Preparation and characterization of FC electrodes and MEAs

Bock, C.

COLLOIDAL CLAY GELATION – RELEVANCE TO CURRENT OIL SANDS OPERATIONS

P.H. J. Mercier[1], S. Ng[2], K. Moran[2], B.D. Sparks[3], D. Kingston[1], L.S. Kotlyar[1], J. Kung[1], J. Woods[1], B. Patarachao[1] and T. McCracken[1]

1. National Research Council of Canada
2. Syncrude Canada Ltd.
3. V. Bede Technical Associates

Abstract: Ultra-fines are predominantly delaminated colloidal clays with dimensions <0.3μm that exist naturally in oil sands and are released during conditioning of surface mined ores. Critical concentrations of these ultra-fines and the cations present in process water are capable of forming flocculated structures with a very high water holding capacity. During primary separation of bitumen these ultra-fines are detrimental to recovery as a result of increased slurry viscosity as well as through slime coating of released bitumen. Disposition into tailings ponds eventually produces mature fine tailings (MFT) as a result of thixotropic gel formation that entraps coarser solids. The ultra-fines concentration of ~3 wt% observed in MFT coincides with the critical gelation concentration determined for suspensions of ultra-fines in salt solutions with cationic concentrations representative of that in pond water. This observation accounts for 100% of the water holding capacity of MFT and also explains why virtually no water is released once an MFT gel state has been formed. Here, we review earlier research in this area and identify the harmful effects of ultra-fines in some current problematic ores.

Keywords: oil sands, ultra-fines, tailings, gelation, sludging, slime coatings, bitumen recovery

1. INTRODUCTION

Colloidal material occurring naturally in oil sands ores comprises phyllosilicate clays only a few layers thick (1-8 nm) with major lateral dimensions <0.3 μm (Kotlyar *et al.*, 1993, 1995). During conditioning in conventional water based separation processes, the dispersion of this ultra-fine material into the oil sands slurry depends on ore type as well as the mechanical and chemical dispersion energy used in the extraction process (Kotltyar *et al.*, 1985). It has been demonstrated (Kotlyar *et al.*, 1996) that in the presence of a sufficient concentration of cations only a small amount of ultra-fines (~3 wt%) is required to form a thixotropic gel with a very high water holding capacity. For ultra-fines concentrations up to this critical gelation concentration (CGC) slurry viscosity appears to increase progressively, thereby inhibiting settling of coarser solids and separation of bitumen droplets from the middlings zone of a gravity separation vessel (GSV). In extreme cases the formation of a dense sludge in the GSV requires operational shutdown. Organic matter adsorbed on these colloidal solids may produce biwettable characteristics that results in strong attraction to bitumen-water interfaces. Slime coatings of extremely small particles are capable of stabilizing bitumen as smaller, more difficult to float droplets (Levine *et al.*, 2000; Kasongo *et al.*, 2000).

When the slurried waste solids from bitumen separation processes are disposed into tailings ponds the coarsest solids separate rapidly to form beaches. Finer suspended material is carried out into the pond, slowly releasing water as it settles to produce mature fine tailings (MFT). The MFT always contains close to 3 wt% of ultra-fines, an amount sufficient to produce a gel with enough internal volume to incorporate all of the water present in mature tailings (Kotlyar *et al.*, 1992). Coarser solids carried into the pond become entrapped within the gel structure to produce the final solids concentration of about 30 wt% observed in MFT.

In this paper we summarize previous research on the role of ultra-fines in bitumen separation from oil sands and MFT formation.

2. ULTRA-FINES PROPERTIES

2.1 Nature of Ultra-fines

Techniques have been developed for the quantitative separation of ultra-fines from both oil sands ores and MFT. These methods involve chemical dispersion of the solids with mild agitation (Kotlyar *et al.*, 1985) followed by sequential application of increasing centrifugal force to separate the solids into size fractions based on differential sedimentation. For separating ultra-fines from MFT (Kotlyar *et al.*, 1992), repeated washing and centrifugation steps allow the original salty water to be replaced by deionised water to produce completely dispersed systems (colloidal sols); the process is completely reversible.

Transmission electron microscopy (TEM) of separated ultra-fines material (<0.3 μm), see **Figure 1**, shows broken, hexagonal clay particles with lateral dimensions of 60 to 270 nm, 1 to 8 nm thickness (Kotlyar *et al.*, 1998). Particle thickness increased with lateral dimension. All ultra-fines material is associated to some degree with organic material (Kotlyar *et al.*, 1992). When the amount of organic is low the solids are predominantly associated with the aqueous phase, intermediate amounts of surface organics produce biwettable characteristics where solids preferentially collect at interfaces, ultimately the highest organic levels result in a fraction that remains exclusively with the bitumen phase (Kotlyar *et al.*, 1988). A wettability study (Darcovich *et al.*, 1989) confirmed that the aqueous ultra-fines were indeed more polar and less hydrophobic than the ultra-fines associated with bitumen. Surface analysis (Bensebaa *et al.*, 2000) indicated patchy surface coverage by both humic and asphaltic components.

An XRD methodology was recently developed to analyze clay minerals in oil sands (Mercier *et al.*, 2008a, b). This XRD technique has produced similar results to existing ultra-fines measuring techniques by estimating the fraction of phyllosilicate mineral crystallites with 1-3 composite layers thickness in clays (<3 μm solids) separated from oil sands. Illite-to-kaolinite mass ratios were shown to increase as particle size decreased. The XRD powder pattern of the smallest size fraction of a waste unit sample (*i.e.* overburden barren clay-size material) was demonstrated to correspond to delaminated illite rather than kaolinite. Application of the new XRD technique to ten oil sands from current operations showed that the specific surface area of illite was significantly greater for four samples identified as problematic in batch-extraction unit (BEU) tests.

2.2 Flocculation and Gelation of Ultra-fines

Settling tests allow evaluation of the size, density and settling rates of particle aggregates or flocs (Kotlyar *et al.*, 1998). The lowest concentration at which a well defined interface formed decreased with ultra-fines particle size and increase in salt concentration. Such hindered settling occurs when flocs interact and no longer settle freely, see **Figure 2**. At equilibrium, the settled volume fraction of the individual size components in the sediment ranged from 0.004 to 0.014 for the finest (60 nm) to coarsest sizes (270 nm). Different mixtures of ultra-fines sizes yield final volume fractions between these values.

Photon correlation spectroscopy measurements to determine changes in floc diameter with time allow flocculation kinetics to be investigated (Kotlyar *et al.*, 1996). **Figure 3** presents results for a solids concentration (0.06 vol%) low enough to allow sufficient time to observe the kinetics. At low concentrations of salt (5 and 10 mM NaCl = 115 and 230 ppm Na^+) the repulsion between particles is still sufficient to inhibit "sticking" collisions (Weitz *et al.*, 1991) and floc growth is slow; this corresponds to a reaction limited regime. At a higher salt concentration (20 mM NaCl = 460 ppm Na^+), floc growth is initially reaction limited but much more rapid. At longer times floc growth slows owing to the increased time required for larger flocs to encounter each other; in this region reaction is diffusion limited. The settling tests summarized on **Figure 4** show that rapid water release for recycle is favoured by fast flocculation whereas slow floc growth produces higher sediment density.

A gelation index (GI) can be determined by NMR measurements (Ripmeester *et al.*, 1993) on clay suspensions in the presence of different cations (Kotlyar *et al.*, 1996). This approach allows the gelation process to be studied for concentrations of ultra-fines and cations typically encountered in actual oil sands separations. The results on **Figure 5** demonstrate that complete ultra-fines gelation, *i.e.*, a GI of 100%, requires sufficient time plus critical ultra-fines and cation concentrations. In this regard total cation concentration is more important than cation valency. An equivalent monocation concentration (EMC) can be estimated using the valency rule (Adam, 1956) that postulates

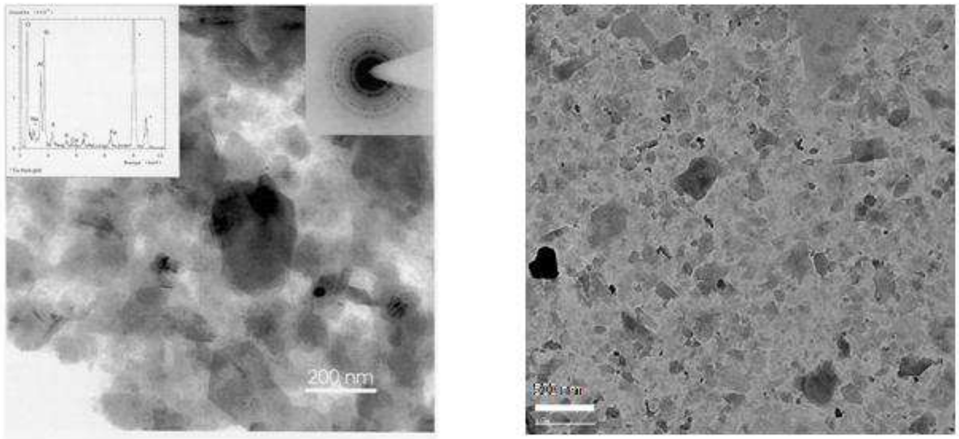

Figure 1: Typical TEM micrographs of ultra-fines separated from Athabasca oil sands.

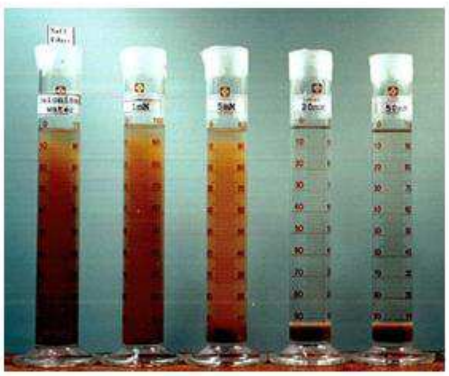

Figure 2: Effect of salt concentration on the settling behaviour of dilute suspensions of ultra-fines. After Kotlyar et al. (1996).

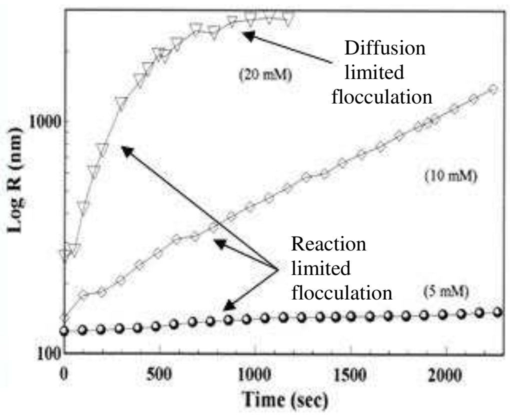

Figure 3: Cluster size (R) versus time in dilute suspensions of ultra-fines for different salt concentrations. After Kotlyar et al. (1996).

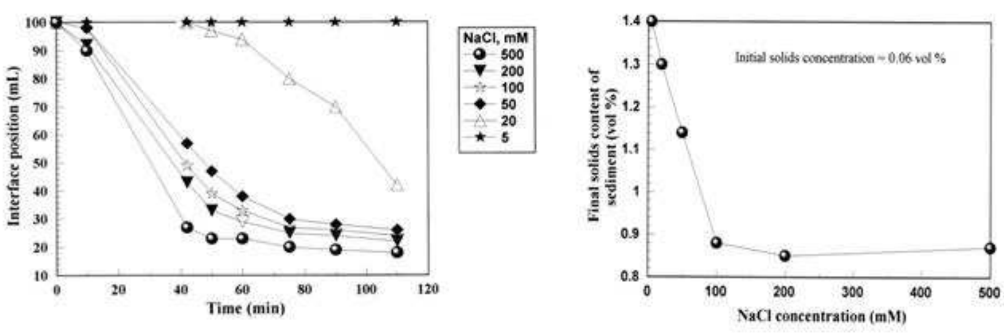

Figure 4: (Left) Time dependence of water release (mL) from dilute suspensions of ultra-fines in salt solutions of different concentrations. (Right) Effect of salt concentration on solids content of sediments after six months settling of dilute suspensions of ultra-fines in salt solution. After Kotlyar et al. (1996).

an order of magnitude increased flocculation effect of divalent over monovalent cations. Depending on overall cation concentration, a space filling gel network is produced in a matter of minutes by an ultra-fines concentration of 1.2 vol% (~3 wt%). The same result is achieved over correspondingly longer time periods for lower concentrations of either ultra-fines or cations. While complete gelation occurs almost instantaneously at 3 wt% ultra-fines, significant effects are noted at a gel onset concentration (GOC) as low as 1.0 to 1.4 wt% (O'Carroll, 2000).

Flocculation, and ultimately gelation, of coarser clay fractions (2 to 3 μm) also occurs in the presence of cations but compared to ultra-fines much higher solids concentrations (>10 wt%) are needed (Tu *et al.*, 2005).

3. APPLICATION TO COMMERCIAL OPERATION

In conventional, water based oil sands extraction, primary separation of bitumen is essentially a gravity based process. Once bitumen is liberated its separation into the froth depends on many factors, including: slurry viscosity (Schramm, 1985), relative density of bitumen to slurry (Shaw *et al.*, 1996), droplet size (Ng *et al.*, 2000) and aeration (Kasongo *et al.*, 2000). Even if all other factors are favourable, high slurry viscosity may be a deciding factor because the free movement of oil droplets through the middlings into the froth will be hindered and perhaps prevented entirely.

In this regard, flocculation and gelation may be associated with reduced segregation of solids and bitumen in GSV middlings. Based on either fines or bitumen contents, the examples given on **Figure 6** represent two ores that were not expected to exhibit poor bitumen recovery. However, the significant difference in segregation behaviour is a reflection of very different processability in the two cases. Poor segregation, with concomitant low bitumen recovery, is associated with the oil sands containing ultra-fines in excess of the GOC (1.8 *cf.* 1.4 wt%). By comparison, a low value ultra-fines content (0.5 wt%) in the other oil sands is linked to good bitumen recovery. Increasing the water to slurry ratio reduces the ultra-fine concentration in the middlings and allows segregation of solids and bitumen while recovery proceeds normally in both cases. Similar effects can be achieved by blending ores with high and low ultra-fines content. Flocculation in the middlings can also be reversed by use of dispersion agents; while sodium hydroxide falls into this category stronger agents such as silicates or phosphates may also be used.

As mentioned previously, a long standing guideline for oil sands processability has been fines (<44 μm) or the related bitumen content (Cuddy, 2000). However, some ores do not fit this profile and the number appears to be increasing as new areas are opened for mining. An explanation for this phenomenon can be seen on **Figure 7** where fines are plotted against the corresponding ultra-fines contents; the dotted curves are the 95% confidence limits for the linear regression. It is apparent that there is a reasonable correlation between fines and ultra-fines in most cases. However, in some instances there is a marked deviation as indicated by the noted anomalous oil sands.

The results on **Figure 8** compares total solids with ultra-fines present in the middlings zones of BEU and pilot tests. The pilot test involved an anomalous ore containing 2.9 wt% ultra-fines, but only 13 wt% fines. During the test, solids content in the middlings progressively increased until it reached ~30 wt%; at this point process failure required a plant shutdown. Ultra-fines content of the middlings was then about 2 wt%, well above the GOC. Usually, the amount of ultra-fines released into the middlings is about 70 % of that in the original ore (O'Carroll, 2000); this is in accord with the results from the anomalous ore in this case.

On average, the amount of ultra-fines in tailings from extraction plants is usually much less than the critical value for gelation; although the cation content of the tailings pond water is normally well above the critical amount, gelation does not occur immediately and a significant amount of water is released. However, time is not an issue in tailings ponds and hindered settling eventually occurs, leading to the progressive accumulation of sludge through MFT formation. The ultra-fines concentration of ~3 wt% observed in MFT coincides with the critical gelation concentration determined for suspensions of ultra-fines in salt solutions with cationic concentrations representative of the chemistry in pond water. This observation accounts for 100% of the water holding capacity of MFT and also explains why virtually no water is released once an MFT gel state has been formed.

4. CONCLUSIONS

Ultra-fines are predominantly colloidal phyllosilicate clays with dimensions <0.3 μm that naturally exist in oil sands and are released into the water phase during processing. In the presence of critical cation concentrations, this oil sands component is capable of forming thixotropic gels at low concentrations. Divalent cations such as calcium and magnesium have an enhanced effect on this process. Even before occurrence of gelation, slurry viscosity or thickening can increase sufficiently to reduce the segregation of coarser solids and prevent bitumen droplet separation. In some cases, adsorbed organic on the surfaces imposes biwettable characteristics on the ultra-fines that result in formation of emulsified bitumen droplets that are too small to float easily. Ultra-fines deposited into tailings ponds continue to flocculate and settle while entrapping coarser particles within the open structure. Eventually mature fines tailings are formed that always contain the same amount of ultra-fines (~3 wt%) regardless of the total solids content. Ultra-fines content therefore represents an important indicator for both bitumen recovery and extent of fine tailings formation. Recent XRD developments for analyzing clay minerals in oil sands may make the determination of this important parameter easier.

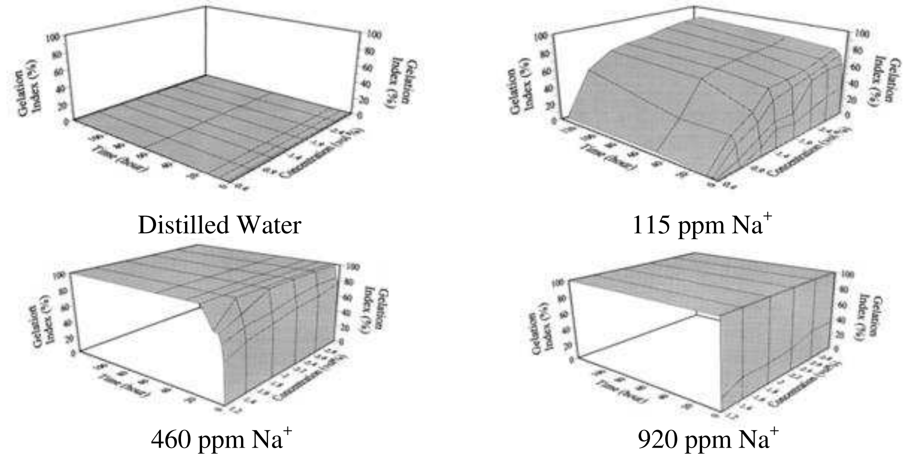

Figure 5: Time and salt concentration dependence of gelation index for dilute suspensions of ultra-fines. After Kotlyar et al. (1996).

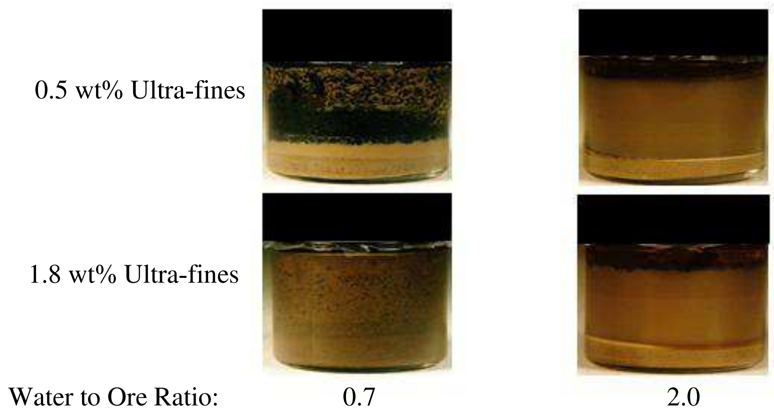

Figure 6: Oil sands with different ultra-fines content at different process water to ore ratios. After O'Carroll (2000).

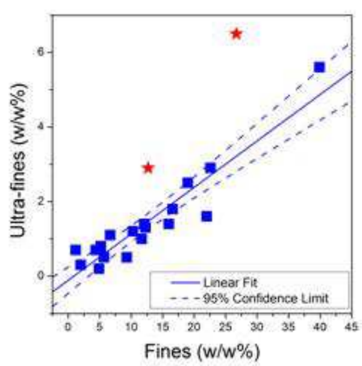

Figure 7: Ultra-fines *vs.* fines contents for a number of oil sands. Data from O'Carrol (2000).

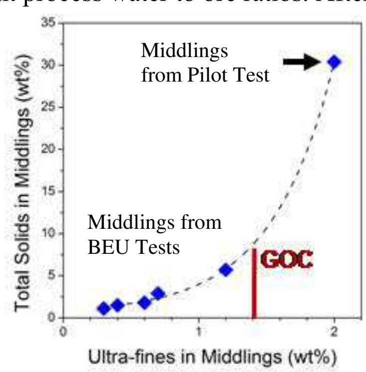

Figure 8: Total solids *vs.* ultra-fines contents in middlings from BEU and pilot tests for a number of oil sands. Data from O'Carroll (2000).

REFERENCES

Adam, NK. (1956). Physical Chemistry, p. 587. Clarendon Press, Oxford.

Bensebaa, F., L.S. Kotlyar, B.D. Sparks and K.H. Chung (2000). Organic coated solids in athabasca bitumen: Characterization and process implications. CJChEng, 78, 610-616.

Cuddy, G. (2000). Empirical studies on the relationship between process water chemistry and oilsands processability. CONRAD Fundamental Extraction Seminar, Problem Ore Workshop, March 28.

Darcovich, K., L.S. Kotlyar, W.C. Tse, J.A. Ripmeester, C.E. Capes and B.D. Sparks (1989). Wettability study of organic rich solids separated from Athabasca oil sands. Ener. & Fuels, 3, 386.

Kasongo, T., Z. Zhou, , Z. Xu, and J.H. Masliyah (2000). Effect of clays and calcium ions on bitumen extraction from Athabasca oilsands using flotation. CJChEng., 78, 674-681.

Kotlyar, L.S., B.D. Sparks, Y. Le Page and J.R. Woods (1998). The flocculation behaviour of nano particles of different size in the presence of salt. Clay Min., 33,103-107.

Kotlyar, L.S., B.D. Sparks and R. Schutte (1996). Effect of salt on the flocculation behaviour of nano particles in oil sands fine tailings. Clays and Clay Min., 44 (1), 121-131.

Kotlyar, L.S., B.D. Sparks, and R. Schutte (1995). Role of bicarbonate ions in the stability of ultra-fines suspensions.J. Environ. Sci. Health, A30(6), 1277-1288.

Kotlyar, L.S., Y. Deslandes, B.D. Sparks, H. Kodama and R. Schutte (1993). Characterization of colloidal solids from Athabasca fine tails. Clays & Clay Min., 41(3), 341-345.

Kotlyar, L.S., B.D. Sparks, C.E. Capes, R. Schutte (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(1), 55-61.

Kotlyar, L.S., J.A. Ripmeester, B.D. Sparks and D.S. Montgomery (1988). Characterisation of organic rich solids fractions isolated from Athabasca oil sands, using a cold water agitation test. Fuel, 67(2), 221.

Kotlyar, L.S., B.D. Sparks, H. Kodama (1985). Isolation of inorganic matter-humic complexes from Athabasca oil sands. AOSTRA J. Res., 2(2), 103-111.

Levine, S., B.D. Bowen and S.J. Partridge (1989). Stabilization of emulsions by fine particles I. Partitioning of particles between continuous phase and oil/water interface. Coll. & Surf., 38, 325-343.

Mercier, P.H.J., B. Patarachao, J. Kung, D.M. Kingston, J.R. Woods, B.D. Sparks, L.S. Kotlyar, S. Ng, K. Moran and T. McCracken (2008a). X-ray diffraction (XRD)-derived processability markers for oil sands based on clay mineralogy and crystallite thickness distributions. Ener. & Fuels, 22, 3174-3193.

Mercier, P.H.J., Y. Le Page, Y. Tu and L.S. Kotlyar (2008b). Powder X-ray diffraction determination of phyllosilicate mass and area versus particle thickness distributions for clays from the Athabasca oil sands. Pet. Sci. and Tech., 26, 307-321.

Ng, S., P. Warszynski,, M. Zembala, and K. Malysa (2000). Bitumen-air aggregates flow to froth layer: II. Effect of ore grade and operating conditions on aggregate composition and bitumen recovery; Min. Engng, 13, 1519-1532.

O'Carroll, J.B. (2000). Factors affecting bitumen recovery from oilsands. MASc. Thesis, Department of Chemical Engineering, University of Ottawa, Ottawa, Canada.

Ripmeester, J.A., L.S. Kotlyar and B.D. Sparks (1993). ^{2}H NMR and the sol-gel transition in suspensions of colloidal clays. Coll. & Surf. A: Phys. Chem. Engng. Asp., 78, 57-63.

Schramm, L.L. (1985). US Patent 4637417, May 3rd.

Shaw, R.C., L.L. Schramm, and J. Czarnecki, (1996). Suspensions in the hot water flotation process for Canadian oil sands. In: Suspensions: Fundamentals and Applications in the Petroleum Industry (L.L. Schramm. (Ed)), 639-675 (Advances in Chemistry Series 251). American Chemical Society, Washington, D.C.

Tu, Y., J.B. O'Carroll, L.S. Kotlyar, B.D. Sparks, S. Ng, K.H. Chung and G. Cuddy (2005). Recovery of bitumen from oil sands: Gelation of ultra-fine clay in the primary separation vessel. Fuel, 84, 653-660.

Weitz, D.A., M.Y. Lin and H.M. Lindsay (1991). Universality laws in coagulation. Chemo. Intell. Lab. Syst., 10, 133-140.