THE ROLE OF ULTRA FINE PARTICLES IN OIL SANDS FINE TAILINGS REDUCTION

by

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Abstract

Syncrude Canada Ltd. and Suncor Inc. extract bitumen from Athabasca oil sands in Northeastern Alberta. The Clark Hot Water Extraction (CHWE) process is used for the bitumen recovery. The waste stream containing 40- 60 wt% of mineral solids suspended in process water, some unrecovered bitumen, water soluble organic matter and salts, is discharged into man-made ponds. The coarse solids almost immediately settle onto beaches. Finer mineral particles remain in the top layer to form a so called "fine tailings" layer, releasing some water which is recycled back into the recovery process. Fine tailings exhibit extremely poor dewatering characteristics.

Accumulated knowledge allows the very high water holding capacity to be attributed to the presence of a gel-like structure created by ultrafine aluminosilicate clays, capable of entrapping coarser solids. The major factors responsible for fine tailings properties are the presence of ultrafines in the parent ore and the ionic composition of the process water.

The research presented here deals with two closely related projects. The first project concentrated on finding an efficient treatment method for already existing fine tailings. The second project was to evaluate process modifications aimed at fine tailings reduction and to develop an understanding of the effect of electrolyte in the process water on the characteristics of fine tailings.

A variety of additives have been tested in an attempt to increase dewatering of fine tailings. In general, increased dewatering was not achieved as a result of chemical treatment. A separated fraction of ultrafines was also subjected to chemical treatment. Once again, chemical treatment alone did not result in an increased amount of released water. It has been concluded that the presence of ultrafines is the major factor preventing the fine tailings from dewatering. The behavior of ultrafines separated from fine tailings was further investigated. A ^{2}H NMR technique was applied to determine the gelation rates for ultrafines at different electrolyte concentrations. The gelation concentration was determined using ultrafines suspensions diluted with salt solutions. Results indicate, that while gelation time varies from minutes to weeks, the gelation concentration is always about 3 - 4 wt%, even at an extremely high salt concentrations

further floc densification (dewatering) is impossible. This is likely a consequence of the rigid fractal nature of the formed flocs. It is believed, that steric hindrance of interfering fractal flocs is the major factor preventing solids' densification.

Although adequate floc densification could not be achieved using chemical treatment, dewatering was increased markedly using freeze-thaw (a physical method). A combination of freeze-thaw and chemical treatment results in a further increase of released water.

Chemical treatment alone can, however be of interest if non-segregating sediments are required for further physical or mechanical treatment. It has been found that in all cases, the chemical addition resulted in strengthening of the gel structure, which leads to non-segregating behavior of the sediments.

An investigation of several non-segregating sludges from Northern Holland was carried out. These sludges, having very poor dewatering characteristics, nevertheless respond to mechanical treatment. An investigation led to the conclusion that in these sludges specific interactions are of primary importance. Strengthening of the gel network (non - segregating sediments) of oil sand fine tailings could also be achieved using mechanisms found in the Dutch sludges. From this point of view, the results of the study of several "difficult" Northern Holland sludges which respond to conventional treatment appear to be very promising.

To evaluate process modifications, samples of different process streams produced during comparison pilot plant runs performed at Syncrude Canada Ltd. were investigated. Using these samples, it was possible to study the effect of process water composition on the properties of intermediate discharge streams, before they are finally recombined and disposed of in the settling ponds. The aggregation state and distribution of ultrafines were determined in all stream samples. These two parameters are believed to depend on process water composition, affecting in turn the dewatering of fine tailings and the segregating behavior of the settling sediments. It was also of interest to determine the contribution of a biwetted solids fraction of ultrafines. For comparison purposes the settling behavior of stream samples, was monitored until no further changes in settling were observed.

In conjunction with the characteristics of parent oil sand ores, results prove that the settling rate was different only up to the point where the gelation onset concentration of the ultrafines fraction was reached, regardless of the ionic composition of water. Modifications to

the extraction process resulted only in marginal differences in the characteristics of the discharge streams. The final volume of fine tailings depends on the ultrafine content in the oil sand ore, and not on the type and concentration of the electrolyte in the process water. Although modified extraction processes resulted in faster settling, the modification produced "dirtier"(containing more clay) secondary froths, thus bringing about other process problems.

Acknowledgments

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List of Abbreviations

BUS	Biwetted Ultrafine Solids
CHWE	Clark Hot Water Extraction process
GCOS	Great Canadian Oil Sands extraction plant
GC	Gelation Concentration
DLVO	Derjaguin, Landau, Verwey, Overbeek Theory
^{2}H NMR	Deuterium Nuclear Magnetic Resonance
IR	Infrared Spectroscopy
k	Boltzmann's constant
OHWE	OSLO Hot Water Extraction process
ORS	Organic Rich Solids
PSV	Primary Separation Vessel
TEM	Transmission Electron Microscopy
UF	Ultrafines
WSS	Wet Sediment Solids
wt%	Weight percent
xG	Centrifugation force relative to acceleration in gravity
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction Spectroscopy

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Chapter 1

Introduction

1.1 General Overview

The world's largest oil sands deposits, located in Northeastern Alberta, contain approximately 300 billion cubic meters of bitumen. It has been estimated that nearly 15 billion cubic meters of bitumen are potentially recoverable by the existing Clark Hot Water Extraction (CHWE) process. Two major extraction plants are operating in the area, Suncor Inc and Syncrude Canada Ltd. Surface mined oil sands are sent to an extraction plant, where about 97 % of bitumen is removed by flotation. The process consists of four major steps [1] outlined schematically in Figure 1.1.

The first step of the process takes place in large conditioning tumblers where temperature is controlled at 80-85°C by the flow rate of steam and hot water injected into the tumbler. Under such conditions oil sands and water form a pulp of 70 -85 wt% solids. Sodium hydroxide is added to maintain pH at about 8.5.

Separation of the pulp takes place in the Primary Separation Vessel (PSV), where the slurry is further diluted to allow for better settling and flotation. The rapidly rising bitumen is skimmed from the top of the separation vessel forming a coherent mass known as PSV froth. Fast settling solids, containing small amounts of bitumen referred to as PSV tailings, are withdrawn from the vessel and used for construction of dikes around the disposal ponds. The medium in which flotation and settling take place is termed PSV middlings. It consists of water, suspended minerals and significant amounts of unrecovered bitumen.

The third step of the process, the scavenging for recovery of the residual bitumen present in PSV middlings, utilizes air flotation as separation method. This results in two additional process streams, secondary froth and secondary tailings. The latter fraction is transported to the tailings disposal pond. A cross-section of the pond is shown in Figure1.2. Combined primary froth and secondary froth is sent to the froth cleaning plant, where it is diluted with naphtha and subjected to two-stage centrifugation. Another waste stream of comprising suspended mineral solids is generated. All waste streams are hydraulically conveyed to the settling ponds; as solids settle clear water is released that can be recycled to the extraction plant.

PSV tailings, discharged onto the pond dikes, settle rapidly. Sand is mechanically compacted to raise the dike level. The suspension which migrates towards the center of the pond exhibits slow settling rate. The remaining tailings streams are discharged over the top of the dike. The coarse sand portion of the tailings creates an extensive beach gently sloping towards the interior of the pond. The unsettled slurry, referred to as beach run offs, drains into the pond. This fraction eventually forms a gel-like system, preventing even coarse solids from sedimenting. The non-settling portion of the pond content is called fine tailings. It consists of an average 66 wt% water, 31 wt% solids, and 3 wt% unextracted bitumen.

A modified method for bitumen extraction has recenly been proposed [28]. Oil sands is slurried with water fortified with calcium ions. Flotation agents and kerosene are added to promote bitumen flotation. This innovative process is called the OSLO Hot Water Extraction (OHWE) process. The OHWE fine tailings stream has been reported [28,29] to be readily treatable to release clear water for recycling and solid sediment for disposal. It has been suggested, that the OSLO process results in faster settling, less toxic and more compact tailings. The sediment is stronger and more permeable than conventional tailings. A comparative study of the Clark and OSLO processes was only performed at the laboratory scale. It was recognized, that a full evaluation would not be possible without pilot plant studies [29].

The objective of this research project was twofold: (1) - to develop a method of eliminating existing tailings by means of an economically suitable treatment, and (2) - to evaluate the effect of process water modification to reduce fine tailings generation or, ideally, to complete elimination of liquid wastes.

Part 1 of the investigation was carried out using chemical treatment of fine tailings provided by Suncor Ltd. No increase in dewatering was achieved, regardless of the type and concentration of the additive. Subsequently, a fraction of ultrafines separated from fine tailings, was used to study the effect of chemical treatment on suspensions of ultrafines. A ^{2}H NMR technique was then applied to determine the critical gelation concentration and gelation rates at different concentrations of salts. A combination of chemical treatments and freeze-thaw methods was found to give significant dewatering of the ultrafines suspension. It was noticed that in all cases of chemical treatment alone, non-segregatting behavior of sediments was observed. Diluted fine tailings exhibit slow, so called "differential" settling. In this case coarse particles and those which have lower resistance to flocculation, settle first, leaving the rest of the solids in suspension. Slow differential settling creates conditions favorable for creation of segregating sediments, in which a clear interface between layers of densely packed solids is visible. Non-segregating behavior observed in the experiment could be of great importance if further treatment of sediments is considered (for example, co-charging with additional sand and before recultivation). Non-segregating behavior was observed in several sludges originating from Northern Holland. These difficult to treat sludges nevertheless respond to conventional mechanical treatment. Possible mechanisms responsible for the Dutch sludge structure formation were studied. Comparison of Dutch sludges with Suncor fine tailings gives a potential opportunity for the mechanical treatment of fine tailings.

Part 2 represents a comparative study of all streams derived from OSLO and Clark hot water extractions performed using both Suncor and Syncrude oil sands. Samples used in the study were obtained during pilot plant runs at Syncrude's research facilities. The samples provided an opportunity to study the properties of discharge streams before they are combined and finally discharged into the settling pond. The study has made it possible to predict whether costly modifications will result in lower discharge and more beneficial process performance.

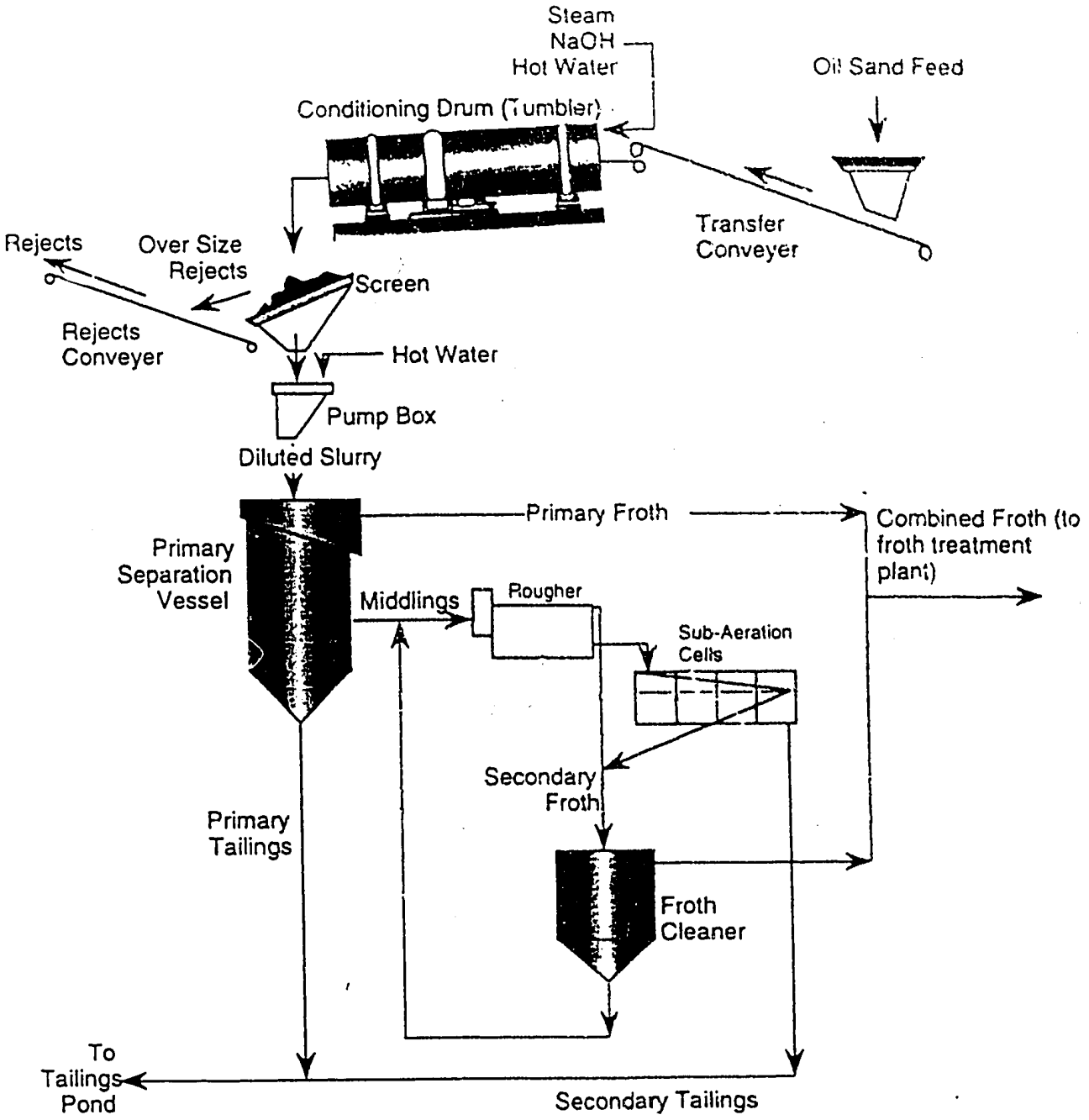

Figure 1. 1 Schematic of the hot water bitumen extraction process.

1.2 Scale of the Problem

Currently, Suncor is operating on its fifth tailings pond. A sixth pond currently under construction, is proposed to be the final depository pond for all the accumulated tailings after the plant's operation terminates. Ponds 2 and 3 have been merged into one pond. The total surface area of the ponds is approximately 6 km^2. The depths in center of the ponds reach 60 m. The total accumulation of tailings in Suncor ponds was 77 x 10^6 m^3 in 1991 [9]. Syncrude has one pond with its surface area extending up to 15 km^2, and depth of 40 m. The total accumulation reached 135 x 10^6 m^3 in 1989 [3].

Residual bitumen and water soluble organics present in the tailings ponds are considered to be a major factor responsible for their environmentally hazardous character. From an economical point of view, tailings containing 3 wt% bitumen discharged at a rate of 650 x 10^3 tonne/day from both Syncrude and Suncor plants implies a loss of 19.5 x 10^3 tonnes of bitumen daily [9]. Moreover, the tailings ponds will become subject to reclamation when the mining companies lease terms expire. In view of the huge volumes to be treated, the method proposed for treatment of tailings has to be both technically suitable and economical.

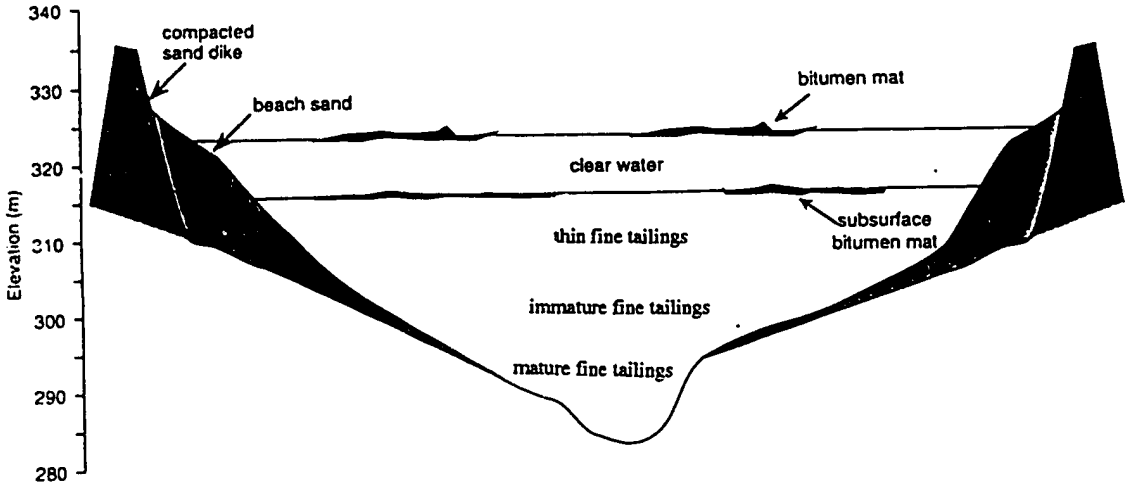

Figure 1.2 Schematic cross section of tailings pond.

1.3 Main Objectives of this Investigation

The targets of this research project are:

- to develop an effective way for fine tailings treatment.
- to study the effect of process modifications for fine tailings reduction.
- to understand the gelation mechanism for clay suspensions from fine tailings.

1.4 Literature Review of Structure and Treatment Methods of Athabasca Fine Tailings

The first commercial project to extract bitumen from Athabasca oil sands in large scale operation was completed in 1967. The Great Canadian Oil Sands (GCOS, now Suncor) extraction plant utilized the Clark Hot Water Extraction process to recover bitumen from oil sands. Unfortunately, since the beginning of the operation the tailings accumulation problem has been underestimated. It was presumed, that after being temporarily impounded the waste product would readily separate into mineral sediment, clear water and a residual bitumen phase. Having realized that the settling process would take much longer than expected, GCOS initiated a research and development program into this matter. For many years research efforts concentrated on treatment of existing tailings, while trying to understand the reason for the system's extreme stability.

Kessick of the Alberta Research Council proposed a fine tailings stability model based on the presence of residual bitumen and organic matter strongly bonded to the clay surfaces [2]. He was able to extract this material and separate it into fractions soluble in different solvents.

Majid *et al.* [4] studied the organic matter associated with solids separated from Suncor fine tailings using IR and NMR spectroscopy. They established that the material consisted mainly of highly substituted multicyclic aromatic compounds with large amounts of oxygen and nitrogen functional groups, and classified it as Type III kerogen. Further successful extractions of organic matter from bitumen free fine tailings resulted in the separation of many types of humic acid [5].

Another approach to understand fine tailings stability was based on a theory assuming organic surfactants such as sulfonic and carboxylic acids were a dispersant of clay particles [9]. In another investigation Schutte *et al.* [10] showed that increasing NaCl concentration up to 0.3M increased the measured yield stress of tailings fivefold. They concluded that the strength of the tailings structure depends on the ionic strength of the liquid phase. They further proposed that energy is stored and released through angular changes in interactions between clay particles primarily governed by attractive-repulsive forces.

Smith *et al.* [29] developed a theory which postulates that slow settling occurs when sodium naphthenates are present. At low calcium concentration, the naphthenates adsorb on the solid particles and increase their electrophoretic mobility which in turn causes slow settling.

Recently Kotlyar *et al.*[6,7,8] attributed the high water holding capacity to the presence of an ultrafine aluminosilicate clay fraction capable of forming a gel. It has been determined that ultrafines content and state of aggregation is a specific parameter of oil sands ores. They found that small particle size, along with specific ionic content of the water and a contribution from biwetted solids, are the most important factors accelerating gelation .

Many attempts have been made to dewater the accumulated fine tailings. The Development and Reclamation Review Committee of the government of Alberta is reviewing different options of area reclamation. As of now, no economically satisfactory method has been identified.

McKinnon and Boerger [11] proposed capping fine tailings with fresh water, so a new ecosystem would develop. They calculated that a 4 m water layer would be sufficient to prevent pond water beneath from wind disturbance. However, increased salt concentration has been found in the surface water. The method is currently being tested in the field for long term system behavior.

For many years, extensive research effort has focused on physical and chemical treatment methods in order to maximize the solidification of tailings' gel, and to recover entrapped water for recycling. For example, Schultz and Morrison [12] used an addition of 25 - 500 ppm of organic flocculants to fine tailings. The flocs created gel rather than settling solids and an additional process would be needed to separate the solids from water. Speight and Moschopedis [13] carried out similar investigation and also did not obtain positive results. They found that

none of the large number of tested flocculants would be effective on tailings having 22 wt% solids content. The best results were obtained when diluted fine tailings were treated with HCl prior to flocculant dosage. The solids settled to 75% of original tails volume after 12 hours. Specken [14] treated diluted tails at 2- 7 wt% solids with 0.03 to 0.14 g/L $KMnO_4$, and subsequently introduced 2 to 30 ppm of an anionic polyelectrolyte. This treatment increased the settling rate of solids by up to 50%. A number of inorganic flocculants with a wide range of concentrations have also been tested on fine tailings. Lime, because of its low cost and well known coagulating properties has attracted attention of many researchers. Lane *et al.* [15] tested addition of lime to fine tailings in amounts of 0.8 - 0.9 g per liter of tailings along with 8 - 10 mg/L of a polymeric flocculant. The addition induced much faster settling of minerals.

Schultz and Morrison [12] added Portland cement to fine tailings, and concluded that larger amounts of cement are required to obtain a similar effect to that shown by samples treated with lime. They also unsuccessfully tested the use of a 10% solution of sodium sulphate to bond water in the decahydrate.

It has been noticed that the presence of calcium in recycled water results in decreased bitumen recovery. One way to overcome this problem was suggested by Yan and Chung [16]. They proposed adding 20 - 500 ppm of Ca^{2+} to the fine tailings stream before its disposal into the pond. This would allow for a relatively fast precipitation of the clay suspension. Excess of Ca^{2+} could then be removed in calcite precipitators. However, Lane *et al.* [15] claimed that most of the Ca^{2+} would be precipitated in the pond by HCO_3^- ions, which are a natural component of the pond water.

Schutte [17] found that pH reduction to 5.5 enhanced coagulation of fine tailings and decreased the concentration of surfactants in supernatant water. He also tested the properties of the water released above the settled tailings and found that after several days its pH returned to neutral. This fact would allow the water to be returned to the environment.

In other work, McKinnon and Boerger [11] confirmed that the addition of acid to fine tailings improved the solids' settling rate and made the released water less toxic, contrary to treatment by lime, flocculant or by mechanical action.

Kessick proposed another variation of hot water extraction [18], in which oil sands is slurried with hot aqueous NaOH solution (pH~9) in a 1:1 ratio in order to form an O/W

emulsion. An adequate amount of $Ca(OH)_2$ is then added in order to invert the emulsion. Too much $Ca(OH)_2$ leads to entrapment of suspended clay in the emulsion. The W/O emulsion can be then dewatered by, for example, adding an organic solvent followed by settling or centrifugation. The organic layer formed is sent to the bitumen processing plant, while the aqueous clay suspension is further treated with an excess of $Ca(OH)_2$. Sodium hydroxide remaining in the solution can then be recycled back to the process.

The possibility of preventing the formation of fine tails by addition of dispersing agents such as $Na_2SiO_3 \cdot 5H_2O$ was investigated by Schutte [25]. The strong dispersing action of sodium silicate can be utilized to prevent gel structure creation, so coarse solids would settle rapidly leaving ultrafines in the form of a low viscosity suspension. The suspension can be recycled back to the extraction process. This method would significantly reduce both the river water intake and fine tailings accumulation. The results are presently being tested in pilot plant runs.

Hepp and Camp [19] noted that either lower (7.5) or higher (9) pH will speed up fine tailings flocculation and allow effective pre-coat filtration or, as proposed by Baillie [20], centrifugation. The latter researcher patented several geotechnical methods which were based on entrapment of fine solids into interstitial spaces between sand grains.

Approaches have been tested to increase dewatering of fine tailings by mixing them with different solids. Schultz and Morrison [12] tested a variety of solids including 1 wt% of sand, and CaF_2, 2% Fe powder, and various concentrations of graphite, charcoal and talc in fine tailings. All of these additives increased settling very little.

Mixing with various solids does not enhance dewatering. It was, however, proposed as a solution to the fine tailings problem in the form of dry landscape reclamation [9]. Scott *et al.* [21] stated that blending tailings with solids would result in non-segregating mixtures. In such a system coarser particles are hindered from settling out from the suspension. This form of waste material is more suitable for handling in dry landscape disposal. Mixing three parts of sand and one part of mature fine tailings would result in a sufficient shear stress at about 65 wt% solids, however, other combinations are possible.

Flintoff and Plit [22] found that gravity settling, enhanced by electrophoresis of diluted fine tailings, increased the solids content in the sediment by 68.3% as compared to a 33.3%

increase through gravity settling alone. However, the authors pointed out the high cost of the proposed method due to the high conductivity of fine tailings.

In his study of electrophoretic treatment of fine tailings, Ritter [23] found that the concentration of particles in recovered water was always higher than 5 wt%. To reduce this, he proposed a pretreatment with CaO or $Ca(OH)_2$ at concentration of 0.5 - 3.5 g/L of fine tailings, in conjunction with pH reduction to between 9 - 10.5 using CO_2. The pretreated mixture was then passed through a container with a moving anode belt on the bottom and a cathode grid submerged in the fine tailings. Negatively charged clay particles collected at the anode as a rigid film of solids (40 wt%). They were further solidified by simultaneously occurring electroosmosis to 65 wt% solids, and were suitable for backfill disposal. As shown in pilot plant runs this method seems to be efficient but is also too expensive.

Another project concerning fine tailings reclamation has been recently investigated. In this investigation Burns *et al.* [24] demonstrated the possibility of effective fine tailings dewatering by natural evaporation. They found that using an appropriately designed fine tailings containment structure would intensify evaporation provided that rainwater could be removed quickly. Drying of fine tailings up to 70 wt% solids should be possible under such circumstances. A very important benefit of such an approach is that there is no need for handling of either the solids or water.

The latter approach of dewatering leads to even better results when the fine tailings subjected to evaporation have been previously conditioned by other methods. Freeze-thaw has been suggested as an effective method [24] to be combined with natural evaporation. This would reduce the fine tailings water content and provide suitable conditions for a less time-consuming operation.

Sego *et al.*[26] studied optimal conditions for dewatering treated and untreated fine tailings by the freeze-thaw method. They concluded that the solids content of fine tailings can be increased from 30 to 70 wt% in a well designed, thin-layered freeze-thaw disposal system. A field scale operation is currently being carried out.

Majid *et al.*[27] investigated the potential utilization of agglomeration techniques to dewater fine tailings. In their study, they used refinery coke as the collector phase to remove hydrocarbon components from the fine tailings. They found that the oil phase agglomeration

technique resulted in sedimentation of 80% of the solids. The diluted suspension of ultrafines could be subsequently dewatered by another 40-50% by treatment with sulfuric acid.

In the past several years a relatively good understanding of tailings structure has emerged. The tailings problem however still remains a major limitation to the bitumen extraction from oil sands. Based on current knowledge future research efforts must be directed towards the elimination of both accumulated fine tailings and future discharge.

Chapter 2

Fundamentals

2.1 Terminology

Some terms frequently used in this work are applied in various disciplines and may be interpreted differently. In order to ensure proper understanding the definitions used in the context of this project are given below:

Aggregation: General term for all the ways in which particles are joined together [32]

Colloid: A suspension in which the particles of the dispersed phase are so small (~1-1000 nm) that gravitational forces are negligible and interactions are dominated by short range forces such as van der Waals attraction and surface charges. The inertia of the dispersed phase is small enough to exhibit Brownian motion [33].

Flocculation: Reversible process in which aggregating particles adhere to one another but do not collapse onto one another [32]. The aggregates are known as flocs.

Fractal floc: A floc which possesses a randomly branching structure with the density decreasing with increasing size [33].

Gel: A dispersion of colloidal particles that form a solid skeleton network enclosing a continuous liquid phase [33].

Gelation: The linking of aggregated clusters into a giant spanning network that reaches acr.oss the vessel [33].

Gelation concentration (GC): The concentration of ultrafines at which further settling of fractal flocs is inhibited by the steric hindrance.

Peptization: The process of redispersing a colloid which has been flocculated.

Sol: A colloidal suspension of solid particles in a liquid medium [33].

2.2 Structure of Athabasca Clays

The main components responsible for the non-settling behavior of fine tailings were identified [7] as aluminosilicates of the kaolinite and mica type.

Kaolinite structure [30] involves a single silica tetrahedral sheet and single alumina octahedral sheet combined in one unit so that the tips of the silica tetrahedron and one of the layers of octahedral sheet form a common layer. All the tips of silica tetrahedrons point towards the center of the unit made of the silica octahedral sheets as shown in Figure 2.1. The dimensions of the sheets of tetrahedral units and of the octahedral units are closely similar in their *a* and *b* directions, and consequently, composite octahedral-tetrahedral layers are formed. In the layer common to octahedral and tetrahedral groups, two thirds of the oxygen atoms are shared by silicon and aluminum, one third remains bonded in a hydroxyl group. This type of sheet unit in kaolinites is continuous in the *a* and *b* directions; any variation between the members of the group lies in the way in which the unit layers are stacked above each other.

The basic structural unit of mica is a layer composed of two silica tetrahedral sheets with one octahedral sheet in between. The tips of the tetrahedron in each silica sheet point towards the center of the unit and are combined with the tetrahedron in a single layer with a replacement of OH by O, (see Figure 2.2). The unit layers extend indefinitely in the *a* and *b* directions, and are stacked in the *c* direction, forming highly irregular platelets of various thickness.

The clay minerals have the property of retaining certain cations around the outside of silica-alumina structural units. This occurs because of the unbalanced net negative charge in the clay lattice, which is compensated for by cations adsorbed on the particle surface. In an aqueous medium these cations tend to diffuse away from the particle surface if a concentration gradient exists, and can be potentially exchanged by other cations. The amount of cations, usually expressed in miliequivalents per 100 g of clay, and referred to as the cation exchange capacity, a very important property in every field in which clay materials are studied. There are three reasons for unbalanced charges in clay lattices [30]:

1. Broken bonds around the edges of silica-alumina units. The number of broken bonds and hence the magnitude of the corresponding net negative charge, increases as particle size decreases. Also lattice distortion tends to increase the number of broken bonds and consequently the net negative charge of a clay particle is expected to increase as crystalinity decreases.

2. Displacement of hydrogen in hydroxyl groups exposed on the broken edges.

3. Substitutions within the lattice structure of trivalent aluminum for quadrivalent silicon in the tetrahedral sheets, and of calcium and magnesium for trivalent aluminum in the octahedral sheets. In clay minerals, substitution within the octahedral layer is the major factor causing net negative charge [31].

Uniform charge distribution creates a constant double layer charge at the clay planar surface, proportional to the degree of substitution in the clay lattice, and independent of the type or concentration of electrolyte in the liquid phase. The potential has a maximum value at the surface and decreases exponentially with the distance from the surface.

The atomic structure at the edge surfaces is different than at planar surfaces. Therefore a possibility exists that the electrical double layer of platelet edges is also completely different. The part of the edge surface at which the broken tetrahedral sheet is exposed may be compared with the surface of a silica particle [31]. It is well known that whereas silica particles carry a negative double layer, their charge can easily be reversed by a small amount of aluminum ions in solution [32]. Because such a small concentration of aluminum can be produced due to the slight solubility of clay in the water, clay edges are likely to posses a positive double layer at the broken silica surfaces[32]. It can be further speculated that silica sheets are preferentially broken at the spots where silicon is replaced by aluminum, creating excess positive charge. Consequently, the whole edge surface may carry a positive double layer, even though the net electrophoretic charge of clay particles is negative.

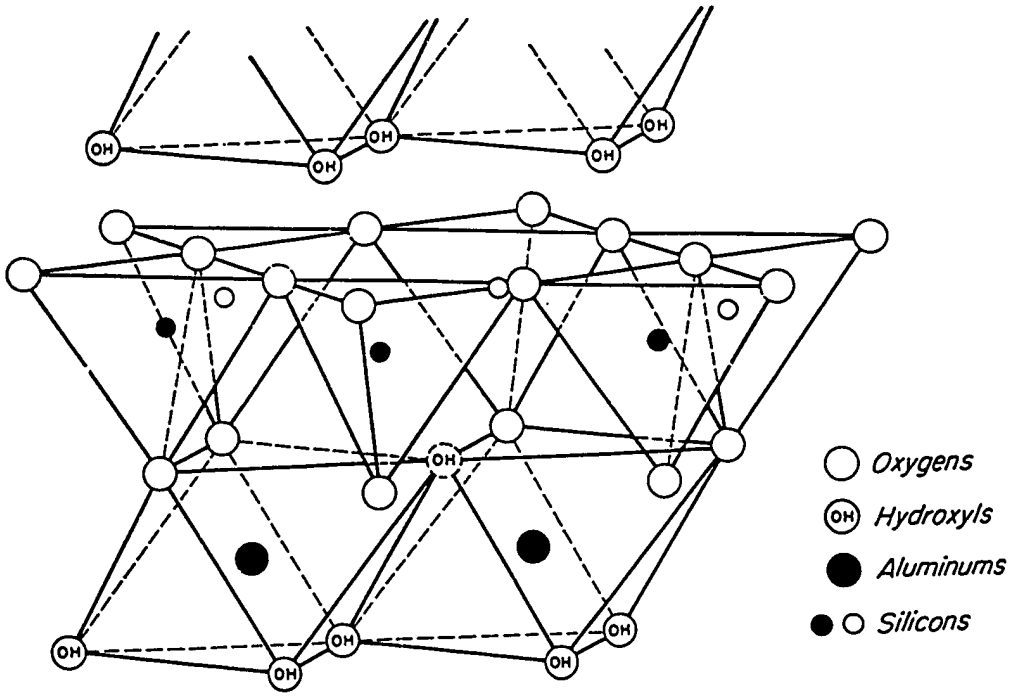

Figure 2.1 Schematic diagram of kaolinite structure.

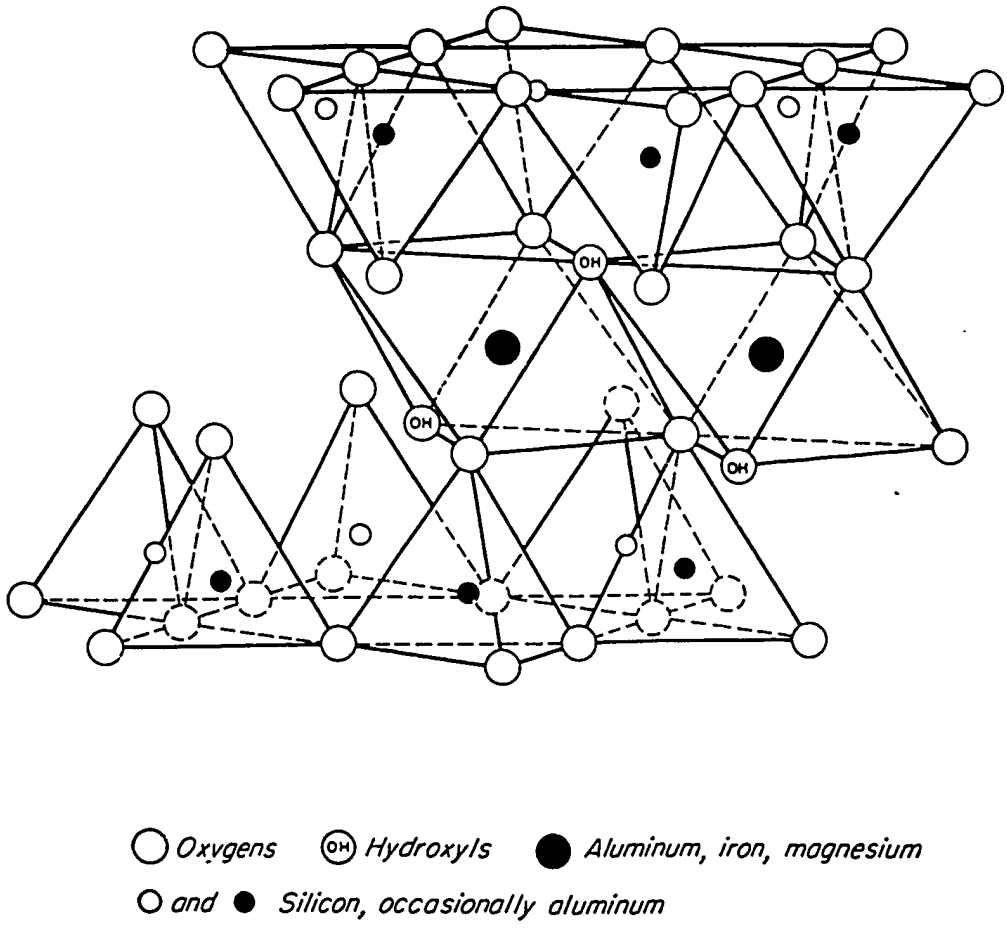

Figure 2.2 Schematic diagram of mica-type structure

Assuming the existence of two different double layers within a clay platelet, the following modes of aggregation of the clay particles are possible:

1. edge to edge (EE)
2. edge to face (EF)
3. face to face (FF)

Although all these types of association (Figure 2.3) are posible modes of aggregation in clay suspensions, only the EE, EF and FF ribbon-like types of association lead to aggregates which would bear the name of flocs. The thicker particles that result from FF association (see Figure 2.3 c) can not be called flocs due to their very compact structure, small surface area and low water entrappment.

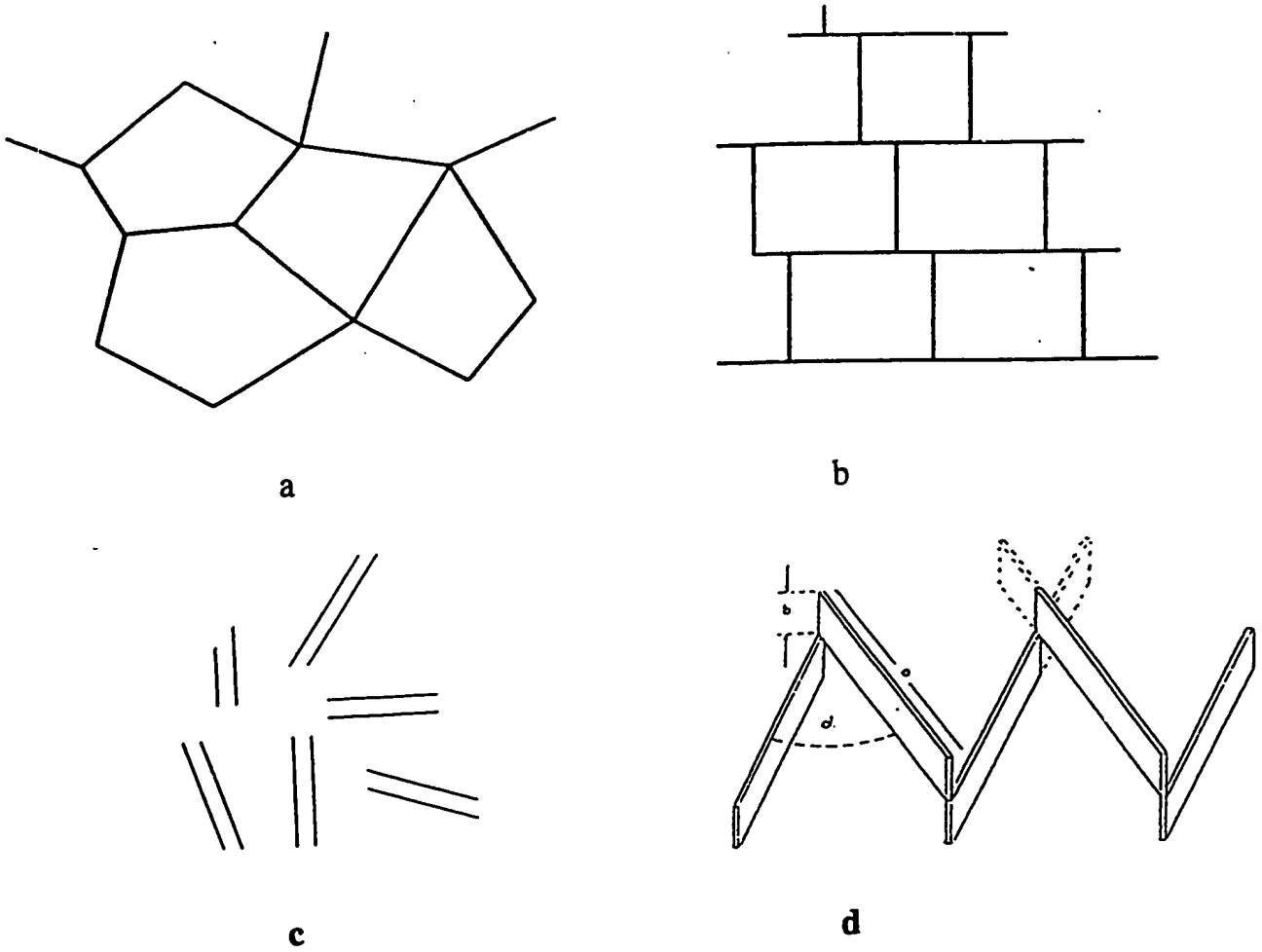

Figure 2.3 Possible particle association in clay suspensions. a) edge to edge (card house), b) edge to face, c) face to face and d) ribbon - like.

2.3 The DLVO Theory

It was anticipated long ago that the stability of colloidal suspensions depends on the electrostatic repulsion between surface charges of particles. Attempts were made to develop a mathematical model of the interactions of two overlapping double layers. The solution to the problem was found in 1941 by Derjaguin and Landau [45] in Moscow and by Verwey and Overbeek [46] in the Netherlands. They showed that a quantitative correlation existed between double layer interaction forces and their dependence on surface potential, ionic strength, and distance between particles. The correlation incorporated electrostatic repulsion as well as Van der Waals and London atraction forces to give a very satisfactory picture of the stability and coagulation of colloidal suspensions. This theory has become an outstanding achievement of colloidal chemistry and it was named the DLVO theory after its creators. The repulsive barrier originates from two types of ions making up the double layer: the charge determining ions, which create charge on the surface of the particles, and the counterions, which are present in the solution in the vicinity of the particle thus screening the charges of potential determining ions. Such a double layer structure, depicted in Figure 2.4, exhibits a linear potential drop in the layer of counterions and water tightly bound to the particle surface called the Stern layer. Beyond the Helmholtz plane (at h=H), in the Gouy layer the counterions are free to diffuse away from the surface. Within the double layer itself, at the slip plane (i.e. interface of the particle moving in an electric field and the surrounding liquid) a specific potential defined as the ξ potential occurrs. The stability of the colloid correlates closely with the magnitude of the ξ potential. In general, a repulsive potential bigger than 30-50 mV is needed to achieve stability [33]. The Gouy layer is characterized by an exponential drop of the repulsive electrostatic potential with the distance *h* from the surface, it follows approximately from Equation 1:

$$V_R \propto e^{-\kappa(h-H)} \quad (h \geq H) \qquad (1)$$

where $1/\kappa$ is called the Debye-Huckel screening length. The parameter κ is given by:

$$\kappa = \sqrt{\frac{F^2 \sum c z^2}{\varepsilon \varepsilon_0 R T}} \qquad (2)$$

where: F is Faraday's constant, ε_0 is the permittivity of vacuum, ε is the dielectric constant of the solvent, and c_i and z_i are concentration and valence of the electrolyte of type i. When the counterion concentration is small and the screening length is large, the repulsive potential extends far from the particle. When the concentration of the counterion increases, the repulsive potential drops more rapidly with distance, since the repulsive force is proportional to the slope of the potential.

$$F_R = \frac{dV_R}{dh} \propto \kappa e^{-\kappa(h-H)} \qquad (3)$$

The repulsive force increases with a small addition of electrolyte (F_R increases with κ) Larger amounts of counterion will result in a collapse of the double layer, elimininating the repulsion and making closer approach of the particles possible, (i.e the exponential term in Eq.3 becomes predominant). Figure 2.5 represents the net effect of the sum of repulsive and attractive forces according to the DLVO theory. Near the particle surface a deep potential energy minimum occurs due to the strong interaction of both opposite forces. Farther away from the particle surface a maximum of potential energy exists caused by the electrostatic double layer (repulsive barrier). When the barrier is greater than approximately 10kT, where k is Boltzmann's constant, collisions produced by Brownian motion will not usually overcome the barrier and no aggregation will occur. On the other hand, in the case when the barrier is reduced to a height much lower than 10kT, every collision results in particles sticking together, leading to a very rapid aggregation limited only by the rate of diffusion [34]. Since the attractive force is unchanged and the repulsive force is reduced a secondary minimum in potential energy occurs, but is not deep enough

to bind the particles instantaneously. This happens when the potential energy barrier is comparable to or slightly larger than 10kT. In such a situation many collisions must take place before the particles will stick to one another, resulting in reaction limited colloid aggregation [35]. However in both modes of aggregation particles form clusters which themselves continue to diffuse, collide, and stick together. The processes of diffusion-limited and reaction-limited aggregation have distinctive features resulting in different cluster structure. The diffusion limited colloid aggregation produces much less compact fractal flocs (i.e flocs which posses a randomly branching structure and decreasing density with increasing size). If the colliding flocs always stick together it becomes difficult for one floc to interpenetrate another so attachment tends to occur at the periphery. The reaction limited colloid aggregation allows more opportunity for the clusters to interpenetrate, so the resulting clusters are more compact. The two different cluster structures are shown in Figure 2.6.

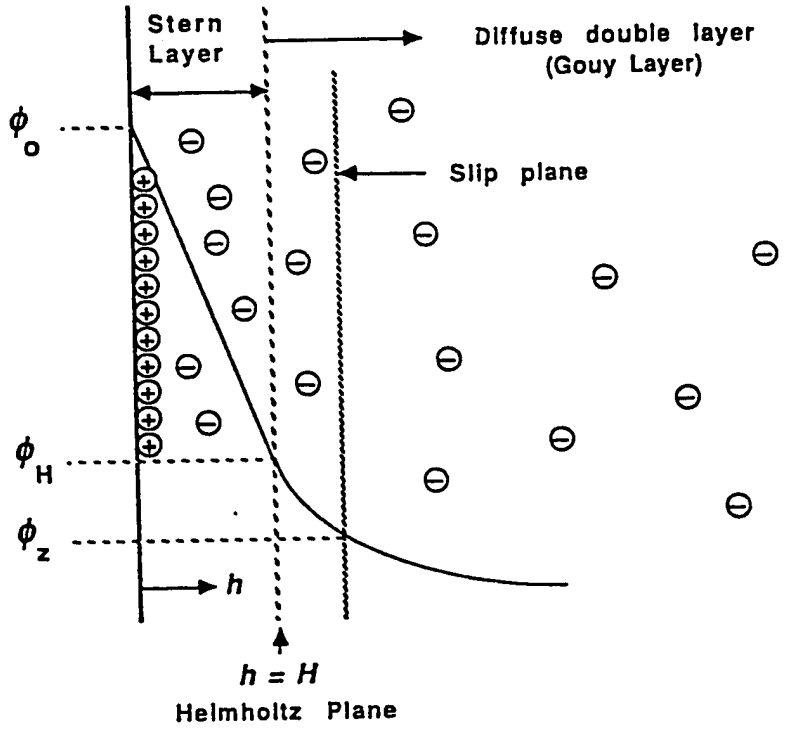

Figure 2.4 Schematic representation of Electrostatic Double Layer.

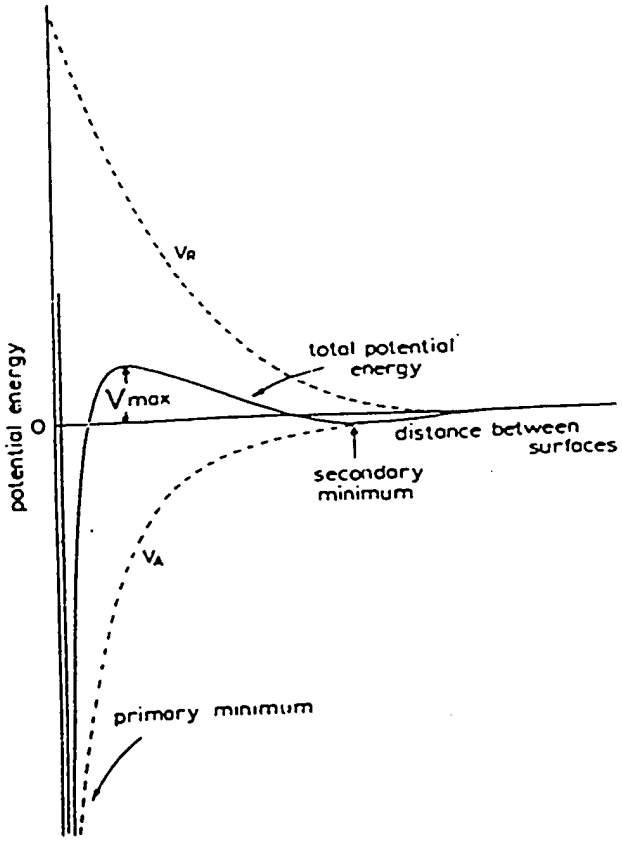

Figure 2.5 Schematic of DLVO potential. V_A=attractive van der Waals potential, V_R =repulsive electrostatic potential.

All these parameters are currently under investigation using both experimental techniques and computer simulations [35].

According to the DLVO theory, coagulation in colloidal systems results from the reduction of surface potential by changing the pH or increasing the concentration of counterion by addition of electrolyte. This, as it can be expected from Eq. 2, can be strongly affected by the valence of the counterion, i.e. the type of electrolyte. The empirical Hardy-Schultze rule, very approximately confirms predictions of the DLVO theory by indicating that the concentration of electrolyte required for coagulation is inversely proportional to the sixth power of the charge of the ion.

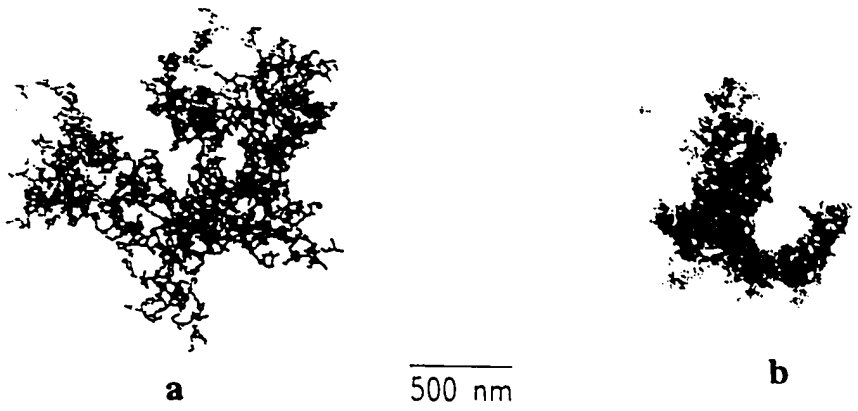

Figure 2.6 Transmission electron micrograph of gold clusters aggregated under: a) diffusion-limited and b) reaction limited conditions.

2.4 Hydration Forces

Hydration forces are short range forces operating at the solid-water interface. Water molecules adsorbed at the interface tend to exhibit specific properties which are different from those of the water present in the bulk. These structured layers are illustrated schematically in Figure 2.7.

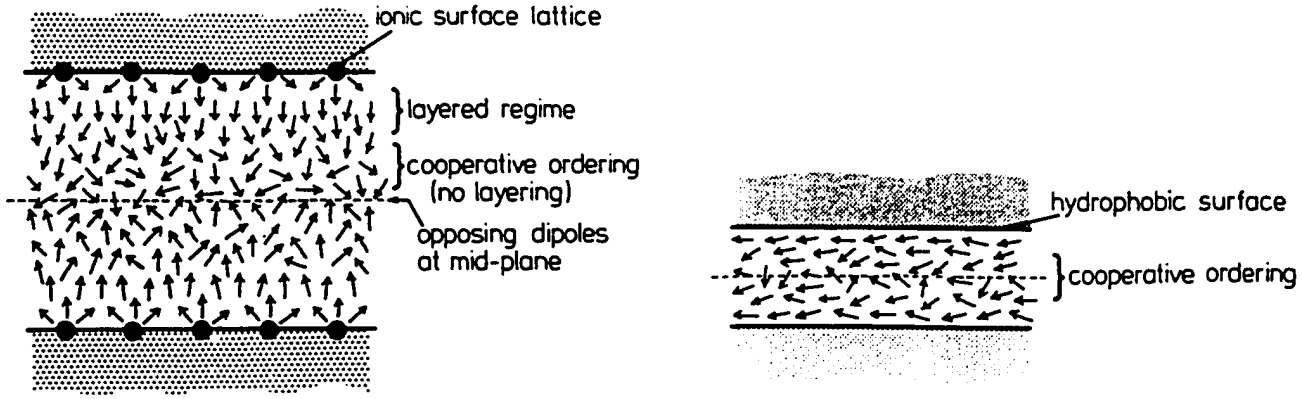

Figure 2.7 Orientation of water molecules at charged hydrophilic surfaces

The interaction is so strong that the adsorbed layer resists freezing. At low concentrations of electrolyte the forces in the vicinity of the surface obey the DLVO rules. At a range of ~1.5 nm from the surface the force oscillates, shown in Figure 2.8, as the individual layers of the molecules are displaced [33]. In water containing higher concentrations of electrolyte, ions adsorbed at the surface develop a layer of hydration that becomes an additional component of repulsion.

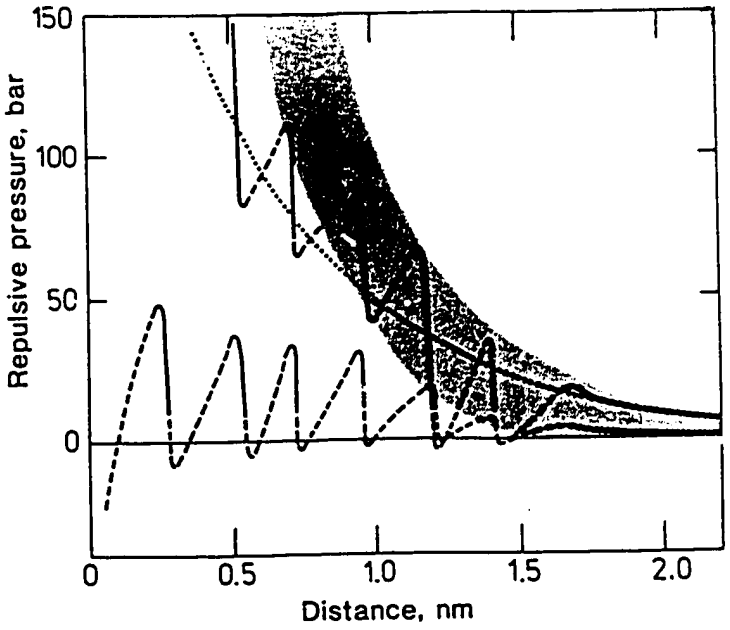

Figure 2.8 Short range hydration forces plotted as pressure against distance.

The most prominent example of the influence of hydration forces on sol stability are colloidal silica systems, which are known not to obey the DLVO theory and remain stable even at pH=2. Silica sols are apparently stabilized by an adsorbed layer of water that prevents coagulation. To destabilize an aqueous suspension of colloidal silica a reduction

of the hydration efect is required. This can be done for example by adding salt to the sol, to produce ion exchange:

$$\equiv Si\text{-}OH + M^{Z+} \Rightarrow \equiv Si\text{-}OM^{(Z-1)+} H^{+} \qquad (4)$$

where M^{Z+} is an unhydrolyzed cation of charge z. Since the Si-OH groups are adsorption sites for water, removal of silanols by binding them in complexes with different cations reduces the stability of silica sols. The amount of silanols to be removed in order to destabilize silica colloids is the same regardless of the valence of the cation used for the exchange.

2.5 Sol-gel transition

Gel formation and sol-gel transformation in colloidal clay suspensions have attracted much attention for many years. NMR techniques have shown a considerable promise in understanding clay-water interactions at a microscopic level [36]. Clay platelets in the suspension are strongly oriented by magnetic field. Water molecules move rapidly back and forth between the bulk water in the suspension and the charged clay surface. This forces the rotating dipole of the water molecule to align its positively charged end towards the negatively charged clay platelet. This ordering of the dipole can be monitored by measuring the quadrupolar splitting of the deuterium nuclear magnetic resonance signal for deuterons in water molecules. The quadrupolar splitting, however can only be detected if the water molecules reside in an anisotropic environment. The same effect can be observed using the ^{17}O NMR signal [36]. It can be easily demonstrated that the gel structure broken by mild manual agitation reappears after certain time. The time required for complete sol-gel transition depends on solids content and water chemistry, and may vary from minutes to weeks. These observations correspond very well with ^{2}H NMR measurements of the splitting as a function of solids concentration and time

at different water compositions. Initially, in a freshly shaken sample the splitting shows its maximum, which is directly proportional to the solids content and to the mole fraction of the oriented water at the periphery of the particles. As the gelation progresses the platelets become more and more entangled in the gel structure, losing their ability to orient themselves in the magnetic field. At equilibrium, when the gel formation is completed, the doublet splitting will diminish to zero. Spectra at intermmediate times can be recorded to obtain an accurate time profile of the gel formation. Therefore quadrupolar splitting, measured as a function of time and clay content, provides valuable information about the kinetics of gelation at specific water ionic compositions.

Chapter 3

Properties of Materials

3.1 Suncor Fine Tailings

The fine tailings samples were provided by Suncor Inc. The samples were retrieved a the depth of about 15 m, using a barge with a winch equipped with a weighed steel cylinder. To ensure that anaerobic conditions are maintained, a pressure regulated pinch valve was attached to a gas line which provided pure nitrogen. After collection, the fine tailings were transferred into 20 L plastic buckets and the lids were subsequently sealed with a masking tape before shipment. The buckets containing samples, received approximately one month after their collection were left overnight on horizontal rollers turning at the rate of ~90-100 rpm. The bitumen layer was then skimmed off and the remaining fine tailings were poured into four 4 L plastic containers, sealed and stored at room temperature for further use. The average sample composition was: 31.6 wt% solids, 3.5 wt% bitumen with the remainder being water with its associated dissolved species.

3.2 Northern Holland Sludges

Three different sludges from Northern Holland (coded H-A, H-B and H-C) were supplied courtesy of Suncor Inc. These stable sludges, originated from Dutch harbours, were recovered by maintenance dredgers. Harbor and river bottom sludges containing

mainly contaminated clay and silt material have very poor dewatering characteristics, but nevertheless are being successfully treated. Their solids content was determined to be 37.4 wt%, 30.8 wt%, 36.9 wt% for the three samples, respectively. Toluene soluble materials accounted only for about 0.2 wt% in each case.

3.3 OHWE/CHWE Streams

Primary Separation Vessel (PSV) middlings, PSV tailings, Secondary tailings, Run-offs, as well as Primary and Secondary froths from five pilot plant runs using Suncor and Syncrude oil sands feeds ores were supplied by Syncrude Research Ltd. The samples were received in 1 L plastic containers and were stored at 5^0C prior to use. The following processes were used for the runs: Clark Hot Water Extraction (CHWE), OSLO Hot Water Extraction (OHWE), and Modified OSLO Hot Water Extraction (M-OHWE). Information about the conditions used in the runs is found in Table III-1. Analysis of the different process waters used for the extractions was performed at Syncrude Research Ltd. and the results are given in Tabie III-2. In the case of PSV middlings there were some froths still associated with the samples. These froths, referred to as PSV middlings froths, were skimmed off and stored in separate containers at 5^0C for further analysis. The remaining samples, after froth removal are referred to as froth-free PSV middlings or PSV middlings. The amounts of various the streams and their solids contents are presented in Tables III-3, III-4 and III-5. PSV tailings had the highest solids content followed by Secondary tailings, PSV middlings and Run-offs. Secondary froths appeared to be "dirtier" than PSV froths and PSV middlings froths, i.e they contained more suspended solids.

Table III-1: OHWE and CHWE bitumen extraction runs for Syncrude and Suncor oil sands

Abbreviation	Description	Extraction medium
M-OHWE	Modified Oslo Hot Water extraction	Mildred lake water treated with gypsum; kerosene + floating agent
OHWE	Oslo Hot Water extraction	Mildred lake water untreated kerosene + floating agent
CHWE	Clark Hot Water Extraction	Pond water + 0.01% NaOH

Table III-2: Water analysis

Water source	pH	HCO_3^-, meq/L	ppm					
			Cl	SO_4	Mg	Na	Ca	K
River water	7.0	2.5	24	38	9.5	21	32	0
Treated river water	6.6	0.1	16	151	9.9	18	43	0
Recycle water	8.0	14.0	280	258	4.6	259	9	10

Table III-3: Amounts of received stream samples

Oil sands	Process	Weight of received samples, grams			
		PSV middlings	PSV tailings	Secondary Tailings	Run offs
Syncrude	M-OHWE	1102 (854)	1576	1085	630
	OHWE	1180 (992)	1643	1082	612
	CHWE	1064 (1060)	1431	989	603
Suncor	CHWE	1001 (975)	1695	967	618
	M-OHWE	1105 (1068)	1690	1032	621

Amount of froth free middlings in parenthesis

Table III-4: Solids content of various streams

Oil sands	Process	Solids content, wt %			
		PSV middlings	PSV tailings	Secondary Tailings	Run offs
Syncrude	M-OHWE	18.4	60.3	25.6	8.1
	OHWE	11.9	58.6	27.7	10.1
	CHWE	16.4	58.8	16.8	6.1
Suncor	CHWE	13.8	56.9	12.2	7.4
	M-OHWE	10.0	64.4	12.4	7.8

Table III-5: Amounts and solids contents of froths

Oil sands	Process	Wt of received samples, gram			Bitumen free solids, wt% of froth		
		Primary froth	Secondary froth	PSV middlings froth	Primary froth	Secondary froth	PSV middlings froth
Syncrude	M-OHWE	601	379	188	6.9	13.4	3.3
	OHWE	603	345	248	7.1	10.9	5.5
	CHWE	834	632	4	7.7	13.7	10.8
Suncor	CHWE	735	406	26	6.4	14.7	9.6
	M-OHWE	687	354	37	6.1	10.9	5.6

3.4 Chemicals

Aluminum chloride ($AlCl_3$) (reagent grade), calcium chloride ($CaCl_2$) (reagent grade), calcium sulfate ($CaSO_4$) (reagent grade), calcium oxide (CaO) (reagent grade), sodium chloride (NaCl) (reagent grade), sodium pyrophosphate ($Na_4P_2O_7$) (reagent grade), sodium bicarbonate ($NaHCO_3$) (reagent grade), sodium hydroxide (NaOH) -reagent grade and sulfuric acid (H_2SO_4) (reagent grade) were supplied by Anachemia Co. of Montreal, Quebec.

Brine containing - 23.7 wt% $CaCl_2$, 4.0 wt% $MgCl_2$, 2.4 wt% NaCl, 1.1 wt% KCl and 40 ppm Fe, was supplied by Energy, Mines and Resources Canada.

Deuterium oxide was supplied by MSD Isotopes, a division of Merck Frosst Canada Inc. It had a minimum isotopic purity of 99.9 atom% D.

Toluene (reagent grade) was supplied by BDH Inc.

Chapter 4

Experimental

4.1 Instrumentation

4.1.1 Deuterium Nuclear Magnetic Resonance

For the NMR measurements about 0.83 wt% of ^2H_2O was added to each sample (25mg of D_2O added to 3g of sample). ^2H spectra were recorded on a Bruker AM-400 NMR spectrometer at frequency of 61.42 MHz. Typically for ^2H, 8 transients were co-added in 16 K datum points at a sweep width of 4000 Hz. The 90^0 pulse lengths were 10 μs, and the delay times 2 s. Before recording the initial NMR spectrum, each sample was vigorously shaken and inserted into the magnetic field. The maximum splitting signal was recorded at this point. It was designated as "zero time splitting". The sample was then removed from the magnetic field and reinserted to record the spectrum after: 30 min; 4 hr; 8 hr; 24 hr; 48 hr, 6 days; 9 days and 14 days.

4.1.2 Ion Exchange Chromatography

Cation analysis was performed using a Waters chromatography system consisting of a Model 510 HPLC pump, IC-Pak C M/D column, Model 712 Wisp autosampler and Model 431 conductivity detector. Nitric acid 3 mM in 1mM EDTA (acid form) was used as a solvent at a

flow rate of 1 mL/min at 20°C. Samples were pretreated with J.T.Baker octadecyl solid phase extraction cartridges in order to remove residual hydrocarbons and then filtered through 0.22 μm membrane filters. Dilutions were made with deionized water.

4.1.3 X-ray Photoelectron Spectroscopy

For X-ray Photoelectron Spectroscopy (XPS), drops of the sample were spread over a clean glass slide and allowed to air dry. The dried solids were then scraped off the glass with a razor blade and pressed onto a piece of indium foil. XPS spectra were recorded using PHI 5500 Instrument using Al Kα as the source of X-rays. The vacuum inside the instrument during the analysis was always below 8×10^{-9} torr. An electron flood gun was used to neutralize the charge developing at the surface of the sample during the recording of the spectra. High resolution spectra were obtained at a pass energy of 29.6 electron-volt (ev). Survey spectra were recorded at a pass energy of 156 ev. Several repetitions were made to assure repeatability of the results. These spectra were used to calculate the atomic fraction of the element I using the software supplied with the equipment based on the formula: $Ci = (IiSi)/\Sigma(IjSj)$, were I is the area under the spectral peak and S is the sensitivity factor. Values of 0.296, 0.711, 0.262, 0.870, 0.213 and 1.791, suggested by the manufacturer were used for the sensitivity factors of C1s, O1s, Si2p, K2p, Al2s and Fe2p3.

4.1.4 Infra-red Spectroscopy

IR transmission spectra were recorded using 520G Nicolet spectrometer. The 32 scans were co-added and an average was taken. NaCl window was used as a background. The resolution was 4 cm^{-1} .

4.1.5 Dynamic Light Scattering

Particle size analysis was performed using an HR-850 Granulometer. Dilutions were made and background signals were recorded using appropriate process waters. Several repetitions at different dilution rates were made.

4.1.6 Transmission Electron Microscopy

For Transmission Electron Microscopy observations a drop of suspended sample was sonicated for 1 minute and then was deposited on a carbon coated copper grid. After 1 minute the liquid was blotted away to leave only a thin layer which was then allowed to air dry. The grid was then examined with a Carl Zeiss Model 902 Transmission Electron Microscope, operated at 80 kV.

4.1.7 pH Measurements

A Fisher Accumet Model 805 MP pH meter equipped with a Fisher Scientific Ag/AgCl electrode and calomel reference electrode, was used for pH measurements.

4.1.8 X-ray Diffraction

X-ray diffraction analysis was performed on powder specimens by random mounting, for the determination of whole mineral composition and in preferred orientation. For detecting small amounts of smectite minerals, the analysis was carried out in preferred orientation. The samples were analyzed using a Scintag PAD II diffractiometer with Co radiation and graphite monochromator. Current and voltage used were 40 mA and 40 kV, respectively.

4.2 Methodology of Sampling

4.2.1 Sampling of fine tailings

Before using the samples, moderate manual agitation was applied. 4 L jars containing fine tailings were gently shaken about 20 times prior to the withdrawal of the amounts needed in each series of experiments. The tailings were poured into 100 mL glass containers and processed immediately after sampling.

4.2.2 Sampling of Northern Holland Sludges

The samples received were found to release a small amount of clear water on top of a relatively homogeneous paste-like sediment. The whole containers, as received, were first agitated in a paint shaker for 15 min, then the contents were split in half and shaken again for 15 min. Finally the two parts were recombined and the amounts needed for the experiments were withrawn using a metal spatula.

4.2.3 Sampling for OHWE/CHWE Comparison Study

Immediately before the application of any treatment or analysis, samples were homogenized as follows: total samples, as received in 1 L plastic containers were shaken for 5 min using a paint mixer. Then, about half of each sample was transferred into another 1 L plastic container and shaken for another 15 min again using the paint mixer. The two subsamples were then recombined and shaken again for 15 min. Manual agitation was then applied before appropriate amounts of the samples were transfered into 100 mL glass jars for further treatment.

4.3 Procedure to Study the Effect of Chemical Treatment

A study of the effect of chemical addition to fine tailings samples as well as to the separated ultrafine fraction was carried out. The samples of fine tailings and ultrafines fraction were treated with several additives at increasing concentrations. Details of fine tailings sample preparation for sedimentation studies are given in Table IV-1. The ultrafines used in this work were separated from the whole fine tailings in the form of an aqueous colloidal suspension (7.6 wt% solids) by mechanical agitation (15 min in Spex shaker), followed by mild centrifugation for 10 min at 200xG. Details of the preparation of ultrafines samples for use in the sedimentation studies are given in Table IV-2. The pH change due to addition of different amounts of chemical

was monitored. For pH adjustment, 1N H_2SO_4 was added to the fine tailings or the ultrafines fraction and the mixtures were manually shaken. With regard to observed pH change with time, a procedure was adopted in which samples were placed under vacuum for 20 min and then allowed to equilibrate overnight before recording the final value. In other experiments 1N NaOH solution or 10 % lime milk was added to the samples previously acidified to different pH, as described above, to readjust the pH to 7.6. Other additives used were $CaCl_2$, brine, lime, gypsum (10 wt% $CaSO_4$ suspension), $NaHCO_3$, and $AlCl_3$. In order to take into account the dilution caused by the chemical addition, an appropriate amount of distilled water was added to fine tailings to adjust the solids concentration as required. The treated fine tailings and ultrafines samples were allowed to settle in 100 mL graduated cylinders or subjected to centrifugation at different speeds.

TABLE IV-1: Sample preparation for settling study on fine tailings.

Additive	Range of the amount added (wt% of fine tailings)	Solids in fine tailings after dilution with additive (wt%)	pH range
1N H_2SO_4	0-9.5	28.8	4.3-8.3
1N H_2SO_4 (1N NaOH)	0.7-7.3 (0.2-4.6)	28.2	2.3-7.2 (7.6)
1N H_2SO_4 (Lime,10% milk)	0.7-7.3 (0.1-2.2)	28.9	2.8-7.2 (7.6)
10% $CaCl_2$	0.3-1.5	31.1	7-8*
Brine	0.18-0.46	30.6	~8*
Lime,10% milk	1.0-4.0	30.4	11.4-12.2
Gypsum,10% milk	0.3-1.5	31.1	7-8*
$NaHCO_3$	0.1-0.4	31.6	8-9*
10% $AlCl_3$	0.3-3.0	30.7	7-8*

* pH estimated using pH paper.

TABLE IV-2: Details of experiments with ultrafine solids suspensions.

Additive	Range of the amount added (Wt% of suspension)	Wt% of solids in suspension after treatment	pH range
H_2SO_4 1N	0.2-8.1	7.0	1.9-7.2
H_2SO_4 1N Freeze-Thaw	0.2-8.1	7.0	2.0-7.0
H_2SO_4 (Lime)	0.2-8.1 (0.2-3.0)	6.9	1.9-6.7*
H_2SO_4 (Lime) Freeze-Thaw	0.2-8.1 (0.2-3.0)	6.9	1.8-6.7*

* - initial pH, prior to readjustment to 7.6

4.4 Sample Preparation for NMR Study

As previously established [37] ultrafine solids are the main component of oil sand fine tailings responsible for its gel-like structure. The gel formation also strongly depends on dispersing medium chemistry.

In the context of this work, it was necessary to identify the pond water components which are active in the gel formation. It was thus important to look at the effect of the salts present in pond water on gelation kinetics. The underlying assumption is that if the problem causing components are known, they can then be eliminated from the Extraction Plant process water and formation of a gel network within fine tailings can be prevented. Another objective was to determine if a salt concentration exists, at which fast floc densification occurs, causing rapid dewatering of the gel structure. It was assumed that concentrations and types of electrolytes naturally present in pond water are appropriate for gel formation, but not for the formation of dense flocs.

The following procedure was employed to investigate the above problem (Figure 4.1). Fine tailings were agitated for 15 min in a high intensity Spex mixer, and then centrifuged at 500xG for 2 hours. These conditions have been found to leave in suspension colloidal solids of average particle size smaller than 200nm which are the most representative fraction for the gelation study [37]. The sediment was discarded and the suspension ultra-centrifuged at 26500xG for 30 min. Clear pore water (i.e water immobilized in the gel structure) resulting from centrifugation, was then decanted and analyzed for cation concentration using Ion Exchange Chromatography. The settled solids were redispersed in distilled water by vigorous agitation in a Spex mixer and the suspension was centrifuged at 46000xG for 30 min. The clear supernatant referred to as the 1st wash water was decanted and the sedimented solids were redispersed in a new portion of distilled water as described above. The suspension was centrifuged at 91500xG for 30 min, and 2nd wash water was collected. The sediment was redispersed again in additional distilled water and left to stand overnight before centrifugation was performed on the following day. To obtain clear supernatant, a 3rd wash water and centrifugation at

360000xg for 30 min was required. Results of the analysis (an average of three runs) of supernatant solutions obtained at this stage of the experiment are presented in Table IV-3.

Table IV-3: Elemental analysis of pore and wash waters, ppm.

Water	Na^+	Ca^{++}	Mg^{++}
Pore	430	5.4	7
1st wash	32.2	0.4	0.2
2nd wash	19.6	0.1	0.1
3rd wash	7.6	0.1	0.02

Using this procedure most of the electrolytes naturally occurring in pond water can be removed, leaving the ultrafine particles in a deflocculated state. Extremely high centrifugation speed was necessary after the third wash in order to sediment the ultrafines completely deflocculated at low concentration of counterions. The 1st, 2nd and 3rd wash waters were subsequently used to redisperse portions of respective sediments and used in the first sequence of NMR measurements.

Subsamples of the deflocculated suspension of ultrafine solids were back-washed three times with solutions of pond salts at different concentrations. The following solutions were used in the study: 5 and 20 mM NaCl (115 and 460 ppm of Na^+), 0.125 mM of $CaCl_2$ (5ppm Ca^{++}), and 20 mM $NaHCO_3$ (1220 ppm HCO_3^- and 460 ppm Na^+). Intensive mixing was again applied to redisperse solids from the sediments and different centrifugation speeds were used, according to the salt type and concentration. To ensure equilibrium saturation of clay by the salt, the solids were redispersed after the first wash and allowed to stand overnight. The chemical content of the waters resulting from the back-washes is shown in Table IV-4. The concentration of solids was kept constant

during the procedure. Diluted samples with 1, 2, 3,4,5, 6, 7, 8, wt% solids were prepared directly in 10 mm NMR tubes, using fresh portions of corresponding salt solutions.

Table IV-4: Evaluation of effectiveness of reverse-washes, ppm.

Salt solution	1st reverse-wash			2nd reverse-wash			3rd reverse-wash		
	Na	Ca	Mg	Na	Ca	Mg	Na	Ca	Mg
5mM NaCl 115ppm Na^+	113	4.1	2.4	122	1.4	0.8	n/a	1.2	0.7
20mM NaCl 460ppm Na^+	439	8.7	5.1	494	6.9	5.9	500	6.0	3.4
20mM $NaHCO_3$ 460ppm Na^+	400	9.1	0.4	4.53	1.5	0.4	4.51	1.1	0.4

4.5 Gravity Settling of Ultrafines in Single Salt Solutions

High concentrations of electrolytes could not be used in the NMR experiments because of a very rapid decrease in the splitting signal. It remained however of great interest to know whether a high electrolyte concentration would result in floc densification. It was decided that the aggregation/sedimentation progress, as well as a sediment compaction factor, could be followed in settling tests. The compaction factor was defined as a ratio of concentration of solids in sediment to initial solids concentration. The same procedure as for the NMR samples was used for sample preparation. The following salt solutions were used in the reverse-washes: NaCl - 10, 20, 50, 100 , 200, 500 and 1000mM, and $NaHCO_3$ - 10, 20, 50, 100, 200, 500 and 1000 mM. Final dilutions were made in graduated cylinders to obtain initial solids concentrations of 0.4, 0.8, 1.2, 1.6, 2.0, 2.4 and 3.2 vol%. The cylinders were sealed with Parawax paper to prevent water evaporation. The values of compaction factor were determined after 120 days.

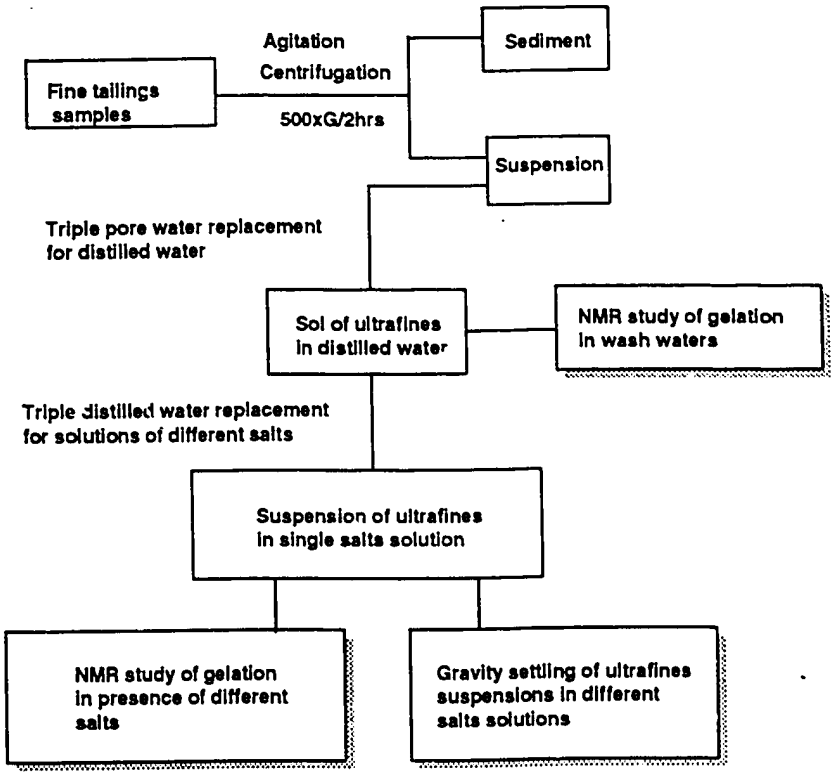

Figure 4.1 Sample preparation for NMR study and gravity settling in single salt solutions

4.6 Procedure for Investigation of Northern Holland Sludges

One of the most unfortunate characteristics of voluminous flocs is their poor dewatering, or consolidation characteristics. Consequently, this investigation was undertaken to compare the characteristics of Athabasca fine tailings with those of other "difficult" but treatable sludges, generated elsewhere. It became of interest to determine whether the mechanisms responsible for strong structure present in the Dutch sludges could be utilized to allow similar treatment of oil sand fine tailings. These sludges, identified as H-A, H-B and H-C were each divided into three portions, numbered as I, II and III, before being subjected to the following treatment:

Portion I: each sample was subjected to vigorous mechanical agitation followed by sequential centrifugation at different speeds.

Portion II: each sample was sub-divided into 4 subsamples. Each subsample (15g) was then diluted with the same amount (60g) of one of the following:

- distilled water
- pore water extracted from tailings samples
- NaOH solution (pH = 10)
- $Na_4P_2O_7$ solution (pH = 9.9).

The diluted samples were agitated manually, allowed to settle for 16 hours and then photographed to record degree of water separation and solids' settling.

Portion III: a sample (15g) of each sludge was agitated vigorously with 1 wt% sodium pyrophosphate solution (60g) and then centrifuged at high speed to separate the solids. While the Athabasca tailings sample produced a clear water layer, all the Dutch sludges gave a dark brown supernatant layer. This coloration is caused by the extraction of natural organic material. Treatment with fresh sodium pyrophosphate solutions was repeated until the supernatant liquid produced from each of the Dutch sludges was nearly colorless. The supernatant solutions, containing dissolved organic matter, were recombined and concentrated under vacuum and nitrogen at 50^0C, in preparation for infrared (IR) spectroscopic analysis. The extracted solids were washed repeatedly with warm distilled water to remove any residual $Na_4P_2O_7$ and then with toluene to remove

toluene soluble matter. The organic-free fractions were then redispersed in fresh distilled water at the same solids concentration as in the original samples. Suspended solids were then classified into particle size fractions by sequential centrifugation at different speeds. Subfractions were analyzed using XPS and XRD techniques. The scheme for sludge treatment is given in Figure 4.2.

The flocculation tests were carried out as follows: Two samples of fine tailings were treated with different amounts of sodium humate solution (5 wt% in 0.05 M sodium hydroxide solution). The samples were shaken vigorously for 5 min and then allowed to settle for 90 days. For comparison purposes a blank sample was treated in the same way except that no humic material was added.

4.7 Freeze-thaw cycle

The procedure of sample preparation for the freeze-thaw experiments is given in Table IV-2. A suspension of ultrafines was obtained from fine tailings as described above. After acid and (acid + lime) treatment they were frozen at -18^{0}C for 17 hours, then allowed to melt at room temperature. Immediately after melting, samples were carefully transferred into the centrifuge and spun at 200xG for 10 minutes. Clear water was decanted and the samples were further centrifuged at 26500xG for 30 minutes. Untreated suspensions of ultrafines were also processed in each series of experiments.

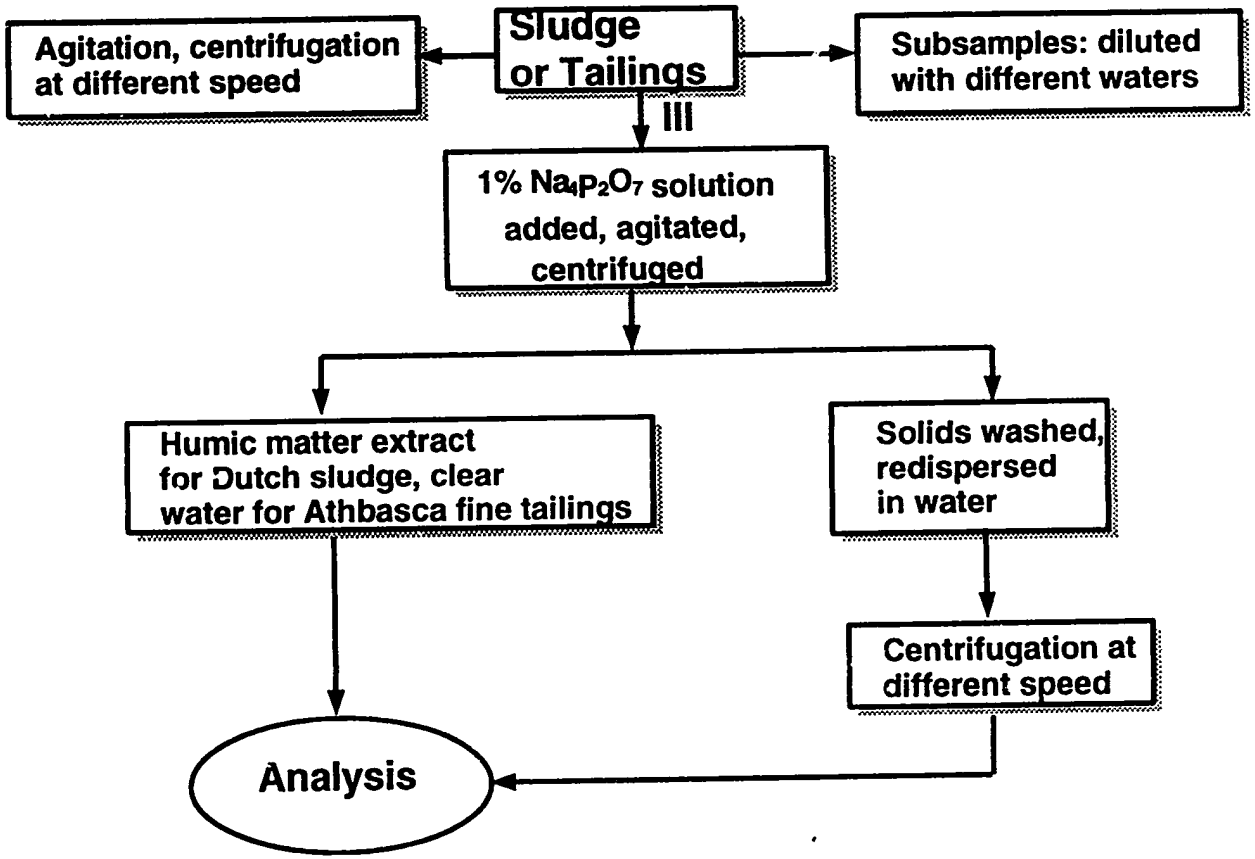

Figure 4.2 Treatment scheme for sludges and fine tailings.

4.8 Procedure to Investigate PSV Middlings and Tailings, Secondary Tailings and Run-offs.

A total of 25 samples were studied: PSV middlings , PSV tailings, secondary tailings, run-offs and oil sands ores derived from all five pilot plant runs, (OHWE-Syncrude, Modified OHWE-Syncrude, CHWE-Syncrude, CHWE-Suncor and Modified OHWE-Suncor). A common characterization procedure is outlined in the flowsheet on Figure 4.3. Processing of froths (15 samples) is discussed in Chapter 4.10.
Before processing, the solids content of each stream sample was determined on a dry residue basis. Constant weight was obtained after approximately 12 hours drying at 110^0C. Each sample (1.5 g) was tested in triplicate to assure the accuracy of the determination. First, the stream samples were separated into two portions. One portion was centrifuged at 26500xG in order replace the process water with a 1 wt% solution of $Na_4P_2O_7$. Deffloculated solids were then fractionated by centrifugation based on particle size.
A second portion was separated into ultrafine (<500 nm) and coarse (>500 nm) solid fractions by a 10-min centrifugation at 200xG. For the separation of ultrafines in PSV tailings a slightly different method was used. The samples were treated with distilled water and the mixture agitated and then centrifuged for 10 min at 200xG. Following these initial treatments the following procedures were applied to all samples.

Suspensions of ultrafines were split into two portions. One portion was separated by centrifugation into fractions containing different floc sizes. The second portion was subjected to emulsion-flotation with toluene for separation of hydrophilic and biwetted components [38].

Sediments obtained from the preliminary separation (200xG/10min centrifugation) were processed to separate Organic Rich Solids, (ORS), i.e. solids with significant amounts of organic carbon tightly bonded to the particle surfaces. Presence of the hydrophobic patches on the surfaces of biwetted particles allows their separation by flotation with toluene. To extract ORS from the sediments of coarse solids the sample was diluted with distilled water, some toluene was added, and gentle manual agitation followed by mild centrifugation (100xG/3min) applied. This procedure was repeated three

times until no appreciable amount of solids was found in the toluene layer. The same procedure was applied to separate residual solids for particle size analysis. In this case however, the selected process waters were used for dilutions. This allowed the determination of particles (floc) size in the original state of aggregation.

4.9 Gravity Settling of OHWE/CHWE Streams

Portions of as-received PSV middlings, secondary tailings and run-offs were immediately transferred into 100 mL graduated cylinders, sealed with Parawax paper and allowed to settle for several months. Photographs were taken periodically in order to record visible differences in the extent of settling, clarity of released waters and layering within the sediments.

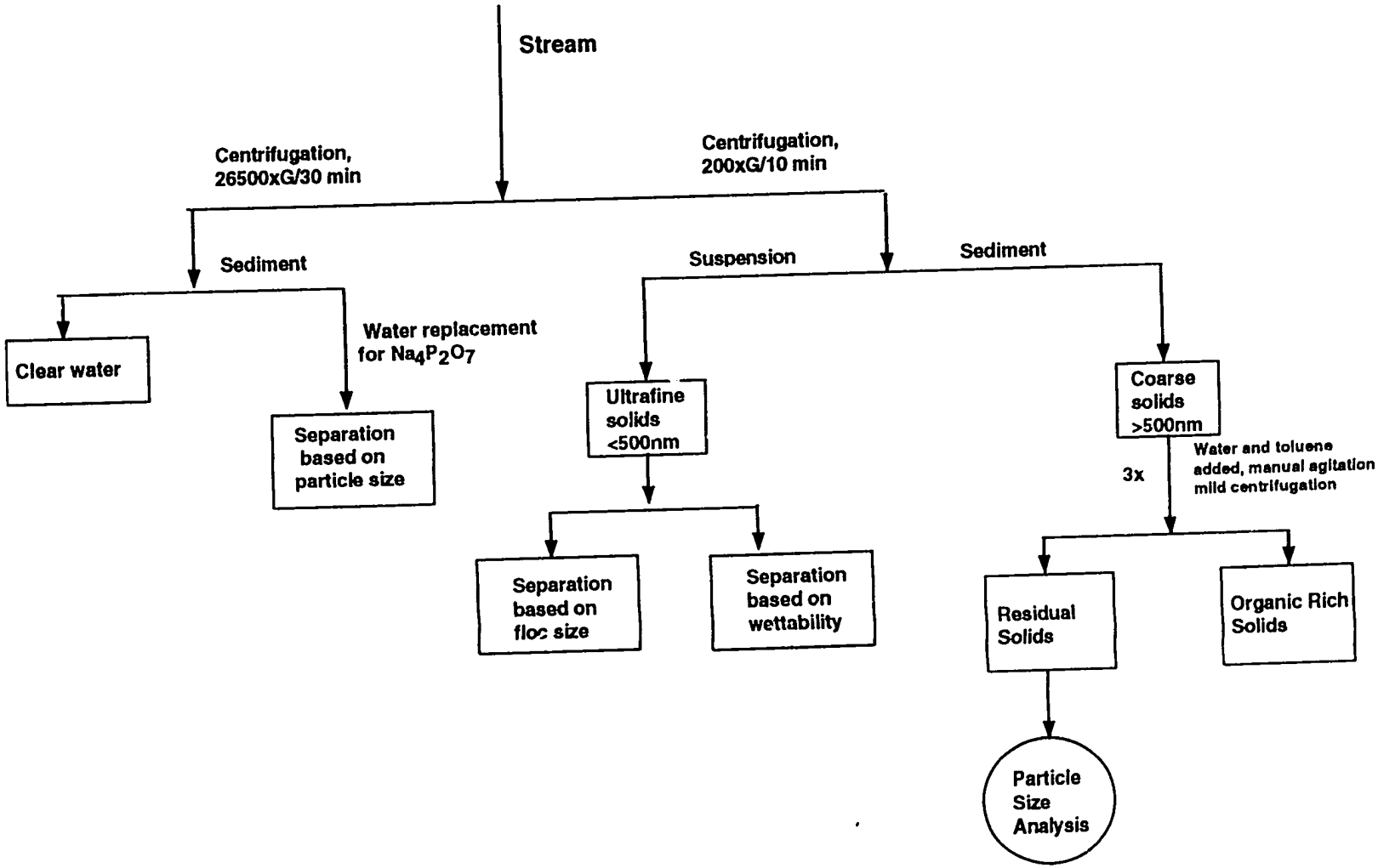

Figure 4.3 Schematic illustration of treatment method for PSV middlings and tailings, secondary tailings and run-offs.

4.10 Treatment of Froths

Samples of froths obtained in different extraction processes were analysed for solids content, contribution of biwetted solids to total solids in froths and particle size distribution. The analysis was carried out in order to determine the effect of process modification on froth quality.

The procedure applied for the treatment of froths is schematically illustrated in Figure 4.4. The treatment of PSV froths and secondary froths initially involved removal of excess bitumen by washing twice with toluene in order to recover the solids. The first wash was carried out using a froth to toluene ratio of 1:4. Samples were shaken in a paint shaker for 15 min and then centrifuged at 1500xG for 30 min. The centrifugation resulted in a bottom layer of solids suspended in the process water and a top layer of bitumen solution in toluene. To ensure complete recovery of solids, this supernatant layer was further subjected to centrifugation at 20000xG for 30min. The sediments containing insignificant amounts of solids (less than 1 wt%) were freed of residual bitumen in three more extractions with excess toluene until the toluene layer was clear. Each sample was submitted for XPS analysis.

The suspension of solids separated from froths was then subjected to a second wash using the same amount of toluene as in the first wash. The mixture was shaken for 15 min and then centrifuged at 1500G for 30 min. The supernatant was once again centrifuged at 20000xG for 30 min, but this time no sediment was obtained. The suspension of solids recovered after the second wash was then diluted with distilled water in a 1:1 weight ratio and separated into ultrafine and coarse fractions by centrifugation at 200xG for 10min. The ultrafine fraction was diluted with distilled water and then separated on the basis of surface wettability (biwetted - BUS and hydrophilic AS) in three extractions with toluene. The suspension of aqueous ultra fine solids (AS) was then classified on the basis of sequential particle size by centrifugation at increasing speeds. The coarse solids fraction was also separated on the basis of wettability after addition of distilled water and some toluene. The mixture was agitated gently by hand and a mild centrifugation (100xG for 3min) was used. The procedure was repeated three times to produce organic rich solids

(ORS), a dense sediment of aqueous coarse solids (RS) and a suspension of ultrafines. The latter was further fractionated by particle using centrifugation at different speeds.

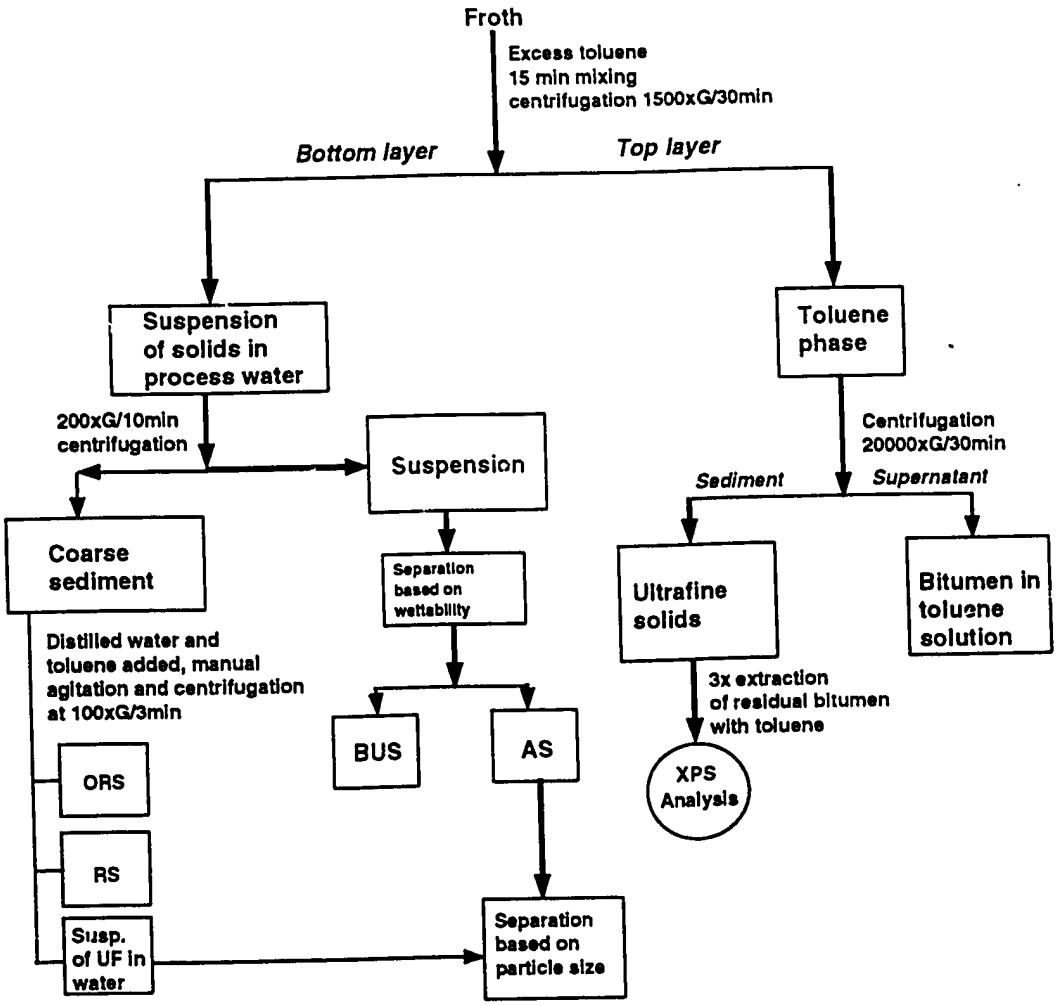

Figure 4.4 Schematic illustration of procedure applied in treatment of froths

Chapter 5

Results and Discussion

5.1 Treatment of Existing Fine Tailings

5.1.1 Chemical treatment of fine tailings

Gravity settling: Figures 5.1 - 5.9 show the effect of various additives on the wet sediment solids (WSS) content over a period of 180 days. It can be seen that:

1) For the blank sample no changes were observed during the first 20 days, whereas for treated fine tailings, changes were observed immediately, possibly as a result of the dilution effect through chemical addition.

2) With the exception of lime, most of the changes occured during the first 40 days of settling.

3) At the end of the observation period the final values for WSS, brought about by the different chemical additions, were in a narrow range of 36 to 39.5 %. This means that in general, the densification of fine tailings did not depend much on the type or the amount of additives used.

4) With respect to all the additives tested, the oil sand fine tailings behaved as a nearly "intractable" system, i.e. dewatering was very slow and the solids content in sediment never approached 50 wt% which is the minimum solids content required for reclamation.

A regression analysis was performend on the data points obtained in gravity settling of fine tailings treated with lime (best results for 2000 ppm). Equation 5 represents the best fit polynomial curve which can be used to model gravity settling of fine tailings after chemical addition see Figure 5.10:

$$\text{wt\% solids} = 30.3351+0.10676t-0.00016t^2-1.43909\times10^{-6}t^3+2.8718\times10^{-9}t^4 \quad (5)$$

where t is settling time in days.

5) Although chemical treatment was not effective from a dewatering point of view, the tailings exhibited non-segregating settling behaviour in the presence of all of the additives tested. Non-segregating sediments (i.e sediments in which solids are evenly distributed within the whole volume) may be of interest if further treatment is considered. Such systems can be handled by already existing techniques. Co-charging with sand, reclamation or direct drying, are the most economical possible methods which can be applied to fine tailings.

Centrifugation (enhanced gravity settling): Mild centrifugation (200xG) of blank fine tailings sample produced two layers: a dense sediment and a suspension containing the ultrafine solids. With acidified samples, under the same conditions, clear water was released, although some segregation into two layers of solids still occured. This difference in behaviour is a reflection of an increase in the strength of the tailings network structure as a result of acidification. This behaviour can be explained on the basis of the results from analysis of the released water,(see Table V-1). Consideration of this data shows that, at low pH, dispersing agents, such as bicarbonate ions, have nearly dissappeared and that the amounts of cations, especially divalent species, has increased dramatically. Some of these cations could have been associated with clay surfaces and are released as a result of changes in the charge at the particle edges that are known to occur at different pHs. The release of Ca^{2+} and Mg^{2+} ions will result from decomposition of the carbonates, calcite and dolomite, typically present in fine tailings. The positive charge on the edges of clay platelets at low pH also increases the likelihood of face to edge attractive interactions between particles.

It should be mentioned that any increase in the strength of the fine tailings network is not necessarily accompanied by improved dewatering through floc densification. In fact, Figure 5.11 shows that for acidified tailings samples at pHs 3.1-6.7, the solids content, after settling at 200xG, was still below the desirable level of 50 wt%. Centrifugation speeds greater than 13500xG were almost equally effective for both treated and blank samples. In all the cases, a maximum solids content of 71-74 wt% was achieved at 26500xG, the highest speed tested. Figure 5.12 compares the solids content of fine tailings acidified to pH 3 both before and after the pH was raised to 7.6 with lime or NaOH. Where lime was used for pH adjustment the solids contents obtained were greater, a fact which could be attributed to higher divalent cation concentrations (see Table V-1). Also in this case the nonsegregating behavior was more pronounced.

Results for centrifugation of fine tailings samples, treated with lime, are shown in Figure 5-13. The solids contents were comparable to those for the acidified samples (see Figure 5-12) although non-segregating behaviour was more obvious. Analysis of the water released in the course of these experiments showed the Ca^{2+}content to be no greater than that in the blank sample, (Table V-1). This indicates that Ca^{2+} cations, introduced with lime, were being removed from the system, most likely in the form of a $CaCO_3$ precipitate. The latter could act as a "binding agent" in the formation of nonsegregating mixtures. It is also likely, that the nonsegregating behaviour would be more pronounced if flocs are first dispersed at very high pH by an addition of 1500-2000 ppm of lime, and then reformed during the precipitation of $CaCO_3$. A comparison of centrifugation results for samples treated with lime only and samples in which lime was used for pH readjustment after acidification, indicates that the solid content was higher in the latter case.

5.1.2 Chemical treatment of suspensions of ultrafines (colloidal solids)

Gravity settling: Supensions of total ultrafines (≤ 500 nm), separated from fine tailings, contained 7.6 wt% solids which is close to the so called " gelation concentration" (GC) , that is the concentration at which gelation is first observed. Samples evaluated for the effect of acid addition (or acid + lime) on gravity settling had a solids concentration of 7 and 6.8 wt% respectively, owing to dilution during sample preparation. Results showing the time dependence of the settling behaviour of these suspensions are given in Figures 5-14 and 5-15. It is interesting to note that, although dewatering is slightly better for samples at lower pH, the maximum solids content achieved was always close to the solid content value prior to dilution. That is, the suspensions tended to approach the GC. Low pH is the condition most favourable for coagulation; here edge to face interactions of the clay particles are possible and the dispersing action of bicarbonate ions is eliminated. Even so, there is no indication of densification of ultrafine flocs within the sediments.

Centrifugation (enhanced gravity settling): Results showing the solids content for ultrafines suspensions, acidified to different pH, and centrifuged under mild (200xG) and extreme (26500xG) conditions are given in Figure 5-16. When 200xG was applied to the samples acidified to pH ≤5 there was a small increase in solids content from 7.6 to about 9%. This is a rather small increase considering that bicarbonates were virtually absent and that a relatively high concentration of Ca^{2+} was present (see Table V-2). When the untreated suspension was centrifuged (26500xG) at its natural pH of 8.4, the solids content reached 27%. This was the highest concentration to which a suspension of ultrafines could be sedimented under high speed centrifugation.

Figure 5-17 gives the solids contents for ultrafines suspensions acidified to different pHs and then subjected to pH readjustment to 7.6 with lime. As found in the absence of lime the solids contents for the lime treated samples were higher at lower initial pH values. Centrifugation of samples with added lime at 26500xG gave results similar to those for the samples without lime addition.

5.1.3 Freeze/Thaw

Acidified suspensions, both before and after lime addition, were subjected to a freeze/thaw cycle. Results showing the solids contents of the sediments, after low speed centrifugation at 200xG, are shown on Figures 5-16 and 5-17. It can be seen that in both cases (with and without lime) this treatment resulted in a large increase in solids content up to nearly 27%, especially for initial pH ≤5. There was no increase in the solids content when high speed centrifugation was applied to the freeze/thaw treated samples.

Table V-1: Fine tailings in the presence of additive. Concentration in water (ppm)

Additive	pH of acidified sample	Bicarbonates + carbonates	Na	K	Mg	Ca
Acids	3.1	n/d	544	27	153	474
	5.1	76	579	43	55.3	195
	6.7	583	533	38	16.9	15.6
	8.4 (blank)	861	382	11	2	3
pH+NaOH	2.5	163	2585	41	199	479
	3.8	n/a	1652	25	116	162
	5.3	181	791	26	46	69
	7.2	444	570	19	17	16
pH+lime	2.6	90	564	34	147	569
	4.0	76	526	36	127	586
	5.4	103	555	35	73	291
	7.2	408	506	23	20	28
Lime	11.6	559	228	7.7	0.1	0.5
	11.7	681	254	8.4	0.04	0.5

n/a - not available
n/d - not detected

Table V-2: Suspension of ultrafines in the presence of additives. Concentration in water (ppm)

Additive	pH of acidified sample	Bicarbonate	Na	K	Mg	Ca
Acid	7.1	830	325	11	3	5
	6.3	422	355	16	7	11
	5.4	103	404	20	13	23
	4.1	n.d.	436	27	26	46
	2.7	n.d.	456	36	44	82
	1.9	n.d.	461	42	61	112
Acid + lime	5.9	132	430	26	31	199
	5.2	142	457	27	32	160
	4.6	136	433	28	35	211
	3.0	114	441	30	42	377
	1.9	114	467	33	57	692

n.d.- not detected

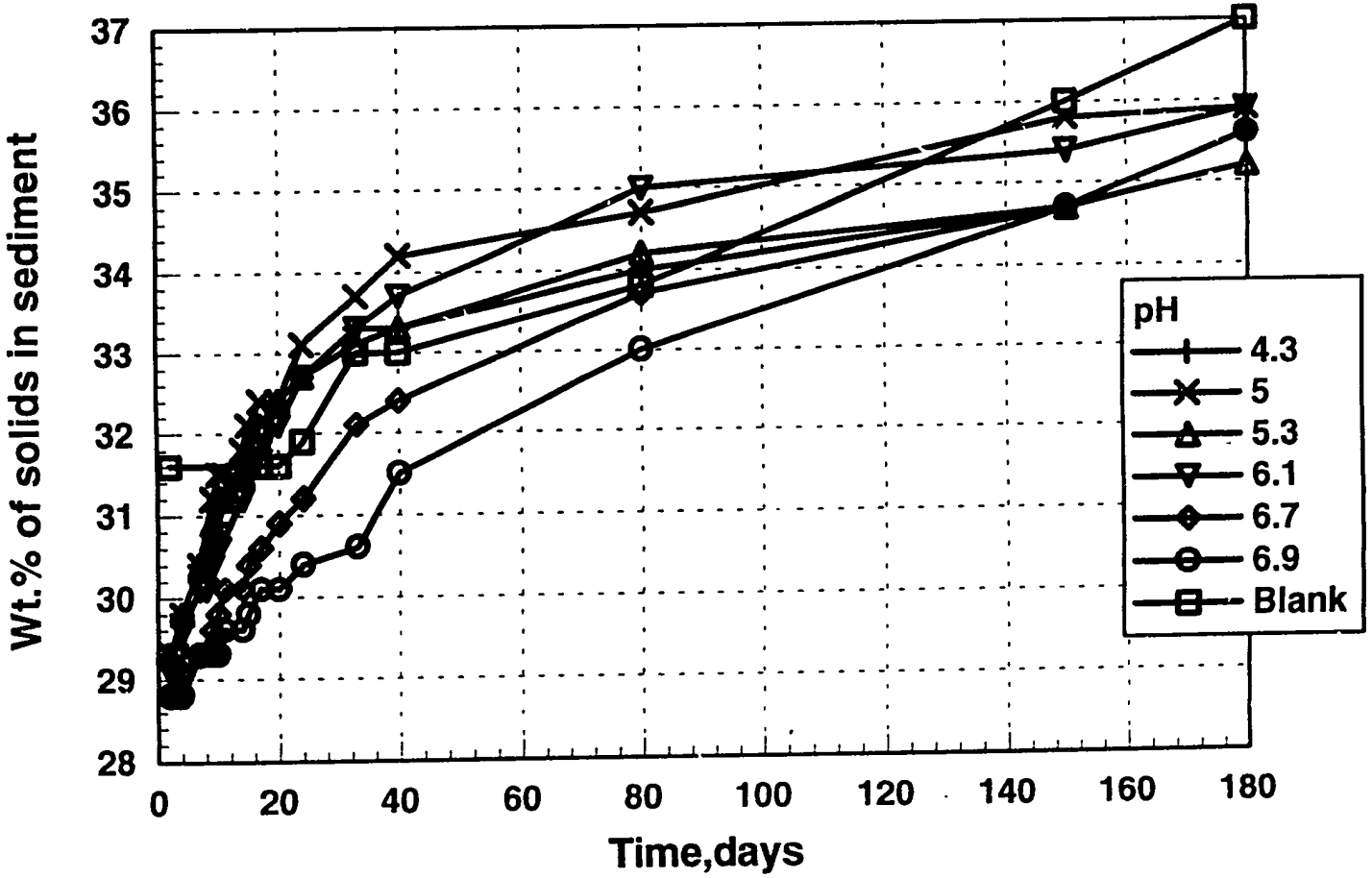

Figure 5.1 Gravity settling of fine tailings at different pH (Blank - untreated fine tailings, pH=8.4)

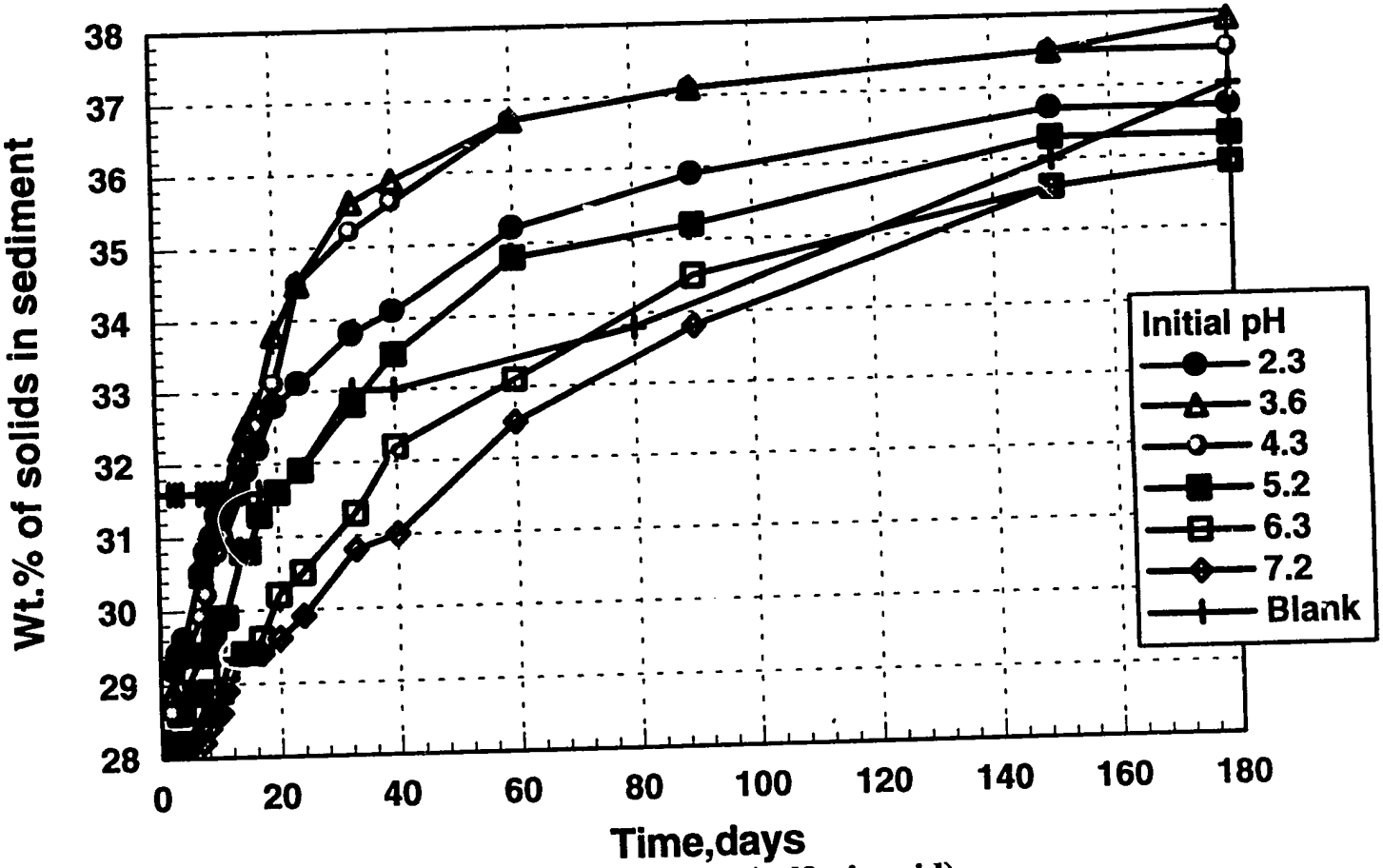

Figure 5.2 Gravity settling of fine tailings acidified(sulfuric acid) to different initial pH and then pH adjusted to 7.6 wit NaOH. (Blank - untreated fine tailings, pH=8.4)

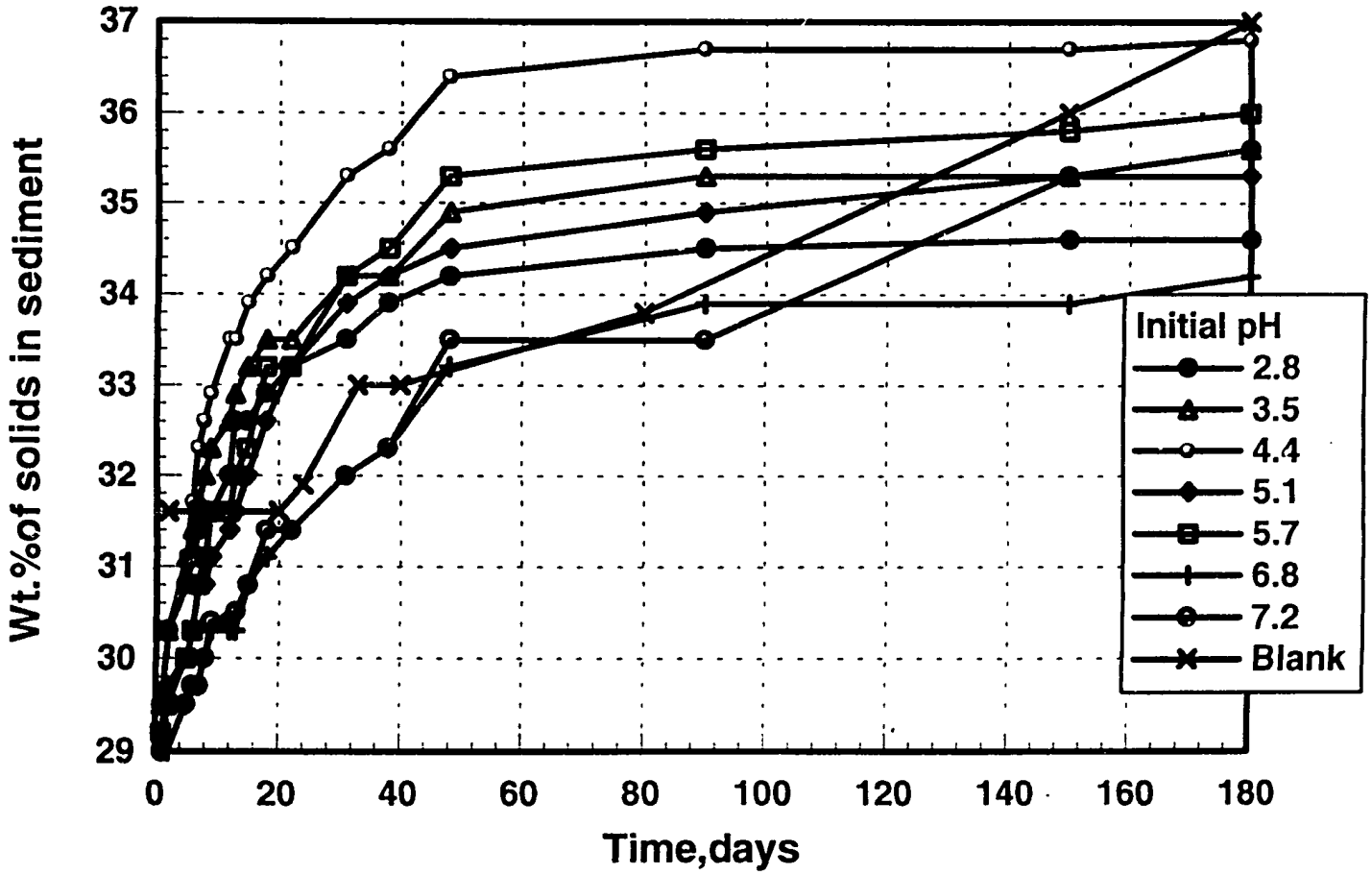

Figure 5.3 Gravity settling of fine tailings acidified (sulfuric acid) to different initial pH followed by pH adjustment to 7.6 with lime. (Blank - untreated fine tailings, pH=8.4)

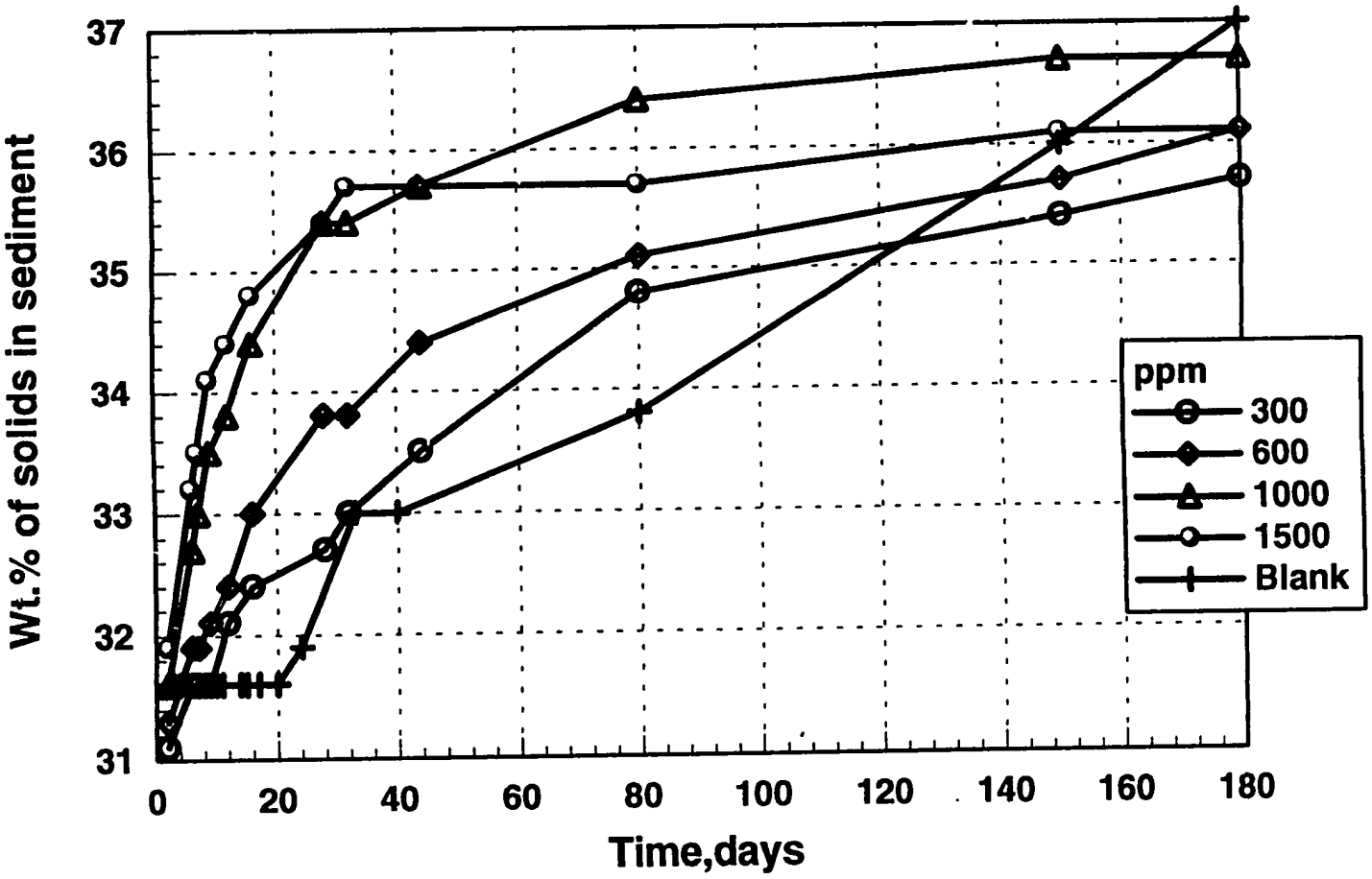

Figure 5. 4 Gravity settling of fine tailings treated with calcium chloride. (Blank - untreated fine tailings)

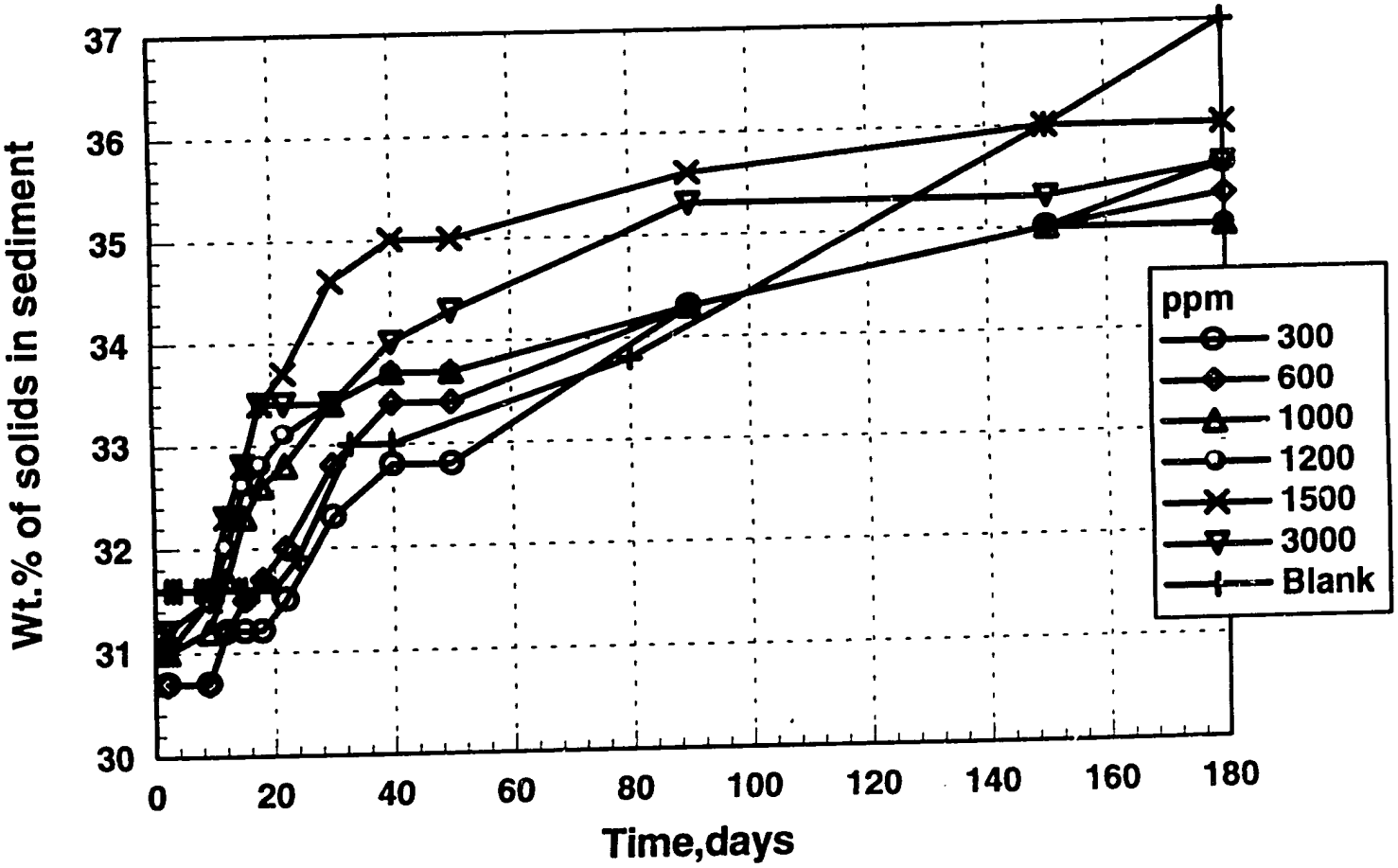

Figure 5.5 Gravity settling of fine tailings treated with aluminum chloride. (Blank - untreated fine tailings)

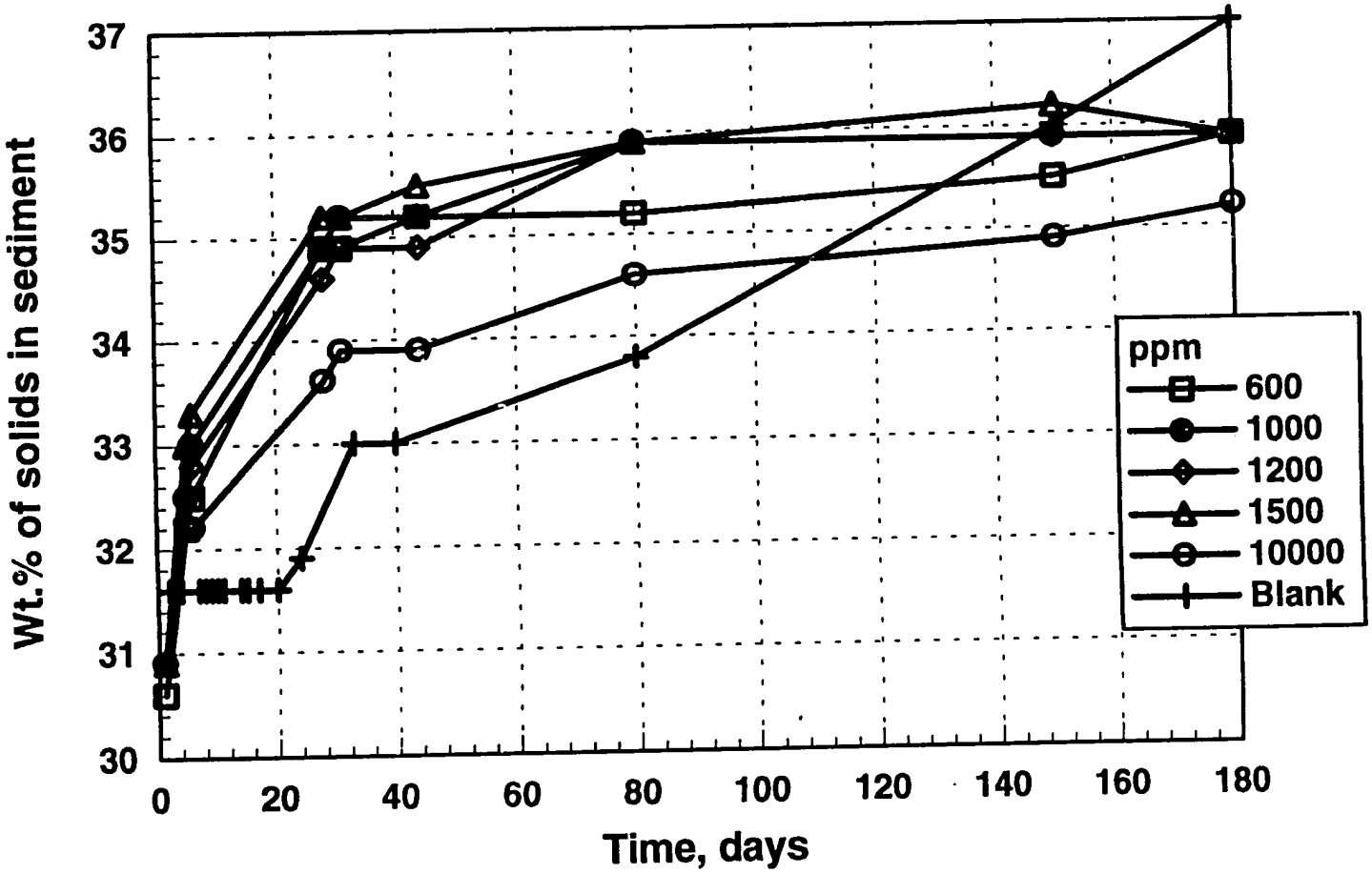

Figure 5.6 Gravity settling of fine tailings treated with brine. (Blank - untreated fine tailings)

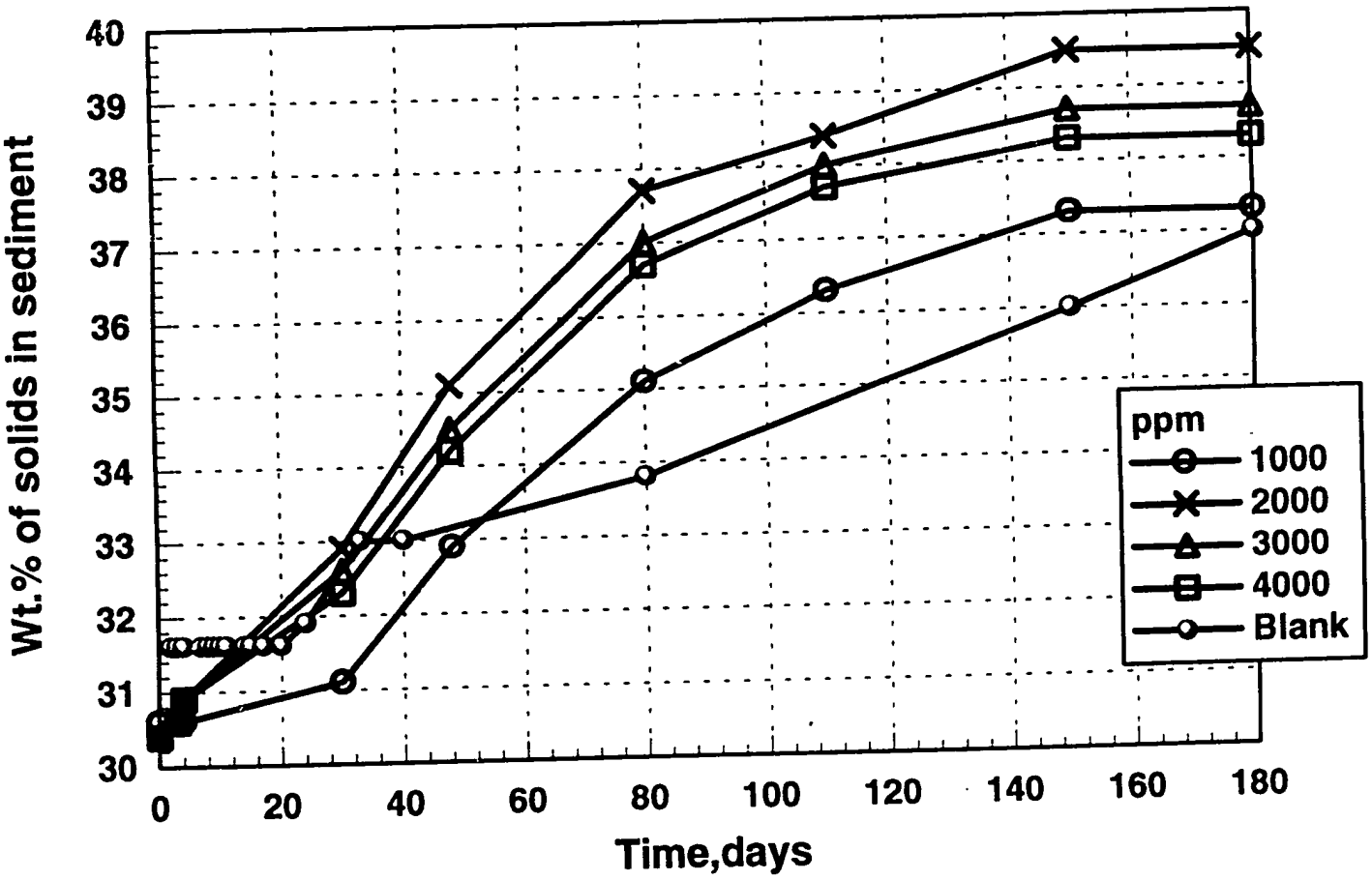

Figure 5.7 Gravity settling of fine tailings treated with lime. (Blank - untreated fine tailings)

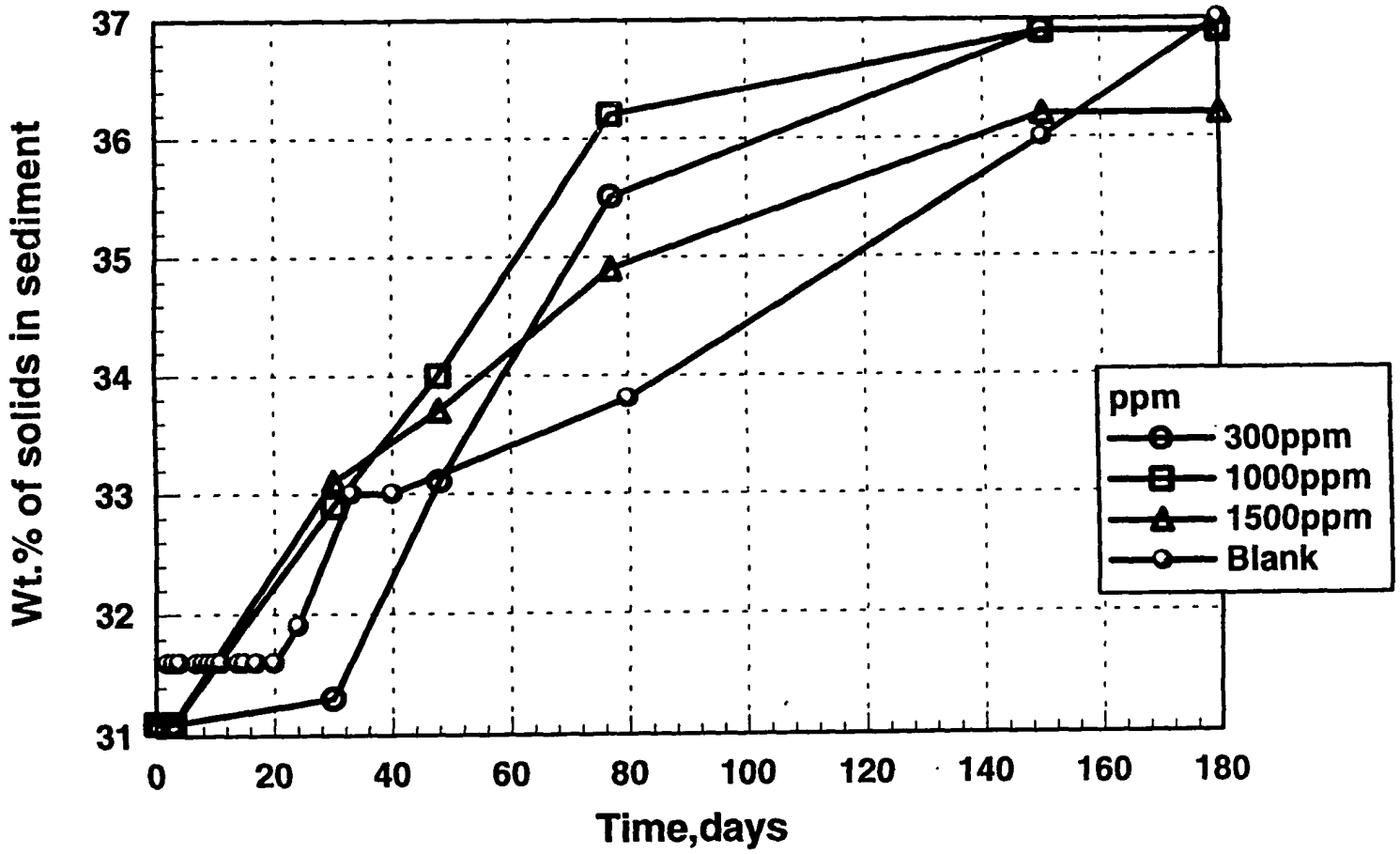

Figure 5. 8 Gravity settling of fine tailings treated with gypsum. (Blank - untreated fine tailings)

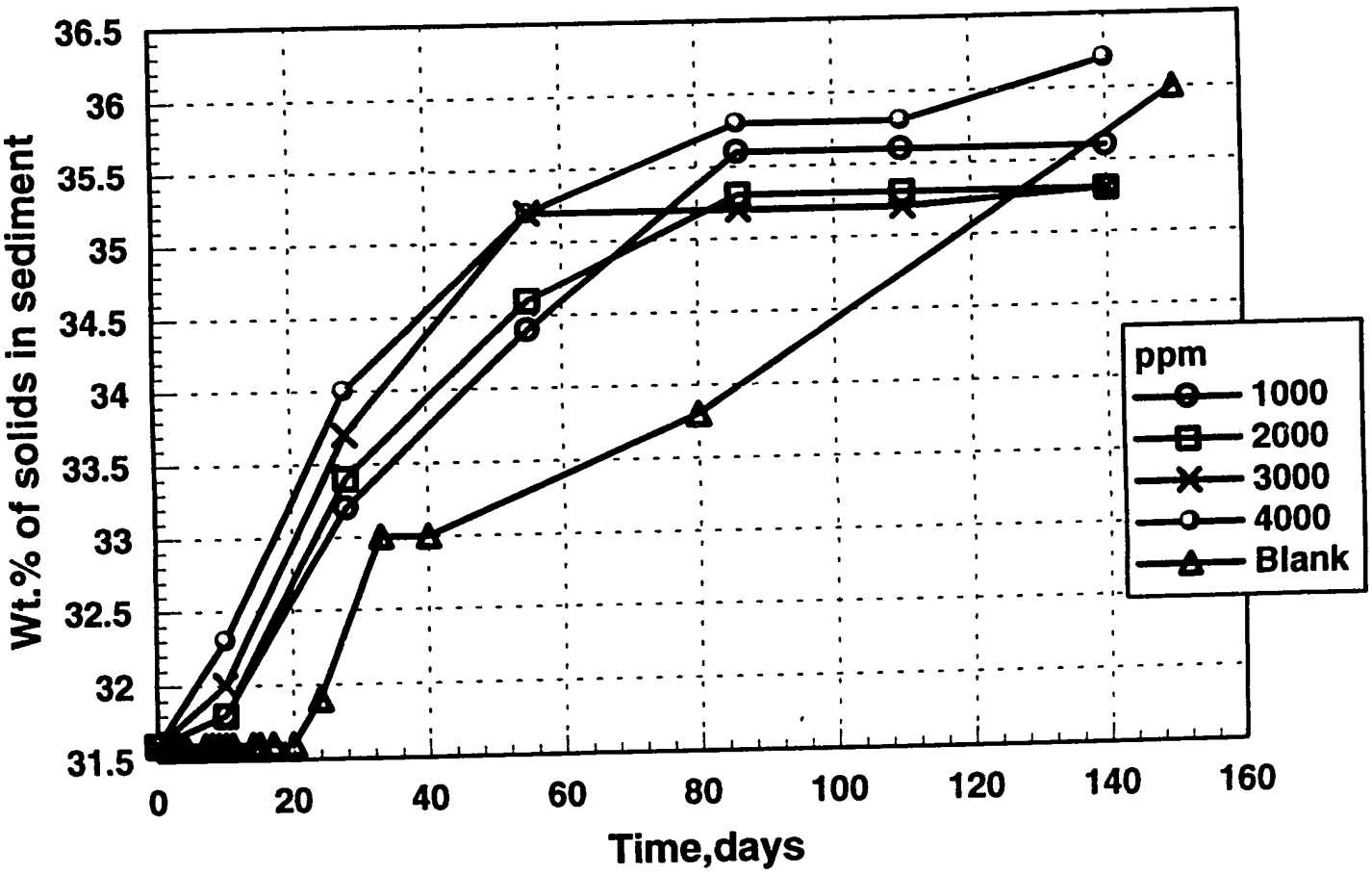

Figure 5. 9 Gravity settling of fine tailings treated with sodium bicarbonate. (Blank - untreated fine tailings)

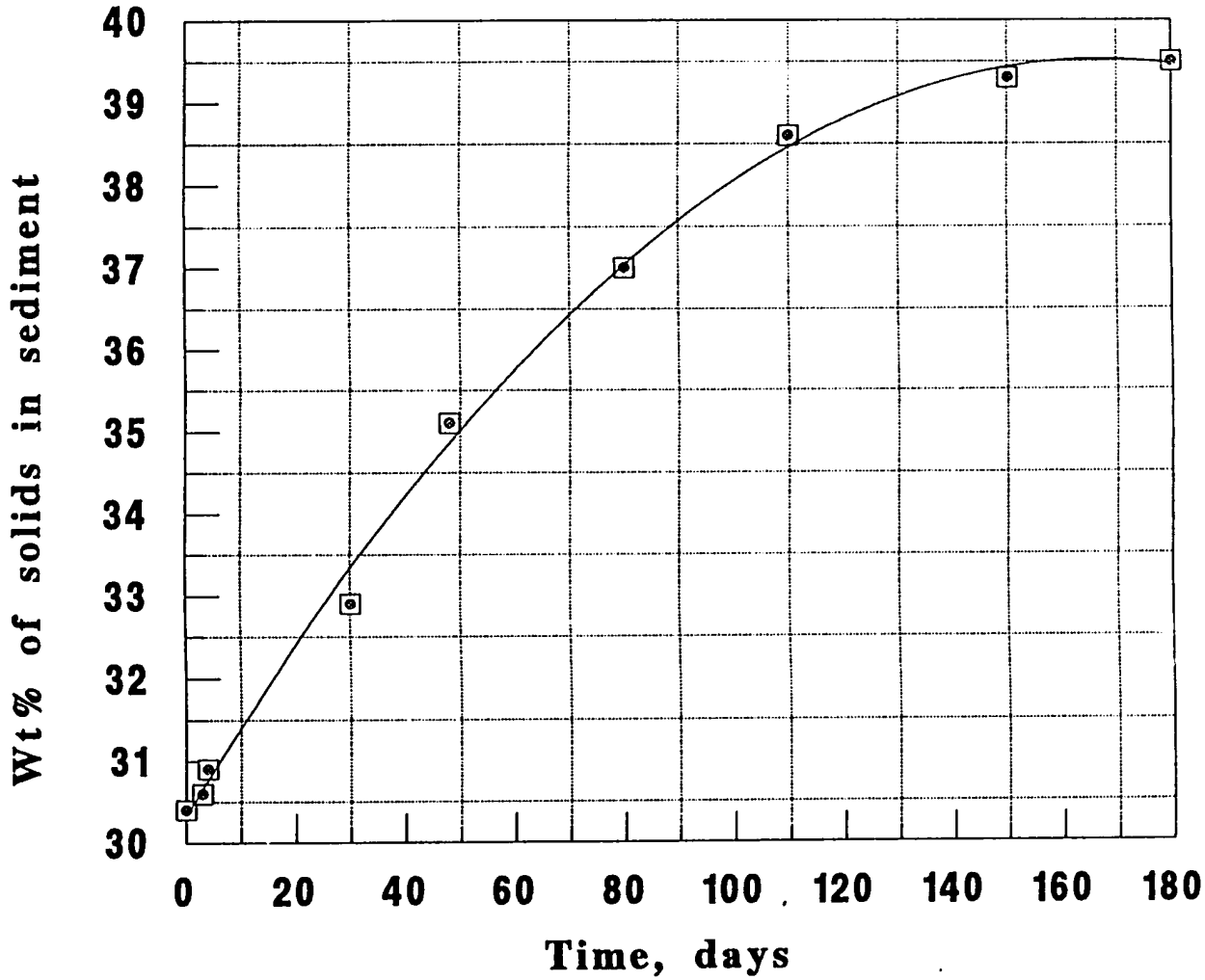

Figure 5.10 Polynomial fit of data representing the best results in gravity settling of fine tailings (2000 ppm lime)

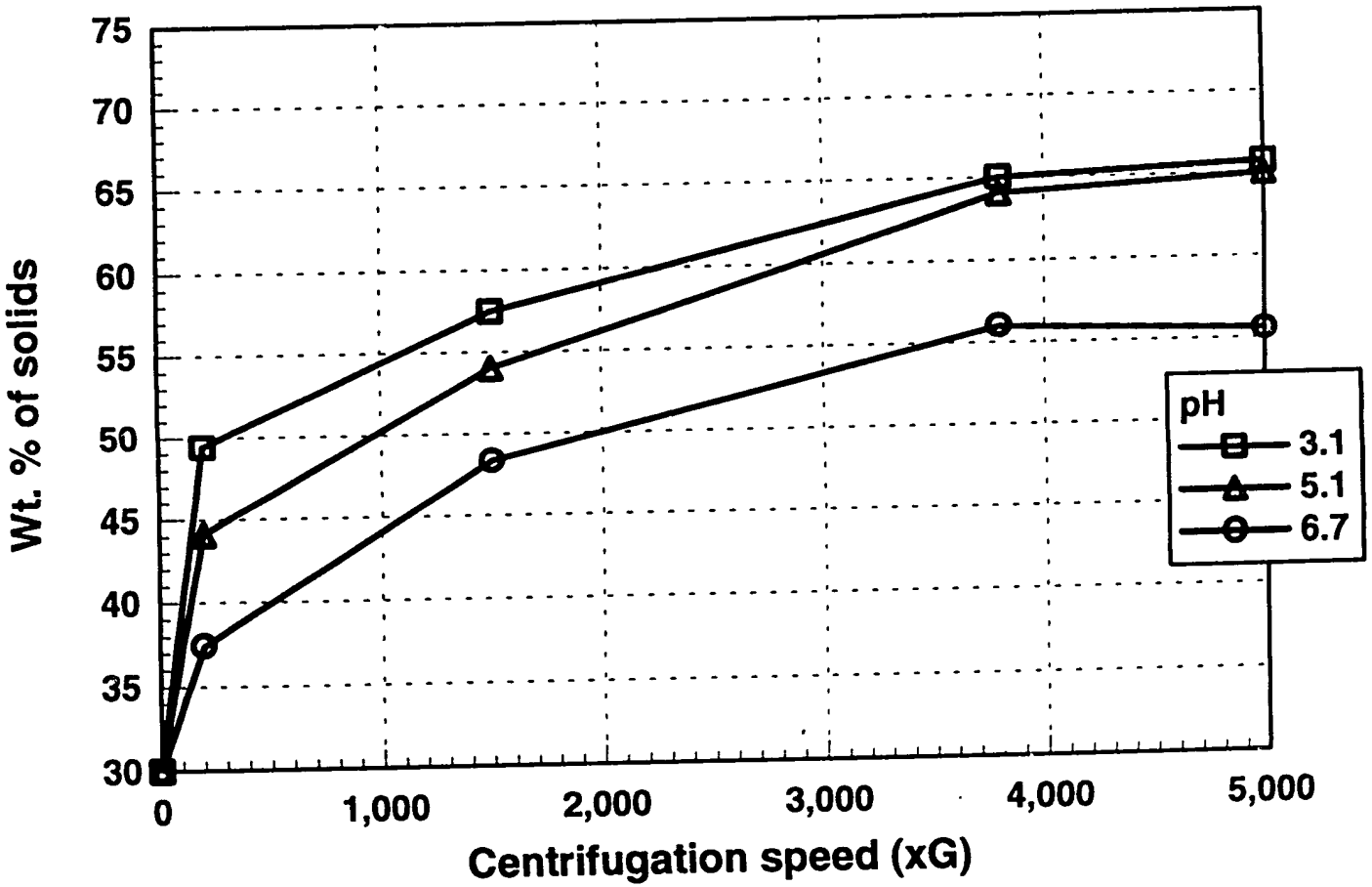

Figure 5.11 Enhanced settling by centrifugation of fine tailings samples at different pH

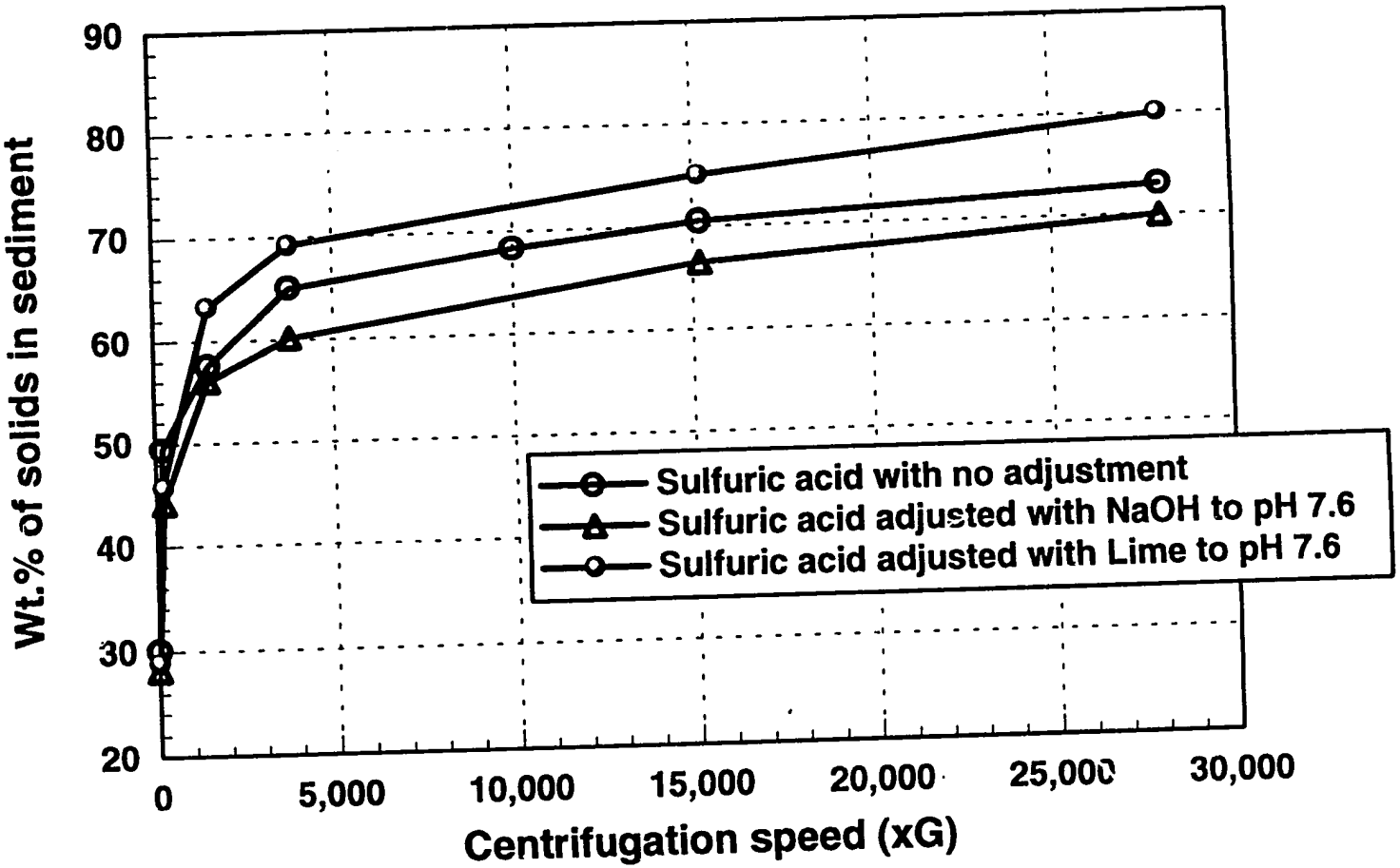

Figure 5.12 Enhanced settling by centrifugation of three differently treated fine tailings samples, initially at pH 3

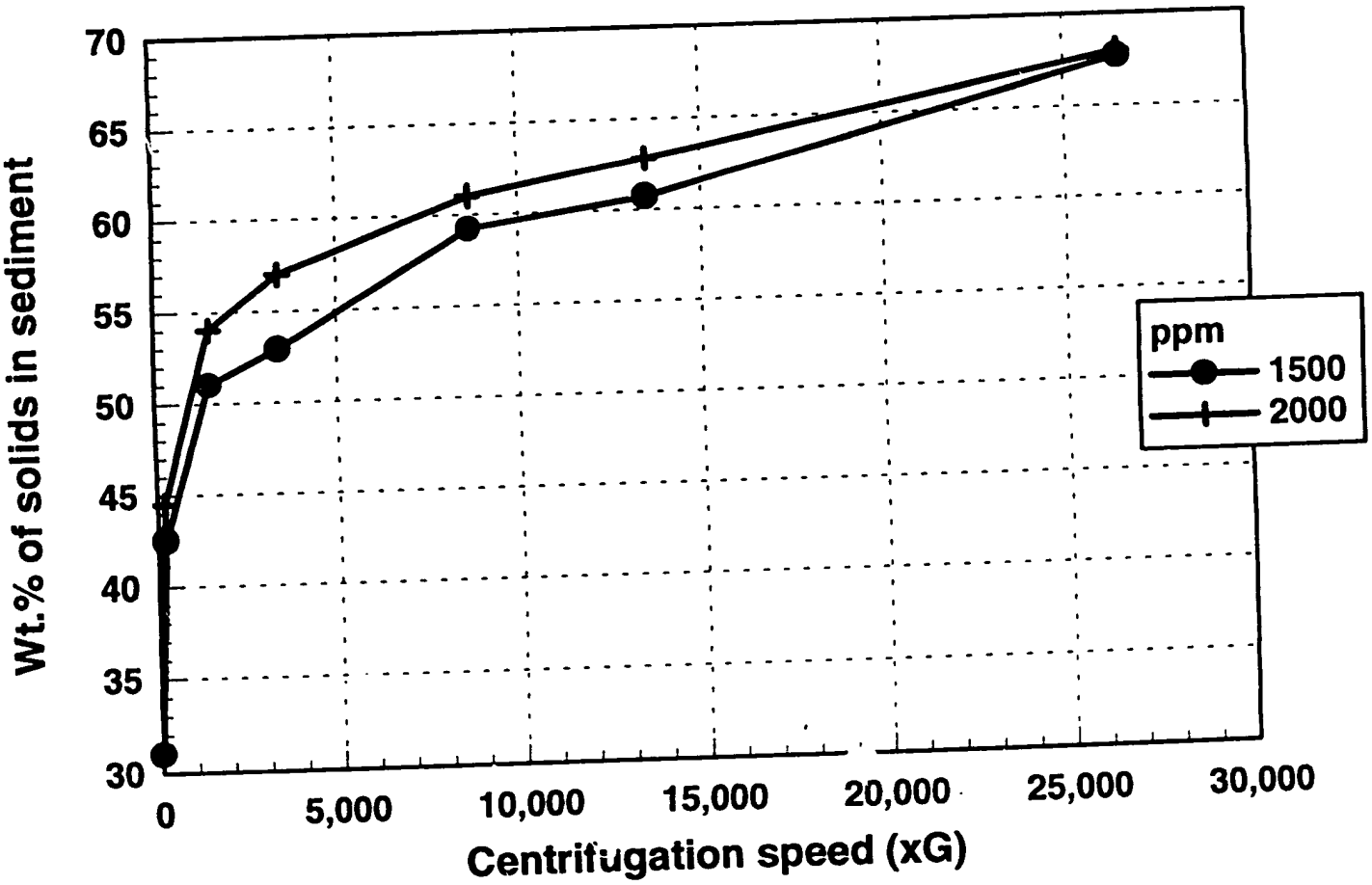

Figure 5.13 Enhanced settling by centrifugation at different concentration of lime

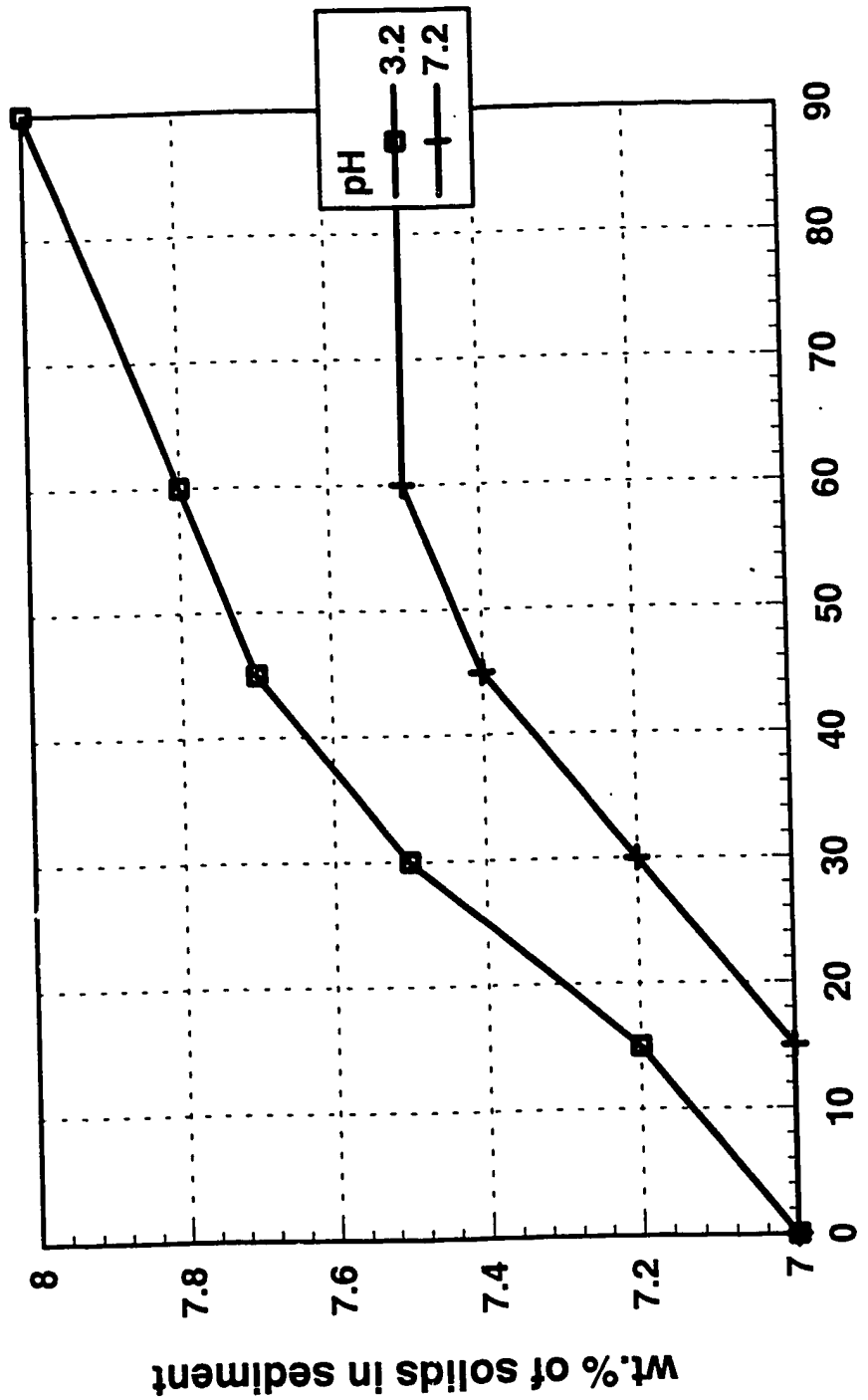

Figure 5.14 Gravity settling of ultrafines suspensions at different pH

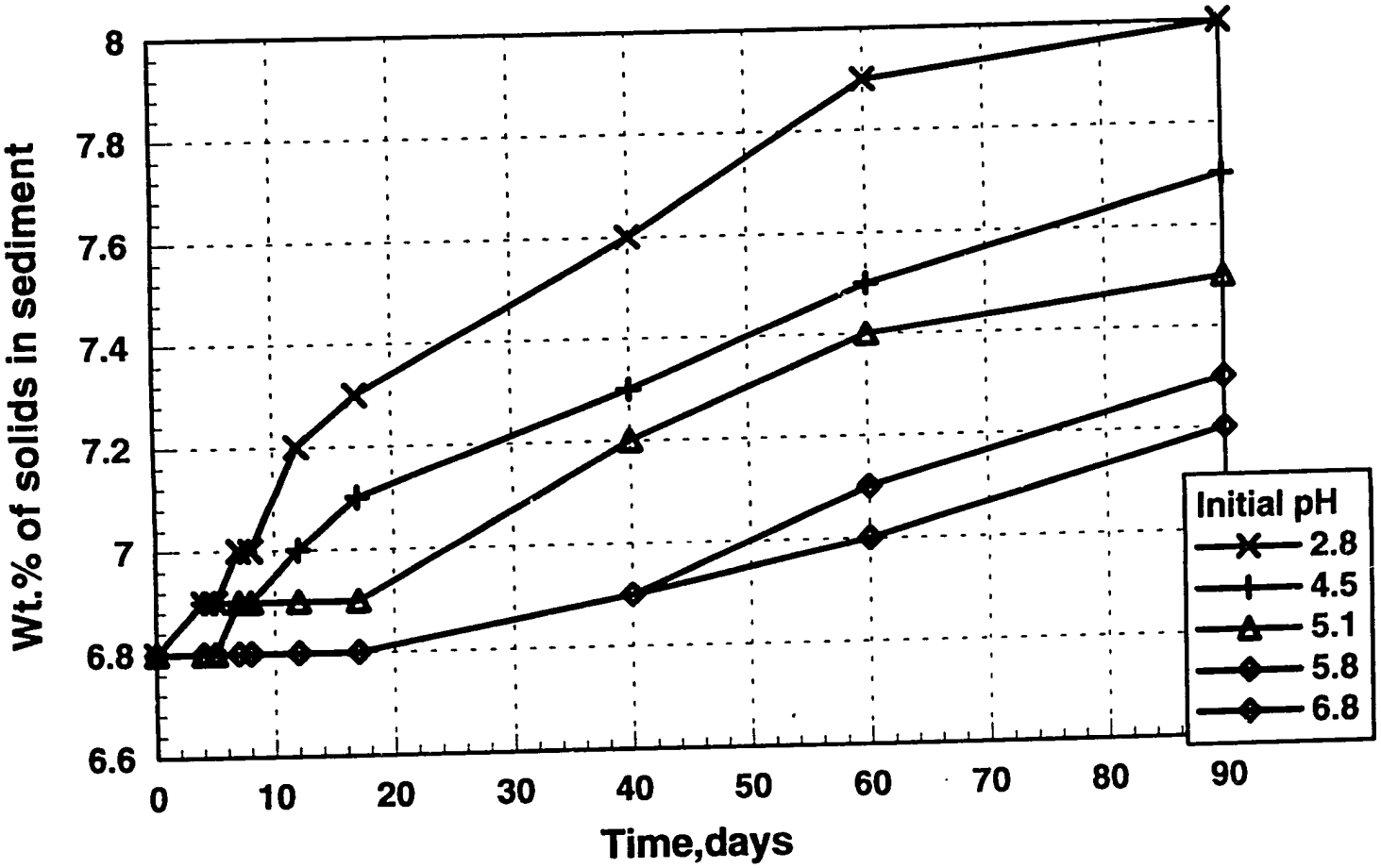

Figure 5.15 Gravity settling of total colloid samples acidified (sulfuric acid) to different initial pH and adjusted to pH 7.6 with lime

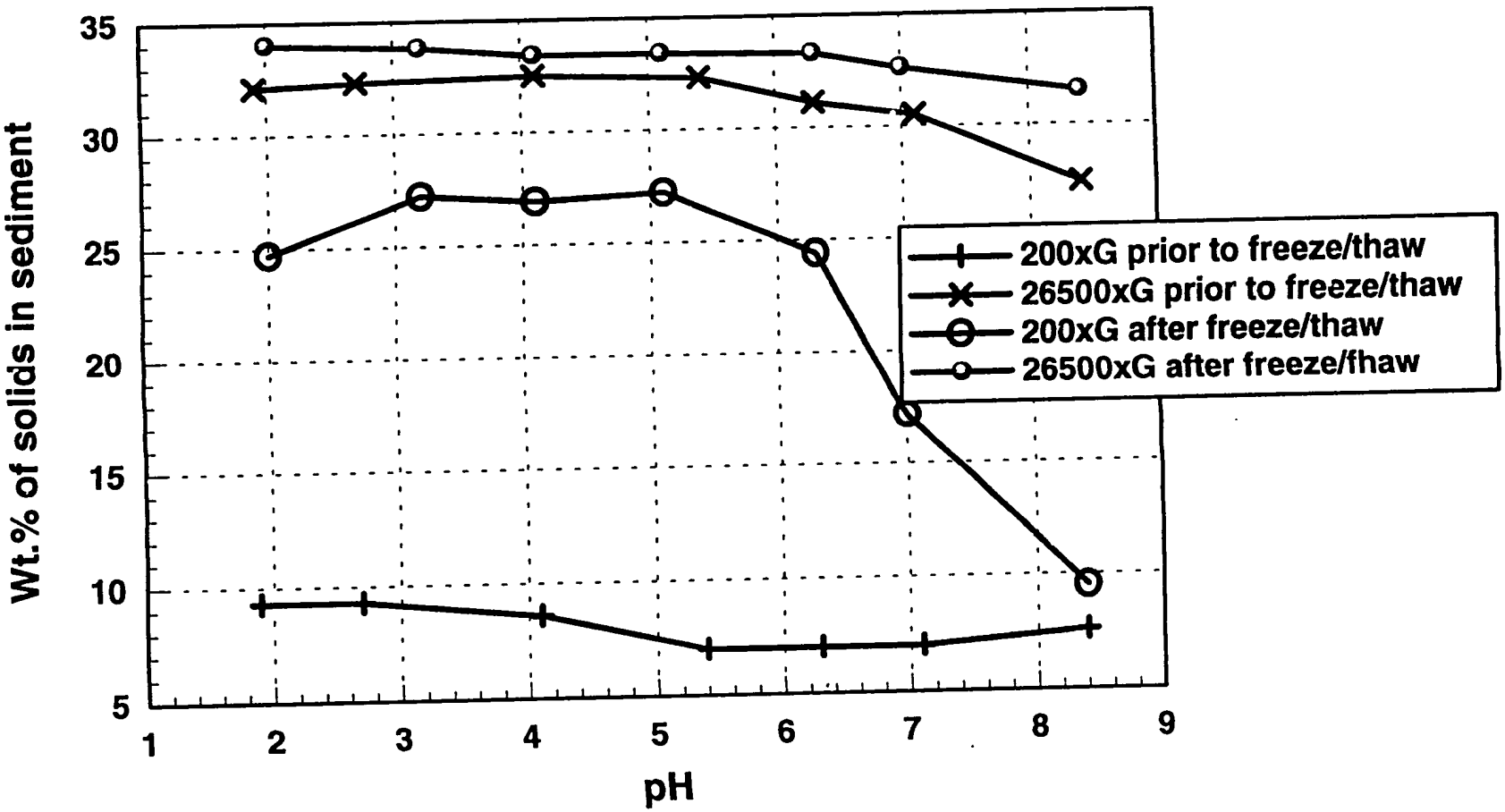

Figure 5.16 Effect of freeze/thaw and centrifugation on dewatering of ultrafines suspension at different pHs

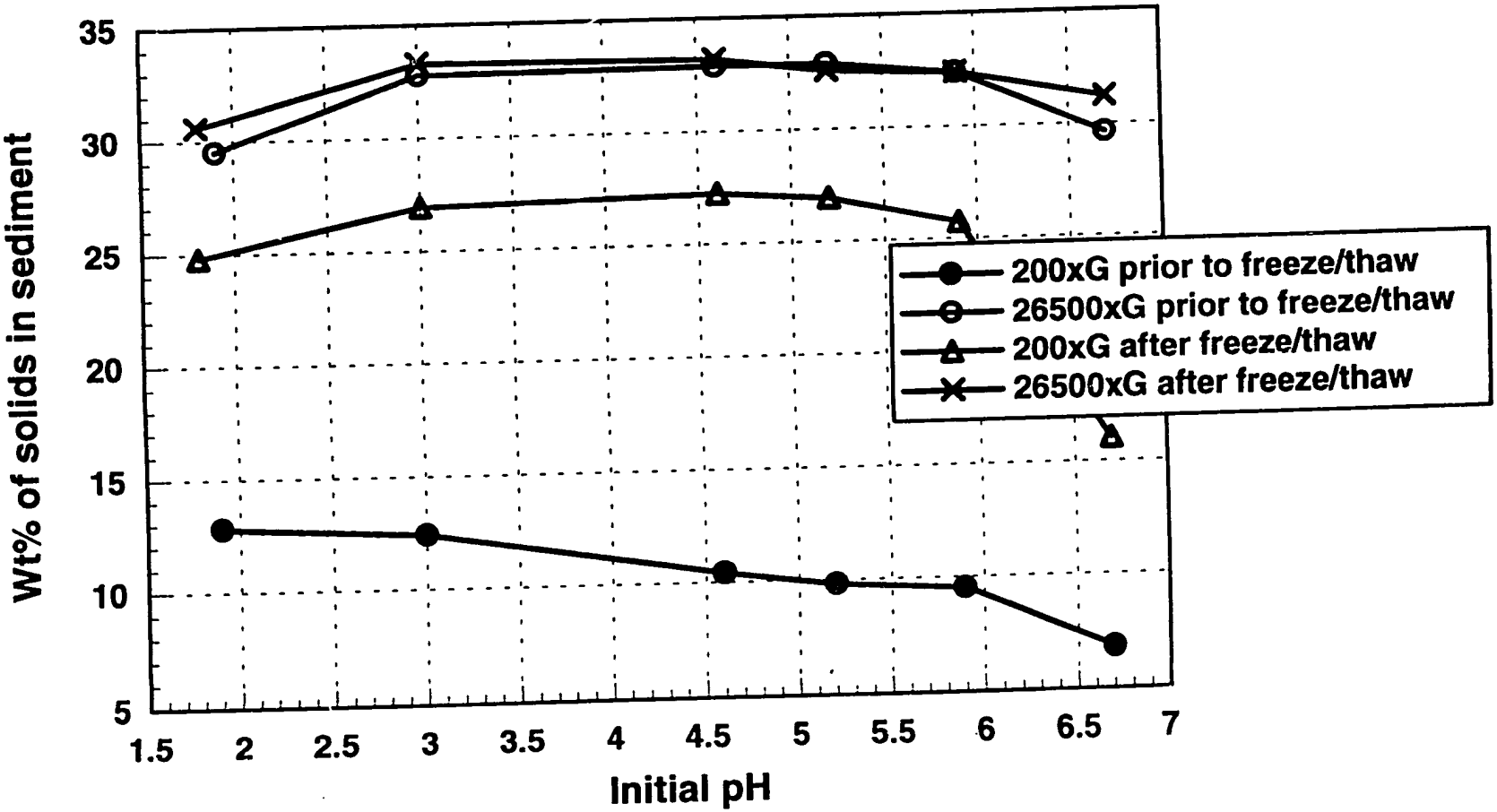

Figure 5.17 Effect of freeze/thaw and centrifugation in acidified ultrafines suspensions, pH adjusted to 7.6 with lime

5.1.4 The NMR Study of UltrafinesGelation at Different Salt Concentration

Deuterium NMR spectroscopy was utilized to obtain information on the sol-gel transformation in suspensions of clay ultrafines at different concentrations of several electrolytes. The electroly e concentration in tailings pond water is high enough to reduce the elecrostatic double layer on the clay platelets sufficiently to cause flocculation.

The sol-gel transformation was initially studied at reduced concentrations of the natural components of tailings pond water. The first series of measurements were carried out using pond water as the dispersing medium. Dilutions were made to obtain samples of 1, 2, 3, 4, 5, 6, 7 and 8 wt% of ultrafine solids. Figure 5.18 shows ^2H NMR splitting versus solids concentration for various time periods. The degree of aggregation of ultrafines is not well pronounced within the first 8 hrs. After 2 days significant changes in splitting for concentrations higher than 4 wt% were observed. The final measurement was made after a period of 28 days. Splitting disappeared in all the samples with solids contents higher than 3 wt%. The clay particles in these samples were completely immobilized in the gel network as reflected in zero splitting signal (see Chapter 2.5). At concentrations lower than 4 wt% some flocs were still settling freely after 28 days.

Subsequently, the natural electrolytes were progressively removed during three consecutive replacements of the pond water with distilled water. After each washing dilutions to 1 - 8 wt% solids were made and change in splitting was monitored for a period of 28 days. The results are shown in Figures 5.19 and 5.20. In summary, the gelation was markedly inhibited by a reduction of cation concentration, in first wash water and it was completely eliminated when the cation concentration was reduced to ~20 ppm (see Table IV-3).

Subsamples of the suspension of ultrafines obtained after three washes in distilled water were then saturated with solutions of mojor individual salts naturally present in pond water. Figure 5.21 shows the sol-gel transformation processes in a dispersing medium containing 5 mM of NaCl (115 ppm Na^+). It can be seen, that at this concentration, gelation progresses markedly in the first 8 hours and then the transformation occurs at a

much slower rate for a period of several days. This could be the result of weak interactions between the particles involved in the gel structure and therefore it is possible that the gel was partially broken by vibrations during insertion of the samples into the magnetic field.

In Figure 5.22 gelation in water containing 20 mM NaCl (460 ppm Na^+) is shown. In this case gelation progresses rapidly. All particles in the samples, containing more then 3 wt% ultrafine solids, are enclosed in a stiff gel network after 8 hours. Subsequently, the effect of the same concentration of sodium in $NaHCO_3$ (460 ppm Na^+ and 1220 ppm HCO_3^-) solution was studied. Figure 5.23 shows the sol-gel transformation in the presence of 20 mM $NaHCO_3$. In such a case the concentrations of sodium and bicarbonate ions are very close to those in the pond water. In fact, the progress of gelation within the first 8 hours in a medium containing 20 mM $NaHCO_3$, is similar to that in pond water alone (compare Figures 5.18 and 5.23). In the case of samples containing $NaHCO_3$ gelation was completed after 28 days only for the highest solids content (8 wt%).

Comparison of the results presented in Figures 5.22 and 5.23 indicates the strong dispersing action of bicarbonate ions. When chloride anions are replaced by bicarbonate anions, at the same concentration of sodium, the gelation time increases dramatically from hours to months. The effect of 5 ppm Ca^{2+} (naturally present in the pond water) on sol-gel transition was also studied. It follows from Figure 5.24 that the presence of 5 ppm Ca^{2+} in the dispersing medium has only a marginal effect on the gelation kinetics of the ultrafine clay particles. Concentrations of salts higher than 20 mM could not be used in the study, due to the very fast gelation progress which was completed in several minutes.
An important observation was made in the course of these experiments. It was noticed that all the samples containing more than 4 wt% of ultrafine solids did not release any water even after long period of time. The question arose whether extremely high electrolyte concentrations might be able to collapse the electrostatic double layer and thus release a major fraction of the water entrapped in the gel network.

5.1.5 Settling of ultrafines in single salt solutions

An attempt was made to study the behavior of the ultrafines in suspensions containing pond water salts (NaCl and $NaHCO_3$) at extremely high concentrations (1000 mM). Final results for both salts are plotted in Figure 5.25 which shows the compaction factor versus the initial concentration of ultrafines in the suspensions at different salt contents. It can be concluded that regardless of the type and concentration of salt used for flocculation, the final ultrafines content in the sediment is always close to the Gelation Concentration (GC). The value of the GC depends on the size and wettability of the ultrafines [24], and is practically independent of the salt content in the dispersing medium.

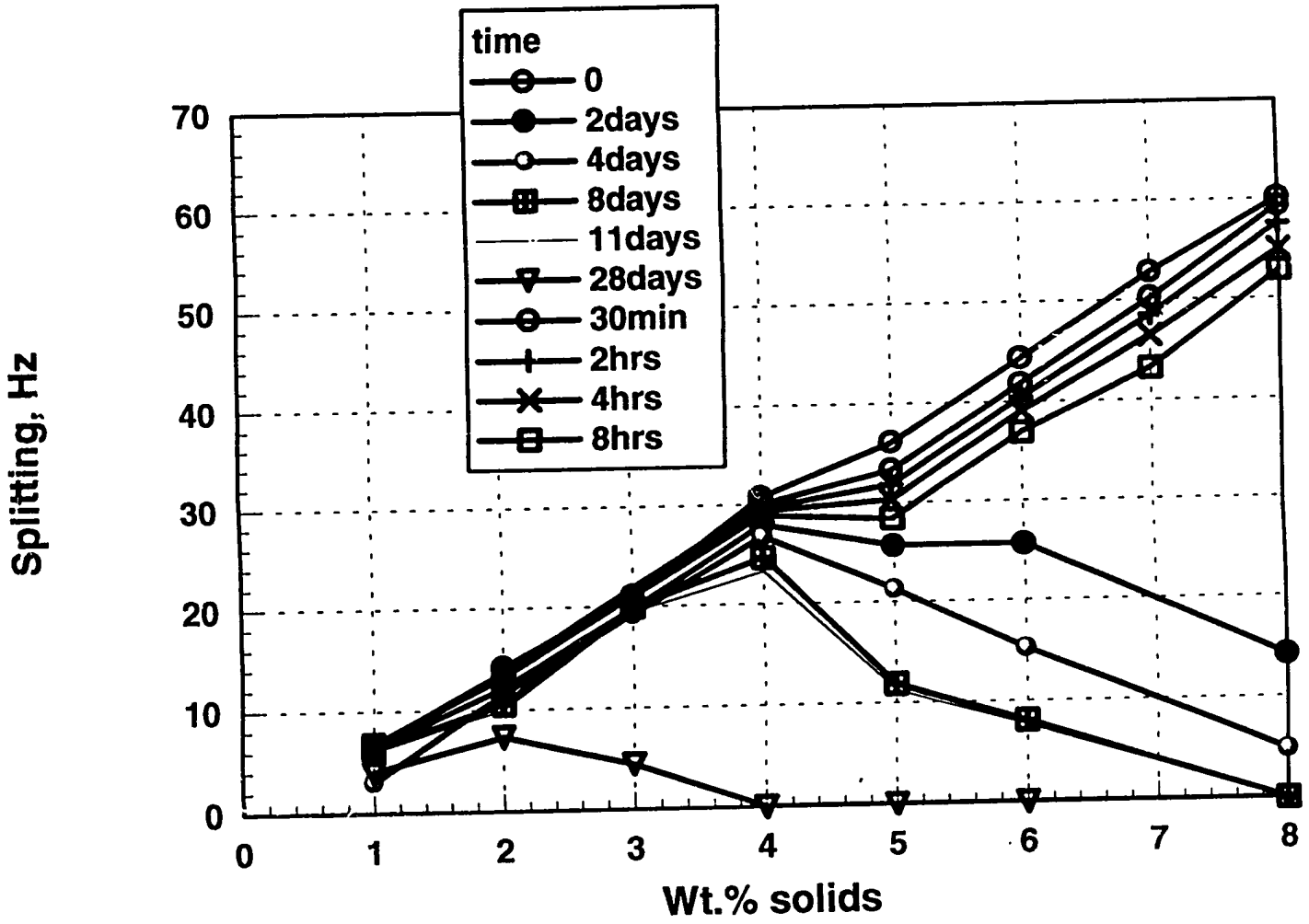

Figure 5.18 Splitting vs. concentration in pond water at different time periods

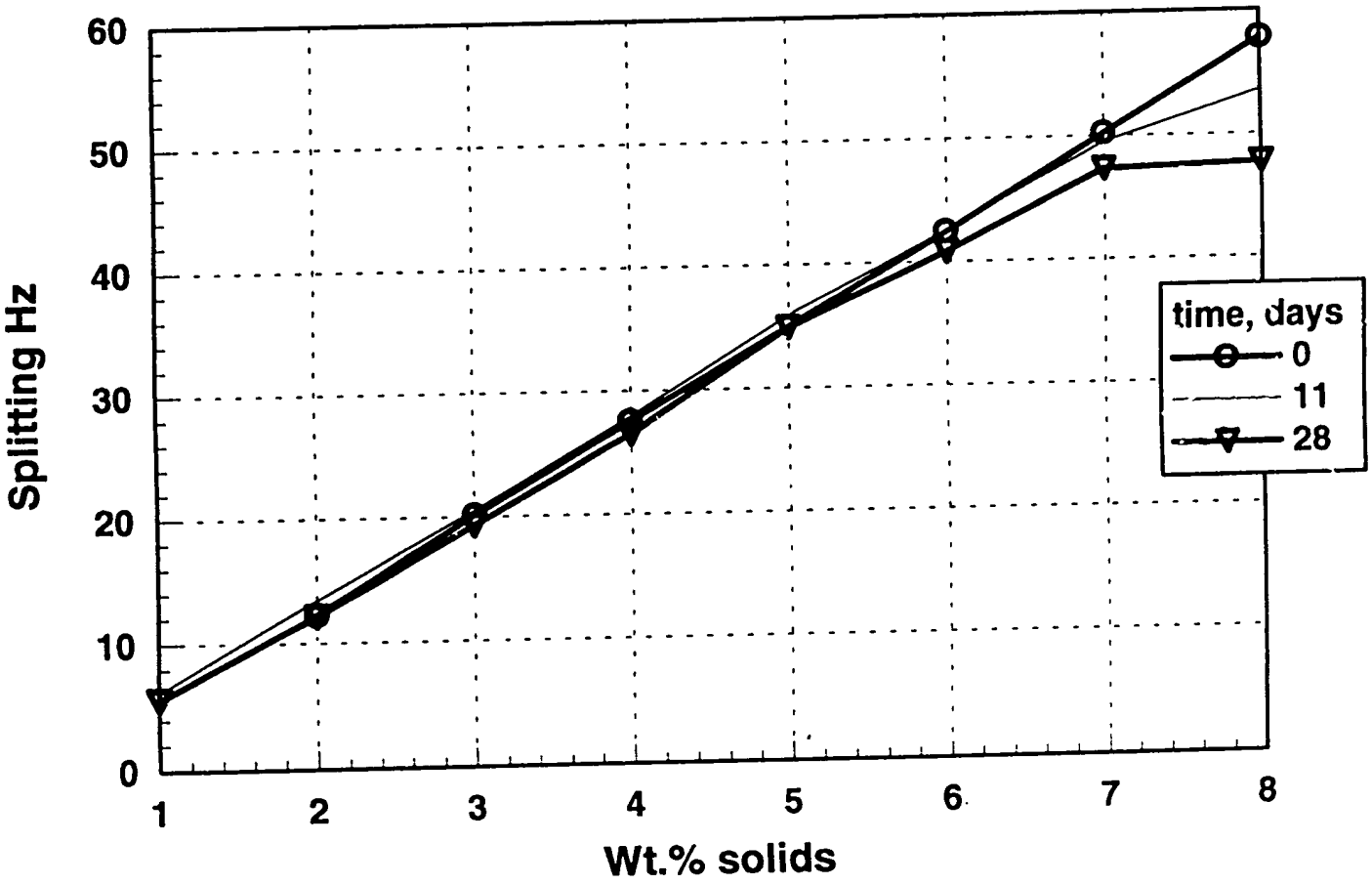

Figure 5.19 Splitting vs. concentration in 1st wash water at different time periods

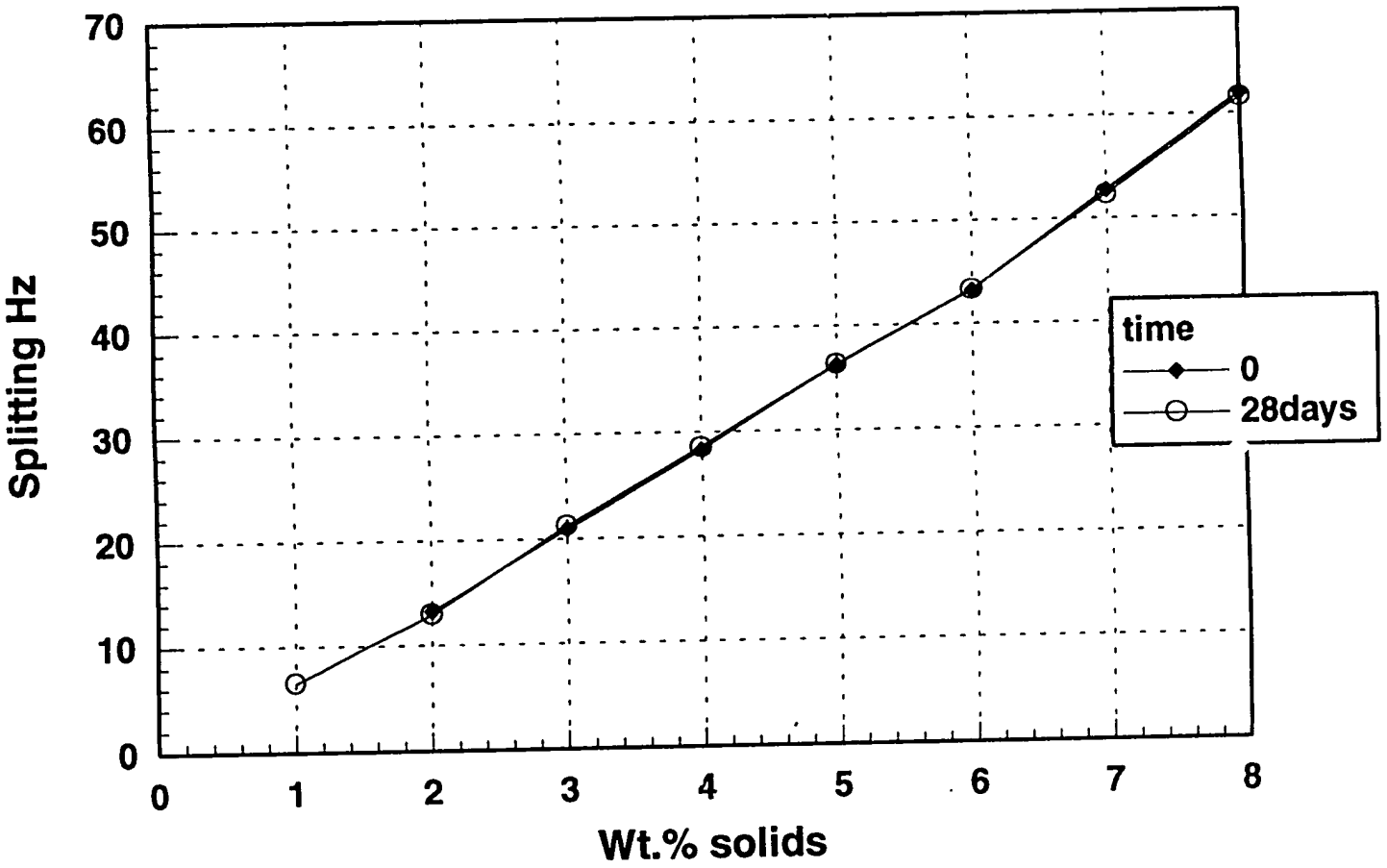

Figure 5.20 Splitting vs. concentration in 2nd wash water at different time periods

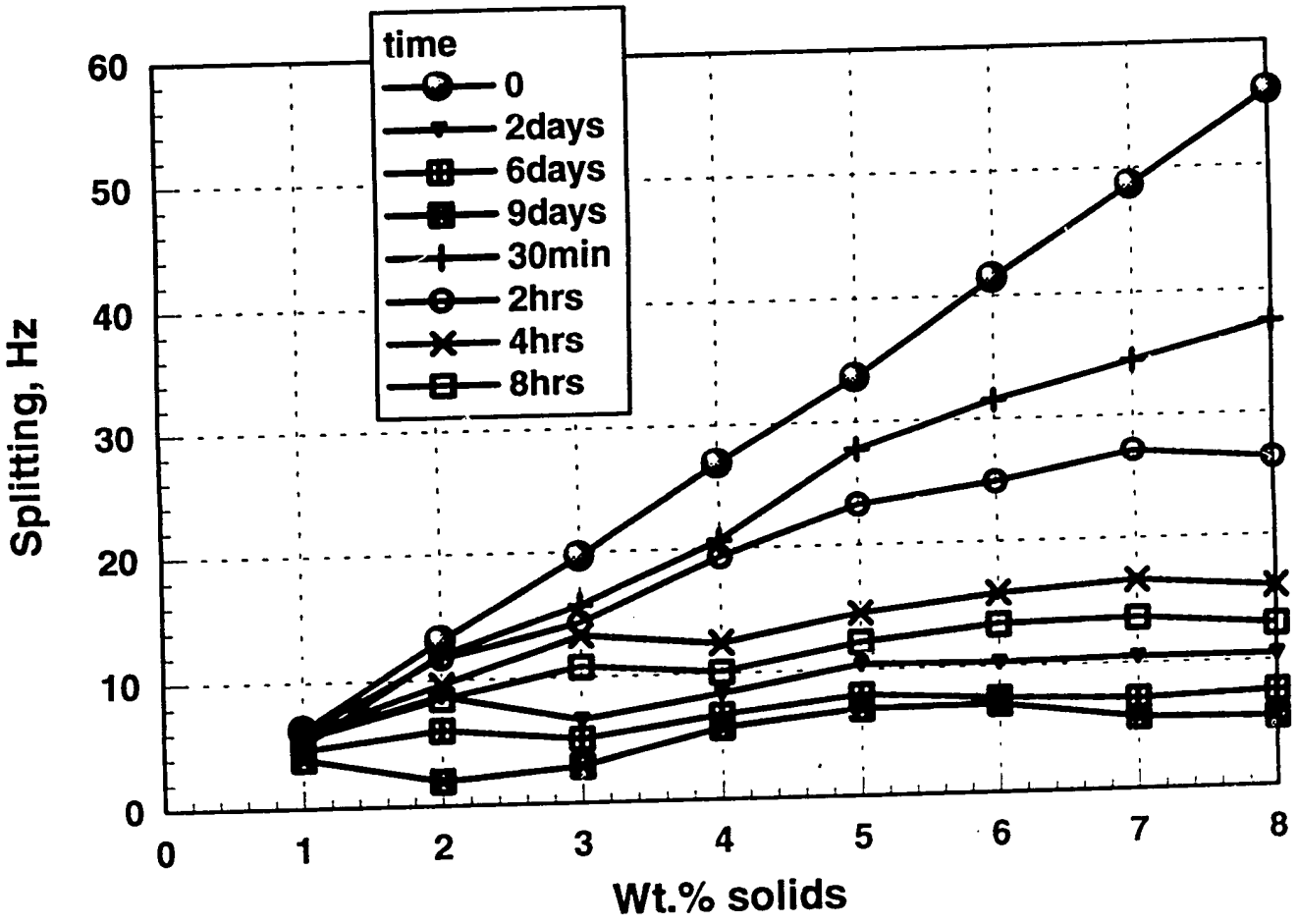

Figure 5.21 Splitting vs. concentration in 5 mM NaCl solution at different time periods

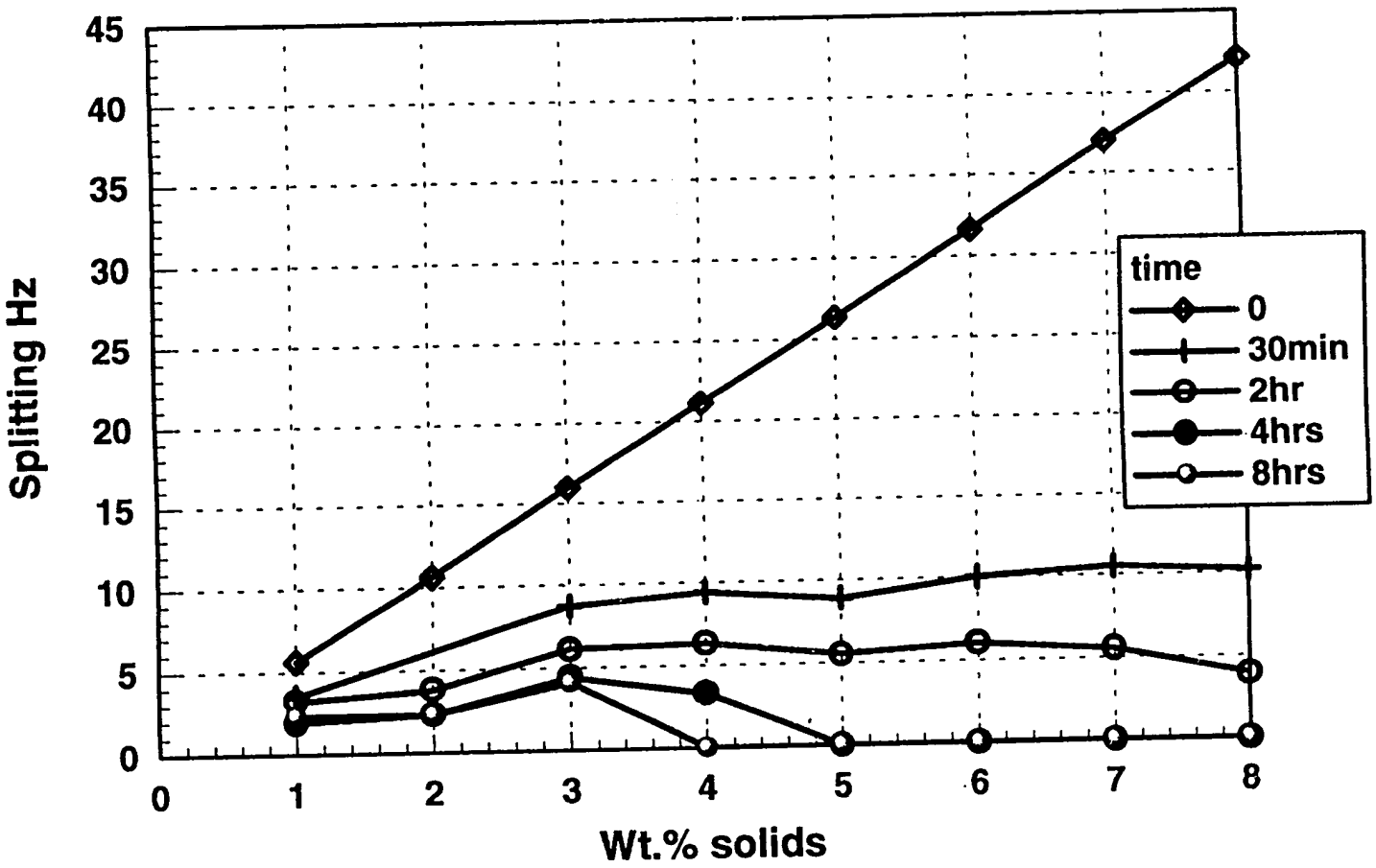

Figure 5.22 Splitting vs. concentration in 20 mM NaCl solution at different time periods

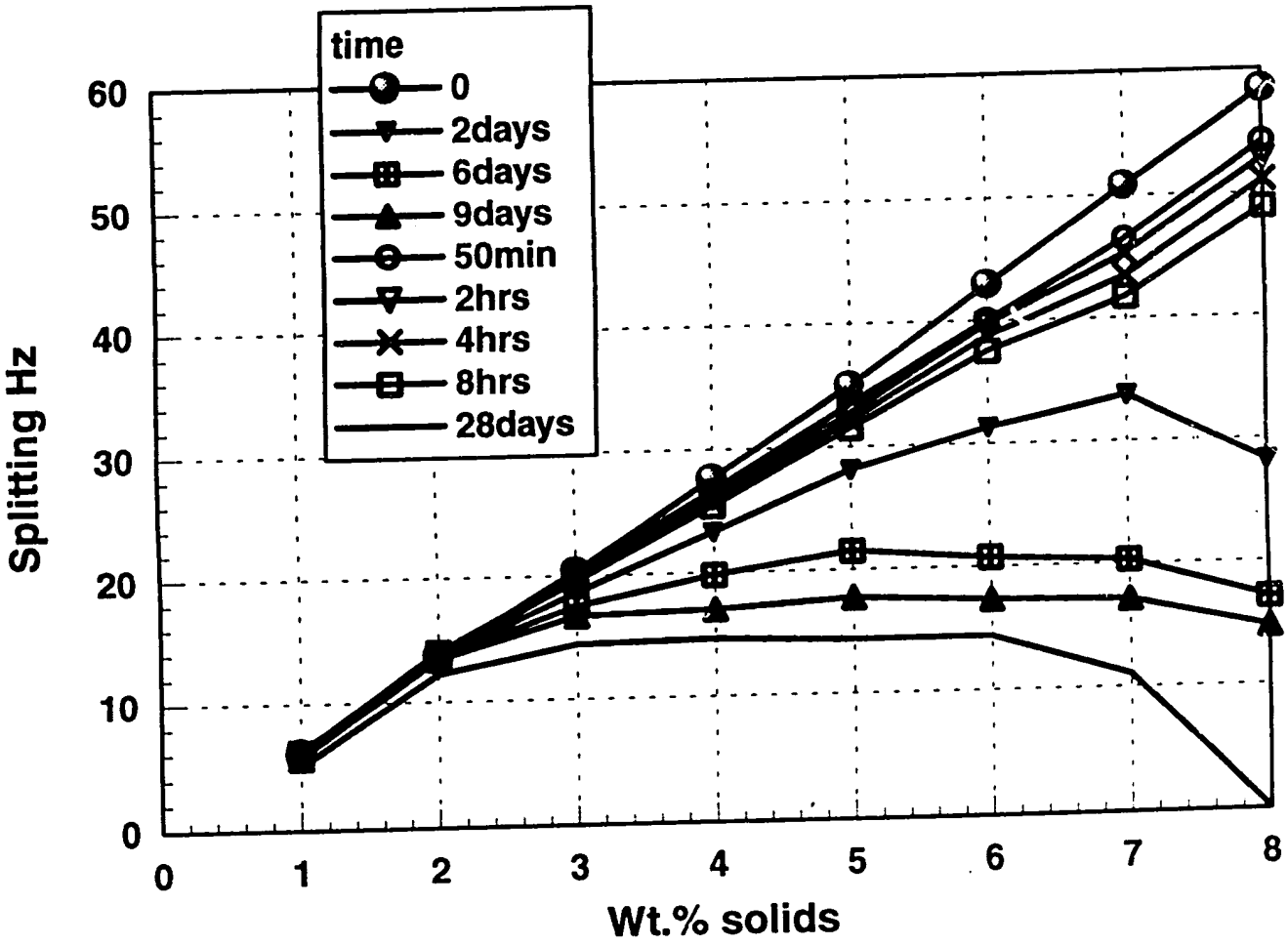

Figure 5.23 Splitting vs. concentration in solution of 20 mM sodium bicarbonate at different time periods

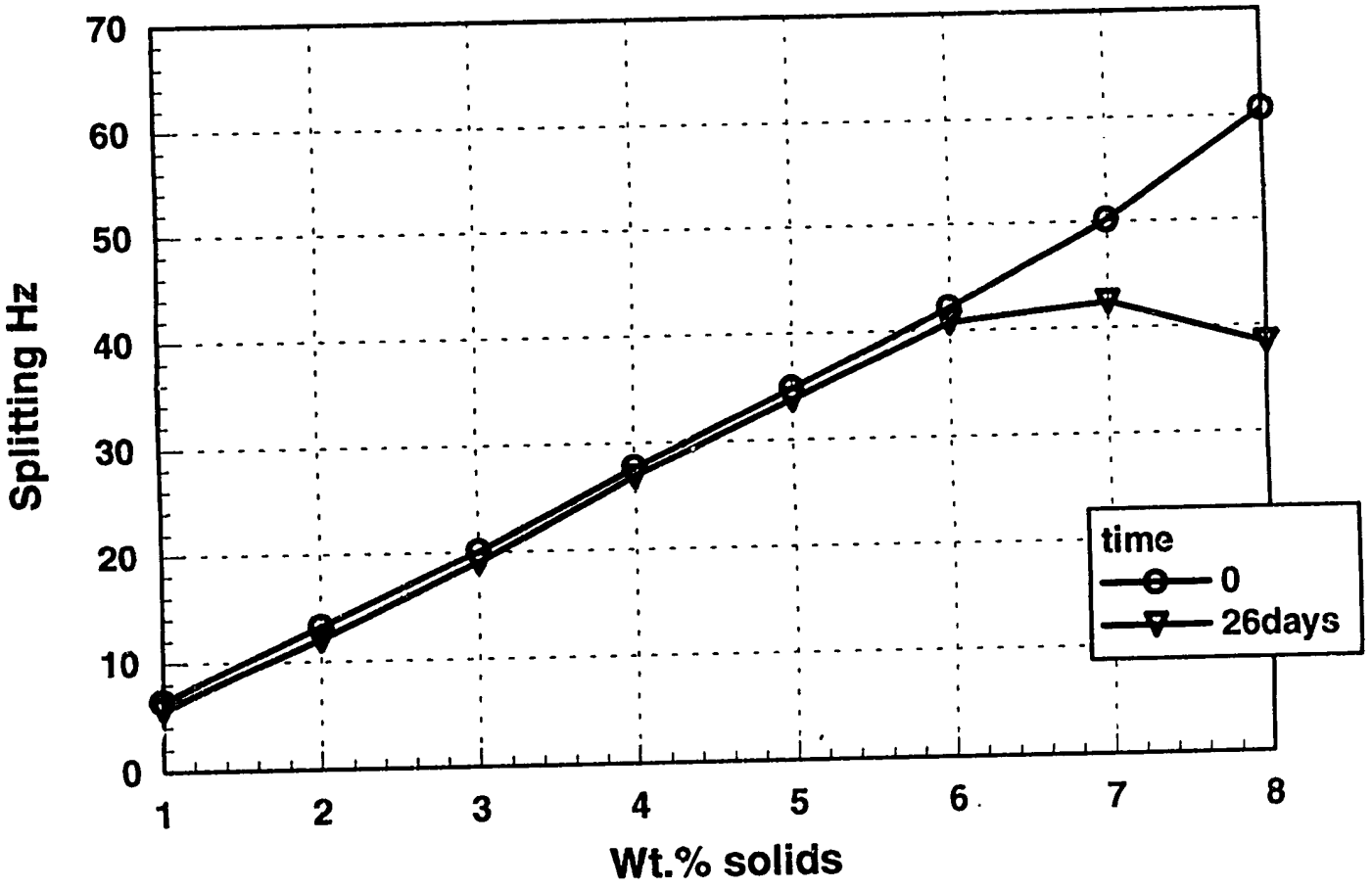

Figure 5.24 Splitting vs. concentration in 0.125 mM solution of calcium chloride at different time periods

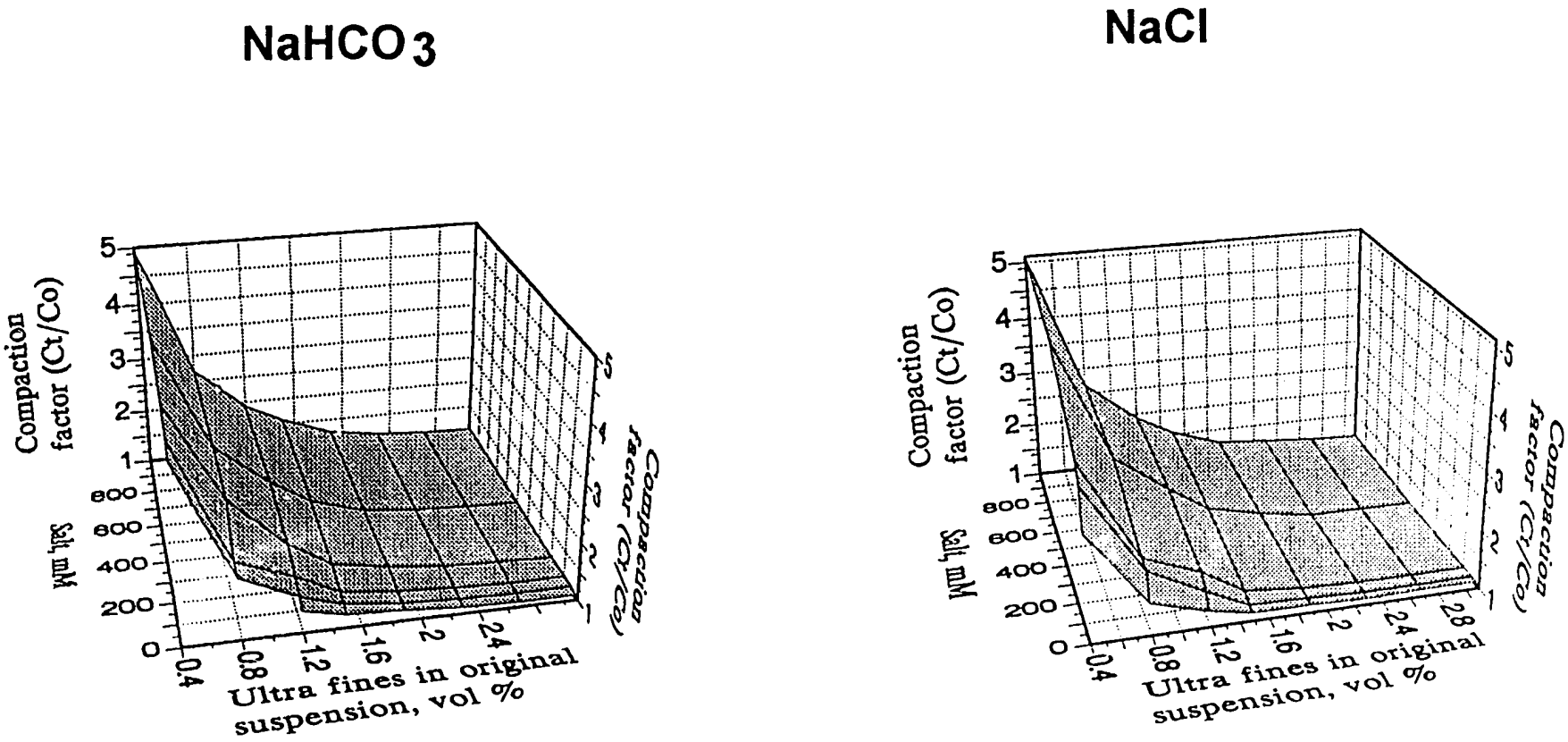

Figure 5.25 Effect of the amount of salt on compaction of ultrafines

5.1.6 Comparison of Northern Holland sludges with oil sands fine tailings

A comparison study of Northern Holland sludges with oil sands fine tailings (Suncor Inc.) was carried out. The Northern Holland sludges contain mainly clay and silt material. The solids content in these sludges is close to that of oil sands fine tailings. Northern Holland sludges also exhibit very poor dewatering characteristics but, contrary to the oil sand fine tailings, they respond to conventional treatment.

The simplest picture of fine tailings structure is that of water entrapped in a loose, three dimensional network of ultrafine solid particles [8]. Such a gel-like system is capable of entrapping other tailings components such as coarser solids, free or emulsified bitumen etc. The structure is thixotropic, breaking into smaller flocs when shear is applied. This property allows most of the entrapped coarse solids and bitumen to be separated from an aqueous suspension of the ultrafine particles by using mechanical agitation, followed by mild centrifugation. The gel-like structure can also be deflocculated with dispersing agents such as NaOH or, especially, $Na_4P_2O_7$ solution. This effect can be attributed to the complexation of the corresponding anions with the exposed aluminum ions at the edges of the clay particles [31]. The gel structure may also be broken into smaller flocs by dilution with either distilled or pond water but the degree of deflocculation is greater in the former case. The effect of water chemistry is completely reversible by simple replacement of one suspending medium for another [37]. These results indicate that, for fine tailings, electrostatic repulsion and van der Waals attractions (DLVO interactions) between particles are important factors. There is evidence that other attractive forces, such as hydrophobic attraction between biwetted particles, could also be of importance (see results for XPS measurements for surface carbon and functionalities in Table V-6). These biwetted solids are known for their ability to accelerate both flocculation and gelation [38] of oil sands fine tailings.

Mechanical agitation, followed by mild centrifugation (200xG for 10 min), caused Suncor fine tailings to separate into a dense sediment of coarse solids and an aqueous suspension of fine particles with no clear water visible. Further centrifugation at 1500xG for 2 hours was required to release any free water, see TableV-3. The Dutch sludges behaved quite differently. There was no segregation of solids for H-A and only very slight segregation of samples H-B and H-C. Also, the Dutch sludges lost water more readily than the Suncor sample (Table V-3).
In order to determine the effect of water chemistry, the Suncor fine tailings and the Dutch sludge H-B, were diluted with distilled water, pore water, NaOH solution at pH 10 or 1% $Na_4P_2O_7$ solution. The fine tailings solids were easily dispersed in all of the aqueous media. In the case of the Dutch samples, $Na_4P_2O_7$ solution was the most effective dispersant for the solids, followed by NaOH solution.

Suncor fine tailings and Dutch sludges were then subjected to the following treatment: addition of 1% $Na_4P_2O_7$ solution, agitation and then sequential centrifugation at 1500xG and 366000xG. After centrifugation of each sample at 1500xG a dense sediment separated to leave a solids free supernatant layer. Centrifugation of the fine tailings resulted in the release of clear, colorless water whereas the aqueous layers associated with the Dutch sludges were quite dark; this colour remained even after centrifugation at 366000xG. This behavior is an indication that natural organic matter, or humic components, are present in the separated water phase.

An infrared spectrum of the organic matter, recovered from the dark brown sodium pyrophosphate extracts from the H-A sample, is shown in Figure 5.26. The corresponding spectra for the organic matter isolated from H-B and H-C were identical to that of H-A and are not shown here. Analysis of the spectrum showed the following main features: a broad band in the region 3600-2000 cm^{-1} and peaks at 1710 and near 1200 cm^{-1}; bands at 1710 cm^{-1}, 1610 cm^{-1} and an unresolved absorption band between 1800 and 930 cm^{-1}. These features are associated with bonded carboxylic acids, polymeric phenols, alcohols and chelated ketones [39]. The spectrum closely resembles those found for humic matter [5].

The solids remaining after removal of organic matter were separated into particle size fractions by centrifugation at different speeds. Average particle size within fractions was determined using Transmission Electron Microscopy. The resulting particle size distributions are given in Table V-4. All samples contained ultrafines (<500nm) solids including particles smaller than 200nm, which are known to be strong gel formers [40]. The mineralogical properties of the different size fractions were examined by X-ray diffraction (XRD). The results showed that in all the Dutch samples mica was the most abundant clay mineral; kaolinite, vermiculite and smectite were present in only trace amounts. The coarser ultrafine solids fraction (>300 nm) contained some quartz, microcline, and placioclase. In the Suncor fine tailings the solids, the main clay minerals were mica and kaolinite.

Surface chemistry of the different solids fractions was determined by X-ray photoelectron spectroscopy (XPS). Before XPS analysis the Suncor tailings solids were separated into biwetted and hydrophilic components by emulsion floatation [38]; no biwetted solids could be separated from the Dutch sludges by the same procedure. The atomic concentrations (atomic %) of the observed elements are listed in Table V-5; the chemical compositions of the surfaces for each of the size fractions were similar. Surfaces are dominated by oxygen with a contribution from carbon, aluminum and silicon atoms. The greatest amount of carbon was associated with the surfaces of biwetted solids from Suncor fine tailings. The amount of carbon associated with the surfaces of solids from the Dutch sludges fell between that found on the biwetted and hydrophilic Suncor particles. Typically, the contribution of iron to the particles surfaces was higher for the Dutch sludges. The Si/Al ratio was greater than expected for mica in the Dutch sludges and for kaolinite and mica in the Suncor tailings. This could result from the presence of non-crystalline silicon rich coatings on clay surfaces, the depletion of Al, owing to weathering of the particles, is also a possibility [41].

Carbon peak envelopes of the XPS spectra for the Dutch samples and biwetted Suncor solids were deconvoluted into different chemical functionalities. The results are listed in Table V-6. No deconvolution was performed on hydrophilic Suncor solids because of the low carbon

contribution in this case. The organic matter associated with the Dutch particles may be considered to be polar in nature because the quantity of carbon atoms linked to oxygen atoms accounted for more than 60% of the total carbon signal. Both phenolic and carboxylic functional groups were detected in rather substantial amounts. This indicated that not all of the humic matter had been extracted with pyrophosphate solution. The percentage of total carbon atoms linked to oxygen atoms on the surfaces of the Suncor biwetted ultrafines was only 7 %. It appears that, in this case, the organic matter is orientated in such a way as to produce more hydrophobic surfaces than those associated with the Dutch sludge solids.

Ultrafine solids were found in both the Suncor and Dutch samples (see Table VI-4). However, unlike the Suncor samples the Dutch sludges contained significant amounts of extractable humic acids. These polyanions are complex components containing a carbon skeleton highly substituted with oxygen-bearing functional groups such as carboxyls and phenols (Figure 5.26). Owing to their ability to bind inorganic minerals as well as organic species, these polyelectrolytes, or polyanions, are known to be extremely efficient flocculating agents [41]. It is believed that the relatively high structural strength of the Dutch sludges, as indicated by their non-thixotropic nature, and their lack of dispersability in either distilled or pore water, results from the presence of this humic matter.

It is common to attribute aggregation in the presence of humic matter to the so-called bridging flocculation mechanism [32]. Bridging flocculation occurs when a portion of the adsorbed molecule lies away from the surface as loops or tails that are able to adsorb onto the surface of a second particle thus producing a link. In this type of aggregation, specific chemical interactions between colloidal particles and organic molecules, rather than the DLVO interactions, may be of primary importance [42].

A preliminary attempt to improve the characteristics of Suncor tailings by adding humate solution gave inconclusive results. While the humate treated tailings produced a more concentrated sediment, significant amounts of ultrafines were also released into the supernatant water layer. Although the latter is an undesirable effect the concentration of dispersed ultrafines

did decrease as humate concentration was increased. These observations appear to support the dual nature of humic materials that may behave as both aggregating and dispersing agents [43, 44]. Further work is required to extend and optimize the results from this preliminary study.

Flocculation tests: Table V-7 summarizes the results of tests to determine the effect of sodium humate on tailings settling. The blank sample produced a small amount of free water and a largely unsegregated sediment containing 37.5w% solids. Treatment with the humate produced a different effect. A fines suspension, rather than free water, was released in both tests. However, in each case the treated samples formed more concentrated sediments than the blank, namely 49 and 58 w/w%, for 0.02 and 0.2 w/w% humate respectively, compared to 37.5 w/w%. Also, the amount of solids in suspension decreased at higher concentrations of humate.

Table V-3 Amount of water released as a result of centrifugation of at different speed. Prior to centrifugation samples were agitated for 15 min by Spex mixer.

Centrifugation Force (xG/time)	Clear Water Released (wt% of sample)			
	H-A	H-B	H-C	Suncor
200/10 min	2.1	8.0	2.4	susp.
200/1h	21.9	17.8	8.9	susp.
500/2h	26.4	28.6	20.6	susp
1500/2h	30.6	35.5	27.8	14.6

Susp. represents suspended solids with no clear water.

Table V-4 Treatment of with sodium pyrophosphate solution. Separation of treated solids by centrifugation.

Centrifugation Force (xG/time)	Average Particle Size (nm)	Amount of Solids (wt% of organic free, dry solids)			
		H-A	H-B	H-C	Suncor
200/10 min	>500	81.5	75.2	78.1	75.5
200/1h	300-500	7.3	6.4	6.0	12.9
500/2h	200-300	4.8	6.3	5.6	5.1
1500/2h	100-200	2.7	3.9	3.4	1.8
91000/30min	<100	3.7	8.2	6.9	4.7

Table V-5 Surface elemental analysis of solids fractions.
Suncor solids were separated into biwetted and hydrophilic components prior to analysis.

Particle Size, (nm)	Sample	Elemental Analysis (Atomic %)								
		C	O	Al	Si	Mg	K	Fe	N	Si/Al
200-300	H-A	6.9	67.8	6.2	12.9	0.6	1.0	2.7	n.d	2.1
	H-B	5.6	68.5	6.3	13.4	0.7	1.1	2.2	n.d	2.1
	H-C	6.3	67.3	6.3	13.9	0.6	1.1	2.4	n.d	2.2
	Athabasca hydrophilic	3.1	69.0	10.1	15.2	0.3	1.1	0.1	n.d	1.5
100-200	H-A	8.7	66.0	5.7	12.5	0.7	0.9	2.3	0.8	2.2
	H-B	7.6	66.4	6.0	13.0	0.7	1.0	2.3	0.7	2.2
	H-C	7.6	67.2	5.6	12.7	0.7	1.0	2.3	0.7	2.3
	Athabasca: hydrophilic biwetted	4.3 40.7	67.0 43.4	10.5 6.5	15.2 10.3	0.3 n.d	1.4 n.d	0.1 n.d	n.d n.d	1.5 1.6
<100	H-A	14.3	61.7	5.4	11.4	0.6	0.8	2.5	1.1	2.1
	H-B	15.1	62.3	4.7	11.5	0.6	0.6	2.5	0.8	2.4
	H-C	12.1	63.8	5.1	11.8	0.6	0.6	2.9	0.8	2.3
	Athabasca hydrophilic	4.3	66.0	10.1	16.8	0.4	1.1	0.1	n.d	1.7

n.d. - not detected

Table V-6 Functionalities of carbon associated with surfaces of solids from Suncor and Dutch Samples (XPS results).

Average Particle size (nm)	Sample	Carbon (% of total)				
		carbon-carbon	hydroxyl,ether	carbonyl	carboxyl	carbonate
200-300	H-A	35.5	45.2	n.d	34.6	n.d
	H-B	29.9	27.4	n.d	22.2	n.d
	H-C	34.6	27.4	n.d	34.6	n.d
100-200	H-A	35.5	37.0	n.d	39.3	n.d
	H-B	33.3	30.1	n.d	28.6	n.d
	H-C	31.2	32.9	n.d	32.1	n.d
<100	H-A	32.9	37.2	n.d	38.3	n.d
	H-B	38.8	32.7	n.d	31.9	n.d
	H-C	28.2	30.1	n.d	29.8	n.d
<300	Athabasca biwetted	93.2	3.3	2.1	1.1	0.3

n.d. is not detected

Table V-7: Effect of addition of sodium humate solution on the settling behaviour of fine tailings.

Sample	Initial Solids Content (wt%)	Humate Added (wt%)	Settling Behaviour		
			Solids Content (wt%)		Water Released (Vol. % of Original)
			Sediment	Suspension	
Blank, Fine Tailings	35.0	None	37.5 (100)[1]	-	8
Test 1	35.0	0.02	49.0 (48)[1]	9.5	-
Test 2	35.0	0.20	58.0 (70)[1]	6.0	-

Note 1: figures in parenthesis represent the percentage of total solids reporting to the sediment

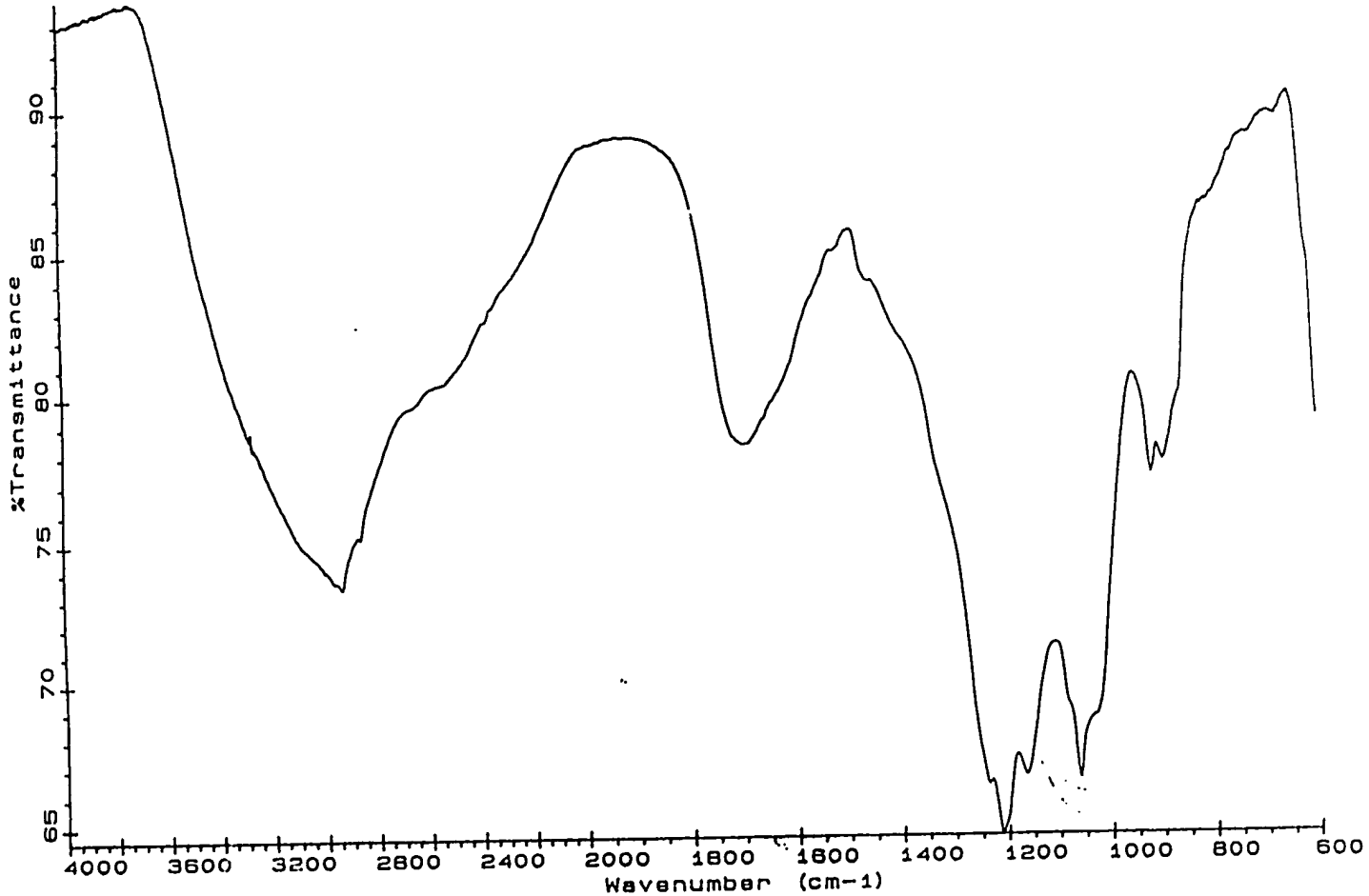

Figure 5.26 Infrared spectrum of humic matter extracted from Dutch sludge (H-A) by sodium pyrophosphate treatment

5.1.7 Conclusions

1. A systematic study of chemical addition to oil sands fine tailings has been carried out. Some initial gains in consolidation were observed but after six months there were no significant differences between any treatment and the blank samples.
2. Similar treatments on the separated ultrafines fraction did not result in any substantial dewatering under either gravity settling or centrifugation at 200xG. This suggests that the ultrafine solids fraction is the reason for the intractable behaviour of fine tailings.
3. The solids content of samples of ultrafines could be increased dramatically by subjecting them to a freeze/thaw treatment.
4. The maximum solids content achievable for the ultrafine solids was 35 wt%. A combination of chemical, physical and mechanical treatments was required to reach this concentration.
5. The results demonstrate that chemical treatment alone is not an effective route for dewatering, although it does result in "stronger" tailings structures which show less segregation by particle size.
6. Gelation time of ultrafines suspensions was investigated using a ^{2}H NMR technique. The gelation process lasts from minutes to months and depends on electrolyte type and concentration in the suspending water. Bicarbonate ions have been found to have strong inhibiting action towards aggregation.
7. The gelation concentration (GC) of ultrafines has been found to be 3 - 4 wt%. At this concentration further flocs densification, by electrolyte addition is impossible.
8. The properties of oil sand fine tailings were compared with those of "difficult" Dutch sludges. Although there was a similarity between the amount and size distribution of solids for the two types of sludges, the strength of their structures was different. This difference is believed to be caused by the presence of substantial amounts of humic materials in the Dutch sludges compared to fine tailings.
9. These results raise the possibility of strengthening the fine tailings structure by an addition of humic matter from municipal or other waste water. A preliminary evaluation of this concept has given encouraging results.

5.2 Bitumen Extraction Processes and Effect of Modifications

5.2.1 PSV Middlings and Tailings, Secondary Tailings and Run-offs.

Flocculated ultrafines. The results of the separation and further fractionation of flocculated ultrafines are shown in Tables V-8 to V-10. It follows from Table V-8 that the contribution of flocs smaller than 300 nm in the stream of PSV middlings was greater than that of the corresponding secondary tailings and run-off samples. This could possibly be attributed to floc densification owing to agitation of PSV middlings in the subsequent process steps. There were no < 300 nm flocs detected in any of the PSV tailings. It can be seen that the streams produced using modified water (M-OHWE) differed markedly from those generated in the CHWE trials. For Suncor feed, in the case of the M-OHWE secondary tailings and run-offs no flocs smaller than 300 nm were present (see Table V-8). In PSV middlings the solids were also present as rather coarse flocs which were relatively easy to settle at 500xG for 2 hours, (Table V-9). In the case of Syncrude oil sands however, secondary tailings and run-offs from M-OHWE runs, contained <300 nm flocs, but their amounts were smaller than those for the CHWE trials. A high concentration of divalent cations (Ca^{2+}) and a low concentration of peptizing components such as bicarbonates and naphthenates is believed to be responsible for such an advanced degree of aggregation. Also, in the presence of excess amounts of divalent cations, insoluble naphthenates and humates are likely to be formed. Such compounds could act as a "cement" between the flocculated particles, thus strengthening the aggregates.

The CHWE runs were carried out with pond water containing both bicarbonates and dissolved organic matter, both known for their inhibiting action towards aggregation. In these cases, although some aggregation does takes place, the flocs produced have a wider variety of sizes, (see Tables V-9 and V-10). PSV middlings from the Suncor oil sand contained lower amounts of "gel formers" (<100 nm) than those from Syncrude oil sands (compare Tables V-9 and V-10). This is in agreement with the results showing that the Syncrude oil sands ore contained greater amounts of fine solids than Suncor oil sands.

Deflocculated ultrafines: To obtain information about the degree of aggregation, the ultrafines were deflocculated with sodium pyrophosphate solution prior to their separation and fractionation by size. The results of these experiments are shown in Tables V-11 to V-13. It can be seen that:

a) the absolute quantities of <300 nm particles present in PSV middlings, secondary tailings and run-offs generated with different dispersing mediums, are relatively close;

b) redispersion with sodium pyrophosphate solution broke the flocs and released bound "gel formers" (<100 nm);

c) the amounts of <100 nm fraction in PSV middlings was greater than that determined for secondary tailings and run-offs. The latter observation could be attributed to the severe agitation during the formation of secondary tailings. Such an action is known [33] to result in floc restructuring accompanied by the formation of stronger and denser aggregates;

d) the absolute quantities of "gel formers" in the corresponding streams from different oil sands were about the same.

To summarize, the results presented in Tables V-8 to V-13 demonstrate that for both OHWE and CHWE runs the ultrafines are present in a flocculated state. The floc size and strength are dependent on the composition of the process water, the amount and the aggregation state of ultrafines in the parent oil sands ore, and also on the type of stream (middlings tailings or run-offs).

Table V-8: Flocculated ultrafines (<300 nm) content of streams

Oil sands	Process	Wt % of stream			
		PSV middlings	Secondary tailings	Run-offs	PSV tailings
Syncrude	M-OHWE	1.1	0.4	0.2	0
	OHWE	1.1	0.7	0.7	0
	CHWE	1.3	0.7	0.9	0
Suncor	M-OHWE	1.3	0	0	0
	CHWE	1.4	0.9	0.9	0

Table V-9: Separation by centrifugation of ultrafine solids from PSV middlings, Secondary tailings and Run-offs produced from Syncrude oil sands (prior to $Na_4P_2O_7$ treatment).

Particle (floc) size, nm	Solids distribution, wt% of dry ultrafines (<300 nm)								
	M-OHWE			OHWE			CHWE		
	PSV middlings	Second. tailings	Run offs	PSV middlings	Second. tailings	Run offs	PSV middlings	Second. tailings	Run offs
200-300 nm (500xG/2h)	100	100	100	72.7	100	100	50.3	71.4	71.4
100-200 nm (1500xG/2h)	0	0	0	27.3	0	0	32.8	28.6	28.6
<100 nm (91000xG/ 30min)	0	0	0	0	0	0	16.9	0	0

Table V-10: Separation by centrifugation of ultrafine solids from PSV middlings, Secondary tailings and Run-offs produced from Suncor oil sands (prior to $Na_4P_2O_7$ treatment).

Particle (floc) size, nm	Solids distribution, wt% of dry ultrafines (<300 nm)					
	M-OHWE			CHWE		
	PSV middlings	Secondary tailings	Run offs	PSV middlings	Secondary tailings	Run offs
200-300 nm (500xG/2h)	100	0	0	61.5	66.7	71.5
100-200 nm (1500xG/2h)	0	0	0	33.8	33.3	28.5
<100 nm (91000xG/ 30min)	0	0	0	4.7	0	0

Table V-11: Dispersed ultrafines (<300 nm) content of streams (<u>after</u> $Na_4P_2O_7$ treatment)

Oil sands	Process	Wt % of stream		
		PSV middlings	Secondary tailings	Run-offs
Syncrude	M-OHWE	1.0	0.7	1.1
	OHWE	1.0	0.8	1.2
	CHWE	1.0	1.3	1.3
Suncor	M-OHWE	1.1	0.9	1.2
	CHWE	1.2	1.2	1.4

Table V-12 Separation by centrifugation of ultrafine solids from PSV middlings, Secondary tailings and Run-offs produced from Syncrude oil sands (<u>after</u> $Na_4P_2O_7$ treatment).

Particle (floc) size, nm	Solids distribution, wt% of dry ultrafines (<500 nm)								
	M-OHWE			OHWE			CHWE		
	PSV middlings	Second. tailings	Run offs	PSV middlings	Second. tailings	Run offs	PSV middlings	Second. tailings	Run offs
200-300 nm (500xG/2h)	37.7	43.5	35.4	37.5	44.2	31.0	31.0	33.3	30.3
100-200 nm (1500xG/2h)	26.0	42.3	46.0	29.6	42.0	43.1	21.5	38.1	38.7
<100 nm (91000xG/ 30min)	36.4	14.2	18.5	33.0	14.0	25.9	47.5	28.6	31.0

Table V-13: Separation by centrifugation of ultrafine solids from PSV middlings, Secondary tailings and Run-offs produced from Suncor oil sands (after $Na_4P_2O_7$ treatment).

Particle (floc) size, nm	Solids distribution, wt% of dry ultrafines (<500 nm)					
	M-OHWE			CHWE		
	PSV middlings	Second. tailings	Run offs	PSV middlings	Second. tailings	Run offs
300-500 nm (200xG/1h)	27.4	27.9	29.6	29.0	36.4	30.4
200-300 nm (500xG/2h)	28.1	30.3	23.6	22.3	30.3	18.8
100-200 nm (1500xG/2h)	14.4	25.1	26.0	16.3	23.8	27.7
<100 nm (91000xG/ 30min)	30.0	16.8	20.8	32.4	9.5	23.1

Biwetted solids. The results showing the contribution of biwetted flocculated solids (BUS) to total flocculated ultrafines in the different streams are given in Table V-14. Of all the streams, Secondary tailings contained the lowest amounts of BUS. It is likely that some of the BUS were removed with secondary froths. The amounts of the biwettable fraction associated with >500 nm are presented in Table V-15. In all cases the amounts of Organic Rich Solids (ORS) increased from PSV middlings through secondary tailings to run-offs. This indicates that coarse hydrophilic solids are being selectively removed at the beaches.

5.2.2 Settling behavior of various streams.

In order to compare the settling behavior of flocs present in the various streams generated with different process waters from both Suncor and Syncrude oil sands, the stream samples were allowed to sediment in 100 mL graduated cylinders. Settling rates, as determined by the position of the interface of the sediment and the clear water, and the equivalent final volumes, or weight percent of solids in the sediments, were monitored.

The middlings produced with M-OHWE settled rapidly, with the rates being faster for Suncor trials. In these cases it took less than four days for the clear water to be released. For CHWE runs, slow and so called "differential" settling is observed. Those particles which have lower resistance to flocculation aggregate and settle first while the rest of the solids remain in suspension above this faster settling layer. Owing to the greater content of <100 nm particles in Syncrude PSV middlings, the settling is slower compared to the Suncor samples and differential settling behavior is more pronounced. Slow differential settling creates conditions favorable for the creation of segregating mixtures. In the latter cases there was a clear interface between the layers of densely packed solids at the bottom of the cylinders and the ultrafine layers on top of them. As opposed to the CHWE runs, in the case of M-OHWE samples with their rapid aggregation and settling, practically non-segregating sediments form a relatively dense layer at the bottom of the cylinders. The behavior of OHWE PSV middlings (Syncrude oil sands) was intermediate between those of M-OHWE and CHWE.

The observations were continued for several months until no more changes in the settling interfaces were detected. In Table V-16, the final concentration of ultrafines (< 300 nm) in the sediments is shown as wt % percent. The results show that the fractal flocs (i.e flocs which possess a randomly branching structure and decreasing density with increasing size) formed in all cases, settle freely until a concentration of 3 - 4 wt % is reached. At this concentration the inter-floc distances are small and the clusters begin to overlap, resulting in the formation of a giant spanning cluster or gel. In the case of Syncrude ore for all processes, the solids packed to nearly the same concentration of 3.0 - 3.2 wt %. For Suncor oil sands ore slightly greater concentrations of 3.6 - 4.1 wt % were reached. This is in agreement with the fact that the latter oil sands has a lower contribution of "gel formers" [40].

Thus, the results show that on one hand, the type and the amount of electrolyte not only affects ultrafines settling rates, and therefore the rate of water release, but also the type of sediment formed. Slow aggregation leads to segregation by particle size, whereas fast aggregation leads to non-segregating behavior. On the other hand it is an intrinsic property of oil sands such as the ultrafines content, rather than the type and amount of electrolyte, that is the most important parameter affecting the solids content of the sediments.

As in the case of PSV middlings, the Secondary tailings produced with M-OHWE water settled rapidly with the rate being faster for the Suncor trial. For both ores, the M-OHWE process produced non-segregating sediments as opposed to segregating sediments formed from slow settling CHWE Secondary tailings. Similar to PSV middlings, Secondary tailings fractal flocs formed in all the cases settle freely until a concentration of 2.5 - 3.2 wt % is reached (see Table V-17).

As found for PSV middlings and secondary tailings, run-offs produced in the M-OHWE trials, settled faster than those generated with CHWE recycle water. Also, similar to the above streams, settling occurred until a concentration of 3 - 4 wt % was reached (see Table V-18). However, unlike the case for PSV middlings and secondary tailings, sediments from the CHWE run-offs did not display segregating behavior.

After 160 days of gravity settling, run-off sediments were subdivided into top, middle and bottom layers. The layers were then deflocculated with sodium pyrophosphate solution and classified on the basis of particle size by sequential centrifugations at increasing speed. Results

presented in Table V-19 show the presence of segregation within all the sediments. The concentration of total solids, as well as of particles smaller than 300 nm (gel formers), increases at a similar rate from the top to the bottom layer in all sediments. Only marginal differences were detected in the characteristics of all the run-off sediments. At least two factors should be considered as being responsible for the lack of visible segregation within the run-off sediments:
1) the finer size distribution of coarse solids associated with the run-offs, (see Table V-20)
2) stronger gel network structure owing to the presence of higher amounts of biwetted components (see Table V-15).

In Table V-21 the results of settling experiments have been summarized in order to compare final ultrafines concentrations in the sediments from the various process streams.

Table V-14: Biwetted ultrafine solids (BUS) in streams as wt% of total dry ultrafines

Oil sands	Process	Stream		
		PSV middlings	Secondary tailings	Run-offs
Syncrude	M-OHWE	42.6	34.9	33.5
	OHWE	41.8	25.0	33.5
	CHWE	47.7	9.5	47.3
Suncor	M-OHWE	36.2	14.8	46.6
	CHWE	31.9	11.5	41.7

Table V-15: Organic rich solids (ORS) in streams as wt% of total dry coarse (>500 nm) solids

Oil sands	Process	Stream			
		PSV middlings	Secondary tailings	Run-offs	PSV tailings
Syncrude	M-OHWE	6.7	8.0	51.5	1.4
	OHWE	1.7	4.0	65.5	1.7
	CHWE	4.4	11.1	36.9	1.1
Suncor	M-OHWE	15.9	21.8	40.7	1.3
	CHWE	10.7	23.6	54.6	1.2

Table V-16: Settling of PSV middlings. Wt% of solids in streams and sediments.

Oil sands	Process	Interface,mL (6 months)	Total solids		solids<300 nm, dispersed state	
			PSV middlings	sediment	PSV middlings	sediment
Syncrude	M-OHWE	35.0	18.4	52.6	1.0	2.9
	OHWE	37.5	11.9	31.7	1.0	2.7
	CHWE	41.0	16.4	40.0	1.0	3.2
Suncor	CHWE	39.0	13.8	34.5	1.2	3.3
	M-OHWE	32.0	10	31.3	1.1	3.4

Table V-17: Settling of Secondary tailings. Wt% of solids in streams and sediments.

Oil sands	Process	Interface,mL (5 months)	Total solids		solids<300 nm, dispersed state	
			Secondary tailings	sediment	Secondary tailings	sediment
Syncrude	M-OHWE	32	25.6	80.0	0.8	2.5
	OHWE	32	27.7	86.6	0.9	2.8
	CHWE	41	16.8	41.0	1.3	3.2
Suncor	CHWE	39	12.2	31.1	1.2	3.1
	M-OHWE	31.5	12.4	39.4	0.9	2.9

Table V-18: Settling of Run-offs. Wt% of solids in streams and sediments.

Oil sands	Process	Interface,mL (48 days)	Total solids		solids<300 nm, dispersed state	
			Run-off	sediment	Run-off	sediment
Syncrude	M-OHWE	31	8.1	26.1	1.1	3.5
	OHWE	30	10.1	33.7	1.2	4.0
	CHWE	35	6.1	17.4	1.3	3.7
Suncor	CHWE	36	7.4	20.6	1.4	3.9
	M-OHWE	29	7.8	26.9	1.2	4.1

Table V-19: Layers in Run-offs sediments after 160 days of gravity settling
Distribution of solids in layers

Oil sands	Process	Layer	wt% of total solids in layers	wt% of solids < 300 nm in layers	wt% of solids < 100 nm in layers
Syncrude	OHWE	Top	16.5	3.0	0.8
		MIddle	22.5	3.7	1.2
		Bottom	29.6	4.2	1.6
	Modified OHWE	Top	21.1	3.0	0.7
		MIddle	25.9	3.8	1.2
		Bottom	29.4	4.1	1.3
	CHWE	Top	12.7	3.7	1.1
		MIddle	18.6	3.5	1.0
		Bottom	23.1	4.9	1.9
Suncor	CHWE	Top	16.7	3.5	0.5
		MIddle	21.4	4.6	1.3
		Bottom	28.2	5.3	1.9
	Modified OHWE	Top	19.1	3.3	0.5
		MIddle	24.5	4.3	0.7
		Bottom	27.0	4.7	0.8

Table V-20: Results of particle size analysis of coarse residual solids (RS > 500 nm) in the original state of aggregation

Stream	Median size (μm) coarse solids settled at 200g/10min (>0.5μm) in streams				
	OHWE Syncrude	M* OHWE Syncrude	CHWE Syncrude	CHWE Suncor	M* OHWE Suncor
Run-offs	22.54	14.94	7.05	15.06	6.62
	26.95	15.78	6.96	13.37	6.63
	25.07	15.36	6.94	12.50	6.62
Seconary Tailing	46.03	36.12	31.48	14.78	19.43
	45.55	37.42	31.28	14.78	14.58
	45.58	35.15	31.37	14.97	14.40
PSV Middlings	25.06	57.75	72.38	14.37	30.09
	27.47	57.30	72.13	14.39	29.35
	28.79	54.91	73.34	14.54	29.15

Table V-21: Summary of the results of settling experiments. Wt% of solids in streams and sediments

Oil sands	Process	solids<300 nm stream			solids<300 nm sediment			solids<100 nm stream			solids<100 nm sediment		
		PSV Middlings	Secondary Tailings	Run offs	PSV Middlings	Secondary Tailings	Run offs	PSV Middlings	Secondary Tailings	Run offs	PSV Middlings	Secondary Tailings	Run offs
Syncrude	M-OHWE	1.0	0.8	1.1	2.9	2.5	3.5	0.4	0.1	0.2	1.0	0.4	0.7
	OHWE	1.0	0.9	1.2	2.7	2.8	4.0	0.3	0.2	0.3	0.9	0.5	1.0
	CHWE	1.0	1.3	1.3	2.4	3.2	3.7	0.5	0.3	0.4	1.2	0.6	1.1
Suncor	CHWE	1.3	1.2	1.4	3.3	3.1	3.9	0.6	0.2	0.5	1.5	0.5	1.4
	M-OHWE	1.1	0.9	1.2	3.4	2.9	4.1	0.4	0.1	0.4	1.3	0.4	1.4

5.2.3 Froths

The general distribution of different types of solids in primary and secondary froths was similar. Hydrophilic, coarse solids were the most abundant particle type followed by biwetted coarse solids (see Tables V-22 and V-23). In the case of secondary froths, the contribution of biwetted ultrafines was somewhat greater than in the corresponding primary froths. Hydrophilic solids were found with the bitumen in all froth samples. The surface of these solids was probed using X-ray photoelectron spectroscopy. The atomic concentrations of the main elements detected are tabulated in Table V-24. There was a similarity between the results for the different oil sands ores and processes. In all cases carbon accounted for more than 50 atom % of the surfaces. The presence of sulfur suggests asphaltene type components. The particles appeared to be aluminosilicate clays with Si/Al ratio of 1.4 -1.5. Elemental iron was not present in all samples. Sodium was detected at less than 1 atomic %. Contrary to the rest of the samples, Syncrude CHWE hydrophobic solids contained chloride and fluoride. Suncor samples contained nitrogen. Deconvolution of the carbon peak envelope into chemical functionalities shows that carbon to oxygen atom linkages on the surfaces of hydrophobic solids account for 14 - 23 atom % (see Table V-25). This suggests that the organic matter on particle surfaces is oriented in such way that the external areas are relatively polar. This information is of interest as it indicates that these solids may act as stabilizers for water in oil emulsion rather than just as particles physically dispersed in the bitumen phase.

Table V-22: Primary froths. Different types of solids as wt % of total bitumen free dry sample

Oil sands	Process	AS	BUS	ORS	RS	Bitumen associated solids
Syncrude	M-CHWE	6.6	2.5	17.2	72.6	1.2
	OHWE	8.7	2.4	20.6	67.5	0.9
	CHWE	7.5	1.7	16.1	74.3	0.4
Suncor	M-OHWE	3.5	1.0	19.4	75.5	0.6
	CHWE	5.9	1.4	20.2	72.0	0.5

Table V-23: Secondary froths. Different types of solids as wt % of total bitumen free dry sample

Oil sands	Process	AS	BUS	ORS	RS	Bitumen associated solids
Syncrude	M-OHWE	5.9	3.4	19.1	71.1	0.5
	OHWE	6.8	4.5	17.2	71.3	0.3
	CHWE	5.0	2.0	7.7	85.0	0.4
Suncor	M-OHWE	5.8	6.6	12.5	74.8	0.3
	CHWE	6.1	3.2	11.9	77.5	0.3

Table V-24: Surface elemental analysis of hydrophobic solids fractions from froths

Oil sands	Process	Atomic %										
		C	O	Al	Si	Mg	Na	S	N	Cl	F	Si/Al
Syncrude	M-OHWE	50.6	31.5	6.4	8.8	n.d	0.2	1.3	n.d	n.d	1.2	1.4
Syncrude	OHWE	51.4	32.4	5.9	8.7	0.2	0.4	1.1	n.d	n.d	n.d	1.5
Syncrude	CHWE	53.7	27.8	5.8	8.2	n.d	0.2	1.2	n.d	0.9	2.2	1.4
Suncor	M-OHWE	52.3	31.2	5.8	8.6	n.d	0.1	1.0	1.0	n.d	n.d	1.5
Suncor	CHWE	54.4	29.8	6.1	8.4	n.d	0.1	1.1	n.d	n.d	n.d	1.4

n.d. not detected

Table V-25: Functionalities of carbon associated with surfaces of hydrophobic solids from froths

Oil sands	Process	% of carbon			
		carbon-carbon	alcohol,ether	carbonyl	carboxyl
Syncrude	OHWE	85.8	9.3	3.3	1.6
	M-OHWE	77.2	17.1	3.7	1.9
	CHWE	81.4	13.2	2.3	3.4
Suncor	CHWE	82.8	11.1	3.4	2.7
	M-OHWE	83.1	11.8	2.9	2.4

5.2.4 Conclusions

1. Solids in OHWE streams settled faster than those in the corresponding streams from the CHWE process. This corresponds to greater degree of ultrafines aggregation owing to the higher Ca^{2+} content and lower HCO_3^- content in the former case.
2. In all the cases, Suncor oil sands gave rise to faster settling streams than Syncrude oil sands.
3. The ultrafines content, particularly of the most active <100 nm fraction, of Suncor oil sands is lower than that of Syncrude oil sands.
4. For all processes the aggregation state of ultrafines, and therefore the settling rate, in PSV middlings is lower than for other streams. Agitation of PSV middlings in subsequent process steps results in floc densification.
5. The CHWE process was associated with slower ultrafines aggregation, allowing coarser solids to settle out independently. The modified OHWE process gave rise to non-segregating sediments from the PSV middlings and secondary tailings streams.
6. The settling rates were different only until the gelation concentration (GC) of the ultrafines fraction was reached. At the gelation concentration steric hindrance inhibits further solids' settling.
7. The final volumes of sediments in the different streams do not depend on process water modification but they do depend on the initial content of ultrafines in the oil sands.
8. During the transition step from secondary tailings to run-offs, coarse hydrophilic solids are selectively removed at the beaches. Higher amounts of biwetted solids, associated with the resulting run-offs, may increase the strength of the gel network. This, in conjunction with the finer size distribution of the remaining coarse hydrophilic solids, could account for the fact that beach run-off streams exhibited non-segregating behavior even in the CHWE trials.
9. For both ores properties of PSV froths such as the amount and type of different solids do not depend on process conditions. This suggests that bitumen flotation occurs prior to solids' aggregation. Secondary froths contain more fine solids and have a greater proportion of BUS, especially for OHWE processes.

10. Process modification did not result in a reduction of fine tailings volume.

    Characteristics of sediments in run-offs (fine tailings) are similar and independent of the type of the process.

11. Process modification resulted in faster settling of solids in the process streams.

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Appendix A

^{2}H NMR Residual Splitting Data

A.1) In pond water

wt% solids	time=0	30min	4hrs	8hrs	2days	4days	8days	11days	28days
1	6.2	6.6	6.1	6.7	6.3	3	6.3	6	4
2	14.1	13.6	13.4	13.1	12.1	11.5	10.5	10	7.3
3	21	20	19.8	19.7	19.7	19.2	19.9	19.4	4.5
4	30.7	30	28.2	27.9	27.9	26.7	24.6	23.2	0
5	36	33.2	32.1	28.3	25.6	21.2	11.8	11.2	0
6	44.3	41.8	38.7	36.9	25.6	15.2	8	7.6	0
7	52.7	50.1	47.1	43.2	n.a.	n.a.	n.a.	n.a.	n.a.
8	60.1	59.3	51.1	52.8	14.1	4.8	0 gel	0 gel	0 gel

A.2) After first water replacement

wt% solids	time=0	2days	4days	8days	11days	28days
1	n.a.	6.5	6.6	6.6	6.2	5.6
2	12.2	13.5	13.5	13.5	13.4	12.1
3	20.1	20.6	20.6	20.7	20.5	19.3
4	27.5	27.8	27.8	27.8	27.9	26.5
5	n.a	36	36	36.1	35.9	34.9
6	42.4	42.6	42.7	42.5	42.5	40.8
7	50.2	49.9	50	49.6	49.5	47.3
8	57.8	56.4	55.8	54.5	53.6	47.7

A.3) After second water replacement

wt% solids	time=0	2days	4days	8days	11days	28days
1	n.a	6.7	6.7	6.5	6.5	6.5
2	13.2	13.1	13.2	13.2	12.9	12.9
3	20.9	21.2	21.1	20.9	21.2	21.2
4	28.2	28.6	28.6	28.7	28.5	28.5
5	36.2	36.3	36.3	36.5	36.3	36.3
6	43.2	43.8	43.3	43.5	43.3	43.3
7	52.7	52.3	52.3	52.5	52.3	52.3
8	62	61.3	61.4	61.8	61.6	61.6

A.4) In 5 mM NaCl solution

wt% solids	time=0	30min	2hrs	4hrs	8hrs	2days	6days	9days
1	6.2	5	5	6	5.6	5.8	4.6	3.9
2	13.1	12	11.7	9.6	8.5	8.7	6	2.0
3	19.6	15.7	14.3	13.3	10.8	6.6	5.1	2.9
4	26.8	20.6	19.3	12.4	10.1	8.4	6.7	5.7
5	33.6	27.7	23.2	14.5	12.2	10.4	8	6.9
6	41.4	31.5	24.8	15.8	13.4	10.3	7.5	7
7	48.6	34.5	27.1	16.6	13.6	10.5	7.2	5.7
8	56	37.5	26.3	15.9	12.9	10.5	7.6	5.5

A.5) In 20 mM NaCl solution

wt% solids	time=0	30min	2hr	4hrs	8hrs
1	5.6	3.5	3.2	1.9	2.3
2	10.6	n.a	3.8	2.3	2.3
3	16	8.7	6.1	4.4	4.1
4	21.1	9.4	6.3	3.3	0 gel
5	26.3	8.9	5.5	0 gel	0 gel
6	31.6	10	6	0 gel	0 gel
7	37	10.5	5.5	0 gel	0 gel
8	42.1	10.2	3.9	0 gel	0 gel

A.6) In 20 mM $NaHCO_3$ solution

wt% solids	time=0	50min	2hrs	4hrs	8hrs	2days	6days	9days	28days
1	6	5.7	6.1	6.1	6.1	6.2	6.1	5.7	5
2	13.7	13.9	14	13.8	13.8	13.6	13.6	13.4	12.2
3	20.3	20.1	19.9	19.8	19.5	18.6	17.5	16.7	14.4
4	27.6	26.6	26.1	25.7	25.4	23.3	19.8	17	14.6
5	34.9	33.4	32.7	32.1	31.5	28.1	21.5	17.7	14.3
6	42.9	40	39.7	38.7	37.5	31.3	20.7	17.3	14.3
7	50.8	46.4	45.2	43.4	41.7	33.7	20.3	17.1	11
8	58.4	54.2	52.9	51.1	48.9	28.2	17.1	14.7	0 gel

A.7) In 0.125 mM $CaCl_2$ solution

wt% solids	time=0	2days	6days	9days	26days
1	6.4	6.6	6.6	6.3	5.7
2	13.2	13.3	13.3	13.1	12
3	20	20.1	20.4	20.2	19
4	27.6	27.7	27.9	27.8	26.8
5	34.7	34.8	34.9	34.6	33.7
6	42.1	42.4	42.6	42.5	40.7
7	50.1	49.9	49.8	49.1	42.4
8	60.6	59.3	58	56.6	38.4

Appendix B

Mass Balances

B.1) Separation of PSV Middlings by Centrifugation

Speed	Amounts of Middlings Settled at Different Speeds (g)				
	OHWE Syncrude (2)	M* OHWE Syncrude (8)	CHWE Syncrude (14)	CHWE Suncor (20)	M* OHWE Suncor (26)
200g/10min	14.39	18.78	15.71	14.20	14.05
200g/1hr	2.73	3.70	1.73	2.30	3.89
500g/2hrs	3.98	4.70	2.50	3.45	4.50
1500g/2hrs	1.68	52.83 clear water	2.09	2.12	57.74 clear water
U/S	57.53 clear water		57.98 suspension	58.30 suspension	
Total	80.31	80.01	80.01	80.37	80.18

B.2) Solids Content of the PSV Middlings Sedimented at Different Speeds

Speed	Wt.% of Solids in Sediments at Different Speeds				
	OHWE Syncrude (2)	M* OHWE Syncrud (8)	CHWE Syncrude (14)	CHWE Suncor (20)	M* OHWE Suncor (26)
200g/10min	49.9±0.08	56.3±0.11	56.3±0.25	57.3±0.21	45.7±0.16
200g/1hr	24.4±0.11	17.5±0.11	29.3±0.14	28.6±0.11	14.1±0.04
500g/2hrs	17.1±0.04	18.2±0.06	20.7±0.09	20.6±0.03	23.2±0.13
1500g/2hrs	15.1±0.03	0.0	16.2±0.08	16.1±0.37	0.0
U/S	0.0	0.0	~0.3 Suspention	~0.2 Suspention	0.0

B.3) Separation of PSV Middlings treated with $Na_4P_2O_7$

Speed	Total Dry Solids Settled at Different Speeds (g)				
	CHWE Syncrude (79.97)	M* OHWE Syncrude (80.88)	CHWE Syncrude (80.13)	CHWE Suncor (80.65)	M* OHWE Suncor (80.18)
200g/10min	10.02	13.34	15.81	11.17	6.56
200g/1hr	0.36	0.32	0.46	0.42	0.33
500g/2hrs	0.30	0.26	0.23	0.31	0.35
1500g/2hrs	0.23	0.19	0.16	0.23	0.18
91000xg/ 30 min	0.27	0.26	0.36	0.47	0.37
U/S	traces	traces	traces	traces	traces

Amounts of samples used in experiment are given in parenthesis

B.4) Separation of Secondary tailings

Speed	Amounts of Secondary Tailings Settled (g)				
	OHWE Syncrude (5)	M* OHWE Syncrud (11)	CHWE Syncrude (17)	CHWE Suncor (23)	M* OHWE Suncor (29)
200g/10min	37.30	36.97	33.79	18.17	25.66
200g/1hr	3.31	5.79	2.52	3.07	9.68
500g/2hrs	3.92	2.40	3.68	3.83	69.74 clear water
1500xg/ 2hrs	51.03 clear water	48.05 clear water	1.50	3.97	-
U/S	-	-	65.16 yellow water	76.84 yellow water	-

U/S - Unsedimented Solids

B.5) Solids Content of Secondary tailings sedimented at Different Speeds

Speed	Wt.% of Solids in Sediments at Different Speeds				
	OHWE Syncrude (5)	M* OHWE Syncrud (11)	CHWE Syncrude (117)	CHWE Suncor (23)	M* OHWE Suncor (29)
200g/10min	68.03±0.0.42	66.80±0.14	67.17±0.14	57.37±0.06	54.42±0.05
200g/1hr	17.55	15.27	23.30	26.46	16.21

500g/2hrs	16.91	15.87	18.22	21.90	0.00
1500xg/ 2hrs	0	0	n/a	n/a	0
U/S	0	0	0	0	0

B.6) Distribution of Secodary Tailings deflocculated with $Na_4P_2O_7$ at different speeds.

	Amounts of Deflocculated Secondary Tailings Settled				
Speed	OHWE Syncrude 95.85*	M* OHWE Syncrude 96.87*	CHWE Syncrude 96.40*	CHWE Suncor 96.75*	M* OHWE Suncor 96.87*
200g/10min	33.69 (69.5)	36.52 (70.6)	22.97 (64.2)	17.35 (57.7)	16.49 (64.60)
200g/1hr	1.37 (28.1)	1.27 (28.4)	1.37 (29.2)	2.79 (27.3)	1.23 (27.7)
500g/2hrs	1.28 (24.3)	1.17 (25.7)	1.30 (27.0)	2.88 (21.9)	1.41 (25.8)
1 1500xg/ 2hrs	0.2907 dry solids (n/a)	0.2621 dry solids (n/a)	0.3777 dry solids (n/a)	0.4686 dry solids (n/a)	0.3141 dry solids (n/a)
91000xg/ 30min	0.1364 dry solids (n/a)	0.1384 dry solids (n/a)	0.2837 dry solids (n/a)	0.0356 dry solids (n/a)	0.2172 dry solids (n/a)

U/S - Unsedimented solids
Wt% of solids in sediments are shown in parenthesis
* - Total amount of tailings used in experiment

B.7) Separation of Run offs

Speed	Amounts of Run offs Settled (g)				
	OHWE Syncrude	M* OHWE Syncrude	CHWE Syncrude	CHWE Suncor	M* OHWE Suncor
200g/10min	10.86	13.50	7.29	9.63	12.43
200g/1hr	5.48	9.57	3.44	3.52	7.71
500g/2hrs	3.31	1.40	4.01	3.63	53.12 clear water

1500xg/ 2hrs	52.37 clear water	59.20 clear water	1.47	1.88	-
U/S	-	-	61.60 clear water	59.66 clear water	-

B.8) Solids Contents of Run offs Sedimented at Different Speeds

Speed	Wt.% of Solids in Sediments at Different Speeds				
	OHWE Syncrude	M* OHWE Syncrud	CHWE Syncrude)	CHWE Suncor	M* OHWE Suncor
200g/10min	44.75	29.11	43.62	46.60	31.46
200g/1hr	16.12	16.51	20.76	21.29	17.90
500g/2hrs	15.71	11.84	16.22	16.71	0
1500xg/ 2hrs	0	0	n/a	n/a	0
U/S	0	0	0	0	0

B.9) Distribution of Run offs deflocculated with $Na_4P_2O_7$ at different speeds

Speed	Amounts of Deflocculated Run offs Settled (g)				
	OHWE Syncrude 100.03*	M* OHWE Syncrude 99.11*	CHWE Syncrude 99.35*	CHWE Suncor 99.06*	M* OHWE Suncor 99.52*
200g/10min	13.10 (53.6)	12.65 (53.5)	8.65 (48.7)	10.92 (53.0)	10.18 (53.4)
200g/1hr	1.83 (30.3)	1.74 (31.6)	1.71 (34.1)	2.05 (33.0)	1.75 (31.7)
500g/2hrs	1.32 (27.6)	1.39 (27.4)	1.49 (26.0)	1.48 (27.2)	1.46 (30.3)
1 1500xg/ 2hrs	0.5189 dry solids (n/a)	0.4664 dry solids (n/a)	0.5463 dry solids (n/a)	0.5890 dry solids (n/a)	0.4730 dry solids (n/a)
91000xg/ 30min	0.2977 dry solids (n/a)	0.1899 dry solids (n/a)	0.4070 dry solids (n/a)	0.5411 dry solids (n/a)	0.4337 dry solids (n/a)

U/S	traces	traces	traces	traces	traces

Wt% of solids in sediments are shown in parenthesis
*** - Total amount of tailings used in experiment**

B.10) Layers in sediments after 160 gravity settling of Run offs. Amounts of layers before sampling for dry residue (total sample collected).

	TOP	MIDDLE	BOTTOM
OHWE-SYNCRUDE	8.14	8.83	14.68
O-M-SYNCRUDE	7.49	10.43	12.36
CHWE-SYNCRUDE	10.00	9.44	12.73
CHWE-SUNCOR	10.63	11.46	10.15
O-M-SUNCOR	9.69	10.03	9.74

B.11) Layers in sediments after 160 gravity settling of Run offs. Amounts of layers after sampling for dry residue (total sample processed).

	TOP	MIDDLE	BOTTOM
OHWE-SYNCRUDE	6.65	7.26	13.29
O-M-SYNCRUDE	6.30	9.04	10.89
CHWE-SYNCRUDE	8.38	8.21	11.23

CHWE-SUNCOR	9.07	9.90	8.20
O-M-SUNCOR	8.20	8.89	8.42

B.12) Layers in sediments after 160 days of gravity settling of Run offs.
Amounts of dry solids settled at different speeds

	O-Syncrude			O-M-Syncrude			CHWE-Syncrude		
Speed	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
200xg 10min	0.8253	1.2261	3.0680	1.0221	1.8291	2.5740	0.5772	0.9078	1.7668
200xg 1 hr	0.0980	0.1478	0.3211	0.0995	0.2007	0.2280	0.1653	0.1498	0.2601
500xg 2 hrs	0.0866	0.1115	0.1992	0.0901	0.1420	0.1711	0.1227	0.1123	0.1920
1500xg 2 hrs	0.0550	0.0722	0.1409	0.0585	0.0961	0.1276	0.0938	0.0870	0.1419
10000xg 30 min	0.0494	0.0821	0.1880	0.0379	0.0869	0.1164	0.0866	0.0739	0.1826
91000xg 30 min	0.0064	0.0048	0.0256	0.0056	0.0180	0.0289	0.0049	0.0101	0.0290

	CHWE-Suncor			O-M-Suncor		
Speed	Top	Middle	Bottom	Top	Middle	Bottom
200xg 10min	0.8852	1.3425	1.8678	1.1453	1.6378	1.6931
200xg 1 hr	0.2064	0.2652	0.2154	0.1459	0.2094	0.2027
500xg 2 hrs	0.1542	0.1902	0.1596	0.1330	0.1638	0.1681
1500xg 2 hrs	0.1179	0.1330	0.1197	0.0948	0.1530	0.1577
10000xg 30 min	0.0309	0.0887	0.1336	0.0357	0.0491	0.0504
91000xg 30 min	0.0103	0.0408	0.0289	0.0063	0.0170	0.0179