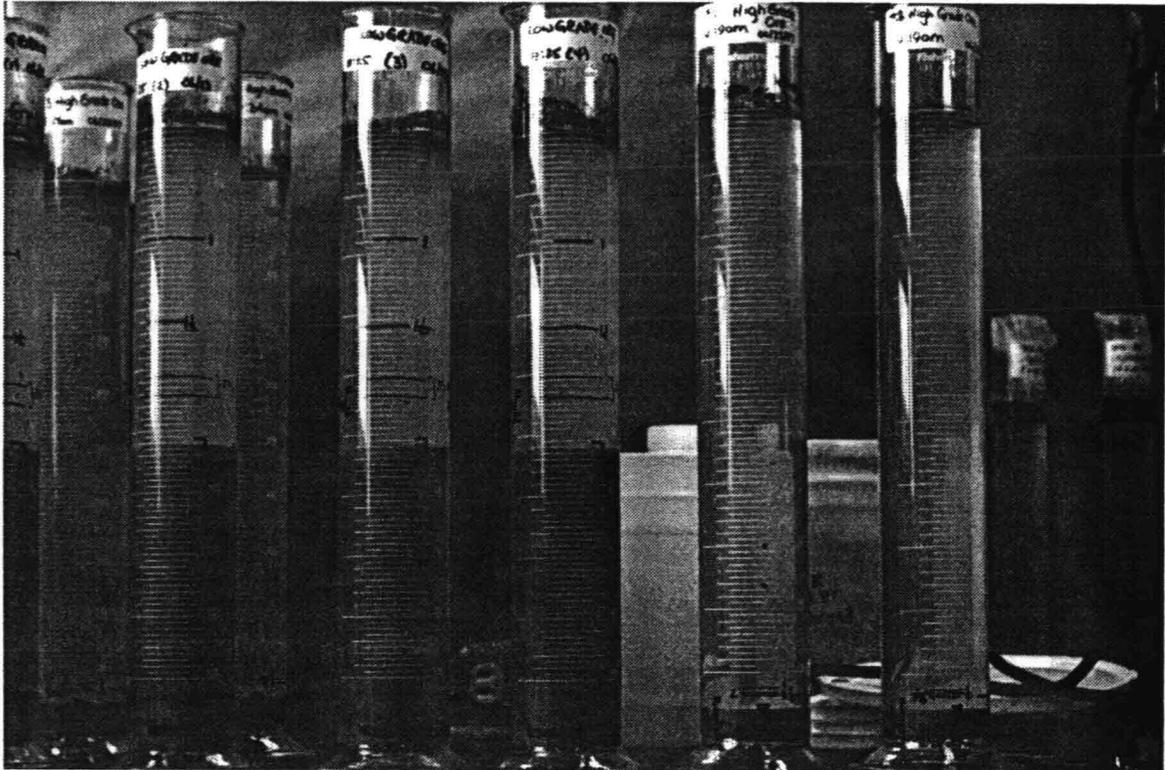
Figure 10: Twenty four hour settling behaviour for a high clay low grade tailings (left) and a low clay high grade tailings (right). Typical induction times for Clark hot water process tailings are one to two weeks before any settling occurs at all. Also note the clarity of the supernatant with the sample containers in the background visible through the water layer.

Calcium content can vary significantly even with season in the Athabasca river (35 ppm summer to 60 ppm winter), (7), making characterization of process water chemistry critical. Table 5 shows the input water chemistry of the pilot plant extraction tests, as well as the tailings water chemistry. The reduction in calcium concentration is due to charge exchange on the clay surfaces and it can be seen that the reduction in calcium is proportional to the amount of clays in the oil sands feed. The initial calcium concentration in the process water is comparable to that in the Athabasca river, givng some degree of confidence in the conclusion that the slurry tank tailings' superior properties

demonstrated in the laboratory will be confirmed with larger scale (pilot and commercial) tests. Appendix B contains a detailed discussion of the long term water chemistry expected with the implementation of the CT process in conjunction with the slurry tank conditioning process. If the Lease 13 ore tested here is typical, then these results indicate no increase in bicarbonate in the tailings release (recycle) water, and no chemical intervention (acidification) would be required to maintain the calcium levels and the resulting favourable tailings settling behaviour.

Table 5: *Water chemistry comparisons for the feed and tailings water. Only the low grade ore results in a recycle water chemistry that increases the bicarbonate level and that may require control.*

FINE TAILS
ION CONCENTRATION
(mg/L)

ICP FILE	Na	S	Ca	Mg	K	pH	HCO3	CO3
FEEDWATER/230697	11.6	18.6	45.1	12.7	0.2	8.0	163	0
River Water (8)	15		40	11	1.4	8.2	134	0
High Grade	25.3	27.6	39.8	13.4	1.5	8.4	165	6
Low Grade	77.9	34.1	18.1	9.7	9	8.2	193	0
Low Grade	81.1	32.9	17.6	10	8.1	8.5	196	11
High Grade	22.2	23.5	38.4	13.2	0	8.4	147	6
High Grade	20.7	22.5	38	12.9	0	8.4	150	13
High Grade	20.8	23	37.8	13.3	0	8.4	150	9
Lease 13	45.3	39.3	33.2	13.1	5.5	8.4	154	2
Lease 13	33.4	40.4	38.6	14	4.2	8.1	134	0
Lease 13	18.4	25.7	42.0	13.4	0.5	8.4	150	4
Lease 13	21.6	29.9	43.9	13.2	1.3	8.3	146	0
Lease 13	28.9	45.1	48.2	14.1	2.6	8.0	127	0
Lease 13	47.7	45.2	38	14.6	8.5	8	163	0
Lease 13	50	46.5	37.6	14.6	8.8	8	162	0
Lease 13	47.5	45.5	36.9	13.7	8.3	8	163	0

CLAY TO WATER RATIO VERSUS TIME

Figure 11 shows the increase in solids content with time for two fine tailings samples. The solids content differences are due to differences in the amount of sand in the two samples. Figures 12 and 13 show the dispersed particle size distributions for the two samples used in these settling tests. The clay content in the medium grade fine tailings is approximately 46%, while the clay content in the high grade fine tailings is only about 30%. Comparison of the clay to water ratio as a function of settling time shows that the clay components are behaving consistently, due to the water chemistry and clay mineralogy of the two samples (which are the same). Plotting the clay to water ratio versus time minimizes interferences due to sand content and gives a method of defining clay consolidation independent of the total solids content. To a good approximation, the sand and silt size material settles very fast and by quantifying the clay behaviour, we can predict fine tailings consolidation as long as we

know the total clay content in the tailings stream. This is shown in Figure 14 where the clay to water ratio versus time relationship is the same for the high and low grade tailings samples in spite of the different solids content. The equation defined by the clay to water ratio versus time relationship can then be used for predictive purposes for clay consolidation. (Assuming water chemistry and clay mineralogy is consistent).

Clay to water ratio = 0.013Ln(Time in Days) + 0.0819   Eq. 1

This equation does not give the complete story because of the nature of the flocculated clay fines in a non-caustic environment. The greater strength of the clay structure results in enhanced consolidation due to applied stresses (from deeper layers of mature fine tailings), assuming the permeability of the mature fine tailings is high enough.
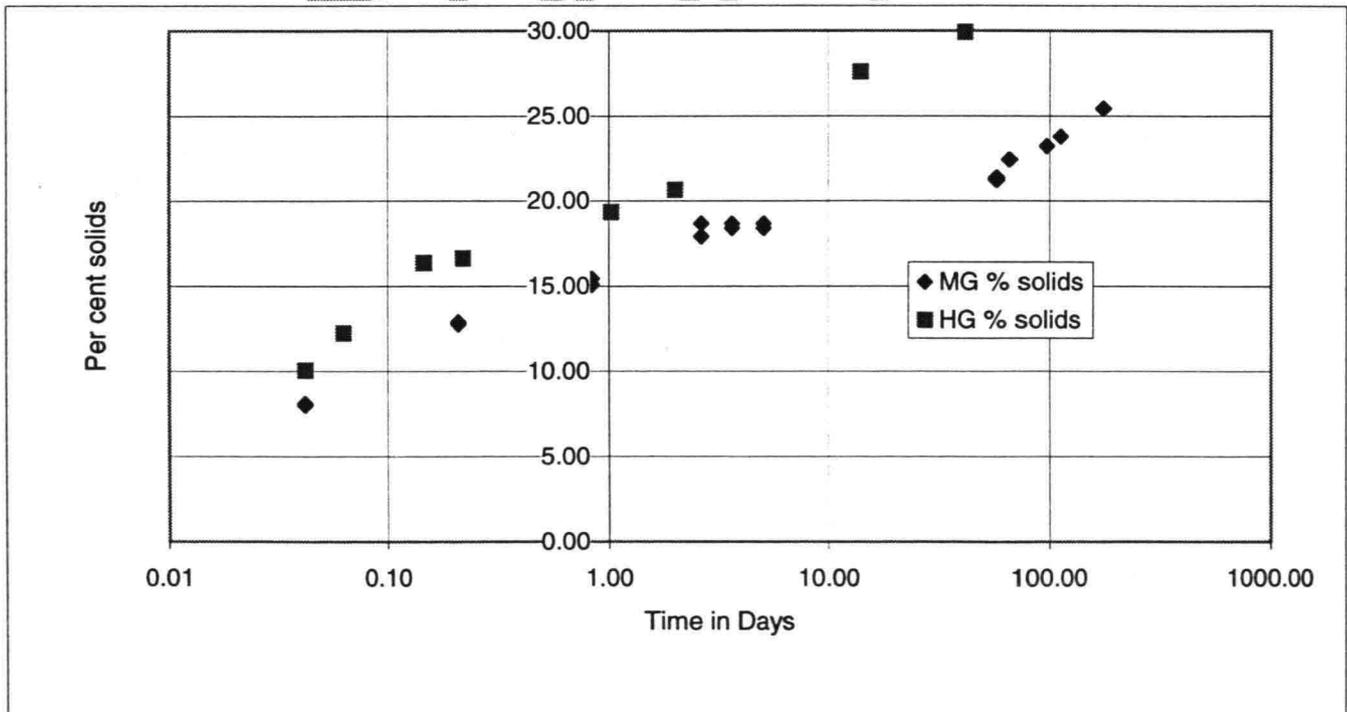
Figure 11: Per cent solids as a function of time for settling tests using medium grade and high grade tailings samples. The difference in the solids content achieved is a result of differences in the clay content of the two samples.
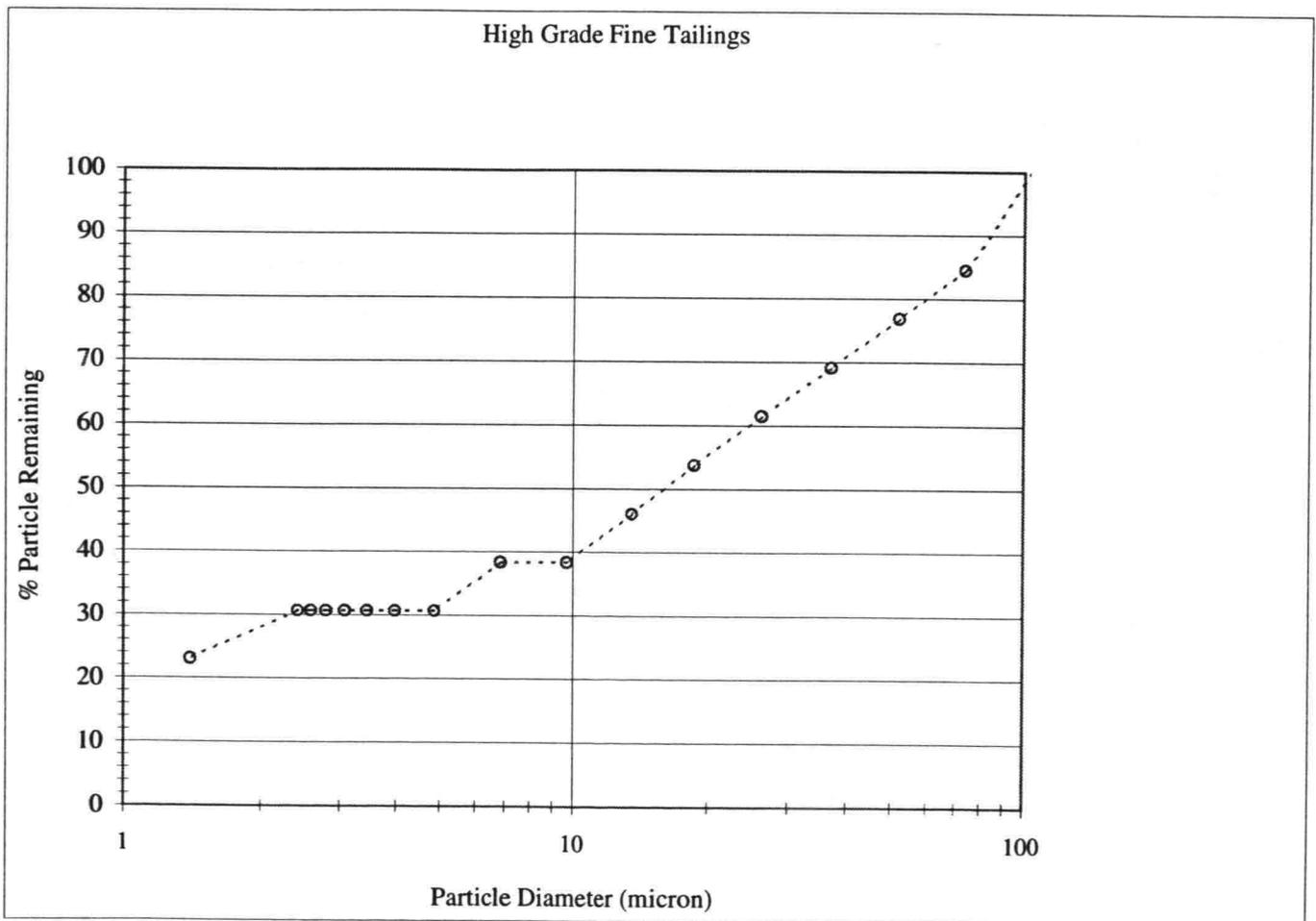
Figure 12: Dispersed particle size distributions for the high grade tailings settling test showing approximately 30% -2µ material.
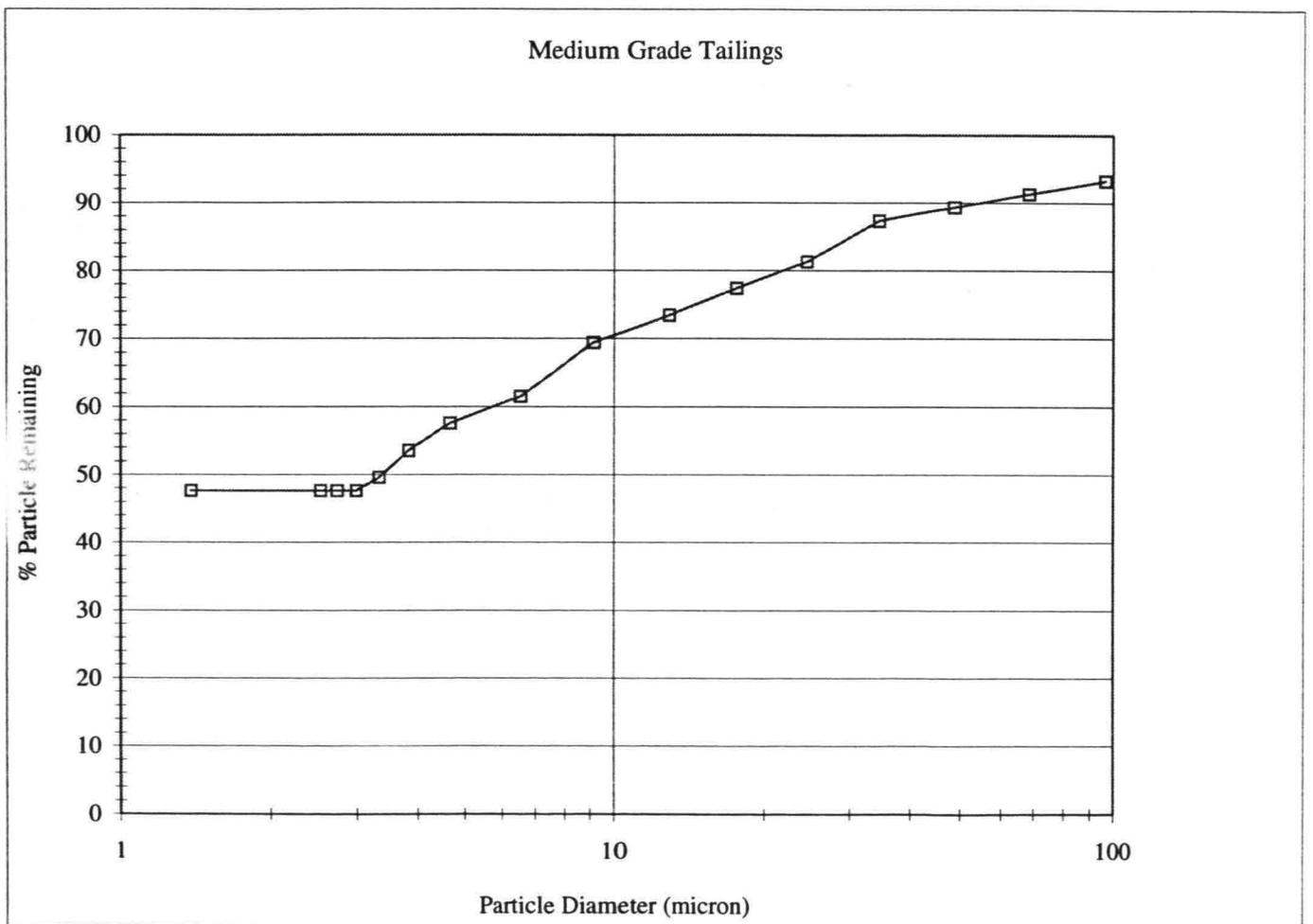
Figure 13: Dispersed particle size distributions for the medium grade tailings settling test showing approximately 46% -2µ material.

Its d. by wt or volume

$\dfrac{C}{W}$
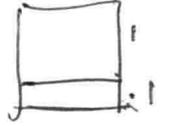
$\dfrac{.1}{1.1}$ 1.1 $\dfrac{.1}{1}$
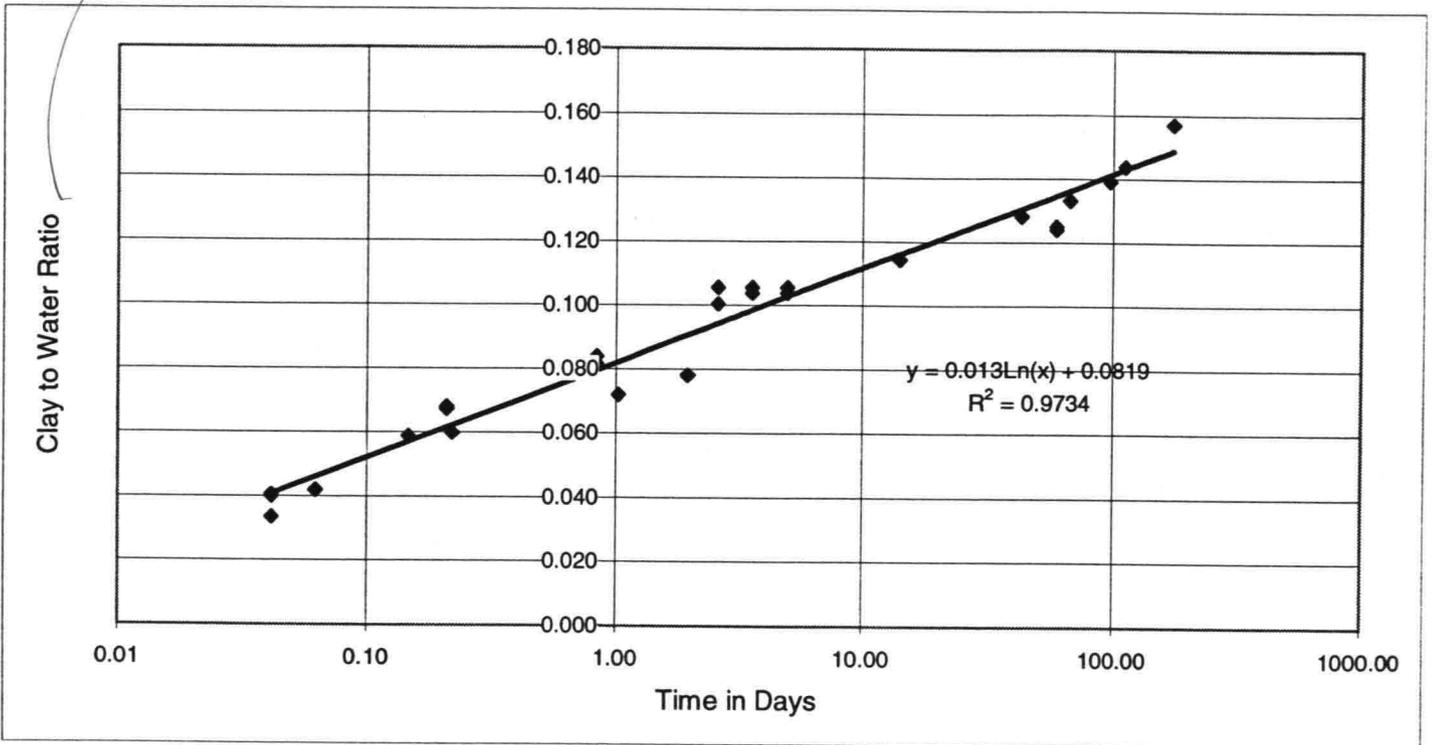
Figure 14: Clay to water ratio for the high and low grade settling tests showing that in terms of clay behaviour, the two tests give the same results. Consideration of the consolidation of the clay component reduces problems in interpretation of the settling behaviour when only the solids content is used. The equation can be used to predict clay consolidation regardless of oil sands feed (because it has already been established that the clays are similar for the four types of oil sands investigated here), as long as the clay content is known.

SPECIFIC RESISTANCE TO FILTRATION (PERMEABILITY)

The specific resistance to filtration (SRF) results are shown in Table 6. Typical Clark tailings results are in the range of 1.5×10^{13} cm/g (9,10). The slurry tank conditioned tailings are between one and two orders of magnitude lower, and in the range of materials that can be commercially filtered. The SRF index is related to the permeability of the clay slurry and the lower resistance for the slurry tank conditioned tailings is indicative of a higher permeability. This higher permeability is in turn indicative of a potential for clay slurry dewatering or consolidation much greater than for Clark process tailings (11). Further studies with larger scale and longer term settling tests are required to confirm this.

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Table 6: Specific resistance to filtration for a variety of slurry tank tailings samples. In all cases the results are better than for typical Clark tailings (1.5×10^{13} cm/g).

49KPa	% solids	SRF cm/g	150KPa	% solids	SRF cm/g
Medium Grade	21.8	5.0E+10	Med Grade	20.7	9.7E+10
Low Grade	28.3	1.3E+12	Low Grade	28.6	2.6E+12
Low Grade	19.6	6.5E+11	Low Grade	19.5	1.5E+12
Med Grade	13.3	6.8E+11	Med Grade	13.2	1.3E+12
Low Grade	75.9	2.1E+11	Med Grade	74.3	4.3E+10
			Low Grade	76.2	1.0E+11

RHEOLOGICAL PROPERTIES

This index test is a direct determination of the strength of the flocculated clays and is related to their ability to accept a stress and to transfer that stress throughout the clay structure. Microscopic investigation of the Clark tailings reveals a weak association of clays which cannot easily support sand grains. The OSLO or non-caustic tailings on the other hand have a different, stronger clay structure

which is able to support a sand surcharge and more rapidly consolidate the clays due to the stress which is transferred to the clay floccs. Sensitive rheological measurements can quantify the strength of the flocculated clays as a function of solids content. Figure 15 shows that the slurry tank tailings develop a significant strength at a much lower solids content than for similar Clark tailings. The slurry tank tailings behave in the same way as OSLO tailings and the ability of the OSLO tailings to support a sand surcharge and enhance consolidation of the clays has been established (12).

The primary purpose of the rheological measurements in this study was to define the gelation properties of the fine tails produced by a non caustic slurry tank conditioning process. The term gel (13) is limited to systems that fulfill the following phenomenological characteristics:

a) They consist of two or more components, one of which is a liquid, in substantial quantity and:

b) They are soft, solid, or solid like materials. In this context, solid or solid like should be defined in terms of dynamic mechanical properties

   i) a storage or elastic modulus $G'(\omega)$, which exhibits a pronounced "plateau" extending to times on the order of seconds or longer and

   ii) a loss modulus $G''(\omega)$ which is considerably smaller than G'.

Comparison of rheological properties in this report will deal with primarily the elastic modulus (G') obtained from dynamic measurements and yield point values obtained from steady state viscometry. Calculated G' and yield point values for pressure filtration fine tails , derived from regression analysis of experimental data obtained from previous studies (14) and slurry tank conditioned fine tailings are listed in Tables 7 and 8 and in Figures 15 and 16.

Table 7: *Calculated elastic modulus values (G' (Pa)) for Syncrude, Suncor, OHWE, CHWE, slurry tank medium and high grade fine tails. The higher G' values indicate a greater strength to the flocculated clay structure, and an ability to support a sand surcharge and transmit the resulting stresses throughout the clays to enhance dewatering. The higher clay content in the medium grade tailings is responsible for the greater G' values compared to the high grade.*

% Solids	Syncrude CHWE	Syncrude OHWE	Suncor CHWE	Suncor OHWE	Slurry tank Med Grade	Slurry tank High Grade

% Solids	Syncrude CHWE	Syncrude OHWE	Suncor CHWE	Suncor OHWE	Slurry tank Med Grade	Slurry tank High Grade
20%	0.2	26.7	1.4	46.6	29.6	31.2
30%	3.9	103	24.7	216	179	118
40%	41.1	281	209	686	641	303

Table 8: Calculated yield point (Pa) values for Syncrude, Suncor, OHWE, CHWE, slurry tank medium and high grade fine tails.

% Solids	Syncrude CHWE	Syncrude OHWE	Suncor CHWE	Suncor OHWE	Slurry tank Med Grade	Slurry tank High Grade
20	0.3	1.8	0.5	2.3	1.2	1.1
30	1.6	5.4	2.8	8.0	3.8	4.2
40	6.1	12.0	10.9	20.0	8.7	10.6

Previous studies at WRC (2) have shown significant differences in the rheological properties of caustic (CHWE) and non caustic (OHWE) processes. Yield point and G' values obtained were lower in CHWE fine tails indicating a more disperse system. Also the magnitude of differences between CHWE and OHWE were much greater at lower percent solids by weight indicating the presence of aggregates in the OHWE system.

As can be seen from Figures 15 and 16, the yield point and G' values obtained for the slurry tank fine tails tend to fall in the same region as the OHWE fine tails indicating a strong correlation of rheological properties to an OHWE non caustic fine tails. It should be pointed out that the proportion of clay fines contained in the slurry tank conditioned fine tails are less than those of the CHWE and OHWE fine tails (for these particular samples). This factor is significant in that it is the clay fines that contribute to the aggregating properties of the fine tails and result in higher rheological properties being measured, especially in a non-disperse medium. It is likely that if similar proportions of clay fines in the slurry tank fine tails existed as in the previous OHWE and CHWE samples, measured values of yield point and G' may be even larger.

The significance of larger yield point and G' values especially at the lower wt % solids implies a greater capacity to aggregate which is controlled by the inherent properties of the clay fines and chemistry of the liquid medium. At low wt % solids, the slurry tank fine tails behave like OHWE fine tails and exhibit superior aggregating properties when compared to the caustic CHWE highly disperse fine tails. This is also demonstrated by the fact that values of yield point and G' can be experimentally

measured below 20% solids, however CHWE fine tails because of their high degree of dispersity, measurable values do not exist. Yield point values for slurry tank medium and high grade fine tails were 0.2 Pa and 0.4 Pa and G' values were 5.5 Pa and 5.6 Pa. As the weight % solids increases, the volume fraction effect is a determining factor in fines aggregation. This is illustrated in Figures 15 and 16 which show that as solids content increases the differences in the yield point and G' values for all the fine tails become smaller.
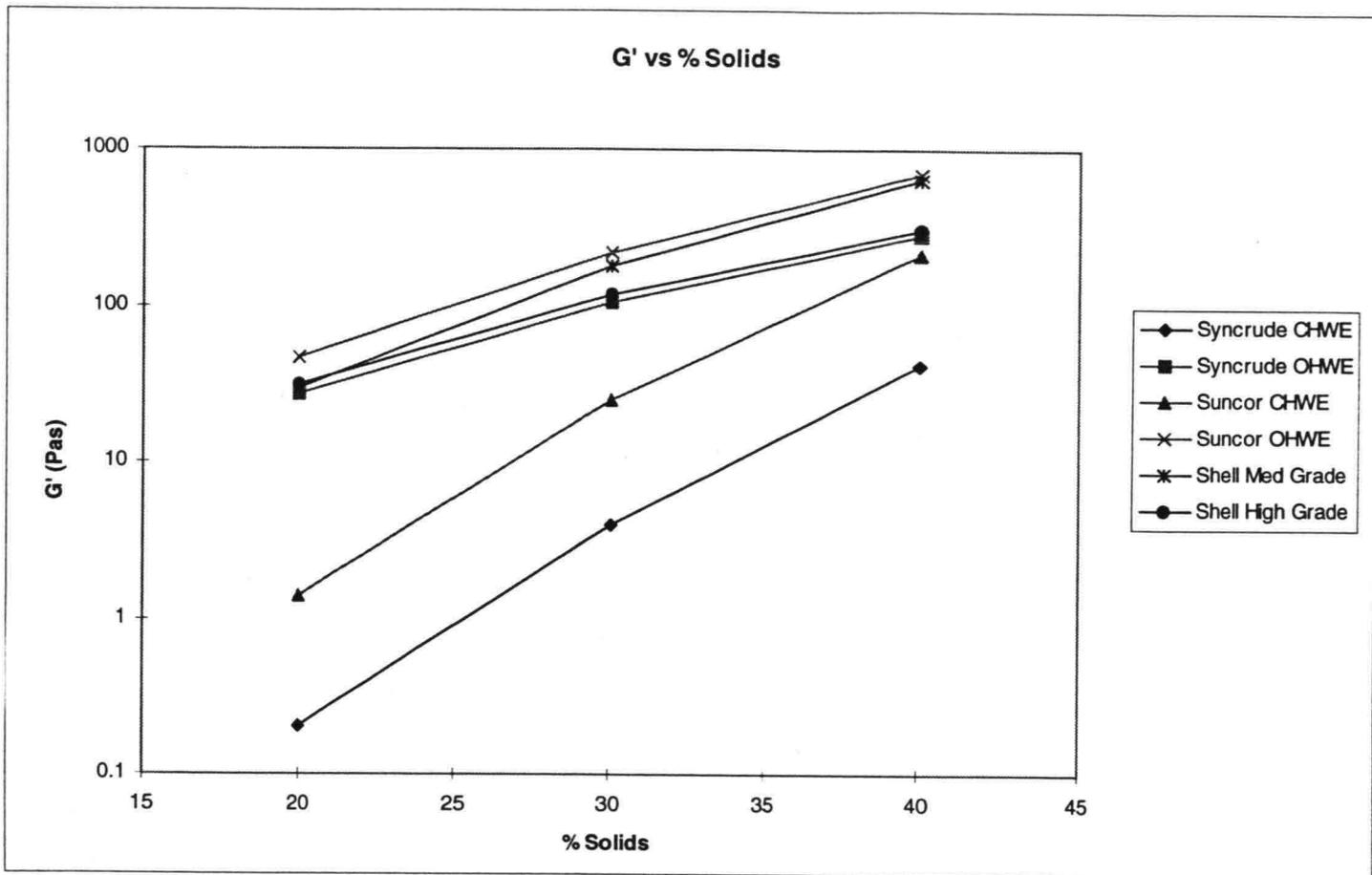
Figure 15: Calculated elastic modulus for Syncrude, Suncor, OWHE, CHWE, slurry tank medium and high grade fine tails, vs percent solids by weight.

Yield Point vs % Solids
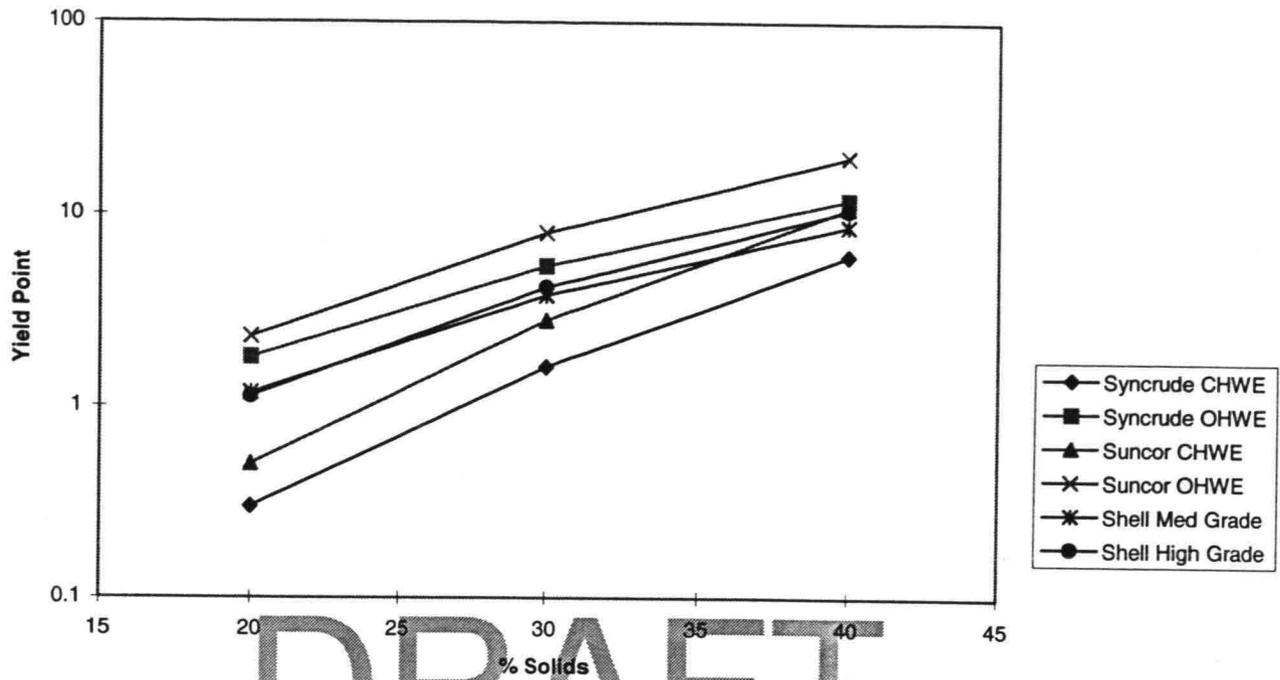
Figure 16: Calculated yield point for Syncrude, Suncor, OHWE, CHWE, slurry tank medium and high grade fine tails, vs percent solids by weight.

TOXICITY

Table 9 shows how the toxicity of tailings release water from the slurry tank conditioning extraction pilot study compares to the current commercial recycle water and a previous pilot study. The slurry tank pilot samples are by far the least toxic, even if one compares them to the OHWE samples.

Table 9: Comparative toxicities for a variety of oil sands extraction tailings water. Although still showing some level of acute toxicity, the slurry tank conditioned tailings would require less treatment to reduce toxicity.

Water Sample	Microtox (IC_{50})
Tailings Pond Water	
Suncor	22-43%
Syncrude	16-50%
OHWE/CHWE Pilot	
CHWE, Syncrude ore	3%
CHWE, Suncor ore	26%
OHWE, Syncrude ore	58%
OHWE, Suncor ore	63%
Shell Pilot Fine Tails Water	
Lease 13	>100%
Suncor low grade (SRC OS)	94%

FROTH CLAYS

A certain proportion of the fine clays will report to the froth and as a result are not part of this investigation of tailings behaviour. It was originally intended that froth fines be included in the tailings for this investigation, but the novel froth treatment process using paraffinic diluents did not produce an appropriate tailings for inclusion in this study. The hydrocarbon content of the froth treatment centrifuge tailings was characterized using TGA-FTIR, and found to have some diluent associated with the solids. These diluent losses will have to be quantified once steady state operation of the froth treatment plant is achieved.

TGA-FTIR results

The sample analysed was centrifuge solids, #4 drum, from the 21-23 July run of the froth treatment plant (split 28 July). The sample was scooped from the material that had settled in the pail.

The sample was run in a BOMEM TG-Plus instrument which consists of a Dupont thermogravimeter (TG) interfaced with a BOMEM MB100 FTIR interferometer. The samples were heated in a He purge (850 ml/min) from 30-80°C at 15°C/min, held for 20 min (drying step), resumed heating to 750°C, held for 10 min (pyrolysis step), then cooled to 400°C, purge switched to He/O_2 (10%), and heated again to 750°C (oxidation step). The balance and thermocouple were constantly monitored while an infrared spectrum of the evolving gases was taken every 30 sec. Values for the weight loss and masses of evolved gases are expressed as weight percent of the initial sample weight.

The following are the average ± S.D. of 2 tests: Drying weight loss (water + hydrocarbon) = 32.5 ± 4.6 wt%

$H_2O = 23.6 \pm 3.9$ wt%

Hydrocarbon = 8.9 ± 0.7 wt% (by difference)

Pyrolysis weight loss = 24.7 ± 1.6 wt%

Oxidation weight loss = 8.2 ± 0.7 wt%

Ash = 34.7 ± 2.2 wt%

Therefore total composition is about 38 wt% hydrocarbon (sum of hydrocarbon from drying phase, pyrolysis weight loss and oxidation weight loss (Only an approximation is made because some of the observed weight loss in the pyrolysis region will be due to inorganic decompositions. This value has been corrected for the amount of water released during pyrolysis on the assumption that this was from the dehydroxylation of clays.); 9 wt% of which is diluent and light ends), 24 wt% H_2O, and 38 wt% inorganics. The nature of the organics can be indicated by the ratio of pyrolysis/oxidation weight losses. For this sample it is 0.331 ± 0.008, which indicates a high (estimated at 60 wt%) asphaltene content (pure asphaltenes give a value of 0.55).

X-RAY ANALYSIS

Since the fraction of the tailings stream that results from subsequent froth processing is relatively small, it will have little impact on the investigation of fine tailings behaviour aside from an increase in sludge make proportional to the amount of fines which report to the froth. Work for the fine tails consortium showed that the impact of mixing froth solids with the fine tailings is negligible. To

confirm that this will be the case, with the slurry tank tailings, the froth solids were separated and characterized. Pyrites were concentrated in the froth fines to some extent, but the mineralogy was otherwise similar to the extraction plant tailings. These results have already been discussed in a previous section.

SUMMARY AND CONCLUSIONS

Slurry tank conditioning of the oil sands and subsequent extraction without process aides results in a fine tailings with properties similar to those obtained from the the OSLO process. Since both the OSLO and slurry tank conditioning processes have a non-caustic water chemistry, the similar clay behaviour is not surprizing. As a result of the non-dispersive water chemistry, improved permeability, and greater sand supporting capability has been shown for the slurry tank conditioned tailings which, coupled with the demonstrated initial rapid settling rate, could result in very favourable tailings properties.

With small scale laboratory tests, the dewatering or consolidation of the clays, although initially rapid, is not significantly better than the Clark tailings over long time periods. However, the greater permeability and load bearing capacity of the slurry tank tailings indicate that with the compaction from deeper tailings deposits, the slurry tank tailings have a much greater dewatering potential than the equivalent Clark process tailings. Further studies are required to confirm this on a larger scale.

Two processes work to make the slurry tank tailings better than similar Clark or even OSLO tailings. The first, a non-dispersive water chemistry, is similar to the OSLO process, and far superior to the Clark process. The second is the control over clay dispersion that is possible with mechanical conditioning. It might be possible to mix the slurry to optimize bitumen release, but minimize clay dispersion. If the clays are not dispersed in the first place, the favourable water chemistry could result in consolidation of clays (increased clay to water ratio) to an even greater extent than has already been demonstrated.

A relationship between clay consolidation and time has been developed which can be used to predict clay behaviour in tailings or recycle water pond design. In addition, the flocc strength demonstrated with the rheology index test indicates that creation of a nonsegregating consolidated tailings mixture should require less reagent than is currently estimated based on experience with the Clark mature fine tailings. This will decrease the ionic strength of the recycle water and significantly

reduce concerns with ultimate reclamation of the mine site. Further work is required to confirm this and to establish the sensitivity of slurry tank conditioning extraction efficiency on water chemistry.

ACKNOWLEDGMENTS

The authors would like to thank Linda Lam, Tammy Giles and Jennifer Koyanagi of CANMET for their thoroughness in carrying out the extensive series of laboratory evaluations.

REFERENCES

1 "Advances in Oil Sands Tailings Research", and Vol. 3-52, edited by the Fine Tails Fundamentals Consortium., 1995. Vol. 1 – p45

2 Mikula, R., Angle, C.W., Zrobok, R., Kan, J., and Xu, Y., "Factors that Determine Oil Sands Sludge Properties", CANMET WRC 93-40 (CF)., 1993

3 Kan, J and Mikula, R. "Particle Size Distribution and Sedimentation of Five OHWE and CHWE Tailings", Division Report WRC 94-51 (CF), CANMET, NRCan, July, 1994.

4 "Standard Specification for ASTM Hydrometers, ASTM Designation: E 100 -81",   Annual Book of ASTM Standards, 74-82, Vol. 05.03, 1991.

5 "Standard Test Method for Particle-Size Analysis of Soils, ASTM Designation: D 422 -63", Annual Book of ASTM Standards, 90-96, Vol. 04.08, 1991.

6 Mikula, R.J., Kasperski, K.L., Burns, R, MacKinnon, M.D., "The nature and fate of oil sands fine tailings, suspensions: fundamentals and applications", ACS Series No. 251, (1995).

7 "Advances in Oil Sands Tailings Research", and Vol. 3-52, edited by the Fine Tails Fundamentals Consortium., 1995. Vol. 4 – p31

8 "Advances in Oil Sands Tailings Research", and Vol. 3-52, edited by the Fine Tails Fundamentals Consortium., 1995. Vol. 2 – p40

9 Xu, Y. and Mikula, R., "The filterability and Surface Tension of Mature Fine Tailings: The Effect of pH and Calcium Ions", CANMET Report WRC 93-37 (CF), 1993.

10 Xu, Y. and Mikula, R., "Filterability of Oil Sands Fine Tailings" CANMET Report WRC 94-55 (CF), 1994

11 "Advances in Oil Sands Tailings Research", and Vol. 3-52, edited by the Fine Tails Fundamentals Consortium., 1995. Vol. 1 – p65

12 "Advances in Oil Sands Tailings Research", and Vol. 3-52, edited by the Fine Tails Fundamentals Consortium., 1995. Vol. 4 – p23

13 Almdal, K., Dyre, J., Wuidt, S., Kramer,O. "Towards a phenomenological definition of the term Gel",Polymer gels and networks 1:5, 1993.

14 Zrobok,R., Kan, J. "Comparison of rheological properties of CHWE-OHWE fine tails from Suncor-Syncrude tests", Division Report WRC94-30 (CF), CANMET Energy, Mines and Resources Canada, September 1994.

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APPENDIX A: Clay content of tailings solids

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Table A-1: The clay content as determined by the methylene blue index for a variety of tailings samples from the slurry tank extraction pilot test program.

ID	Oilsand Type	Sample Date	%w/w MINERAL	METHYLENE BLUE	Clay in Solids	Total Clay	C:W ratio
1146	High Grade	05-Jun-97	2.42%	60	2.9%	0.07%	0.0007
346	High Grade	12-Jun-97	4.18%	271	11.9%	0.50%	0.0052
343	High Grade	12-Jun-97	6.06%	38	1.9%	0.12%	0.0012
344	High Grade	12-Jun-97	10.15%	28	1.5%	0.15%	0.0017
1104	High Grade	04-Jun-97	10.94%	18	1.1%	0.12%	0.0013
345	High Grade	12-Jun-97	11.48%	36	1.8%	0.21%	0.0024
1147	High Grade	05-Jun-97	12.49%	108	4.9%	0.61%	0.0070
535	High Grade	09-Jun-97	13.69%	39	2.0%	0.27%	0.0031
424	High Grade	18-Jun-97	16.77%	17	1.0%	0.17%	0.0020
425	High Grade	18-Jun-97	19.10%	14	0.9%	0.17%	0.0021
1105	High Grade	04-Jun-97	22.50%	25	1.4%	0.31%	0.0039
1476	Lease 13	26-Jun-97	1.99%	36	1.8%	0.04%	0.0004
1475	Lease 13	26-Jun-97	4.60%	41	2.0%	0.09%	0.0010
163	Lease 13	25-Jun-97	5.90%	532	23.1%	1.36%	0.0145
1474	Lease 13	26-Jun-97	6.69%	33	1.7%	0.11%	0.0012
162	Lease 13	25-Jun-97	6.86%	450	19.6%	1.34%	0.0144
1473	Lease 13	26-Jun-97	8.32%	35	1.8%	0.15%	0.0016
1441	Lease 13	25-Jun-97	9.68%	637	27.6%	2.67%	0.0296
1442	Lease 13	25-Jun-97	11.91%	93	4.3%	0.51%	0.0058
1443	Lease 13	25-Jun-97	14.80%	33	1.7%	0.25%	0.0030
1444	Lease 13	25-Jun-97	34.06%	35	1.8%	0.61%	0.0092
1404	Lease 13	25-Jun-97	35.69%	9	0.7%	0.24%	0.0037

Table A-1 continued: The clay content as determined by the methylene blue index for a variety of tailings samples from the slurry tank extraction pilot test program.

ID	Oilsand Type	Sample Date	%w/w MINERAL	METHYLENE BLUE	Clay in Solids	Total Clay	C:W ratio
1713	Low Grade	07-Jul-97	6.35%	131	5.9%	0.37%	0.0040
1712	Low Grade	07-Jul-97	8.08%	229	10.1%	0.82%	0.0089
1583	Low Grade	03-Jul-97	12.52%	192	8.5%	1.07%	0.0122
1835	Low Grade	03-Jul-97	14.35%	122	5.5%	0.79%	0.0092
1585	Low Grade	03-Jul-97	14.46%	83	3.8%	0.56%	0.0065
1657	Low Grade	04-Jul-97	15.24%	106	4.8%	0.74%	0.0087
1834	Low Grade	03-Jul-97	15.56%	306	13.4%	2.09%	0.0247
1710	Low Grade	07-Jul-97	17.84%	108	4.9%	0.88%	0.0107
1711	Low Grade	07-Jul-97	18.43%	48	2.3%	0.43%	0.0053
1526	Low Grade	02-Jul-97	19.78%	30	1.6%	0.31%	0.0039
1586	Low Grade	03-Jul-97	21.85%	126	5.7%	1.24%	0.0159
1659	Low Grade	04-Jul-97	23.26%	140	6.3%	1.46%	0.0191
1584	Low Grade	03-Jul-97	25.08%	146	6.5%	1.64%	0.0219
1662	Low Grade	04-Jul-97	25.47%	48	2.3%	0.60%	0.0080
1660	Low Grade	04-Jul-97	25.60%	48	2.3%	0.60%	0.0081
1833	Low Grade	03-Jul-97	27.43%	19	1.1%	0.30%	0.0042
1527	Low Grade	02-Jul-97	28.14%	49	2.4%	0.67%	0.0093
1658	Low Grade	04-Jul-97	34.00%	126	5.7%	1.93%	0.0293
1661	Low Grade	04-Jul-97	39.43%	48	2.3%	0.92%	0.0153
412	Medium Grade	18-Jun-97	9.06%	255	11.2%	1.02%	0.0112
442	Medium Grade	19-Jun-97	13.13%	48	2.3%	0.31%	0.0035
169	Medium Grade	18-Jun-97	13.31%	236	10.4%	1.38%	0.0160
1267	Medium Grade	19-Jun-97	13.36%	292	12.8%	1.71%	0.0197
1297	Medium Grade	23-Jun-97	13.36%	292	12.8%	1.71%	0.0197
1268	Medium Grade	19-Jun-97	13.50%	260	11.4%	1.54%	0.0178
1298	Medium Grade	23-Jun-97	13.50%	260	11.4%	1.54%	0.0178
456	Medium Grade	19-Jun-97	14.71%	249	11.0%	1.61%	0.0189
1266	Medium Grade	19-Jun-97	14.92%	256	11.3%	1.68%	0.0197
1296	Medium Grade	23-Jun-97	14.92%	256	11.3%	1.68%	0.0197
444	Medium Grade	19-Jun-97	15.18%	162	7.2%	1.10%	0.0129
457	Medium Grade	19-Jun-97	16.35%	312	13.7%	2.23%	0.0267
445	Medium Grade	19-Jun-97	16.45%	135	6.1%	1.00%	0.0120
1365	Medium Grade	24-Jun-97	18.71%	189	8.4%	1.57%	0.0193
443	Medium Grade	19-Jun-97	20.21%	222	9.8%	1.98%	0.0248
1366	Medium Grade	24-Jun-97	25.82%	269	11.8%	3.05%	0.0411
1367	Medium Grade	24-Jun-97	26.33%	309	13.5%	3.56%	0.0484
1368	Medium Grade	24-Jun-97	27.22%	424	18.5%	5.02%	0.0690

APPENDIX B: Recycle water quality predictions for long term recycle scenarios

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Water quality predictions for long periods of recycle are dependent upon the oil sands connate water chemistry. River water inputs are assumed to be constant (rightly so). The following analysis outlines expected long term changes in water chemistry assuming a variety of connate water, and assuming that production of CT will require chemical additions similar to those necessary when Clark process mature fine tailings are used. The completely benign water chemistry observed for the lease 13 ore in the present study in terms of increasing bicarbonate content, coupled with the increased flocc strength for the non-caustic tailings (implying that less reagent will be needed to create CT) makes the following analysis a worst case scenario.

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Lease 13 West Mine Water Management: Water Chemistry

OUTLINE

Preliminary estimates of the water quality for the Shell Lease 13 oil sands development are discussed in terms of water impact on extraction and for ultimate reclamation. Important inputs to any water model relating to oil sands extraction are the connate water chemistry and the amount and type of any process aides. Connate water chemistry was estimated from historical data and since mine water chemistry was also not available, it was estimated to be similar to the connate water chemistry. Although no process aides will be used for extraction, calcium and sulphate will be used in the consolidated tailings (CT) process. By not using caustic or other clay dispersing agents, rapid clay settling is expected relative to conventional (Clark) commercial operations (see Figure 1). A series of index tests showed favourable tailings behaviour for the slurry tank conditioned tailings relative to the Clark process tailings. These tests include double hydrometer tests, rheology and specific resistance to filtration. The test details are published in the Fine tailings consortium report and the results on the slurry tank conditioning samples are in "Characterization of Slurry Tank Conditioning Process Tailings", R.J. Mikula, D. Omotoso, R. Zrobok, and V.A. Munoz (CANMET Report in preparation).
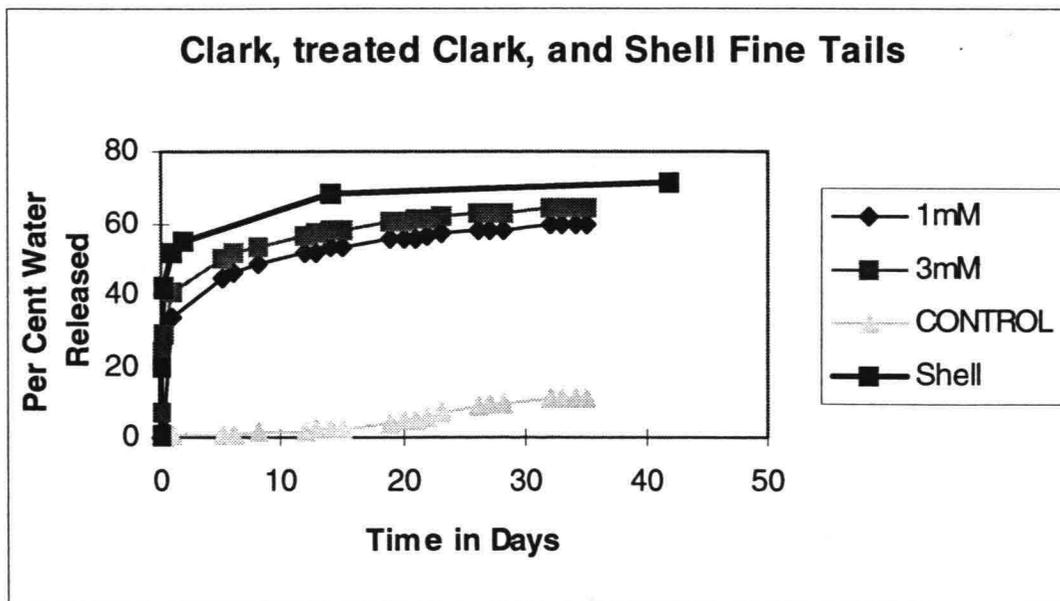
Figure 1: Comparison of the settling rate for the Shell extraction fine tailings compared to Clark and gypsum treated Clark tailings. (1mM = 40 ppm Calcium).

In order to maintain this rapid, favourable tailings behaviour, it may be necessary to control the water chemistry. Bicarbonate in the oil sands (connate water) might eventually result in a recycle water chemistry similar to that in the Clark process. When or if this occurs will be a function of the connate water chemistry. If it is necessary to control bicarbonate levels then this could be accomplished by using an acid-lime CT process where the acidification step will remove bicarbonate. If bicarbonate control is not an issue, then gypsum may be preferred in the CT process for handling or cost reasons. In terms of the water chemistry for extraction, recycle, or discharge, the chemistry of the CT process (gypsum $CaSO_4 \cdot 2H_2O$ or acid $H_2S \; SO_4$ – lime $Ca(OH)_2$), is still dominated by the sulphate concentration. There are sinks for the calcium in charge exchange on the clay surfaces and precipitation as calcite $CaCO_3$. Implementation of the CT process will therefore automatically limit the bicarbonate level and help to prevent development of the elevated pH which will result in slowly settling clays.

The preliminary assessment of the water chemistry which follows assumes a gypsum CT process. The loss of calcium via precipitation and charge exchange have been accounted for. The bicarbonate can be controlled if necessary by using an acid lime CT process without changing the conclusions about the water chemistry. The final decision as whether acid lime or gypsum will be used for the CT process should depend upon a thorough evaluation of the connate water chemistry of the ores being mined.

Estimates of the water quality are provided for the recycle water, beach and fine tails pore water and for the consolidated tailings (CT) release water. The consolidated tailings deposit pore water will be the same as the CT release water for the purposes of this preliminary analysis. Water quality will depend upon a number of factors, including the river water and oil sands connate water chemistry, as well as the relative volumes of water expected for recycle and from CT release. The estimates of water quality for the various streams was done for what is thought to be typical of lease 13 as well as for a worse case connate water chemistry. The following "snapshots" are discussed:

One year after recycle begins

When the plant begins to produce CT

Immediately after mine closure

The far future equilibrium is only speculated upon

Water chemistry assumptions:

The input water chemistries are summarized in Table 1. The water flows are from the tailings management case provided by AGRA and Golder, with implementation of the CT process in stages. Note

that no adverse impacts on either extraction or tailings behaviour would be predicted and in most scenarios the ionic loading only approaches that experienced by Suncor and Syncrude at this point in time and will be much less than that predicted for Suncor and Syncrude with their implementation of the CT process. Organics released to the tailings pond are estimated from the Suncor and Syncrude operating experience and are discussed in a separate section.

Table 1: Summary of the relevant input data for the preliminary water quality model.

Jan-99	River Water	Recycle Water	CT release	Basal Aquifer	Pond Inventory	CT make cyclone UF	MFT	CT Weight	Ore Mtonnes	Clay
Jan-99										
Jan-99	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
May-00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Nov-00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
May-01	0.00	0.00	0.00	0.00	1.04	0.00	0.00	0.00		
Nov-01	0.50	0.00	0.00	0.00	2.30	0.00	0.00	0.00		
Jul-02	23.91	0.00	0.00	1.43	12.38	0.00	0.00	0.00	44.6	2.7
Jan-03	52.54	0.00	0.00	2.19	35.01	0.00	0.00	0.00	89.1	5.3
Jan-04	9.58	41.42	0.00	1.90	20.00	0.00	0.00	0.00	87.1	5.2
Jan-05	22.79	28.26	0.00	1.90	20.00	0.00	0.00	0.00	87.5	5.2
Jan-06	23.36	24.59	5.03	1.90	20.00	7.30	4.45	33.57	90.3	5.4
Jan-07	21.18	22.35	9.99	2.05	20.00	12.12	7.39	55.74	90	5.4
Jan-08	19.92	23.75	10.92	1.54	20.00	12.24	7.48	56.34	90.8	5.4
Jan-09	15.34	27.12	11.58	1.32	20.00	12.09	7.30	55.40	90.3	5.4
Jan-10	12.69	22.60	15.95	1.32	20.00	17.30	10.47	79.34	86.1	5.1
Jan-11	11.50	22.10	18.55	1.32	20.00	19.95	12.16	91.74	87.1	5.2
Jan-12	11.83	22.22	17.35	4.02	20.00	20.63	12.53	94.74	90.3	5.4
Jan-13	10.53	20.39	20.12	3.14	20.00	22.62	13.82	104.11	88.3	5.3
Jan-14	10.18	21.09	22.13	2.75	20.00	23.40	14.37	107.91	91	5.4
Jan-15	6.94	21.39	26.54	2.75	20.00	23.97	18.28	120.71	94	5.6
Jan-16	5.94	21.41	26.13	2.75	22.64	22.46	17.10	113.03	88.2	5.2
Jan-17	5.94	23.61	22.28	2.04	21.10	22.17	16.88	111.57	87.1	5.2
Jan-18	5.94	21.87	23.67	1.55	20.51	22.17	16.88	111.57	87.1	5.2
Jan-19	5.94	21.22	25.03	1.34	20.86	22.17	16.88	111.57	87.1	5.2
Jan-20	5.94	21.47	26.35	1.34	22.49	22.17	16.88	111.57	87.1	5.2
Jan-21	5.94	23.30	23.46	1.34	21.28	22.17	16.88	111.57	87.1	5.2
Jan-22	5.94	21.62	24.38	0.79	20.67	21.97	16.53	110.00	87.1	5.2
Jan-23	4.38				17.22					
Jan-24	4.38				13.78					
Jan-25	4.38				10.33					
Jan-26	4.38				6.89					
Jan-27					3.44					
Jan-28					0.00					
Jan-29					-3.44					

Recycle water:

Recycle water chemistry changes with time as a result of connate water inputs and due to the impact of process aides and tailings treatment. With slurry tank conditioning, there are no process aides to consider, and the most significant impact on recycle water chemistry is the addition of gypsum to create consolidated tailings. The spreadsheet charts (for the typical case) illustrate the increase in ion concentration when CT release water is added to the process water. These increases were modelled taking into account only equilibrium water chemistries and with sulphate assumed to be a conservative ion (it undergoes no chemical or physical reactions which would remove it from the water). In fact, it is likely that sulphate reducing bacteria would serve to remove significant amounts of sulphate from the system either as hydrogen sulphide or as pyrite. In spite of this simplification, the predicted water chemistries are not significantly higher than those currently experienced at Suncor and Syncrude. The charts which plot ionic concentration for a variety of ions as a function of time show a rapid increase in sulphate with the implementation of the CT process. Note that this represents the worst case scenario and also serves to illustrate the importance of defining discharge or water treatment options early in order to minimize impact on the environment due to the relatively innocuous nature of the discharge water before extensive recycling has taken place. Note also that the water chemistry of the deposit pore water is an average of the concentration found throughout the mining operation. The graphs in the appendix show that the beach and CT deposited first will have the lowest ionic strength and will be the most favourable candidates for discharge. The CT and beach deposited later in the mining operation have higher ionic strengths but the amount of the pore water is decreased.

CT Release water:

The CT water chemistry assumes a gypsum addition rate of 600 ppm based on grams of gypsum per tonne of CT. For a CT solids content of 66%, this implies an addition rate of about 1000 ppm based on grams of gypsum per cubic meter of CT. Work at CANMET and at U of A demonstrated that this addition level is more than adequate to reliably create CT (CANMET report 97-13, Consoldiated Tailings: Technical support for the Suncor Commercial Trial by Mikula et al). Furthermore, it is the target addition rate for the Suncor commercial operation (Don Sheeran, personal communication).

The basis of the CT process is manipulation of the fluid phase (clays and water) rheology to suppot the sand grains which provide the driving force to consolidate the mixture. Within a certain clay and total solids content, enough gypsum must be added to "treat" the clays, with an excess that determines the release water chemistry. It has been experimentally determined that the residual calcium in Syncrude's field trial was about 60 ppm, and about 120 ppm for Suncor's field trial. (*Shaw, B., Cuddy, G., McKenna, G., and MacKinnon, M., Non-segregating Tailings: 1995 NST Field Demonstration, Syncrude Research Report 96-2, April (1996)., and Mikula, R.J., and Kasperski, K.L., Nonsegregating tailings release water chemistry: Preliminary report, Division Report WRC 95-23 (CF), CANMET, Natural Resources Canada, (1995)).* One hundred (100) ppm calcium in the CT release water was used for this modelling exercise.

Mine Drainage Water:

Due to lack of detailed information on the flows and water chemistries of the two streams (Komex memo KI97-4577), the chemistry of the mine drainage water was assumed to be the same as the connate water for the oil sands. Water chemistry for the mine drainage water is not expected to be significantly different (in terms of total dissolved solids (TDS)) from connate water (2000 to 4600 mg/L) for the Cretaceous water and similar to the river water in the case of the Quaternary water (300 to 700 mg/L TDS). Mine drainage waters are often discharged to the environment and the data in Tables 2 and 3 show that even at mine closure the extraction water has comparable chemistry to the mine drainage water

Table 2: *Water Chemistry assumptions for the various streams. River water, Syncrude and Suncor pond data is from the "Advances in Oil Sands Tailings Research" document published by the Fine Tailings fundamentals consortium. The connate water chemistries are from the "Sodium Chloride Projections for the Tailings Pond and Dry Bitumen at the Alsands Plant" (420.06) by R.L. Proulx.*

Ions	pH	Ion Conc.	HCO3	Ca	Na	K	Mg	Cl	SO4	cat:an	TDS
River	7.75	mg/L	130	32	13	1	10	11	22	1.04	219
Connate (worst case)	7.60	mg/L	1670	31	1120	310	15	870	110	1.10	4126
Connate (typical case)	7.46	mg/L	540	4	270	50	4	130	40	1.02	1038
Syncrude Pond	8.0	mg/L	851	5	550	9	3	220	210	1.00	1848
Suncor Pond	8.2	mg/L	950	19	366	18	11	43	72	1.00	1479

20 meg/l

Table 3: *Recycle water at mine closure after 14 years of CT process tailings treatment.*

Recycle water	HCO3	Ca	Na	K	Mg	Cl	SO4	TDS
Worst case connate (after 14 years CT)	879	84	531	146	12	429	1917	3998
Typical case connate (after 14 years CT)	329	81	133	24	7	69	1883	2527
Syncrude (current)	851	5	550	9	3	220	210	1848
Suncor (current)	950	19	366	18	11	43	72	1479

Impact of changing water chemistry:

None of the water chemistry scenarios modelled result in ionic strengths that will impact extraction. Only the worst case connate water chemistry situation results in recycle water (even after 20 years) that is significantly higher in TDS than the current Syncrude and Suncor recycle water before implementation of the CT process. Furthermore, recent work at CANMET has demonstrated that the slurry tank conditioning is not as sensitive to water chemistry as the Clark process.

Tailings Behaviour:

In terms of tailings behaviour, bicarbonate concentrations greater than about 300 mg/L can begin to adversely impact tailings behaviour (slow settling similar to the Clark process tailings). If this is the case, then chemical control of bicarbonate can be achieved with acidification. In order to estimate the cost of acidification, calculation of the amount of H_2SO_4 required to maintain the connate bicarbonate at the river water level is used (Table 4).

Table 4: *Sulphuric acid required to reduce the worst case connate water bicarbonate to river water levels*

	cost/tonne of H2SO4 = $200 *		
bicarb difference river and oil sand	tonnes/a HCO_3	tonnes/a H_2SO_4	cost/a
810	2754	2212	$442,400

*Van Waters and Rogers quote 20/6/97

Actual costs would be less because elevated Calcium from the creation of CT will tend to remove bicarbonate and the equilibrium bicarbonate level might easily be less than about 200 ppm (which is unlikely to impact extraction tailings behaviour). Furthermore, the more favourable connate water chemistry will not require bicarbonate reduction at all.

Extraction Behaviour:

The impact of elevated calcium on extraction has been investigated by several researchers and varies considerably. Work at CANMET has shown that the impact of calcium (and other divalent ions) is a function of ore type and conditioning. For high grade ores the impact is considerably less than for lower grades (based on clay content). Similarly, more aggressive conditioning also minimizes the impact. Little or no impact on extraction was observed with calcium concentrations less than about 120 ppm (3 mMole/L) for a wide range of ore types. *(Wallace, D., Henry, D., and Takamura, K., A Physical Chemical Explanation for deterioration in the Hot Water Processability of Athabasca Oil Sand due to Aging, Fuel Science and Technology International, 7 (5-6), 699-725, (1989)., Mikula, R.J., Munoz, V.A., and Kasperski, K.L., Comparison of Tailings Behaviour for Several Bitumen Extraction Methods, Division Report WRC 96-19 (CF), CANMET, Natural Resources Canada, (1996)., Kasperski, K.L. and Mikula, R.J., Modeling the effect of gypsum addition on Suncor plant water chemistry: Interim report, Division Report WRC 95-13 (CF), CANMET, Natural Resources Canada, (1995).*

Even the worst case water chemistry scenarios do not result in calcium concentrations that exceed 100 ppm (2.5 mM/L), nor do they result in total dissolved solids contents which would be expected to have a detrimental effect on extraction.

Reclamation/Discharge:

Impact of residual organics:

Organic contamination of the tailings ponds occurs via loss of bitumen to the tailings and loss of light hydrocarbons from the froth treatment processes. Froth treatment involves the addition of a light hydrocarbon to the froth in order to reduce the bitumen viscosity, followed by removal of the water and solids. In the novel froth treatment technology being investigated by Shell, a significant amount of asphaltenes are rejected along with the solids. If these tailings are burned to utilize the hydrocarbon content in the asphaltenes, the impact on mine water chemistry will be minimal since the resulting ash material could simply be landfilled.

However, if these tailings are combined with the other extraction plant tailings, there will be an impact on the organic loading to the tailings pond. Asphaltenes can be treated like lost bitumen in terms of their impact on recycle water chemistry (i.e. safely ignored). In terms of the light hydrocarbon used as a diluent, some will be lost to the water and clays and the amounts are best estimated using the existing operating experience as a worst case.

The following estimate of the soluble organic content of recycle water is based on observed values in the current operations at Suncor and Syncrude. Measured dissolved organic concentrations vary from 55 - 85 mg/L. These compounds are mostly carboxylic and sulphonic organic acids, including naphthenic acids. Some examples of naphthenic acids concentrations are: >100 mg/L in fresh tailings water, 82 mg/L in Suncor pond water, and, for comparison, 1-2 mg/L in Athabasca River water. Naphthenic acids are emphasised because it is believed that this is the source of the toxicity of oil sands extraction tails. However, it has been shown that naphthenic acid concentration shows a positive correlation with NaOH addition. In the case of a non-caustic extraction process, the expected napthenic acid level (and hence toxicity) will be much lower.

There are also some light ends, which are either lost to the atmosphere or trapped in the fine tails. There are only trace amounts of phenols in recycle water (< 1 µg/L), although values ranging from 25 - 152 µg/L have been measured at various depths in the fine tails of Syncrude's pond. Other organics, such as polyaromatic hydrocarbons (PAH's) are either not detected, or exist in trace quantities (< 0.01 µg/L). (Reference: Fine Tailings Fundamentals Consortium, "Advances in Oil Sands Tailings Research", 1995.) The use of low aromatic content diluents (currently proposed) will minimize the amount of PAH and phenols and the relatively low pH of the slurry conditioning process will minimize the napthenic acid level.

Long Term Effects:

Inorganic Ions

As can be seen from the tables and charts, sulphate is by far the most important ion in terms of concentration in the various release and pore waters. Once chemical equilibrium has been established (what we have modelled here), the only changes to inorganic chemistry make-up in the long-term would be from non-chemical or external causes. Examples of these could be dilution (water being added) or concentration (water evaporating), or surface- or ground-water draining into the system , carrying with it some unknown quantity of ions. Since the precipitation/evaporation ratio is very close to one for the Fort McMurray area, this is not an important factor. Note that long term leaching of pore water from the deposit

is difficult to model and the concentrations of pore water shown in the charts as a function of time are the beach pore water and CT deposit chemistries expected at that time. Leach water chemistry will be significantly lower in sulphate and other ions and in the worst case will be an average of the early deposits and the later ones.

Another important mechanism for the reduction of sulphate due to bacterial action. In the current ponds at Syncrude and Suncor, sulphate levels are generally lower at lower depths of the pond. This is believed to be due to the action of sulphate reducing bacteria and/or interaction with various organic compounds (humic acids). Similar reductions could be expected (but were not modelled) in this process.

Even though the inorganic ions are not expected to change significantly with time, it has been determined that the concentrations expected for CT treatment of tailings at the current Suncor operation could meet discharge criteria since at the predicted levels they are not a concern with regards to toxicity. *(W. James, "Water Quality Review and Treatment Recommendations for Water Released from Suncor's Tailings: Final Report", Alberta Environment Report, 1994).* For the slurry conditioned tailings, the long term ionic loading is significantly less than that predicted for the Syncrude and Suncor operations when they implement the CT process.

Organic Ions

Soluble organics in tailings water will decrease over time, mainly due to bacterial action. Toxicity of oil sands extraction tailings water has been correlated with organic content (specifically the naphthenic acids), and studies have shown that over time (years), if the water has been decanted from the tailings solids, it naturally de-toxifies. *(Fine Tailings Fundamentals Consortium, "Advances in Oil Sands Tailings Research", vol. 2 (1995).*

Table 4 shows how the tailings release water from the Shell pilot studies compares to the current commercial recycle water and a previous pilot study. The Shell pilot samples are by far the least toxic, even if one compares them to the OHWE samples (which is also a non-caustic extraction process).

Table 4: *Comparison of toxicity with fresh tailings release water for a variety of extraction processes.*

Water Sample	Microtox (IC_{50})
Tailings Pond Water	
Suncor	22-43%
Syncrude	16-50%

OHWE/CHWE Pilot	
CHWE, Syncrude ore	3%
CHWE, Suncor ore	26%
OHWE, Syncrude ore	58%
OHWE, Suncor ore	63%
Shell Pilot Fine Tails Water	
Lease 13	>100%
Suncor low grade (SRC OS)	94%

SUMMARY

Water chemistry and water quality estimates, even after 20 years of extraction operation do not result in water qualities that raise any concerns either in terms of tailings or extraction behaviour. Operation at lower pH than the current Clark process will directionally result in better tailings behaviour in terms of both settling rate and napthenic acid contamination (the major determinant of toxicity). Further work is required to quantify the expected napthenic acid levels in order to develop possible treat and release water handling options. Preliminary studies have suggested that predicted levels of inorganic ions are not likely to require reduction before discharge, and with the expected low organic (especially napthenic) loadings, treating and releasing mine process waters may be possible before mine closure as part of the reclamation process. For conventional (Clark) tailings, a year without fresh tailings input will result in significant reductions in toxicity due to degradation of napthenic acids. Since the slurry tank conditioning process operates at a lower pH, significant amounts of napthenic acids are unlikely to be present in the first place (especially with pH or bicarbonate control via acid addition). As a result, the water quality is not expected to be different one year after extraction stops. In addition, the long term water quality (leachate from the beach or CT deposits for example would not be any different than current ground water in terms of the inorganic chemistry. There will be an increase in sulphate, but given that the surrounding soils are sulphate poor, the excess sulphate will rapidly be depleted to original ground water levels. Furthermore, the amount of gypsum required as a process aid could be significantly less for the slurry tank conditioned tailings and that would result in a further reduction in the ionic loading of the recycle water.

Future Studies:

Quantification of the sensitivity of the slurry tank extraction process to divalent ions and to increases in ionic strength.

Definition of the segregation boundary for non-caustic tailings.

Further work on the toxicity of slurry tank extraction tailings water.

Determine the rate at which sulphate is removed from the water phase by interaction with organics and/or bacterial action.

CHARTS AND TABLES

Table 5: *Recycle water chemistry comparisons for the final year of operation for various connate water chemistries compared to the existing commercial operations. All values in ppm (mg/L)*

Worst Case Connate Water

Recycle Water								
year	HCO3	Ca	Na	K	Mg	Cl	SO4	TDS
Recycle begins (2004)	399	32	206	55	11	161	37	901
CT begins (2006)	437	46	219	59	11	182	232	1185
Final Year (2022)	879	84	531	146	12	429	1917	3998
CT release and pore water								
CT begins (2006)	428	100	227	61	11	177	996	2001
Final Year (2022)	881	100	531	146	12	430	2488	4589
Beach pore water								
Recycle begins (2004)	439	32	235	63	11	183	40	1002
CT begins (2006)	477	45	253	67	11	204	242	1299
Final Year (2022)	876	66	532	146	12	427	1263	3323

Typical Case Connate Water

Recycle Water								
year	HCO3	Ca	Na	K	Mg	Cl	SO4	TDS
Recycle begins (2004)	202	27	58	10	9	32	25	362
CT begins (2006)	212	41	61	10	9	35	218	585
Final Year (2022)	329	81	133	24	7	69	1883	2527
CT release and pore water								
CT begins (2006)	209	100	63	10	9	34	982	1408
Final Year (2022)	330	100	133	24	7	69	2454	3117
Beach pore water								
Recycle begins (2004)	212	26	65	11	9	35	26	383
CT begins (2006)	222	40	69	12	9	38	226	614
Final Year (2022)	329	59	133	24	7	69	1229	1851

Recycle Water Quality (typical case connate water)

Beach Pore Water (typical case connate water)

CT Release Water (typical case connate)

Recycle Water Quality (worst case connate water)

Beach Pore Water (worst case connate water)

CT Release Water (worst case connate)