Novel Methods for Treating Oilsands Tailings

by

Dominic Kealan Thompson

A thesis submitted in partial fulfilment of the requirements for the degree of

Master of Science

in

Chemical Engineering

Department of Chemical and Materials Engineering

University of Alberta

Abstract

Oilsands tailings are a waste product comprising primarily a stable alkaline suspension of clay in water. This waste product of oilsands mining is environmentally hazardous to store and expensive to safely dispose of. This work presents two novel ideas for dealing with the waste. The first is treatment with alkoxysilanes. Five alkoxysilanes were tested: bis(3-trimethoxysilylpropyl)amine; 3-aminopropyltrimethoxysilane; (3-glycidoxypropyl)trimethoxysilane; methacryloxypropyltrimethoxysilane; and tetramethoxysilane. Of these, bis(3-trimethoxysilylpropyl)amine and 3-aminopropyltrimethoxysilane were found to be effective at reducing Capillary Suction Time. Further tests were conducted with bis(3-trimethoxysilylpropyl)amine, including: 1) optimisation of pretreatment conditions; 2) determination of the effect of carbon dioxide on its performance; 3) determination of its interaction with a conventional polymer flocculant; and 4) investigation of its effect on suspensions with other solids concentrations. The second is treatment with carbon dioxide close to its critical point. This treatment is found to improve measures of dewatering potential, including Capillary Suction Time. No evidence is found for an additional supercritical effect and the mechanism is found to be the well-documented pH reduction.

Table of Contents

Illustration Index

Index of Tables

1 Introduction

Oilsands are composed of bitumen in a matrix of sand and clay, and are found principally in Venezuela and Canada. The store of energy in this type of deposit is large. In the Canadian province of Alberta alone, the oilsands formations contain approximately 27.5 X 10^9 m^3 of economically recoverable bitumen. Table 1 puts this into context.

Table 1: Comparison of oil flows and stores.

Description	**Quantity of oil (10^6 m^3)**
Alberta oilsands reserves	27 500
Western Canada resource	350 000
Saudi Arabian reserves	42 609
World reserves	222 000
Canadian annual consumption	128
World annual consumption	5 300

Most of this bitumen occurs in deep formations, but around 15% can be mined from the surface. This is still a substantial amount, and because of the ease with which the bitumen can be removed from shallow deposits, they account for 50% of production.

Almost all bitumen mined in this way is liberated from its ore by the “Clark Hot Water Process”. In this simple procedure, crushed ore is mixed with hot, dilute sodium hydroxide solution. The bitumen melts[1], and acidic components of it are saponified in the alkaline conditions. With sufficient agitation, the sand, bitumen and clay in the ore are separated from

---

[1] The bitumen is theoretically a liquid even at ambient temperature, but its viscosity is so high that for all practical purposes it is solid.

each other and dispersed in the water. When air is blown into this suspension, the bubbles attach to bitumen droplets because of the high surface energy at the bitumen-water interface. This causes the droplets to float to the surface, where the bitumen froth is easily removed.

Once agitation stops, sand particles readily settle, but the clay remains suspended, and only slowly settles over a period of months or years. Even then, the particles settle to a liquid containing around 30% solids, which resists further settling. This material is termed Mature Fine Tailings, or MFT.

It has been estimated that for every unit volume of bitumen produced, there is twice as much MFT produced, as shown in Figure 1.1. This represents a cumulative storage problem. Around 176 km^2[1] of Northern Alberta are covered by tailings lakes. Since oilsands mines have only been operating for about 50 years, and only on a large scale for 30 years, it is not yet known if the MFT will ever settle into distinct solid and liquid phases. In the meantime, the tailings lakes must be assumed permanent. Such unnatural water features are damaging to the environment even in their normal operating condition, and a huge liability in case of failure.

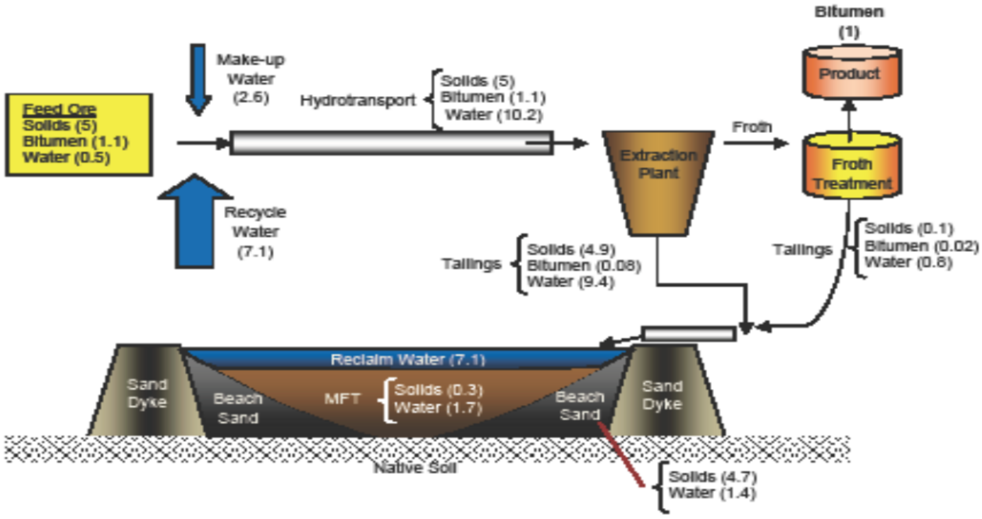


Figure 1.1: Oilsands production mass balance.

The bitumen held in Northern Albertan oilsands reserves is valuable, but one of the main factors restricting its monetisation is environmental uncertainty and practical difficulties caused by tailings. Therefore, the motivation for wastewater research in oilsands processing is strong.

This work focusses on oilsands waste water, which, due to its particular water chemistry and its bitumen content, is a hard test for any water treatment method. It is anticipated that any treatment for MFT will, therefore, be applicable to other mineral processing tailings, and perhaps other water treatment fields.

2 Literature Review

2.1 The nature of oilsands waste water

Oilsands tailings consist mostly of fine clay particles suspended in a dilute aqueous solution of sodium hydroxide and surfactants formed during the extraction process. Although the solids settle over a period of weeks or months, they do not settle completely. A sludge is formed consisting of around 30% solids, which does not settle further over a reasonable timespan.

The suspended clay particles are held apart from each other by strongly repulsive electrostatic forces. In addition, because the particles are so fine (less than 2 µm), water does not easily flow away from the particles, even under capillary action. One way of testing this “filterability” is the Capillary Suction Time (CST). This test is described in detail in Section 3.2.2. A low time indicates good filtering.

Many methods have been tested with a view to finding a way of either causing the Mature Fine Tailings (MFT) to settle into solid and liquid phases, or increase the filterability to an acceptable level so that the liquid can be removed by filtration. The two simplest and most effective are flocculation and coagulation.

In flocculation, a water-soluble polymer (which may be organic or inorganic) is dissolved in the MFT. Polymer chains adhere to clay particles, forming a bridge between them. For entropic reasons, the chains have a tendency to coil in on themselves- when they do, the clay particles are brought closer together into “flocs”- loose agglomerations of particles which settle more readily than individual particles, due to their size. These flocs also contain a lower proportion of water than the suspension as a whole, and there is more space between flocs than there was between the loose particles. As a result, water flows more readily away from the particles and hence the filterability is improved.

In coagulation, ions are added to the water to reduce the electrostatic repulsive force between particles, so that the attractive forces (van der Waals especially) dominate. Any salt will work for this, but it is desirable to use a salt with multivalent ions because, for a first approximation, the concentration required is inversely proportional to the sixth power of the valency. For MFT, many salts have been tested[2]. One of the most effective is calcium sulphate, and this is used in practice because of its local abundance.

2.2 Forces on small particles

Clay particles in static aqueous suspension are subject to at least three forces:

- Gravity
- Electrostatic force
- Van der Waals forces[3]

Gravity causes the large particles to settle. It is proportional to the cube of the particle radius, with the result that it is much more significant for large particles. Once moving, particles are subject to hydrodynamic forces, which are proportional to the square of effective radius and are related to velocity. These two forces cause sand particles (greater than 44 µm) to settle relatively quickly- within a few hours - and clay particles to settle more slowly[4].

The electrostatic force arises from surface charge on the particles- which is due to isomorphous substitution and pH effects[5]. It is proportional to the surface area of the particle. This force is strong enough to oppose gravity and prevent settling in small particles (on the order of 2 μm). Van der Waals forces arise from dipole interaction (permanent, instantaneous and induced) and are proportional to the radius of the particle[6].

Since the clay particles are similar to each other, and will therefore have the same degree and type of isomorphous substitution when in the same medium, they must have the same charge. We can immediately see that the electrostatic force should therefore cause the particles to repel each other. In an ionic solution, this simple state of affairs is complicated by the formation of a double layer of charges[7] [8] [9]. Close to the charged clay particle, opposing charged ions from solution adhere tightly to its surface to form the Stern layer[10]. Further from the surface, the particle exerts its influence to a lesser and diminishing degree. At the slipping plane, shear forces in the fluid are able to move those ions which are under the influence of the particle. At the boundary of the double layer, the concentration of ions is the same as in the bulk liquid. This is shown in Figure 2.1.

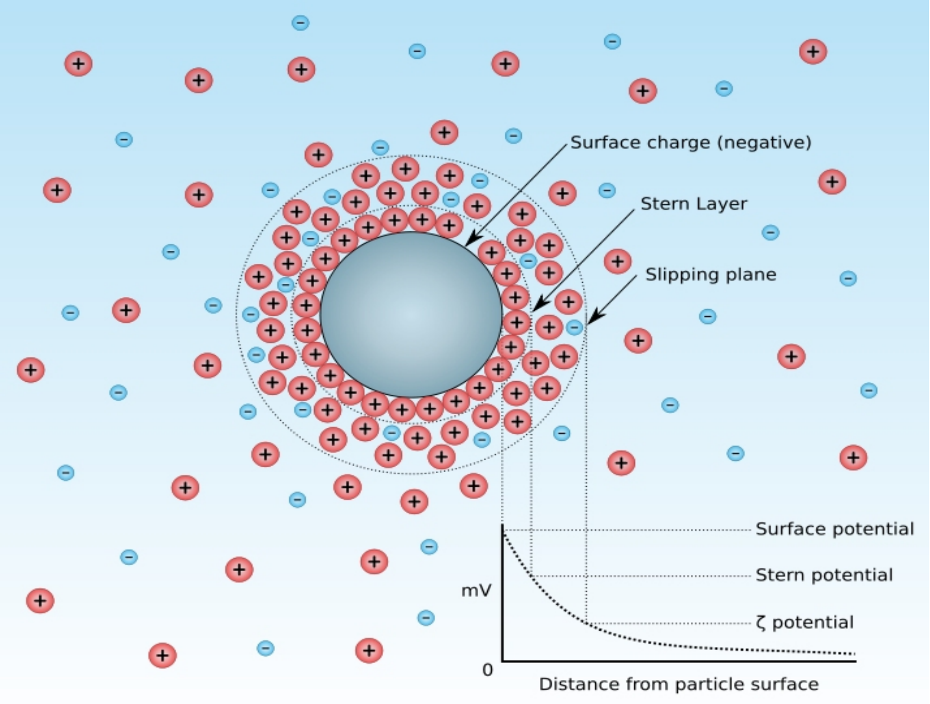


Figure 2.1 Ion distribution around a charged particle (public licence from creative commons).

The Zeta potential is the potential difference between the two sides of the slipping plane, and is used to represent the magnitude of the electrostatic repulsive force.

Van der Waals forces are stronger than this repulsion, but operate on a small length scale[11]. Figure 2.2 shows the free energy of particles as a function of distance.

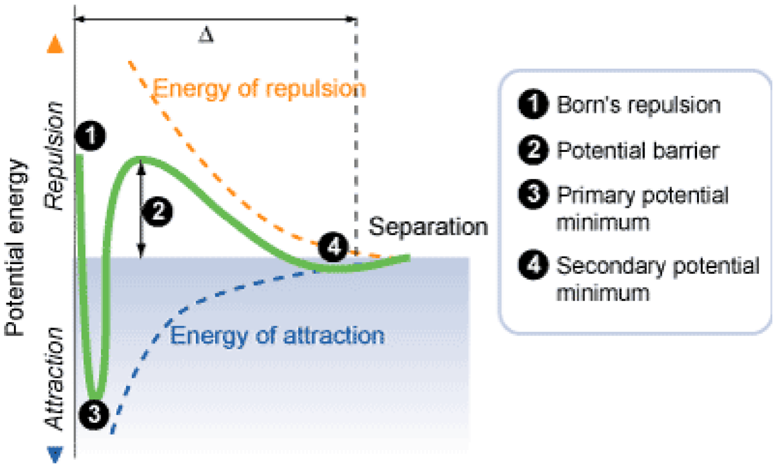


Figure 2.2 Interaction energy between two small particles as a function of separation. (Adapted from http://www.inkline.gr/inkjet/newtech/tech/dispersion/).

At the primary minimum, particles are held firmly together by van der Waals forces (primarily London dispersion forces- i.e. instantaneous dipole-induced dipole interaction). This is coagulation and is a strong union of particles. At the secondary minimum, particles may form loose agglomerations, but under normal circumstances these are easily broken by thermal motion. This is flocculation. Between these minima, there is an energy barrier (the primary maximum) which prevents the particles getting close enough to each other to experience the deep attraction which occurs at the primary minimum.

This energy barrier is related to the Zeta potential, which represents the electrostatic repulsion, and by extension, the stability of the colloidal suspension.

The Zeta potential, and the repulsive force, can be reduced by changing the composition of the dispersion medium. Adding a salt to the solution reduces the Zeta potential, so that the energy barrier becomes small enough that it can be overcome by thermal motion. When this occurs the particles can easily fall into the primary minimum and will remain closely united. Figure 2.3 shows the free energy curves with respect to particle separation for increasing salt concentrations (from 1 to 5). The energy barrier becomes smaller as salt concentration increases, and eventually disappears. A multivalent salt such as calcium sulphate or aluminium trichloride will be much more effective than a 1:1 salt, and this method is often used for potable water treatment, for example. However, in oilsands tailings treatment, this is not a viable method, because when the water is re-used in oilsands extraction, the reduced Zeta potential in the now-saline solution would prevent dispersion of the clay particles, limiting the amount of bitumen that can be recovered.

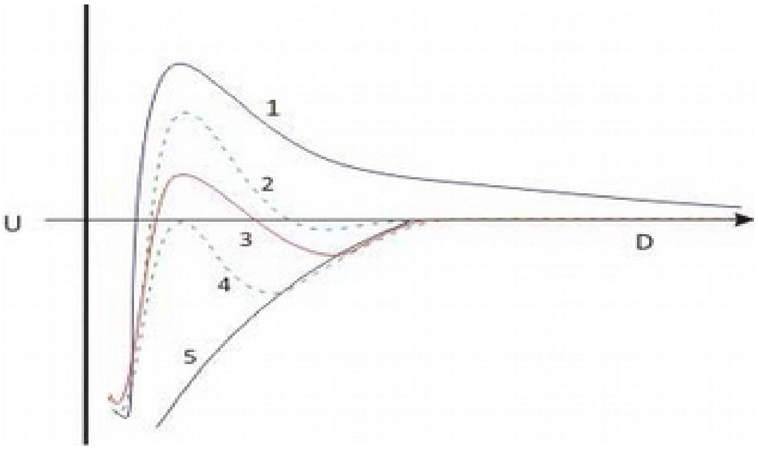


Figure 2.3 Free energy curves as a function of separation for increasing salt concentrations. From http://nptel.ac.in/courses/103104045/pdf_version/lecture37.pdf.

2.3 Flocculation

We have seen in the previous section that coagulation is an effective way to remove clay particles from water, since it causes the strongest attraction between particles and is unlikely to be undone by thermal motion. However, it is not feasible in oilsands processing because the most practical way of achieving it, adding a multivalent salt to the tailings, has a deleterious effect on the water when it is re-used. On the other hand, natural flocculation cannot be relied on to bring particles together so they settle out under gravity. The agglomerations formed at the secondary minimum are weak, and easily overcome by thermal agitation. To settle well, a floc must be larger than a comparable group of coagulated particles, because the floc has a higher water content and hence lower density. Easily separated by random thermal motion, flocs rarely achieve a sufficient size to settle. Moreover, the secondary minimum does not always exist at low ion concentrations, as seen in Figure 2.3.

A solution to this problem is to use polymer flocculants. A polymer flocculant is a water-soluble polymer that is able to bridge the gap between clay particles and keep them close enough together that they remain flocculated. This allows much larger flocs to form, which settle more readily.

The properties of an ideal polymer flocculant are as follows:

- Will bond to the clay particles- it is important that the polymer adheres to the particles which are suspended, so that it is able to bridge the gap between them. The polymer may adhere by its backbone, by side chains or by functional groups attached to it.
- Have long chains, which can bond to a large number of particles. Other factors being equal, the more particles that are in a floc, the quicker the floc will sink.

- Should not adsorb too much water- since this will cause the flocs that form to have a large amount of water as well as clay particles, which will reduce the density and adversely affect settling. On the other hand, it is important that the polymer disperse in the liquid so that it can gather distant particles. It is therefore important to have the correct balance of hydrophobicity and hydrophilicity.

Many polymers, such as non-ionic polyacrylamide, will bond to suspended particles in the absence of electrostatic forces[12]. It is beneficial, however, for the polymer to adhere by electrostatic attraction, and so cationic and anionic polymers are used depending on the charge of the particles present[13].

All polymers have an entropic tendency to coil in on themselves rather than have an extended conformation[14]. This means that clay particles to which the polymer is bonded will be brought together into flocs. Some polymers also have an opposing tendency to spread out, due to self-repulsion of ionic groups or high hydrophilicity. There also exist polymers which can change from extended conformation to coiled when their environment changes, e.g. after a temperature increase or a pH change[15]. These switching polymers have the advantage that they can bond to large numbers of remote particles when extended and bring these into flocs when conditions change and the polymer changes to the coiled state.

One polymer which has been found to be effective for flocculating fine solids in oilsands tailings is polydiallyldimethylammonium chloride (PDADMAC)[16]. MFT is composed of the smallest particle present in oilsands tailings, and as such PDADMAC was chosen as a standard when comparing the novel flocculants described in this thesis. The structure of PDADMAC is shown in Figure 2.4. The molecular mass of PDADMAC used in these comparisons was 200,000 – 350,000, which is classified as medium.

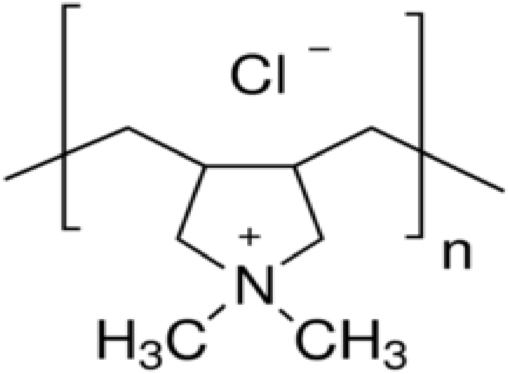


Figure 2.4: Structure of PDADMAC.

2.4 Performance metrics

In scientific literature on oilsands tailings flocculation, it is common to use initial settling rate (ISR) and capillary suction time (CST) of the freshly flocculated suspension to measure the performance of flocculants and flocculation stratagems. These are used because the polymers are tested on whole tailings or diluted MFT, both of which are quite dilute suspensions and so the ISR is significant. Most of the work in this thesis is with undiluted MFT. High ISRs are not possible with MFT and moreover, are not particularly desirable, since the MFT has already been stored for years and it is inconsequential whether treatment takes a few days instead of being complete in a few minutes. The properties of a good treatment for MFT are altogether different. Treatment of MFT is different from whole tailings for the following reasons.

MFT is concentrated. This means that it may be economic to use methods which are more expensive on a unit volume basis than would be the case for whole oilsands tailings treatment.

MFT already has a high solids content. The solids content of MFT, at about 30%, is approximately ten times higher than whole oilsands tailings. For reclamation purposes, about 70% solids is required. This means MFT treatment is more about removing water than removing solids.

MFT is stable. Whereas whole oilsands tailings will undergo very large volume reduction on their own, this is not the case for MFT. MFT production is cumulative, and oilsands mining has been going on long enough that the volume of MFT in storage is greater than the volume required to hold whole oilsands tailings while it settles. The land required for MFT tailings ponds is directly proportional to the volume of MFT stored. This makes volume reduction an important short-term goal, and this has been reflected in recent legislation which specifies targets for MFT volume reduction.

The important metrics for MFT post-treatment are:

1. volume reduction;
2. yield strength;
3. ease of further dewatering.

Volume reduction is important because this is specified by the Alberta Energy Regulator. A smaller volume of tailings also means less land is occupied by tailings ponds prior to final remediation.

Yield strength is important because it is necessary for the material to behave as a hard solid for successful remediation.

Polymer flocculants rarely achieve sediments which contain a sufficiently low proportion of water to behave as a solid. (Generally, 70% solids is required for this). For suspensions with very high solids concentrations, it becomes increasingly difficult to remove further water. Therefore, an important measure of a flocculant's performance is its effect on subsequent dewatering processes. After flocculant treatment, a suspension may be further dewatered by gravity drainage, evaporation, freeze-thaw action or capillary action. Efficient application of any of these methods requires that water move readily through the suspension. A good measure of this is CST.

For these reasons, certain metrics were chosen for measuring the improvement in MFT properties. These are presented in Table 2.

Table 2 Measurement of performance parameters.

Performance parameter	Metric chosen	Reason for choice
Volume reduction	Mudline drop	Percentage drop in mudline is identical to percentage reduction in volume, since release water is no longer classed as MFT.
Yield strength	Solids content	The primary determinant of yield strength is solids content. While apparent yield strength may be affected by thixotropic and temporary viscosity effects, solids content is unchanging.
Ease of further dewatering	Capillary suction time	CST measures the rate of water removal from a sample by capillary action. In high solids suspensions, this is limited by rate of water movement through the suspension itself. Other dewatering methods are also limited by this, including surface evaporation, gravity drainage, freeze-thaw, so it is an appropriate measure.

2.5 Silicon chemistry

Conventional polymer flocculants are carbon-based compounds. Just as carbon's tetravalency gives it the flexibility to form the alkanes, alkenes, alcohols, aldehydes and so on, so can tetravalent silicon form an almost equally varied and numerous class of compounds. The silicon equivalent of alkanes are silanes, which have the general formula $Si_nH_{(2n+2)}$. The structure of the third homologous silane, trisilane, is shown in Figure 2.5.

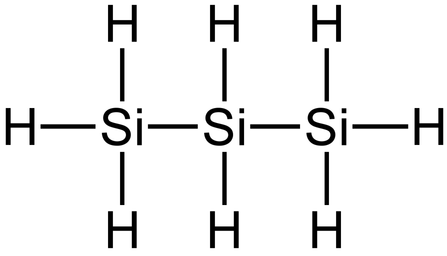


Figure 2.5: Structure of trisilane.

The silanes become less stable with increasing n, which limits their length to about 8 silicon atoms[17]. However, silicon-based polymers are still possible, because the stability of the silicon chain is increased by side-groups of alkanes. Figure 2.6 shows an example of such a polymer.

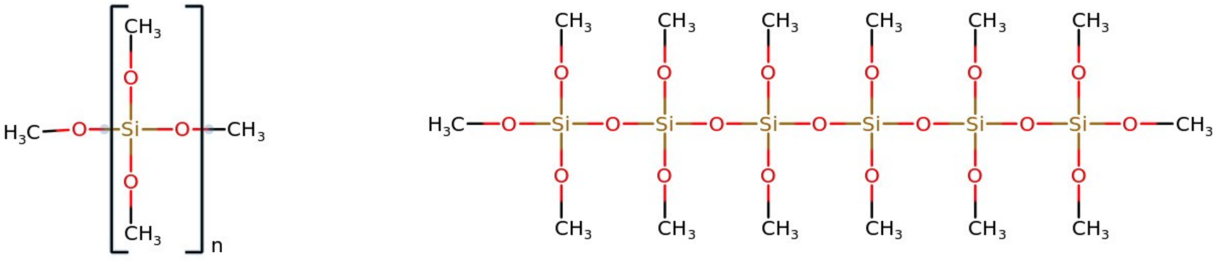


Figure 2.6 Polymer of tetramethoxysilane.

The corresponding monomer of the polymer shown in Figure 2.6 is the alkoxysilane tetramethoxysilane, shown in figure 2.7.

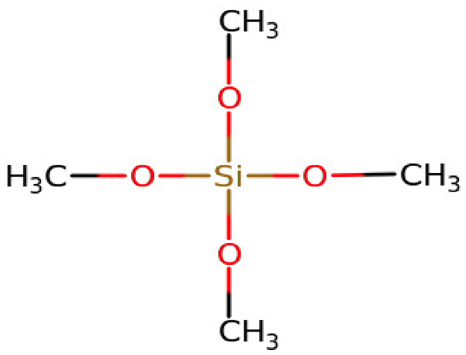


Figure 2.7: Structure of tetramethoxysilane.

The reaction from the monomer to the polymer proceeds via hydrolysis to the silanol and alcohol. The reactive silanols then undergo condensation in which they react with each other to form polymers[18]. This is shown in Figures 2.8 and 2.9.

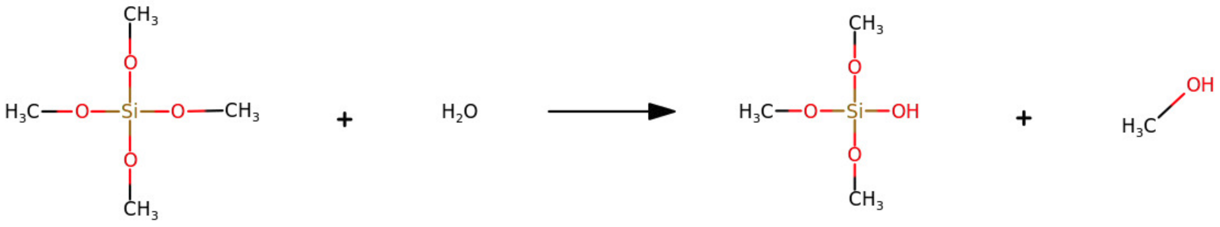


Figure 2.8 Hydrolysis of tetramethoxysilane, producing the reactive silanol intermediary and alcohol byproduct.

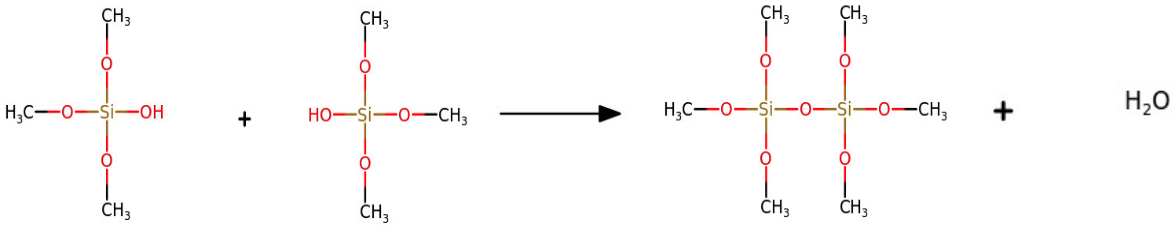


Figure 2.9 Condensation of silanol intermediaries.

In practice, the hydrolysis and condensation reactions shown in Figures 2.8 and 2.9 respectively can happen on any of the silicon bonds and in any order[19]. This gives rise to complex structures which are branched and may have unreacted alkyl groups and silanol groups.

Polymerised alkoxysilanes bond to clay (and other substrates) by two different mechanisms[20]. Their primary application is in surface treatments, because of the strong bonds they form to substrates and the change in surface properties which results, and this area of application has been extensively studied. When polymerised alkoxysilanes approach the surface of a clay particle (Figure 2.10), the molecule can bond to the surface hydroxyl groups of clay particles by hydrogen bonding or by dehydration-condensation reaction as shown in Figures 2.11 and 2.12[21] respectively.

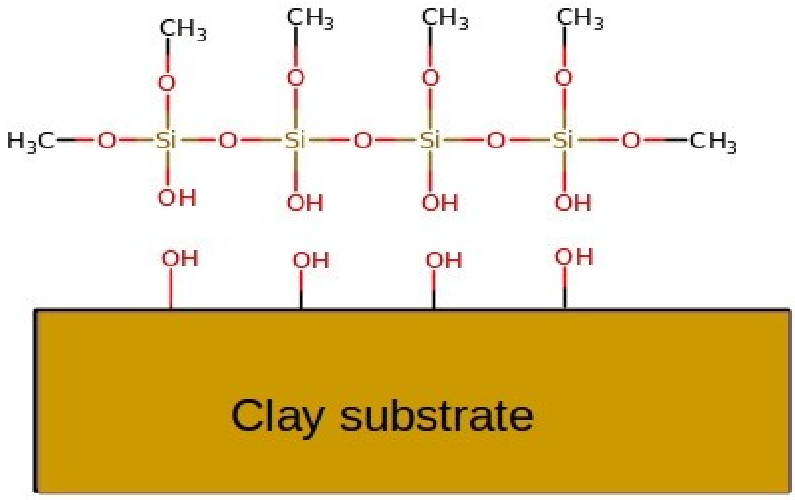


Figure 2.10: Oligomer alkoxysilane apporaching a clay surface.

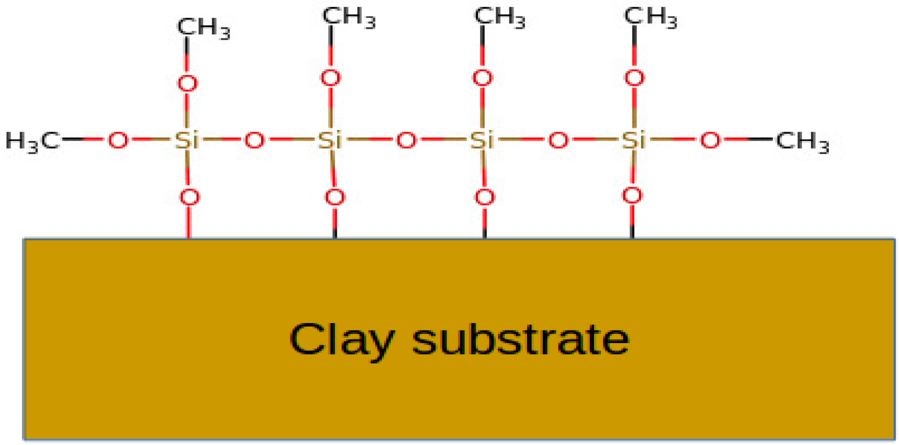


Figure 2.11: Oligomerised alkoxysilane attaches to clay surface by dehydration-condensation.

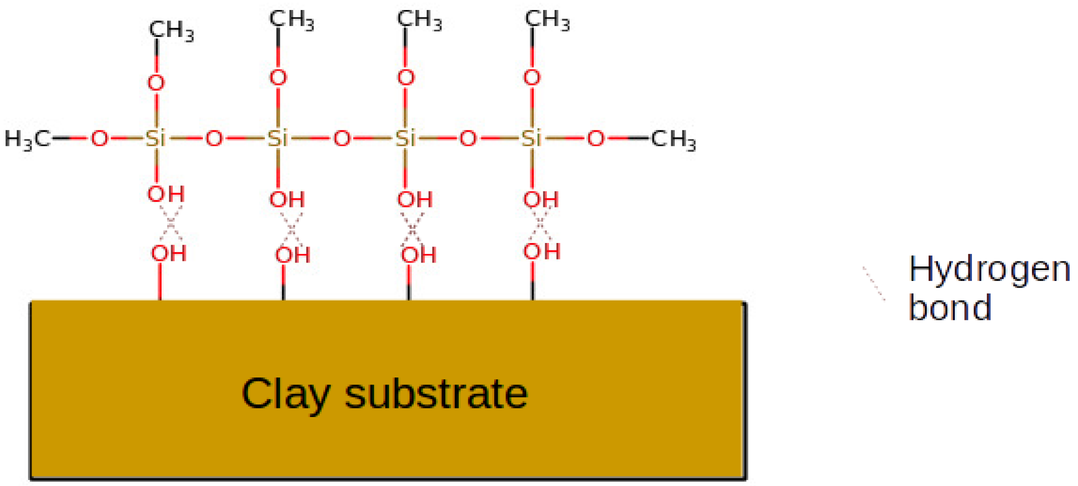


Figure 2.12: Hydrogen bonding may still take place where chemical bonding by dehydration-condensation does not occur.

Alkoxysilanes can form polymers, which are water-soluble, and it is this bonding to clay substrates which makes polymerised alkoxysilanes possible flocculants.

In Section 2.3, three important properties of polymer flocculants were listed. These were:

- Bonding to clay particles;
- Long chains;
- Correct degree of hydrophobicity.

The hydrophobicity of a polymer is largely determined by its functional groups[22]. Polyalkoxysilanes fulfil the first criteria due to the mechanisms already outlined.

Polyalkoxysilanes may or may not have long chains, depending on the conditions of their polymerisation. An acidic environment and a low ratio of water to silicon promote weakly branched polymeric networks, whereas a high water to silicon ratio and a basic environment promote highly branched “colloidal” particles[23]. Intermediate environments produce intermediate polymer structures. The rate of hydrolysis is reduced by complexity of the alkyl groups- such as functional groups- but is lowered most by the alkyl groups being branched[24].

When they bond to a silica surface, alkoxysilanes change the exposed surface from silica to whichever organic functional group they have. For this reason, they are used in many and varied surface treatments. They are used to preserve old buildings, by rendering the surface of the masonry impervious to water without changing the appearance[25]. They are used as surface treatments for laboratory glass, to increase its hydrophobicity, and for preservation of wood[26]. They are used in many applications for increasing the bond strength between glass (or metal) surfaces and organic resins or polymers[27], and between fibres of different composition in composite materials[28].

It seems that, given the alkoxysilanes’ polymerisation potential, and their bonding to clay particles, that they are reasonable candidates as bridging flocculants. This topic has not been extensively studied, but there are reports of copolymers of a silane with an organic polymer having flocculant properties[29]. Silane compounds have also been documented as surface modification agents having an effect on flocculation. For example, colloidal silica nanoparticles have been shown to exhibit a reduced zeta potential when functionalised with methyl polyethylene glycol silane[30].

2.6 Carbon dioxide in mine tailings treatment

In mining, the target material (which may be a mineral, such as bauxite, haematite, malachite etc, or an energy product, such as bitumen), is often intimately mixed with a waste material, and it is necessary to separate the target material from the waste before further refinement can take place. There are several technologies which are used for this, but the two most important are froth flotation and solution complexing. Both generate aqueous waste which must be treated before discharge to the environment.

In froth floatation, crushed ore is mixed with water and soluble chemicals which selectively adhere to the surface of particles of the target material, and make them hydrophobic. When air bubbles are blown into the mixture, the target material attaches to them and rises to the surface, while the debris sinks or remains in suspension. The tailings from this process consist of a suspension of fine particles in water, together with dissolved material. The tailings cannot be reused indefinitely because both the fine particles and the dissolved substances adversely affect the separation of target material from waste, and their concentration in the extraction water soon becomes unacceptably high.

The exact nature of these tailings depends on the nature of the ore being treated. In addition to the inert material, typically there will be trace metals (either those being targeted or other metals in the ore formation), sulphides (which oxidise in the atmosphere to sulphates) and, in the case of oil sands floatation, residual bitumen.

Tailings also arise from extraction processes which rely on solubility rather than surface forces. For example, gold ores can be subjected to cyanide leaching. This treatment renders gold and some other metals soluble by cyanide complexing. Once the aqueous fraction is separated from the solids, the gold is precipitated from solution. The tailings from this process contain cyanide and non-target metals which were also made soluble but not retained with the gold.

The usual method of dealing with froth flotation tailings is to impound them within a dam and possibly use polymer flocculants to enhance the settling process. Filtration is also sometimes used.

Froth floatation is used extensively in bitumen extraction from oil sands. The tailings from this process are particularly troublesome, more than other mining processes, because:

- Bitumen is a high demand, low-value product. It has been extracted on such a large scale that tailings ponds now cover a significant land area.
- There is normally a high proportion of fine clay in oil sands ore.
- The water chemistry of the tailings is unfavourable for clay settling, since it is modified (using sodium hydroxide and surfactants) for the specific purpose of separating clay particles from each other in the presence of bitumen.

This review outlines the current and proposed uses of CO_2 in mine tailings treatment, although CO_2 is also sometimes used in mineral extraction. For example, it can be used in froth flotation in place of air, offering slightly different surface properties. It can also be generated on the surface of the desired mineral (in the case of carbonates exposed to acid), which offers better attachment over introduced air bubbles[31].

2.6.1 Carbon dioxide as coagulant

In oil sands tailings treatment, CO_2 has been found to be an effective coagulant when used in the non-segregating tailings process[32]. CO_2 is used in this fashion commercially by Canadian Natural Limited.

When added to Mature Fine Tailings, CO_2 rapidly causes further settling and release of clean water. This water also has a lower turbidity compared with normal settling. CO_2 causes a reduction in pH. Lower pH reduces the electrostatic repulsion between particles and so improves settling. In order to determine whether the improved settling was due to pH change or to some other property of CO_2, the study referenced above compared CO_2 with modifying the pH to the same level using hydrochloric acid. It found that the effect was due simply to pH.

Also, when the pH was taken below around 6, the hydrochloric acid continued to give improvements in settling rate and supernatant clarity, whereas the CO_2 performance deteriorated. This pH level corresponds to a CO_2 partial pressure of around atmospheric, and so the reduced performance can be attributed escape of CO_2 to bubbles or “fizz”. When the CO_2 concentration in the liquid phase is at this level, gas bubbles escape from the liquid. Not only does this represent an escape of CO_2 from the system, and concomitant increase in pH, but these bubbles also recirculate sediment, thereby undoing any benefit that was accrued.

Unlike salt-based coagulation using calcium sulphate, in which the salt remains in the water and causes problems when the water is re-used, the CO_2 does not have an adverse effect on the extraction process. The study did not indicate whether the CO_2 can be removed from solution, but since process water is alkaline at least partly because of the NaOH it contains, it seems likely that the pH reduction occurring due to CO_2 addition is not fully reversible by a low energy method (such as stripping with inert gas or pressure reduction). It also seems likely that it will be less detrimental to extraction than the build-up of salts that would occur if a mineral acid were used instead, although this has yet to be investigated.

2.6.2 pH adjustment

In some tailings, such as “red mud” from alumina production, very high pH is itself a problem, even the main environmental liability associated with the waste. In this case, CO_2 addition is an effective method to bring the pH closer to neutrality[33].

In order to reduce leaching of metals from solid tailings, it is generally advisable to keep the pH high[34]. The presence of alkali metal carbonates however, acts as a buffer to metal solubility and the risk of metals becoming soluble in groundwater is therefore reduced by storage of tailings within carbonate aquifers[35].

However, there are some exceptions to the rule that high pH reduces solubility. Arsenic becomes more mobile at high pH, due to decreased adsorption reactions[36]. Carbon dioxide could potentially be used as a pH adjusting agent to reduce pH and decrease arsenic mobility in soil or groundwater.

2.6.3 Switchable polymers

Some water-soluble polymers show physical property transitions in the presence or absence of CO_2. For example, they may change from sol to gel, or from gel to sol[37]. Similarly, the Lower Critical Solution Temperature may be adjusted by the concentration of CO_2[38]. These processes are reversible by removing the carbon dioxide, for example by stripping with an inert gas.

Temperature-sensitive polymers, which transition from sol to gel at a particular temperature, have already been shown to be useful in flocculating fine particles from oil sands tailings; in the disperse phase, the polymer chains adhere to clay particles in suspension, and, when the temperature is changed, the polymer chains draw in on themselves, bringing the clay particles with them and expelling water. Polymers which are sensitive to CO_2 instead of temperature may offer a similar benefit, but may be cheaper to operate because there is no need for heat transfer.

2.6.4 Supercritical complexing

Supercritical CO_2 with organic complexing agents can be used to extract metals from solid or liquid material[39]. The complexing agents act as an intermediary between the metal ion and supercritical CO_2 to make the metal soluble in the supercritical phase. The metal is then dissolved in the CO_2 and is easily separated from it by distillation. The technique can be used for removing uranium from solid wastes, including tailings[40].

2.6.5 Supercritical carbonation

Tailings ponds also arise from combustion of solid fuels when a wet scrubber is used to remove dust from flue gases. Depending on the mineral content of the fuel, the ash from combustion may possess cement-like properties (in fact, ash from coal-fired power stations is often used in cement). In Estonia, direct combustion of oil shale for electricity production has produced tailings ponds. It has been suggested to use supercritical CO_2 to form a hard cap over these ponds; the CO_2 would react with the minerals in the ash to form hard carbonates[41].

2.6.6 Carbon dioxide sequestration

Some mine tailings react with carbon dioxide, allowing it to be sequestered as a solid and preventing its release to the atmosphere[42]. This occurs when the tailings contain a mineral such as magnesium silicate; the carbon dioxide reacts with the mineral to form carbonates and silicates. This happens naturally rather slowly, but can be sped up by contacting the silicate with a high concentration stream of carbon dioxide. This enables long-term storage of CO_2 and prevents it polluting the atmosphere.

2.6.7 Conclusions

Carbon dioxide has some current and some postulated uses in the treatment of mine tailings. Many of these are based on its acidity when in aqueous solution. The effectiveness of carbon dioxide in treating mine tailings is limited, but, in as far as it works, it is a uniquely attractive material. In many contexts in the mining industry it is abundantly available as a waste product, and particularly where mining meets the energy industry- in oil sands and coal mining.

If not captured, CO_2 is a harmful waste product which causes global warming. Although the potential applications to mine tailings do not store CO_2 for a significant time, some silicate-containing tailings offer the ability to permanently capture CO_2.

3 Treatment of MFT with Alkoxysilanes

3.1 Introduction

As discussed in the Chapter 2, alkoxysilanes can form oligomers or polymers after combinations of sequential hydrolysis and condensation reactions in aqueous alcoholic solution, and they also bond to other materials which include Si-O-Si structures, such as certain clay minerals, via silicate bonding. It is therefore plausible that alkoxysilanes could polymerise and bond with suspended clay particles, in a manner similar to conventional polymer flocculants, although via a different mechanism. Once bonded together by alkoxysilane bridges, the clay particles might undergo flocculation, if they could be brought close enough together by the tendency of the alkoysilane polymer to minimise its surface area- a phenomenon also discussed briefly in Chapter 2.

The present chapter describes experiments which were designed to test this hypothesis. Most of the experiments were conducted in MFT, which is an already dense suspension of clay particles – by definition, the particles have settled as much as they will under the influence of gravity in the existing water chemistry. This is a hard test for any flocculant, but a relevant one for the oilsands industry, since MFT is the final state of tailings in an untreated state, and there are very large quantities already awaiting further remediation.

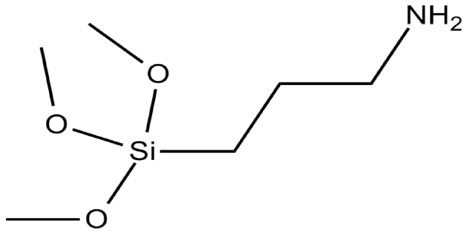
This chapter will first describe:

- preliminary experiments done to determine the testing conditions;
- the main set of experiments, done to screen alkoxysilanes for efficacy at flocculating MFT, and to select one alkoxysilane for further tests; and finally;
- further tests, such as testing the alkoxysilane in whole tailings, in the presence of an acidifying agent, and in combination with a conventional polymer.

3.2 Preliminary experiments

3.2.1 Introduction

As described in Chapter 2, initial results from the experiments showed that, of the four compounds tested, two were efficacious for flocculation, although they had not been proved in MFT. These were 3-aminopropyltrimethoxysilane and bis(3-trimethoxysilylpropyl)amine. These will henceforth be abbreviated to 3-amino and bis-amine respectively. The chemical structures are shown in Figures 3.1 and 3.2.

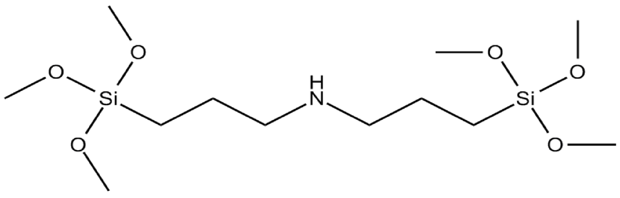


Formula: $C_6H_{17}NO_3Si$

Molecular weight: 179.29

Density: 1.027 g/mL at 25 °C

Figure 3.1: Chemical structure of 3-amino.



Formula: $C_{12}H_{31}NO_6Si_2$

Molecular weight: 341.56

Density: 1.04 g/mL at 25° C

Figure 3.2: Chemical structure of bis-amine.

The aims of the preliminary experiments were:

1. to find out whether these compounds were effective flocculants in MFT;
2. to decide protocols for testing other alkoxysilanes; and
3. to decide suitable further tests.

At this stage it is helpful to recall the reactions that take place in alkoxysilanes in aqueous alcoholic solution. Figure 3.3 shows the hydrolysis of 3-aminopropyltrimethoxysilane.

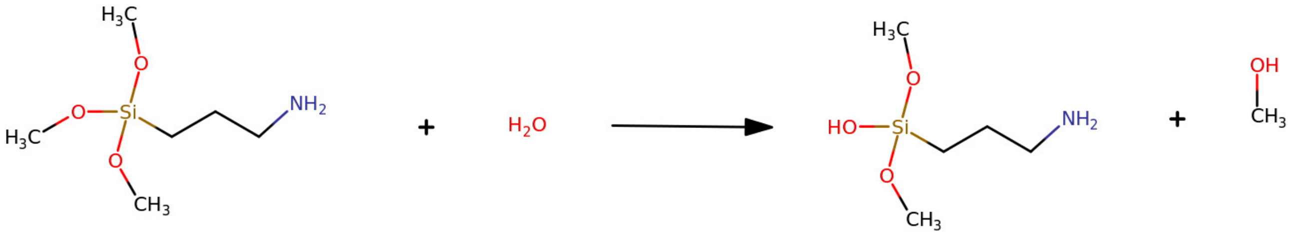


Figure 3.3: Hydrolysis of 3-aminopropyltrimethoxysilane.

The silanol hydrolysis product can undergo further hydrolysis on the remaining alkyl groups, as shown in Figures 3.4 and 3.5.

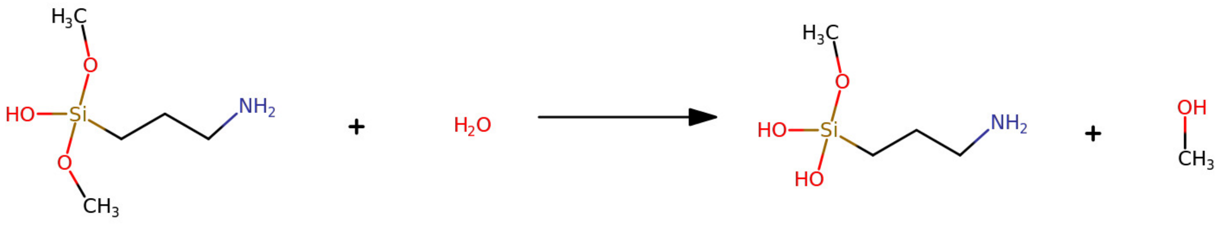


Figure 3.4: Further hydrolysis of the silanol hydrolysis product of 3-aminopropyltrimethoxysilane.

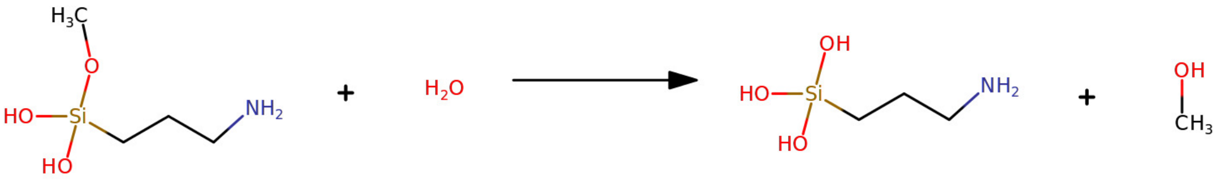


Figure 3.5: Hydrolysis taking place on the final alkyl group.

These silanols are reactive and readily undergo condensation reactions with each other. These could produce many types of compounds, depending on the degree of hydrolysis of the reactants. In the simplest case a dimer will be produced as shown in Figure 3.6.

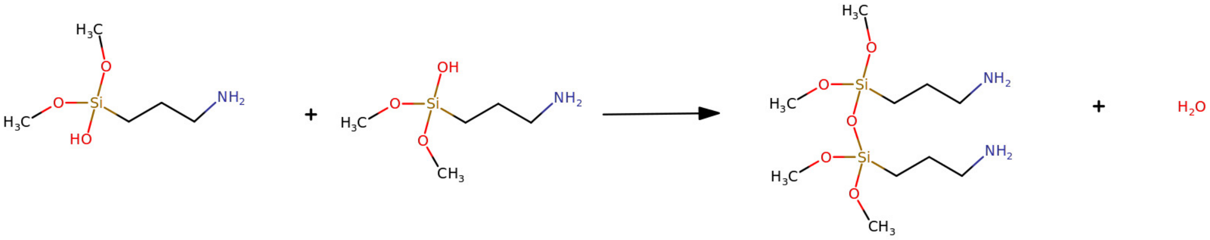


Figure 3.6: Hydrolysis products of 3-aminopropyltrimethoxysilane undergo condensation to form a dimer.

If all reactants are secondary hydrolysis products, a straight-chain polymer will form as illustrated in Figure 3.7.

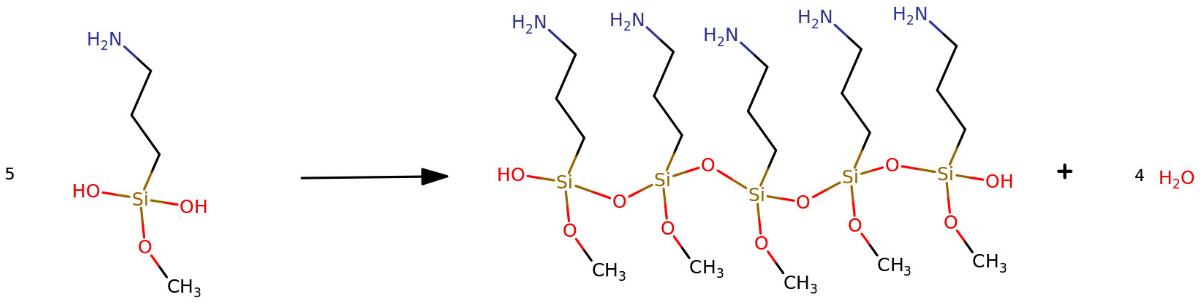


Figure 3.7: Condensation of secondary hydrolysis products forming straight chain polymer.

All three hydrolysed products of 3-amino may undergo condensation reactions. Also, condensed products may undergo further hydrolysis on remaining alkyl groups. Clearly, this can lead to very complex structures, including oligomers and polymers with a high degree of branching.

3.2.2 Trial of method

3.2.2.1 Methods and observations

We conducted flocculation tests with 3-amino and bis-amine to replicate our preliminary results but used MFT instead of kaolin.

A mass of 1 g of the compound was withdrawn using a syringe through the sealed lid (in order to reduce exposure to atmospheric oxygen). This was dissolved in a solution consisting of 8 volumetric parts of ethanol to 2 parts deionised water. The volume was brought up to 10 ml with this ethanol solution. This concentration has been used in the prior experiments and also in previous work done in this group. Both compounds dissolved easily.

The solution containing bis-amine rapidly turned into a cloudy gel, which shows that it was colloidal, and that there were excessive condensation reactions leading to highly branched polymers. The 3-amino solution remained clear and colourless. The samples were then held in a water bath at 60°C for 30 minutes to allow hydrolysis to take place. This procedure was chosen because it has been previously used within the group, and shall be referred to as the Standard Hydrolysis Technique. After this step, both samples were unchanged in appearance. Manipulation of the bis-amine gel revealed that it behaved like a brittle solid. The flocculation tests require that the flocculant be in liquid form, so only the 3-amino sample was tested in

MFT. The procedure is described below.

The bulk sample of MFT was stirred to homogenise it, and then five portions of 200 g each were taken. Each sample was in turn stirred at 500 rpm for two minutes and then 200 rpm for 8 minutes. Just after the start of stirring, the allotted quantity of flocculant solution was introduced into the MFT, using a pipette under the surface to ensure thorough distribution. The syringe was rinsed with the MFT to ensure all the flocculant went into the MFT. This technique was used throughout the experiments; flocculation is known to be sensitive to factors such as stirring speed and duration[43], and container shape[44], and so it is important to be consistent. For the rest of this paper, this technique will be referred to as the Standard Flocculation Technique. The quantities of solution used were 0, 500, 1000, 1500, 2000 μl, corresponding to nominal trials of blank MFT, 500, 1000, 1500, and 2000 ppm volume/mass.

After the mixing step, the samples were poured into measuring cylinders to a level of 73 ml. They were sealed and allowed to settle undisturbed for 72 hours.

Various tests were then performed to determine the efficacy of 3-amino as a flocculant, including mudline, Capillary Suction Time (CST), and solids content. Note that percentage change in mudline is the same as percentage reduction in tailings volume. These tests are used throughout this work and were performed as follows.

Mudline and total fluid level were measured visually using 1ml markings on a measuring cylinder, taking care to ensure that the sightline was in a horizontal plane and that the measurement was taken at the bottom of the meniscus, where present.

CST is a measure of how well a sample can be dewatered using capillary action. This is a relevant metric if the sample will be dried using a belt filter, or by deposition on top of a fine-grained soil, both of which make use of capillary action. It was measured using a Triton Type 319 multi-CST machine and Jackson brand filter paper. The test works by measuring the time taken for water to move a certain distance along the paper after the moist sample is placed on it.

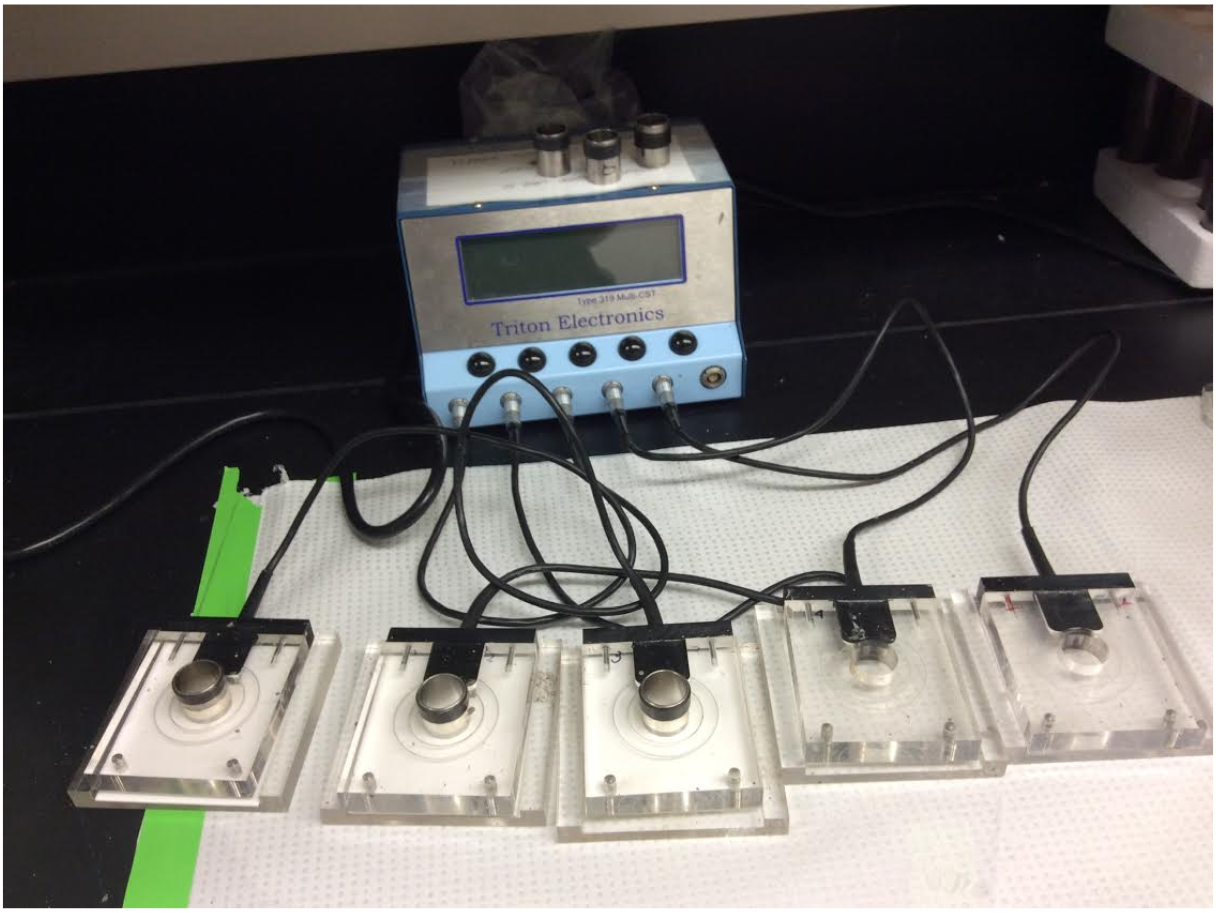


Figure 3.8: CST machine with 5 measurement heads.

The sensor and annulus were placed on the filter paper, with the textured side up. The annulus was filled with tailings, MFT or sediment using a pipette, ensuring that the sample was fully in contact with the circle of filter paper below the annulus and that there were no air bubbles.

Some samples were too viscous to draw into a pipette. In this case they were spooned into the annulus with a spatula. The sensors detect when the filter paper has become damp and the time taken for the dampness to spread between the sensors is measured automatically by the machine.

Solids content was measured by calculating the ratio of dry mass to wet mass. The mass was measured before and after drying in a fan-assisted oven at 60°C overnight. The dry mass was measured immediately after removal from the oven in order to prevent adsorption of atmospheric water.

3.2.2.2 Results and discussion

Figures 3.9 to 3.11 show the mudlines, ie MFT volumes, CST and solids content of the samples respectively.

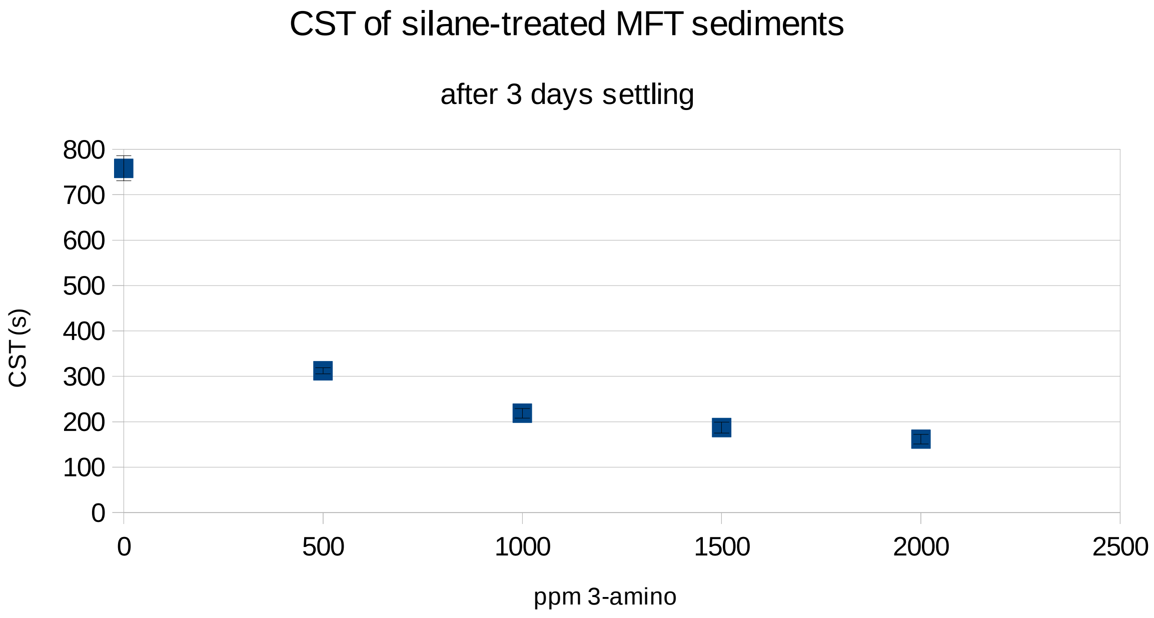


Figure 3.9 CST of silane-treated sediments.

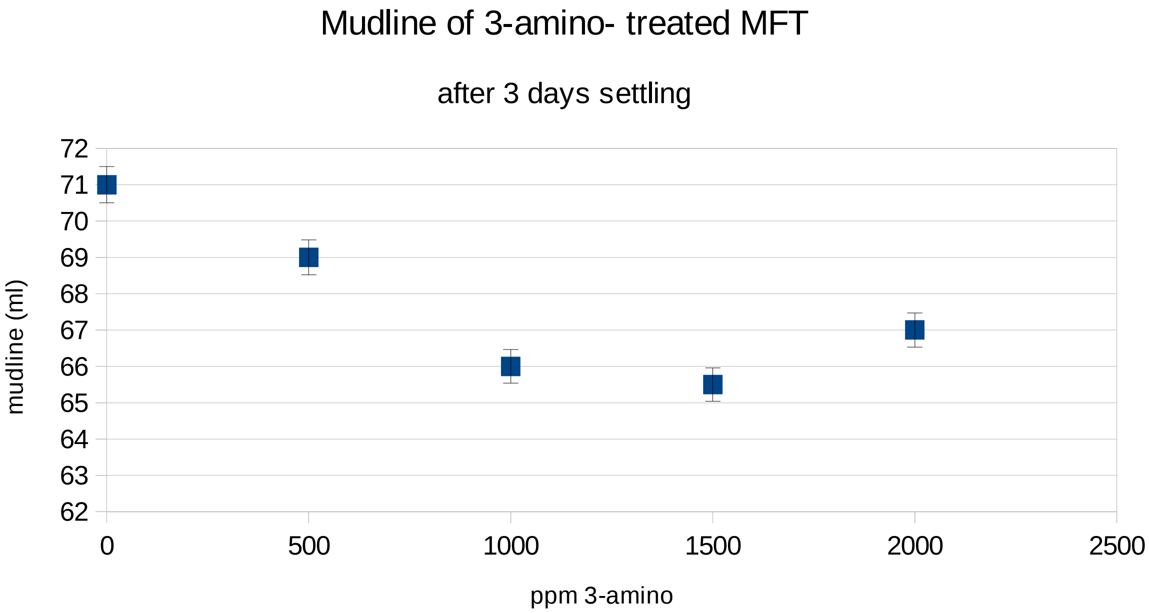


Figure 3.10 Mudline of 3-amino-treated MFT.

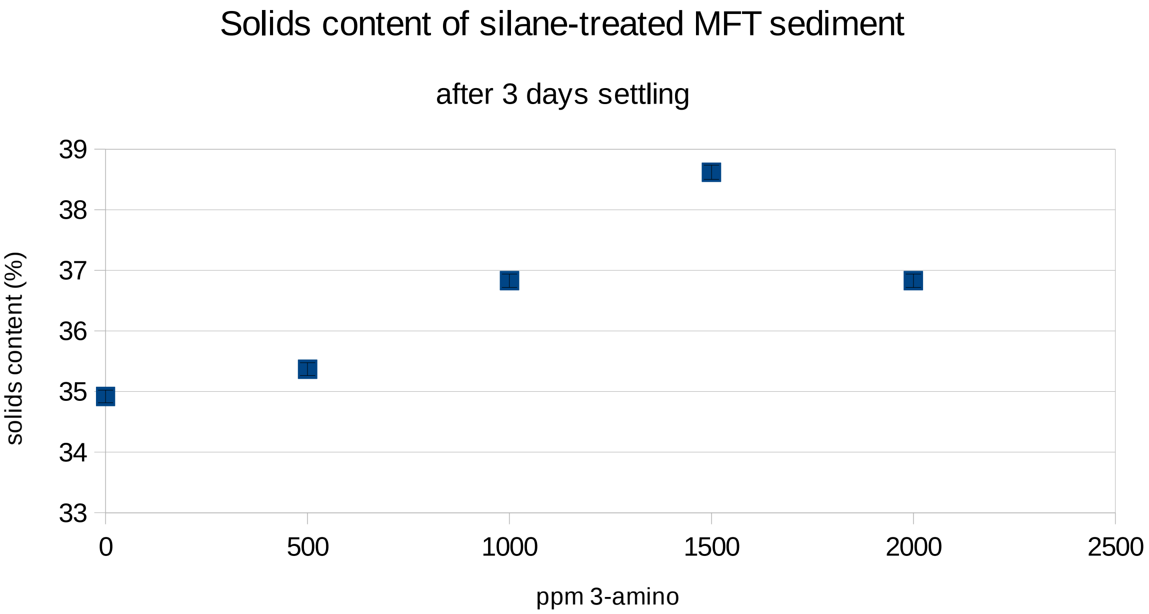


Figure 3.11 Solids content of silane-treated MFT sediment.

The results show a clear, dose-dependent improvement in properties after treatment with 3-amino. The mudline test showed an optimum at 1500 ppm, after which more flocculant was deleterious.

As expected given this result, the sediment solids content also increased up to 38.6% at 1500 ppm and then dropped. This is because the mudline is an indicator of the degree of separation between solid and liquid phases- a lower mudline means that there is more free water and so the sediment must contain a higher proportion of solids, as well as having a smaller volume.

CST did not show an optimum at 1500 ppm, but continued to decrease slightly. If greater doses of flocculant were used, the CST will probably tend asymptotically to about 250 s or else show an inversion point around this value. This characteristic is common to many conventional polymer flocculants, viz it is possible to overdose on flocculant. This overdosing causes reduced performance and stabilisation instead of flocculation.

The pH of the stock solution, sediment and release water were also measured. The MFT was neutral, the stock solution was alkaline (pH 11) and the sediments and release water showed alkalinity which increased with 3-amino concentration.

Treatment with 3-amino improves the properties of MFT with respect to solid-liquid separation. Moreover, this is not due to pH change, since pH increased slightly with addition of 3-amino and we expect properties of MFT to get worse in alkaline conditions (see Section 5.6). It seems that the effect is therefore due to flocculation.

Since 3-amino is an effective at treating MFT, it is likely that some structurally similar alkoxysilanes are also effective. The main body of the experiments, therefore, tested five distinct alkoxysilanes. For each compound/dose combination, the same tests were conducted after centrifugation and, separately, after normal gravity settling.

Before these systematic experiments were done, however, tests were conducted using “in-situ hydrolysis”. It was hypothesised that the bis-amine might work to reduce CST even if it were not oligomerised first in a separate step, because it might form oligomers inside the MFT and directly cause flocculation as soon as these oligomers were formed. The same hypothetical effect might occur with 3-amino.

3.2.3 In-situ hydrolysis tests

From the preliminary experiments, it was found that bis-amine and 3-amino are affected differently by contact with ethanol/water solution. Bis-amine rapidly turned into a solid gel at room temperature – indicating excessive condensation reactions - , whereas 3-amino was apparently unaffected by 30 minutes at 60°C. Even after two weeks at room temperature, the solution was only slightly cloudy.

Since it is impractical to mix the bis-amine with ethanol/water solution prior to introducing it to MFT, it was decided to try adding it directly to MFT, without the hydrolysis step. Hydrolysis is expected to take place in the MFT itself, and this may be just as effective, or more so, than external hydrolysis, because the monomers are expected to bond to the clay first and will already be homogeneously dispersed throughout the MFT when polymerisation takes place. Therefore there is no risk of the polymer remaining – and only acting in - localised “hotspots”, as for conventional polymer flocculants. Additionally, in these conditions there are two effects which tend to reduce the degree of branching which occurs, relative to using a “pre-hydrolysis” step in aqueous alcoholic solution. These are:

1. when dispersed in a dilute solution, self-condensation reactions will be slower;
2. hydrolysed intermediates will likely bond to a clay particle on at least one -OH group, preventing condensation at that group.

In-situ oligomerisation may be effective because monomers will quickly bond to the surface of one of the many small particles, so that long chains are possible despite the high ratio of water to silicon promoting colloidal particle formation. For comparison, 3-amino was also tested using the same procedure.

3.2.3.1 Methods and observations

A small quantity of the alkoxysilane in question was withdrawn from the sealed bottle using a syringe and stored in a covered container with minimal headspace for the duration of the experiments. The Standard Flocculation Technique was followed, except that the pure alkoxysilane was added instead of hydrolysed alkoxysilane solution. The concentrations of alkoxysilane tested were 500, 1000, 1500 and 2000 ppm on a (mass alkoxysilane)/(mass MFT) basis. In all cases, the MFT was apparently unaffected by the end of the fast stirring stage. However, it became viscous by the end of the slow stirring stage, and the viscosity increased with the dose of alkoxysilane.

The pH of the sample was also measured. The sample was split between a measuring cylinder, for the settling tests, and a centrifuge tube for centrifugation tests. The settling sample was left undisturbed for 72 hours. The centrifugation sample was subjected to 910 g.

After centrifugation or settling, the mudlines (ie volumes) were noted and the sediments tested for CST and solids content.

3.2.3.2 Results and discussion

The graph in Figure 3.12 shows a comparison of CST for the sediment after settling for 72 hours for 3-amino and bis-amine.

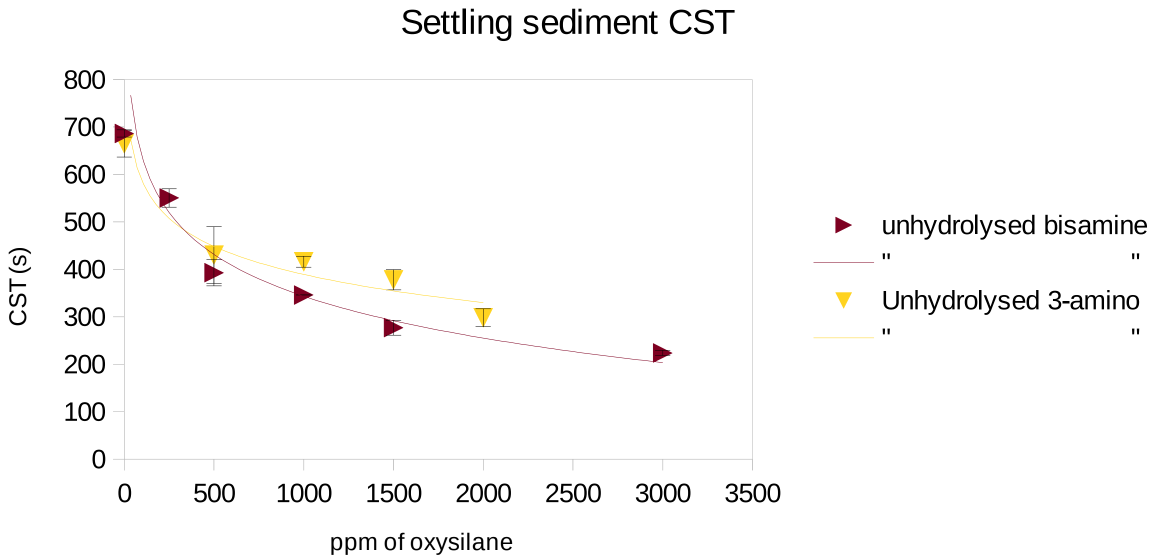


Figure 3.12 CST of gravity-settled sediments.

Figure 3.13 shows the drop in mudline (ie reduction in volume) following treatment with alkoxysilane.

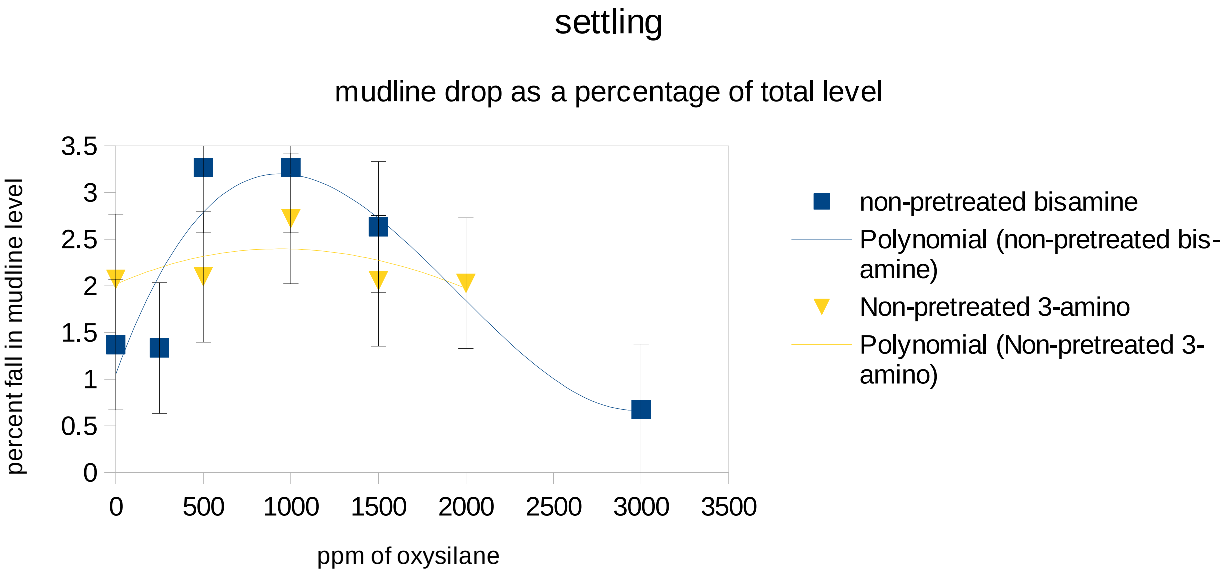


Figure 3.13 Settling for unhydrolysed alkoxysilanes.

The pH of the samples increased slightly with dose of alkoxysilane, as Table 3 shows:

Table 3: pH of treated sediments

Alkoxysilane concentration (ppm)	**0**	**500**	**1000**	**1500**	**2000**
Bis-amine sediment pH	7.63	7.92	8.13	8.43	8.46
3-amino sediment pH	7.64	8.02	8.43	8.84	9.18

In Figure 2.3.2.1, it can be seen that bis-amine and 3-amino treatments have similar trends; there is a steep drop in CST at a relatively small dose of alkoxysilane, followed by further, but diminishing, reductions thereafter. Bis-amine is more effective than 3-amino over most of the range tested.

Silane treatment also improves settling and reduces the volume of waste, as shown by the graph of mudline. On the other hand, the mudline shows an optimum dose, which is followed by decreased performance. This is the same as what was found in Section 3.2.2.

The pH increases with alkoxysilane treatment, because the alkoxysilanes have high pH. Increased doses have a diminishing effect, due to the logarithmic nature of pH and the buffering capacity of the suspended clay in MFT.

Figure 3.14 compares CST for the two in-situ tests and hydrolysed 3-amino.

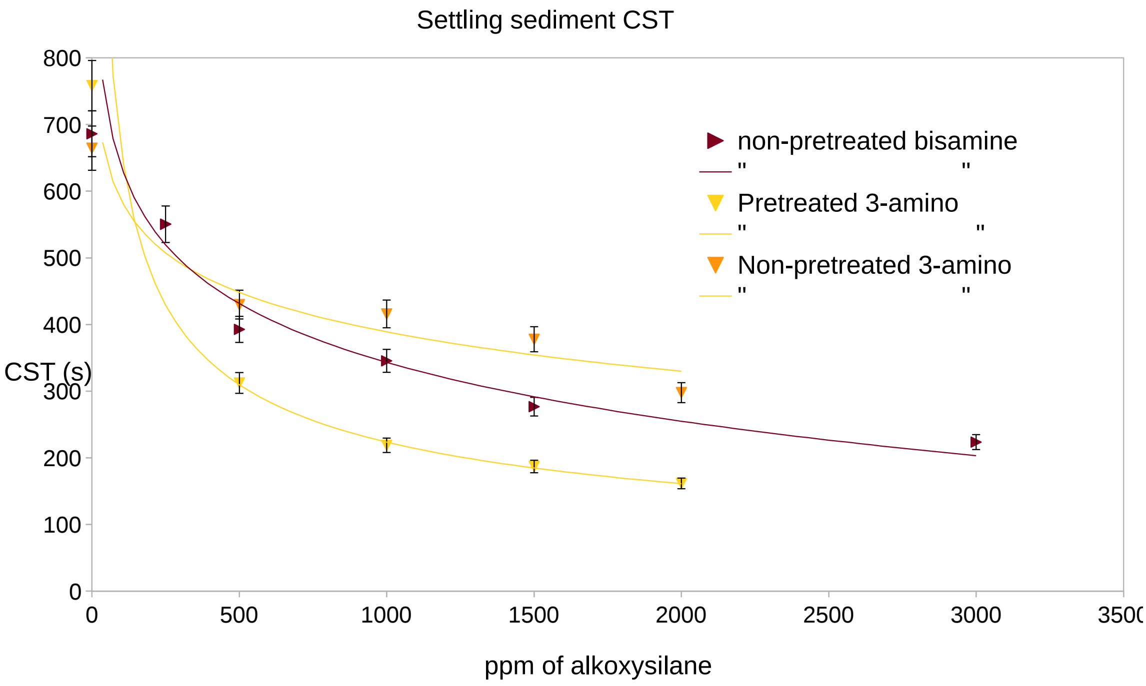


Figure 3.14: CST of gravity-settled sediments.

Figure 3.14 shows that pre-treatment hydrolysis has a significant effect on 3-amino performance; the same concentration shows greatly improved performance after the hydrolysis step. There are two possible explanations for this behaviour: either it is an independent effect of ethanol; or it is the result of the pretreatment step of reacting 3-amino with ethanol. The control experiment outlined in the next section was performed to determine which was dominant.

3.2.4 Control for ethanol

3-amino performed better with the pre-treatment step (reaction in the presence of ethanol, at 60°C for 30 minutes), than in the in-situ tests (adding 3-amino directly to MFT). The aim of the pretreatment step was to hydrolyse the 3-amino, so that it formed oligomers which would be more effective flocculants than 3-amino monomers. However, it was also thought that 3-amino might form oligomers in MFT, without pretreatment with ethanol. After testing this hypothesis, it was shown that in-situ 3-amino *did* improve the dewatering properties of MFT, but 3-amino with pretreatment was even better. It was not clear, however, if this was simply due to the ethanol used in pretreatment having flocculation effects of its own. To determine whether the efficacy of 3-amino is improved by ethanol, or ethanol is itself effective, a control test was performed with ethanol in MFT, but in the absence of any alkoxysilane.

3.2.4.1 Methods and observations

Three beakers each containing 200 g MFT were prepared, and flocculation tests performed with pure ethanol solution. The quantities used in the tests corresponded to the amounts of ethanol solution used in tests using 0, 1000 and 2000 ppm of alkoxysilane. The Standard Flocculation Technique was followed, and 0 ml, 2 ml and 4 ml of 80% ethanol in aqueous solution were added respectively to each beaker. The three samples were then allowed to settle for 3 days.

3.2.4.2 Results and discussion

Figure 3.15 shows the mudline for the three concentrations of ethanol solution tested:

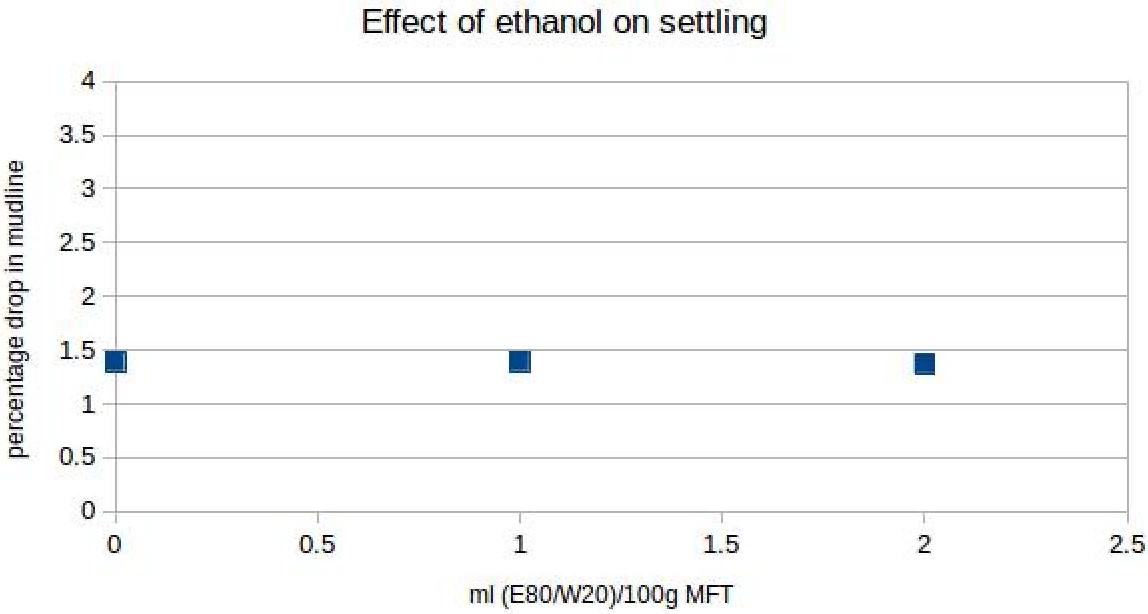


Figure 3.15 Control for ethanol, showing no change in volume reduction.

Additionally, the CST was measured for the central data point, and found to be 776.4 seconds, which is comparable to, but slightly higher than, the CST of untreated MFT sediment.

Ethanol solution has no discernible effect on MFT settling, and may be slightly detrimental to CST. Since the performance of 3-amino is improved with the ethanol pretreatment step, it is reasonable to conclude that it is ethanol hydrolysis, and concomitant oligomerisation, that is important in improving the properties of MFT.

3.2.5 Determination of optimum centrifugation time

For the rest of the experiments, in which alkoxysilanes will be compared for efficacy in gravity settling and centrifugation settling, it is necessary to choose a consistent technique for the centrifugation tests. The conditions of this technique should give sufficient separation of solid from liquid, but should be gentle enough that there is variation due to the presence or absence of alkoxysilane. As well as time and centrifugal force, other parameters, such as volume and timing should be fixed. These other parameters are relatively easy to select- a fixed volume of 50 ml was chosen (or one full centrifuge tube), the centrifugation was done within two hours of the flocculation, and the tests on the centrifugation samples were done within two hours of centrifugation.

The next section outlines the experiments done to find a suitable conditions of time and effective force. For convenience, and easy comparison to gravity settling, the centrifugal force is given in terms of g, the gravitational force on the surface of the earth.

3.2.5.1 Methods and observations

Five different concentrations of bis-amine in MFT were each centrifuged at 910 g for 10 minutes and 64 minutes. After ten minutes, the separation between liquid and solid phases increased with dose of bis-amine. After 64 minutes, all concentrations showed very good separation and a clear liquid phase.

3.2.5.2 Results and discussion

Figures 3.16 and 3.17 respectively show the mudlines after 10 minutes and after 64 minutes at 910g.

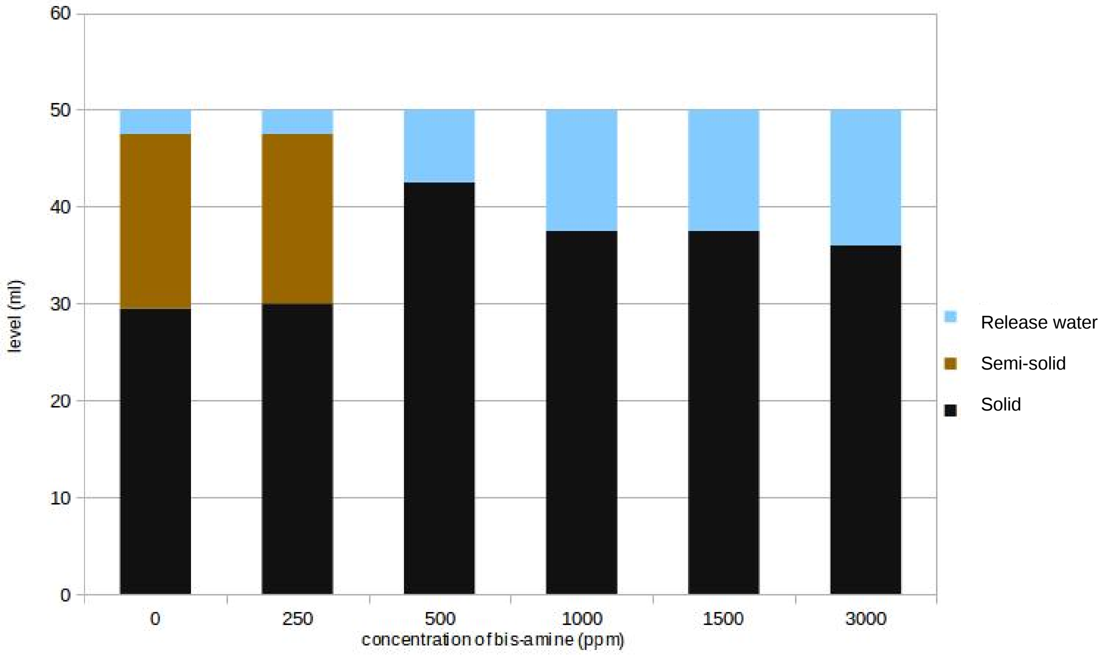


Figure 3.16 Graphic showing upper and lower mudline heights after 10 minutes centrifugation. Error: +/-1ml

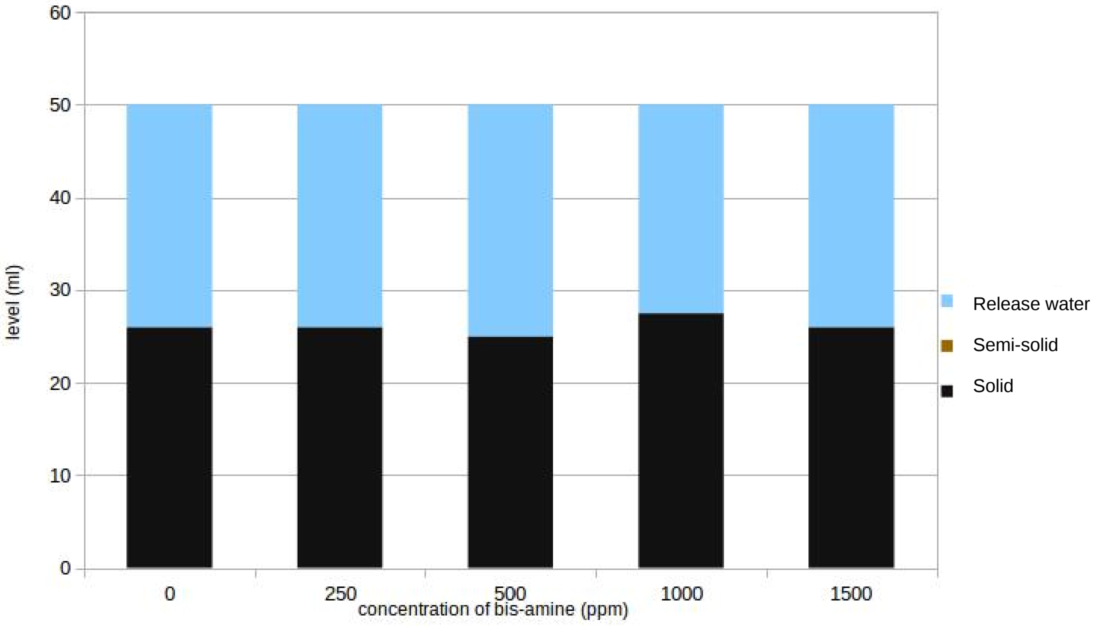


Figure 3.17: Graphic showing mudline heights after 64 minutes centrifugation. Note that here, there is only one mudline. Error: +/-1ml

After 10 minutes, the release water was turbid for 0 and 250 ppm bis-amine, and clear for doses of 500 ppm and above. After 64 minutes it was clear at all concentrations.

The longer centrifugation time separated solids and liquid well to effectively discriminate between doses of alkoxysilane– all concentrations gave very good separation and there was no difference between high and low doses of alkoxysilane. The shorter centrifugation time, 10 minutes, did show the effect of adding alkoxysilane; higher doses produced better separation, while lower doses gave a smaller amount of solid and an intermediate semi-solid material (which was either a very viscous liquid or very soft solid) indicating that only partial separation occurred.

This result suggests that 10 minutes is a better centrifugation time. It gives good divergence in settling between alkoxysilane dose and so this centrifugation time was chosen as the time for further experiments.

3.2.6 Determination of suitability for hydrolysis

The previous experiments demonstrated that a pre-hydrolysis step had a favourable effect on the alkoxysilane's flocculation ability. However, this effect can only be realised if the alkoxysilane remains a liquid, since a solid will not disperse in the MFT. Therefore, the two other monomeric alkoxysilanes to be tested (glicyl and metha) were subjected to the same reaction conditions as bis-amine and 3-amino in the preliminary experiments. 10% vol alkoxysilane was dissolved in an 80% ethanol/20% water solution, and held at 60°C for 30 minutes. Both alkoxysilanes dissolved readily and they were not visibly affected after 30 minutes – they were still clear, colourless solutions. The experiment was continued for 24 hours. The status of the solutions was checked periodically, and they only began to show cloudiness toward the end of the 24 hours. This result is in agreement with Salon, Bayle et al, who conducted hydrolysis tests on metha, 3-amino and other alkoxysilanes and found that 3-amino reacted much faster than the others[45] (they did not perform tests on bis-amine). For clarity, table 4 shows whether the Standard Hydrolysis Technique should be used.

Table 4: Suitability of Standard Hydrolysis Technique by alkoxysilane.

Oxysilane	**notes**	**Standard Hydrolysis Technique appropriate?**
Bis(3-trimethoxysilylpropyl)amine (Bis-amine)	Turned cloudy and solid within 3 minutes at room temperature.	no
3-aminopropyltrimethoxysilane (3-amino)	Remained a clear, colourless solution	yes
(3-glycidoxypropyl)trimethoxysilane (glycil)	Remained a clear, colourless solution	yes
methacryloxypropyltrimethoxysilane metha	Remained a clear, colourless solution	yes
Tetramethoxysilane (oligomer) (tetra)	Already oligomerised	no

3.2.7 Main experiments

3.2.7.1 Methods and observations

The remaining alkoxysilanes were tested for their ability to dewater MFT, using the same method as in the preliminary experiments:

1. hydrolyse as per the Standard Hydrolysis Technique, if appropriate;

2. add to 200 g of MFT, following Standard Flocculation Technique;

3. divide sample into settling and centrifugation streams;

4. settling at normal gravity for 3 days; centrifugation at 910 g for 10 mins;

5. measure mudline, sediment CST and solid content for both streams.

The mudlines for the centrifugation tests posed a problem not encountered under gravity settling- many, although not all, centrifuged samples showed two distinct mudlines. Where this occurred, there was a supernatant layer of clear or slightly turbid water, overlying a layer of very turbid liquid or semi-solid sludge, and finally a layer of firm solid at the bottom. The pertinent question, then, is where to measure the mudline, and on which layer is it most appropriate to measure CST.

Both mudlines were measured, but the upper mudline is the most relevant here, for the following reason. The middle layer, consisting of a very turbid liquid or semi-solid, can not be legitimately treated as either water or solid waste. It most closely resembles the original MFT, and in practice it would probably be returned to the MFT holding space to be treated a second time. On the other hand, the difference between the total level and the level of the upper layer, determines how much water is released from the MFT, which is a useful parameter. This water can either be re-used in an oilsands plant or disposed of after minimal further treatment. The bottom layer, which is a firm solid, is probably hard enough and dry enough to be disposed of as landfill. It may require some further dewatering, but is likely to resist further settling by gravity, so capillary suction time is relevant to measure further potential for dewatering. For the purposes of comparison, therefore, the upper mudline was used to compare settling performance under centrifugation, and the bottom layer was measured for CST.

3.2.7.2 Results and discussion

Figures 3.18 and 3.19 show the percentage of settling, for gravity and centrifugation tests respectively.

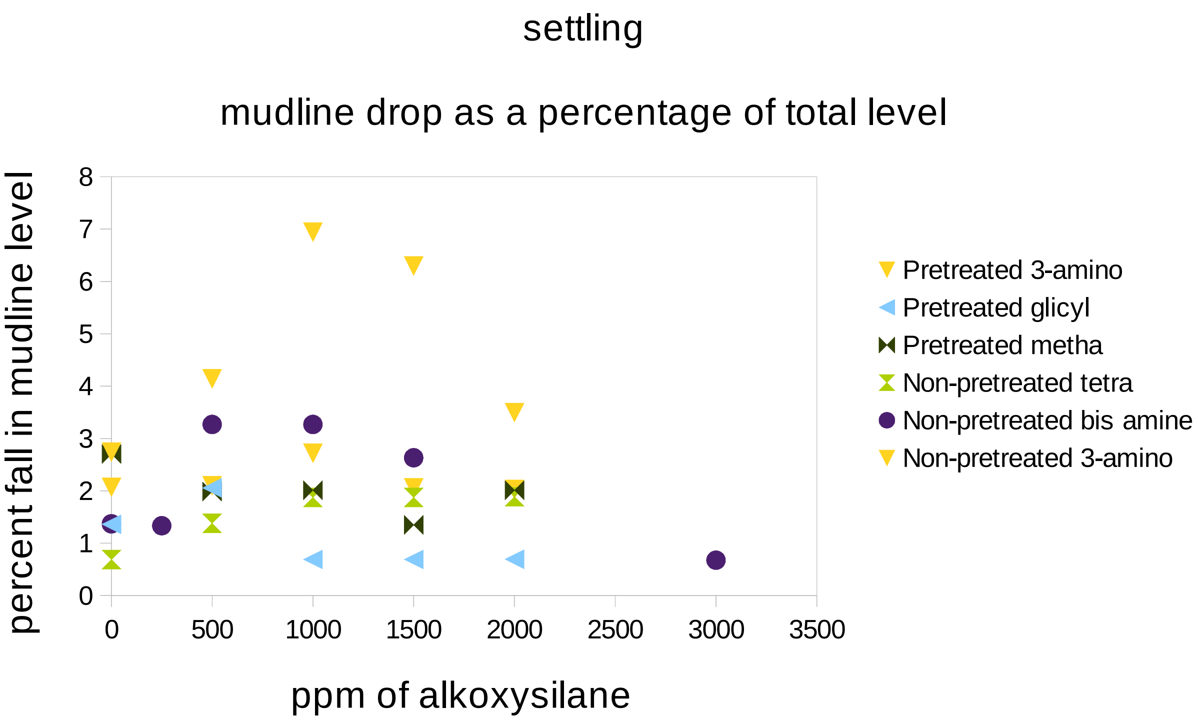


Figure 3.18 Mudline drop for all alkoxysilanes. Error (+/-) 0.7 percentage points

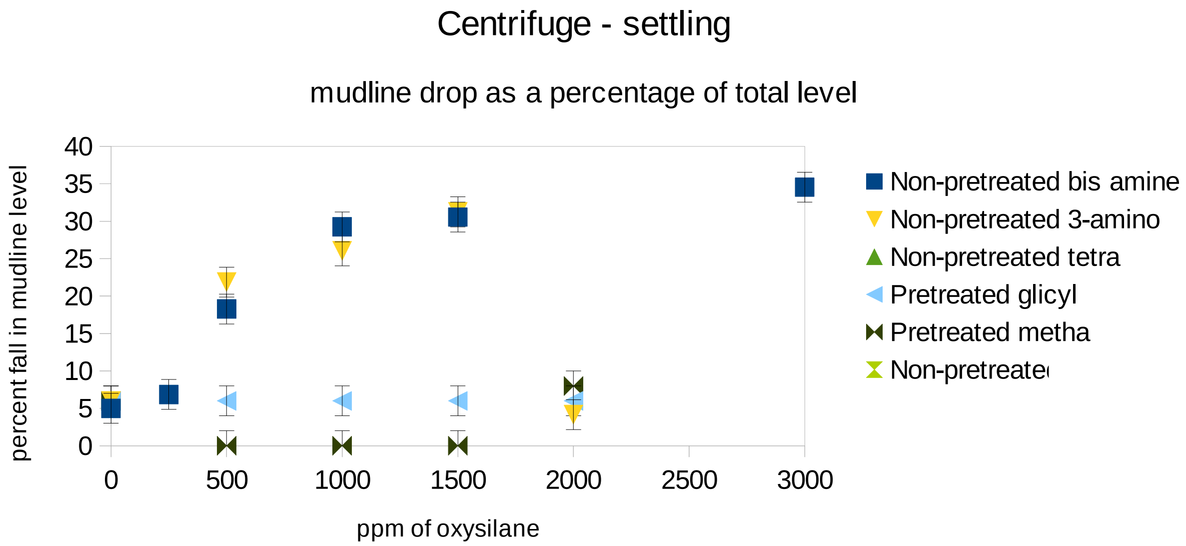


Figure 3.19: Mudline drop with centrifugation for all alkoxysilanes

Figures 3.20 and 3.21 show the CST of sediments derived from gravity settling, and centrifugation, respectively.

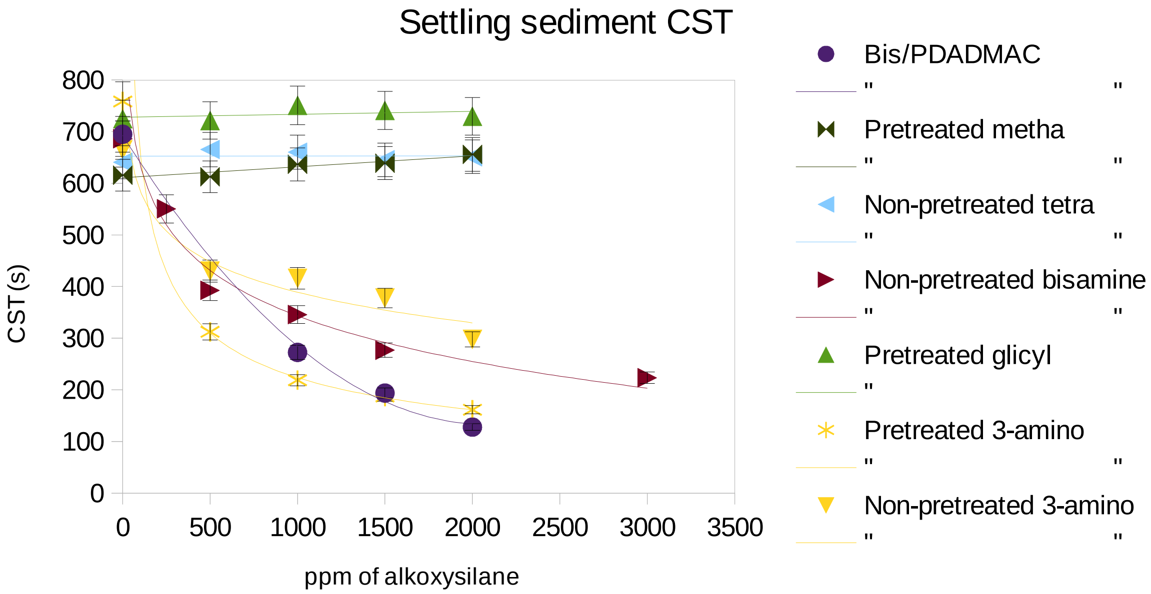


Figure 3.20: CST of sediments

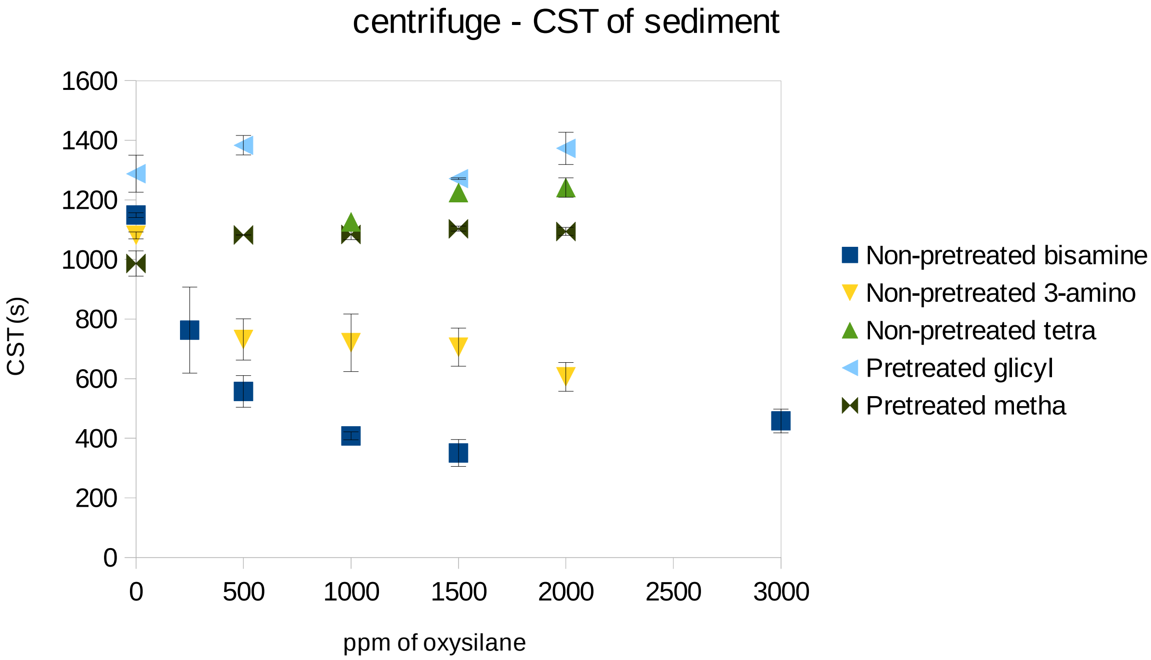


Figure 3.21: CST of centrifuge sediments

The results above show the two metrics used for determining improvement in MFT properties, for gravity and centrifugation paths. Let us first discuss the results for gravity settling.

Of the five alkoxysilanes tested, bis-amine and 3-amino showed an improvement in consolidation and volume reduction, as measured by mudline drop. The drop is small, but given the already high solid content of MFT, removal of even 7% of the water, as measured for a concentration of 1000 ppm of 3-amino, will have a significant impact on the ratio of solids to water (32:61 versus 32:68), and on the yield strength of the material, particularly when mixed with sand in a process such as the composite tailings process.

The most obvious improvement, however, comes in CST. Again, 3-amino and bis-amine are the two alkoxysilanes with the most significant effect. As noted previously, hydrolysed (ie pretreated) 3-amino outperforms the unhydrolysed counterpart.

The settling under centrifugation tests is around 5% in the absence of alkoxysilanes. (Recall that this is settling to the upper mudline level, representing release of clean water). At 910 g, the net force after accounting for buoyancy is much greater than with gravity settling, but the time is also much smaller, and so the overall settling is similar.

However, it seems that the *relative* settling between alkoxysilane-treated and plain MFT is greater when it is subject to centrifugation. This is true for most of the alkoxysilanes, but not for 3-amino. For example, without alkoxysilanes and in normal gravity, MFT typically settles by 1.5%. Bis-amine only increased this to 3%. However, under centrifugation, the respective figures are 5% and 30% - a six-fold improvement.

The CST of centrifugation sediment is much greater than MFT – this is expected because the solids content is higher – about 50% compared with 30% - and hence the water content is lower. Since CST is a measure of how easy it is to remove water from sediments, this result is not unexpected. If there is less water in the material, it will be harder to remove and will not so readily migrate from the sediment under capillary suction. The bis-amine test gave the lowest CST, and also the best separation (there was only one mudline).

In terms of settling, the conventional polymer, PDADMAC, performed much better, as shown in Figure 3.22.

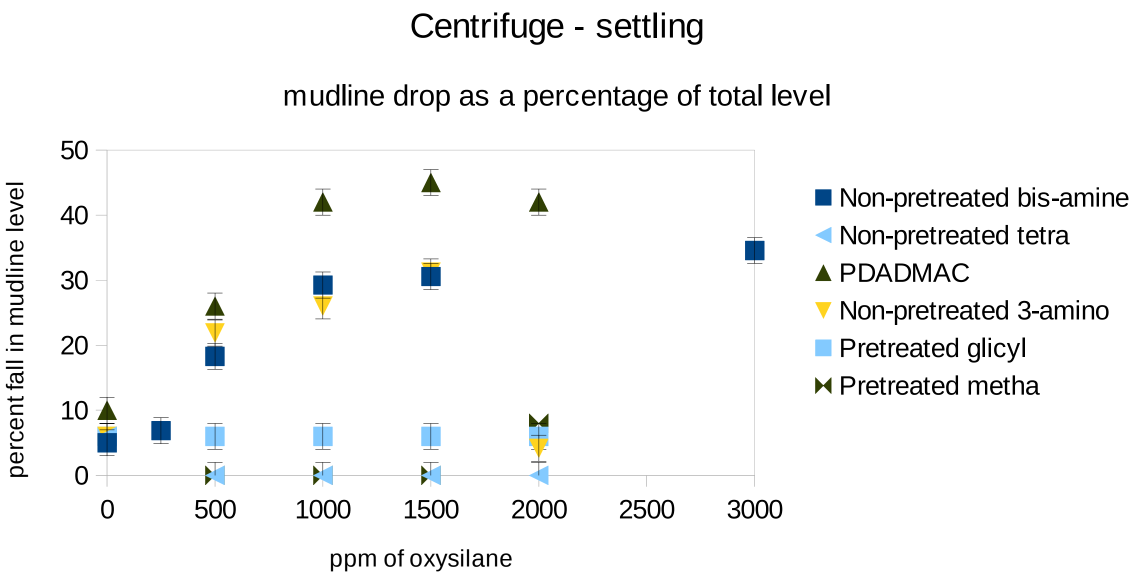


Figure 3.22: Centrifugation settling

However, bis-amine performed better than the polymer for CST, as shown in Figure 3.23.

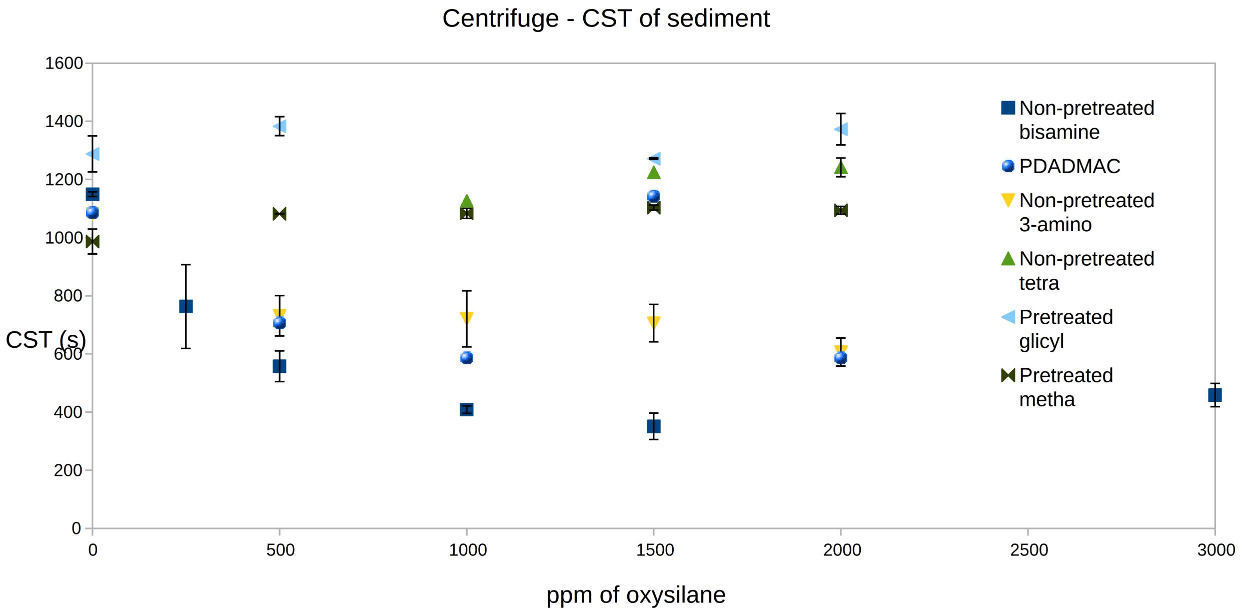


Figure 3.23 Centrifugation sediments CST

This is probably due to a combination of bis-amine being effective at reducing CST, and the higher mudline (ie lower solids content) in bis-amine compared with PDADMAC.

For the further tests, bis-amine was selected as the alkoxysilane to be tested. Bis-amine exhibits good reduction in CST and, unlike 3-amino, does not require a pre-hydrolysis step. This is important for a process such as MFT dewatering, which is done on a large scale, but per unit, is a low-value-added process. To ensure consistency, a repeat of the bis-amine tests was performed and similar results, within experimental errors, were found for settling and CST.

3.3 Further experiments

3.3.1 Different concentrations of ethanol/bis amine

To determine whether a useable bis-amine oligomer could be prepared in advance of flocculation, combinations of various concentrations of bis-amine, water, ethanol and ethanoic acid were prepared. As a rule these generally suffered from gel formation, with the rate increasing with water content. As an illustrative guide, Figure 3.24 shows, from left to right, 10% bis-amine in 80%, 50% and 20% ethanol solution, 200 seconds after mixing at room temperature. It was decided to proceed with in-situ hydrolysis for the further experiments, because in-situ gives promising results in terms of CST reduction in MFT and would be much more cost-effective in an industrial scenario.

Figure 3.24: Increasing Opacity of bis-amine with water concentration.

3.3.2 Effect of CO_2 saturation on bis-amine performance

3.3.2.1 Introduction

Since bis-amine hydrolysis is improved in acidic conditions, it was hypothesised that larger polymer chains would form and MFT properties would be further improved at low pH. Since dissolved CO_2 increases acidity, it seems reasonable that injecting CO_2 into MFT would improve polymerisation of alkoxysilanes. Furthermore, as discussed in chapter 2, MFT's dewatering performance is improved in acidic conditions, and indeed this technique is already in commercial use at Canadian Natural, where CO_2 is injected into MFT to increase water release and viscosity. To find which factor causes a greater improvement, an experiment was conducted to compare the CST and settling of MFT without bis-amine, in the presence of CO_2.

3.3.2.2 Methods and observations

A regulator was fitted to a CO_2 cylinder to provide a constant stream of gas at just above atmospheric pressure. This was conducted by a tube to a syringe, which was held in a fixed position in a container of MFT. The MFT was stirred continuously at 500 rpm to ensure thorough mixing.

A preliminary experiment was conducted to determine an appropriate length of time for CO_2 injection. In this experiment, the pH was measured periodically. When it stabilised, this was taken as the time at which the MFT was saturated with CO_2(ie no more will dissolve). It was found to stabilise at pH 6.22 after 1 hour.

After the preliminary experiment, two trials were conducted sequentially. In both trials, CO_2 was injected for one hour and then the standard technique was followed for adding alkoxysilane (two minutes fast stirring; add alkoxysilane (if not a blank test); 8 minutes slow stirring). One test was conducted without alkoxysilane, and the other with 1000 ppm unhydrolysed bis-amine. This concentration was chosen because it gives the optimum improvement in properties without CO_2. During this time CO_2 injection was continued, because stirring without CO_2 could cause the dissolved CO_2 to dissipate.

In both cases, the MFT became gradually more viscous with CO_2 addition. In the test with bis-amine, the viscosity increased markedly after addition of bis-amine. A froth also formed when the bis-amine was added.

3.3.2.3 Results and discussion

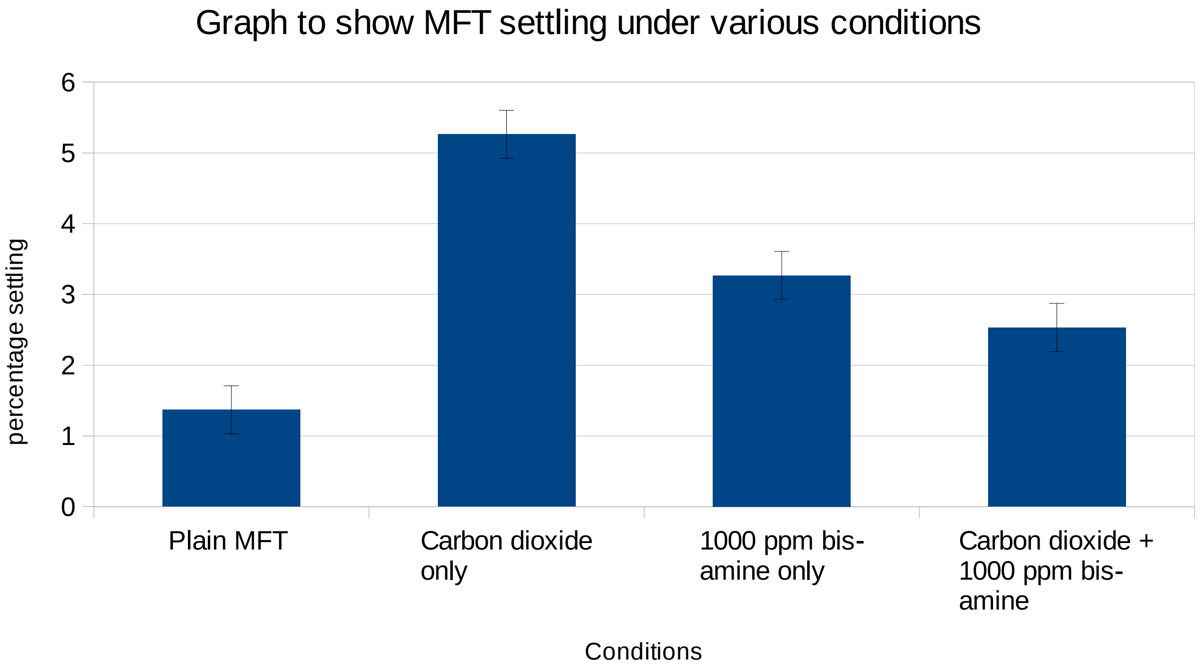


Figure 3.25 MFT settling comparison.

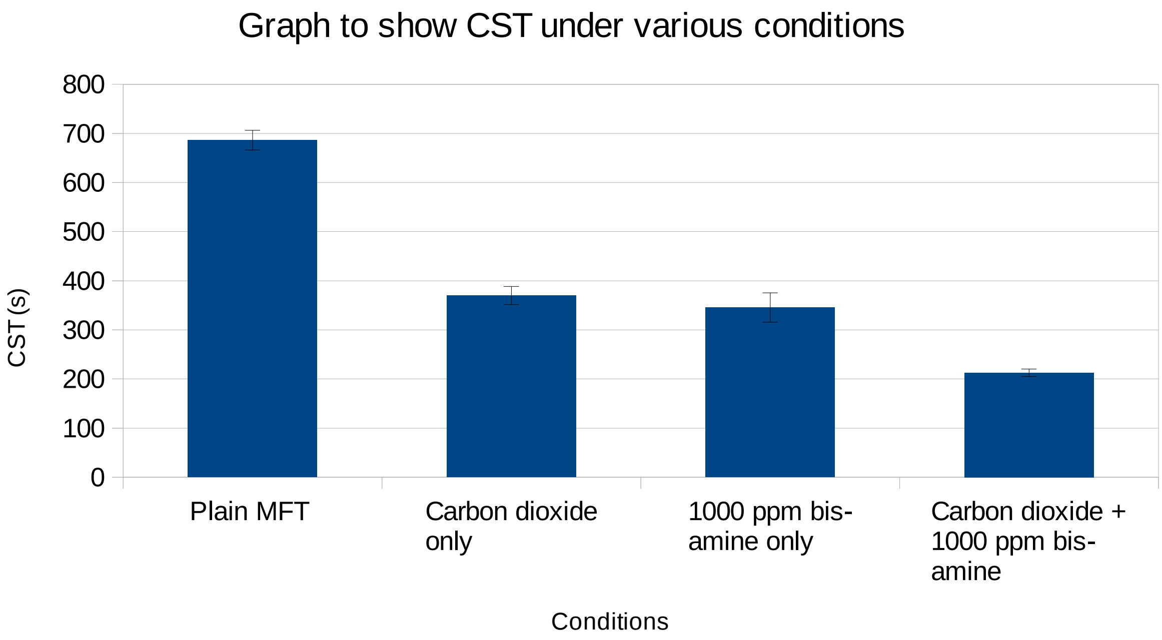


Figure 3.26 MFT CST comparison.

The results show that CO_2 has a marked beneficial effect on settling – larger than that obtained from adding bis-amine. This is no doubt due to the lower pH it causes. The test with both CO_2 and bis-amine showed worse performance than bis-amine alone, although the difference is small and within experimental errors. This result is contrary to our expectation that CO_2 would improve the performance of bis-amine.

For CST, both CO_2 and bis-amine cause an improvement, to a degree which is similar between the two. When combined the effect is even greater. This is in contrast to settling, where the combination was less beneficial than either alone.

It is possible that bis-amine has a stabilising effect on tailings. This can occur when a polymer bridges particles, but does not bring them closer together. This would explain why CST improved in bis-amine with CO_2, but settling did not. We can postulate two explanations for this: either the acidic environment of polymerisation affects the structure of the polymer formed, by changing the ratio of hydrolysis to condensation reactions for instance, or changing the degree of branching; or the CO_2 affects the hydrophobicity of the polymerised alkoxysilane, so that it is less attracted to itself. In acidic conditions, alkoxysilanes are more likely to form long, unbranched structures[ii]. Such structures are typically better flocculants than branched polymers, because for equal molecular mass, they are able to reach further and adhere to more and more distantly spaced particles. The bis-amine showed greater stabilisation in CO_2-saturated solution, however, which means there is another reason. It is possible that CO_2 affects the hydrophobicity of the bis-amine chain, making it more attracted to water, so there is less driving force for chain coiling and the resultant settling.

3.3.3 Whole tailings

While MFT is a concentrate of the clay solids in oil sands tailings, it is also useful to treat whole tailings so that clay particles can be removed and water returned, almost immediately. It takes a significant period of time for clay particles to settle naturally from oilsands tailings into the more dense MFT, with the result that tailings ponds must be large in order to have a viable rate of water availability. It is therefore potentially advantageous to treat oilsands tailings directly.

With this in mind, experiments were conducted on a whole oil sands tail, to determine whether bis-amine is able to flocculate the whole tailings. An ionic analysis of this material is shown in Section 3.5.

3.3.3.1 Method and observations

Whole oilsands tailings were homogenised and then divided into 200 g samples. The same stirring technique as for MFT was followed and bis-amine was introduced in the same manner. The dose range was from 0 to 200 ppm in intervals of 50 ppm, which corresponds to approximately the same range as for MFT, on a bis-amine-to-solids ratio.

The treated whole OST was allowed to settle under the influence of gravity for 3 days, and the mudline noted, and CST of the sediment was measured. Note that in OST, as in MFT, the volume of waste is reduced by an proportion equal to the proportion of mudline drop, and CST is also again a viable method for measuring the propensity for further dewatering.

3.3.3.2 Results and discussion

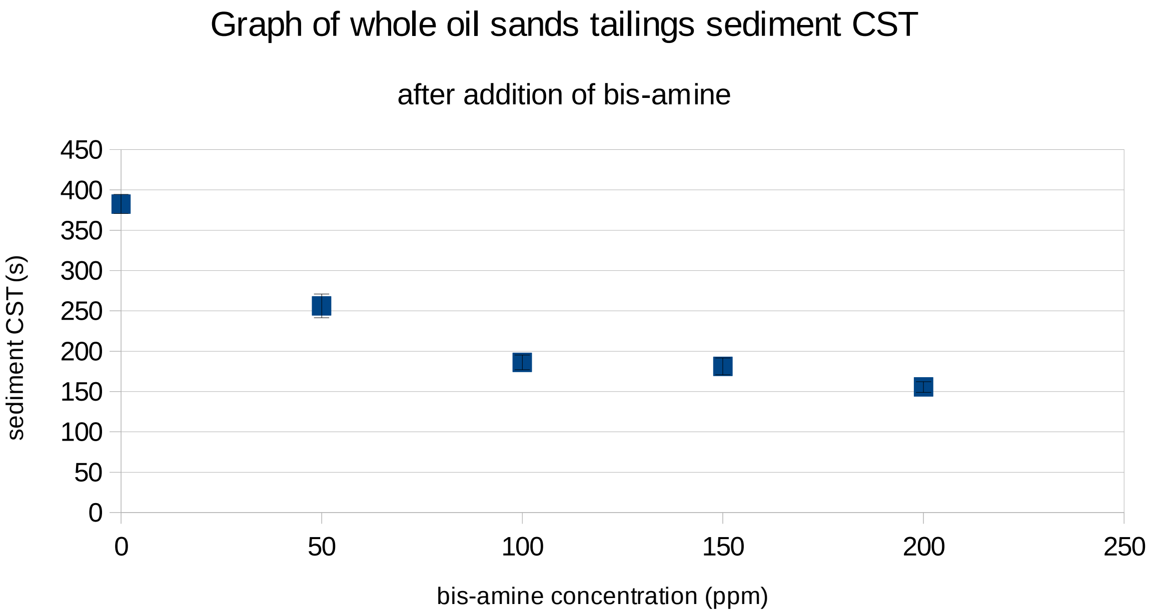


Figure 3.27: Effect of bis-amine on CST in oilsands tailings.

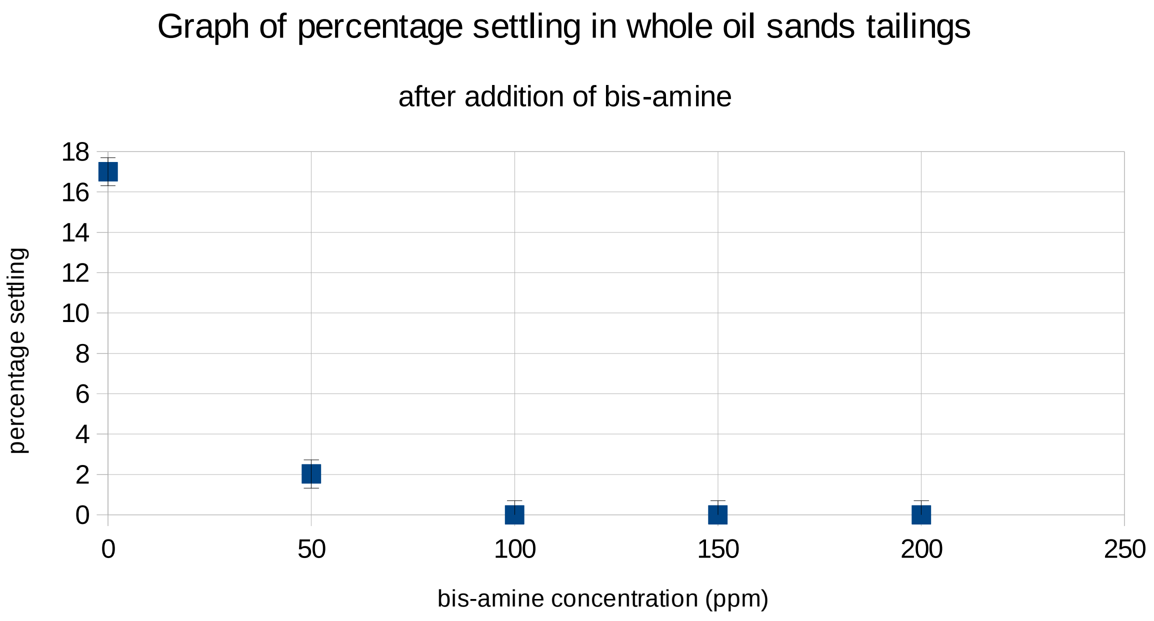


Figure 3.28: Percentage settling in bis-amine treated oilsands tailings.

Untreated whole oil sands tailings settles considerably in the space of three days, as demonstrated by the 0 ppm concentration of the first graph. This is because whole oil sands tailings is fresh and unstabilised- it settles readily at first, and continues to settle by diminishing degrees until MFT is reached- which is recalcitrant to further settling.

In contrast to our expectation that bis-amine would flocculate and improve the settling of whole oil sands tailings, it seems to have the opposite effect- that it prevents settling and stabilises the suspension.

However, it does improve the CST of the sediment that is formed. This is partially because the sediments with bis-amine contain more water, which means they will have lower CSTs because the water is necessarily easier to remove. This can not be the only effect, though, because sediment CST continues to decrease past 50 ppm, even though the stabilisation of settling is essentially complete by this point. It seems likely that bis-amine does indeed lower CST, even on an equal solids basis, while at the same time preventing settling of the tailings. This could be because the bis-amine bonds strongly to clay particles, but does not have enough attraction for itself to fold in and bring the clay particles closer together. This would mean that the clay particles remain suspended, held apart by a gel-like formation of bis-amine, but the water between clay particles is, nevertheless, able to escape from the gel when drawn out by another force, such as capillary suction. This would explain why CST is improved with increasing dose of bis-amine.

Whilst a decrease in CST is desirable, it is not desirable if it occurs at the expense of natural settling. A decrease in CST is only valuable if the oilsands tailings are subject to a capillary suction process, such as a filter belt or dewatering in layers on a hydraulically conductive substrate. As shown in this experiment, whole oil sands tailings will dewater significantly in a few days with minimal intervention, and so this process cannot be economic in its current state. However, the reduction in CST shows that bis-amine is effective to some degree, and further work should examine the ways in which oligomer structure and functional groups affect dewatering.

3.3.4 Combination with PDADMAC

3.3.4.1 Introduction

We have seen that bis-amine seems to have a stabilising effect on both whole oil sands tailings, and at high concentrations, on MFT. This effect is undesirable and competes with the beneficial improvement in CST. The improvement in CST is likely due to bonding between the bis-amine and clay particles, whereas the reduction in settling is likely because the oligomer chains repel themselves, so that the clay particles do not move closer to each other and remain suspended.

Conventional polymer flocculants bond with clay, but then furl in on themselves so that clay particles are brought together into flocs. It was thought that if a polymer were added to the suspension of clay particles bonded to bis-amine, then it might bridge the bis-amine oligomers and overcome their self-repulsion, so that flocs were formed. In addition, the alkoxysilane might act as a coupling agent and improve adhesion between the polymer and clay.

3.3.4.2 Methods and observations

Trials of flocculation in MFT were conducted with a 50/50 mix of PDADMAC and bis-amine. They were conducted in the range 0-2000 ppm, at intervals of 500 ppm (total, ie PDADMAC + bis-amine). The standard technique was followed.

The viscosity increased as the polymer was added, and the effect increased with dose of (bis-amine + PDADMAC).

3.3.4.3 Results and discussion

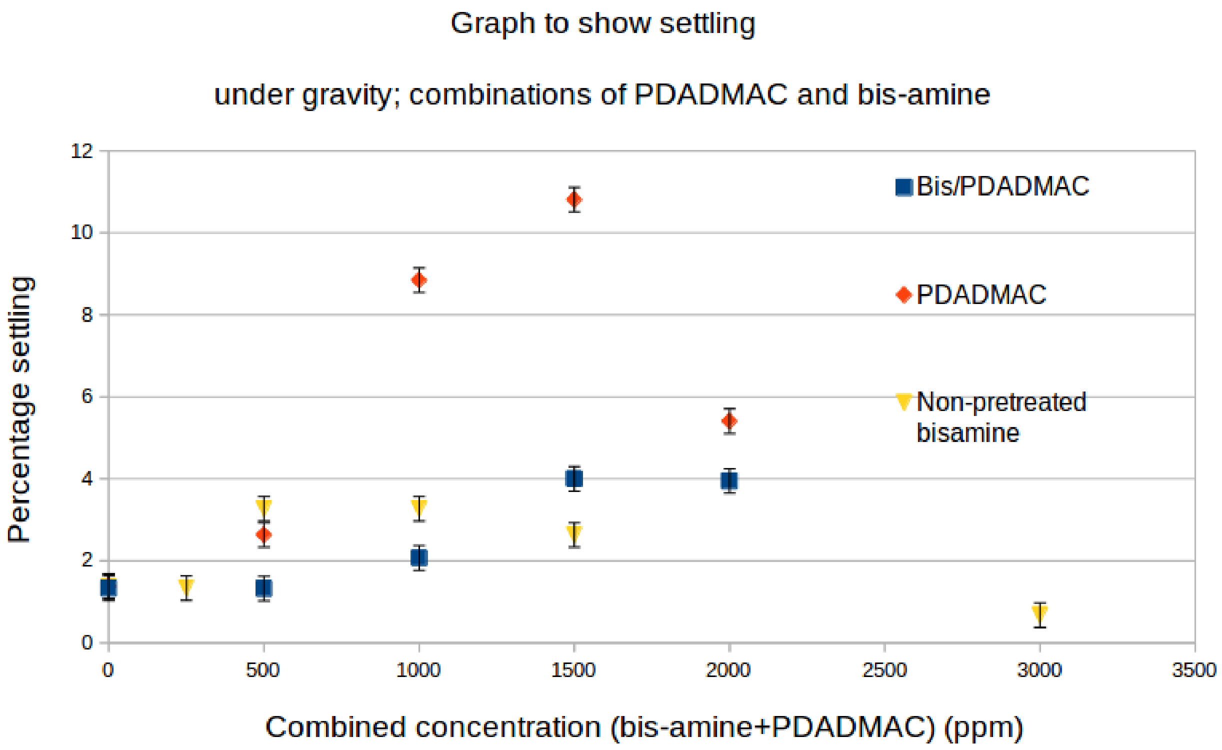


Figure 3.29 comparison of bis-amine performance with and without polymer (settling).

At their respective peaks, the polymer by itself causes much more settling than bis-amine by itself. The mix of the two falls short of a “rule of mixtures”, that is to say, bis-amine and PDADMAC are less than the sum of their parts, as regards settling. This could be due to increased stabilisation caused by bis-amine in the presence of PDADMAC, or vice versa, ie bis-amine causes PDADMAC to stabilise the suspension.

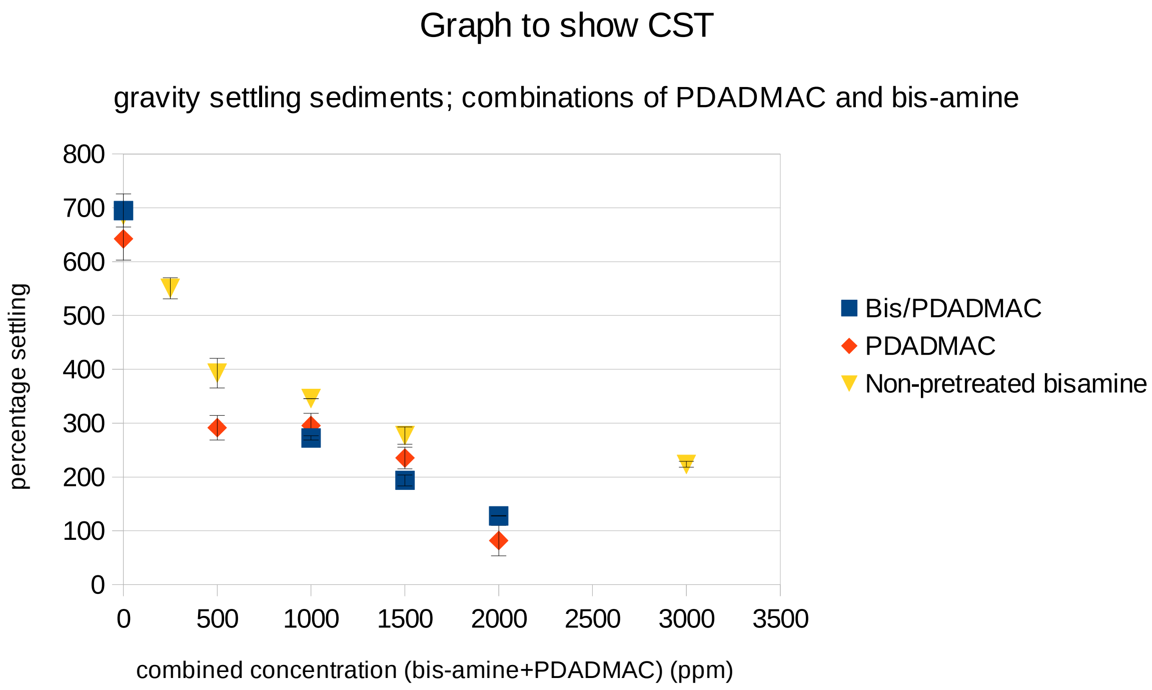


Figure 3.30: Comparison of bis-amine performance with and without polymer (CST).

All the combinations of polymer and alkoxysilane are broadly similar in their effect on CST, but it does indeed seem that, in the 1000-1500 ppm range, the combination is better than either component individually. Again, this could be a result of the relatively high settling in PDADMAC-treated MFT in that concentration range, meaning that the sediments contain less water and so have higher CSTs.

It seems that in order for there to be significant benefit from combining polymer with alkoxysilane, there should be stronger bonding between them than there is between PDADMAC and bis-amine.

3.3.5 Effect of pH in methanol hydrolysis

An alternative bis-amine pretreatment technique was tested, based on existing work in the literature[46]. The technique was designed to suppress condensation and favour hydrolysis reactions. Recall that acidic conditions favour hydrolysis over condensation. Recall also the hypothesis stated earlier that increased hydrolysis reactions would favour flocculation, since longer oligomer chains would be produced. Three different pH values were used to vary the relative rates of condensation and hydrolysis reactions.

3.3.5.1 Methods and observations

A solution of 90 parts methanol to 5 parts water was prepared. This was acidified using anhydrous ethanoic acid to a pH of 4, 5 or 6. 5 parts bis-amine was added. The resulting solutions were left to react for 18 hours. They were then used in the Standard Flocculation Technique at a concentration of 1000 ppm bis-amine. After 18 hours, the solution at pH 4 was colourless and completely clear, and the solutions at pH 5 and 6 showed increasing white cloudiness.

3.3.5.2 Results and discussion

The increasing turbidity of bis-amine solutions with pH supports the literature with regard to condensation reactions being favoured at high pH and hydrolysis at low pH. The percentage settling is shown in Figure 3.31 as a function of pretreatment pH.

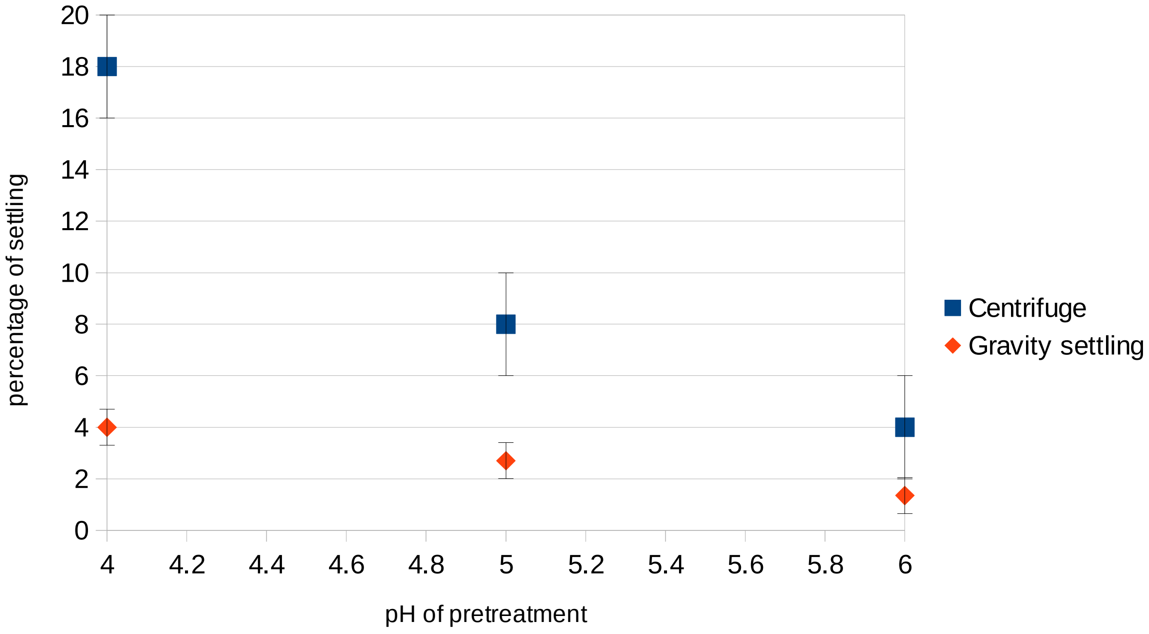


Figure 3.31: Percentage of settling as a function of pretreatment pH for centrifugation and gravity settling.

The degree of settling increases with acidity of pretreatment. This applies to both centrifugation and gravity settling. This supports the hypothesis that longer, less branched bis-amine chains would promote flocculation.

3.4 Appendix I: Error calculation

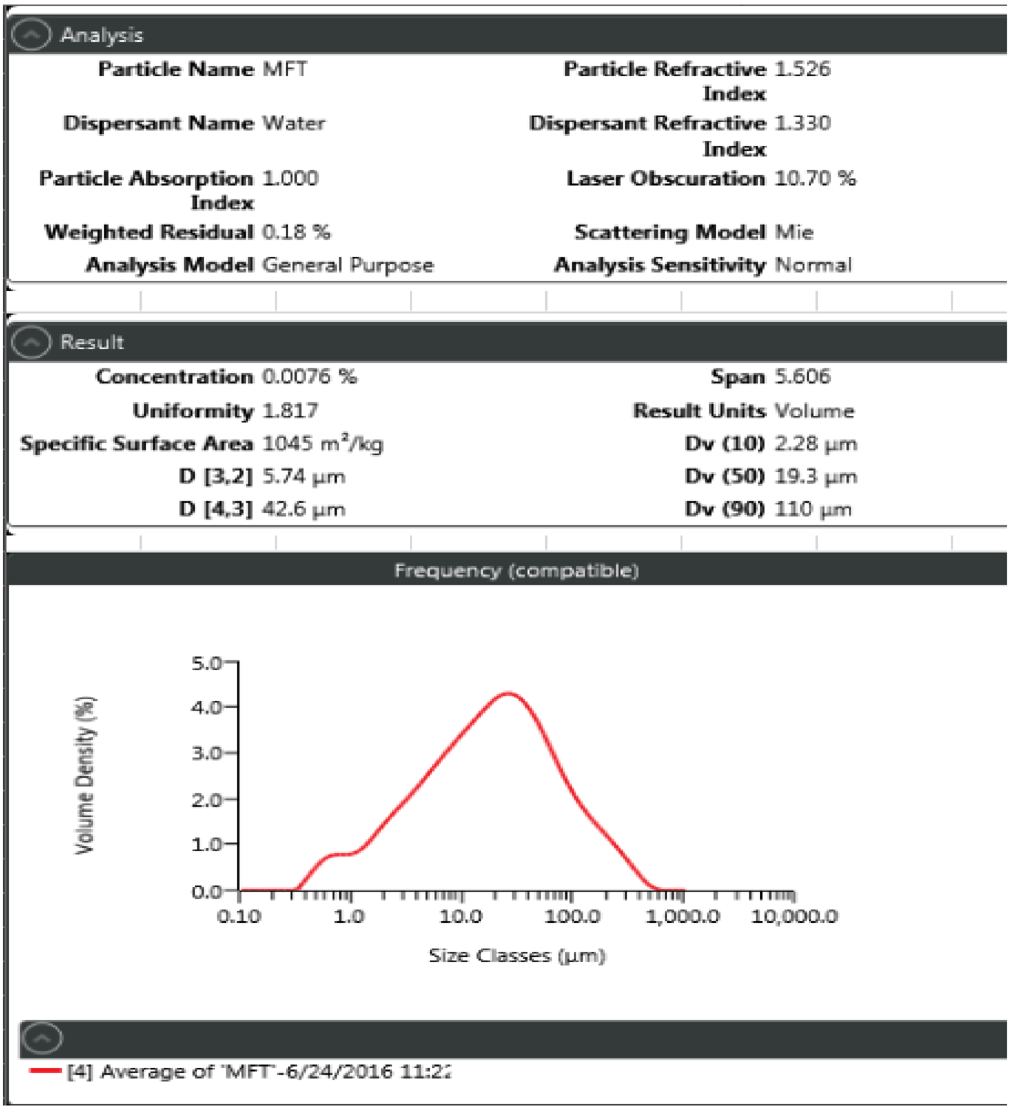
CST results show some random error, and for this reason the error bars are (+/-) the standard deviation of all results (ranging from 2 to 5 readings), plus equipment precision error. Wherever possible, the CST tests were repeated if the first two measurements differed by more than 10%, and the average and standard deviation were taken for all tests, unless there was a clear anomaly.

The other measurements are subject only to equipment precision error and the bars are calculated according to this.

For example, centrifugation mudlines have an error of +/-1 ml. The total volume is 50 ml. The percentage error is therefore:

(+/-)1 X 100/50 = (+/-)2%

3.5 Appendix II: Analysis of MFT



Analysis

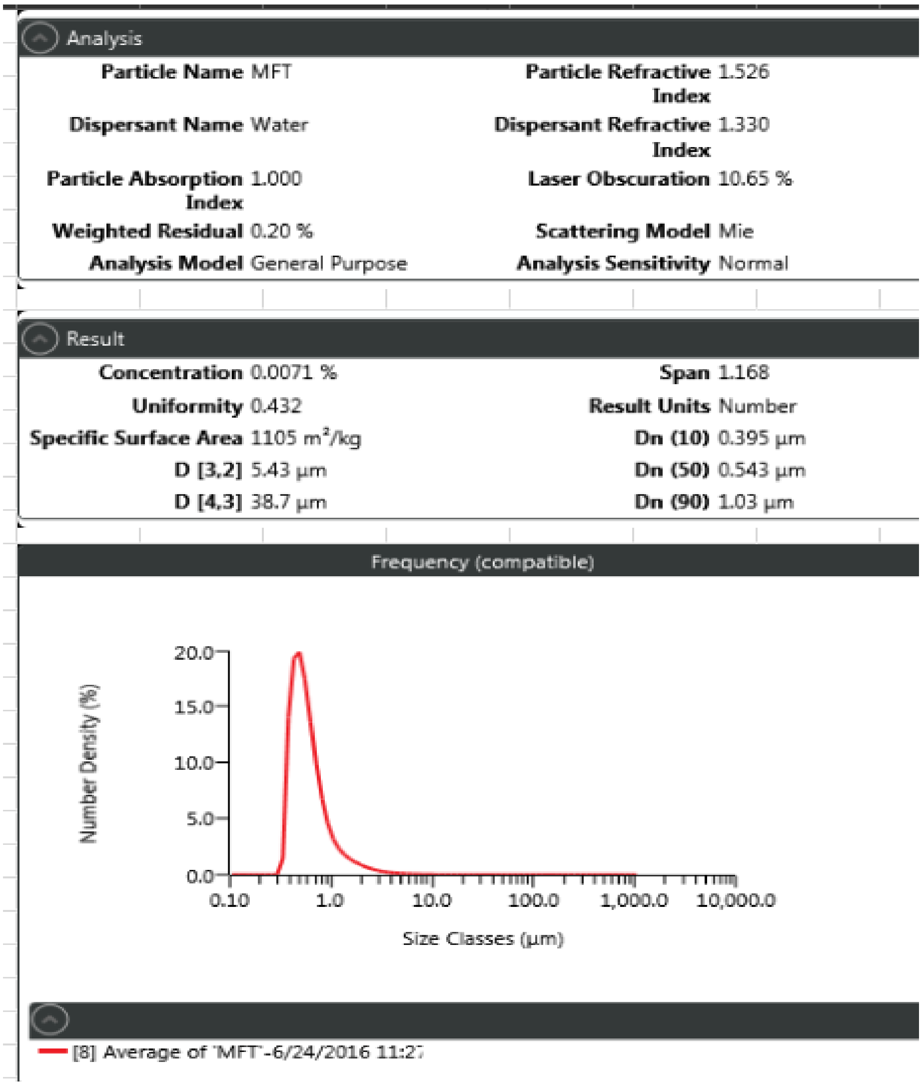
Particle Name	MFT	**Particle Refractive Index**	1.526
Dispersant Name	Water	**Dispersant Refractive Index**	1.330
Particle Absorption Index	1.000	**Laser Obscuration**	10.70 %
Weighted Residual	0.18 %	**Scattering Model**	Mie
Analysis Model	General Purpose	**Analysis Sensitivity**	Normal

Result

Concentration	0.0076 %	**Span**	5.606
Uniformity	1.817	**Result Units**	Volume
Specific Surface Area	1045 m²/kg	**Dv (10)**	2.28 µm
D [3,2]	5.74 µm	**Dv (50)**	19.3 µm
D [4,3]	42.6 µm	**Dv (90)**	110 µm

Frequency (compatible)

[4] Average of 'MFT'-6/24/2016 11:2



Analysis

Particle Name	MFT	**Particle Refractive Index**	1.526
Dispersant Name	Water	**Dispersant Refractive Index**	1.330
Particle Absorption Index	1.000	**Laser Obscuration**	10.65 %
Weighted Residual	0.20 %	**Scattering Model**	Mie
Analysis Model	General Purpose	**Analysis Sensitivity**	Normal

Result

Concentration	0.0071 %	**Span**	1.168
Uniformity	0.432	**Result Units**	Number
Specific Surface Area	1105 m^2/kg	**Dn (10)**	0.395 µm
D [3,2]	5.43 µm	**Dn (50)**	0.543 µm
D [4,3]	38.7 µm	**Dn (90)**	1.03 µm

Ion analysis OST:

251.6 ppm Na^+, 17.3 ppm K^+, 12.4 ppm Mg^{++}, 25.6 ppm Ca^{++}

4 Effect of solids content on alkoxysilane performance

The effect of bis-amine in MFT and oilsands tailings has been investigated, but intermediate solids contents have not been investigated. In order to more fully understand the effect of bis-amine treatment at other solids contents, a statistical experimental design was planned with MFT solids content and bis-amine dose as variables. This experimental design allows for efficient analysis of variables without the need for a full-factorial set of experimental conditions[47].

4.1 Methods and observations

A Composite Central Rotatable Design was used with each variable at five coded levels. For the analysis of the data these are required to be cover the whole range required for that variable, and to have intermediate values at the mid-point, and plus/minus 1/(2 X root 2) of the range. For simplicity, these are referred to as (-1.41, -1, 0, +1, +1.41), where 0 represents the mid-point of the range. The benefit of this statisitcal design is that not every combination of variables needs to be tested. The model comprised 12 runs including 4 replicates at the central point. Because solids contents varied between tests, the bis-amine dose was measured on a per mass of solids basis, rather than per total mass as in previous tests. The trials performed are shown in Table 5.

Table 5. The experimental CCRD design of MFT solids content and bis-amine dosage, with both real and code values (in parentheses) and the observed values of the analysed responses.

Trial	Experimental values		CST (s)	Normalised mudline (volume reduction)	Solids content (wt %)	Solids concentration factor	Turbidity (NTU)
	MFT solids content (wt%)	Bis-amine dosage (ppm)					
1	6 (-1)	1464 (-1)	181.0 ± 7.2	0.08 ± 0.01	45.3 ± 0.0	7.0	860.0
2	28 (+1)	1464 (-1)	296.5 ± 9.4	0.56 ± 0.01	43.6 ± 3.3	1.6	7.3
3	6 (-1)	8536 (+1)	33.4 ± 2.5	0.13 ± 0.00	43.2 ± 0.8	6.7	7.2
4	28 (+1)	8536 (+1)	152.4 ± 5.8	0.56 ± 0.01	46.8 ± 2.0	1.7	17.3
5	2 (-1.41)	5000 (0)	67.6 ± 1.7	0.05 ± 0.00	28.3 ± 6.4	14.2	279.0
6	32 (+1.41)	5000 (0)	325.7 ± 26.1	0.60 ± 0.02	53.1 ± 1.4	1.6	17.7
7	17 (0)	0 (-1.41)	393.0 ± 3.8	0.18 ± 0.00	52.9 ± 0.1	3.1	4136.0
8	17 (0)	10000 (+1.41)	46.8 ± 0.8	0.39 ± 0.00	39.1 ± 0.7	2.3	5.0
9	17 (0)	5000 (0)	73.1 ± 1.9	0.36 ± 0.01	45.4 ± 0.9	2.6	4.4
10	17 (0)	5000 (0)	76.8 ± 1.9	0.36 ± 0.01	44.9 ± 0.1	2.6	10.4
11	17 (0)	5000 (0)	76.9 ± 2.0	0.36 ± 0.00	44.0 ± 0.0	2.6	5.7
12	17 (0)	5000 (0)	70.8 ± 0.4	0.36 ± 0.00	45.1 ± 0.1	2.6	7.4
Control	*32 (+1.41)*	*0 (-1.41)*	*708.8* ± *12.3*	*0.64* ± *0.00*	*50.4* ± 1.8	*1.6*	*155.0*

The trials with lower solids contents were prepared by mixing MFT with DI water. Immediately after flocculation, the CST was measured. Within two hours of flocculation, the sample was subject to centrifugation at 910 g. The sediment volume reduction was measured periodically up to 60 minutes. The turbidity of the resulting release water was measured, as was the solids content of the resulting centrifuge cake.

4.2 Results and discussion

A multiple regression analysis of the model and construction of response surface graphs were performed by Statistica, version 13. A quadratic polynomial regression model was constructed from the statistically significant terms for each output: CST, normalised mudline, solids concentration factor and turbidity.

Note that for the equations in this section, the coded value of the input variables should be used. For example, if we wanted to find the value of CST at a bis-amine dosage of 7500 ppm, we would need to interpolate between 5000 ppm (coded value = 0) and 8536 ppm (coded value = 1). The coded value at 7500 ppm is therefore 0+1X(7500-5000)/(8536-5000) = 0.707. This is the value that would need to be substituted for D into the equation for CST.

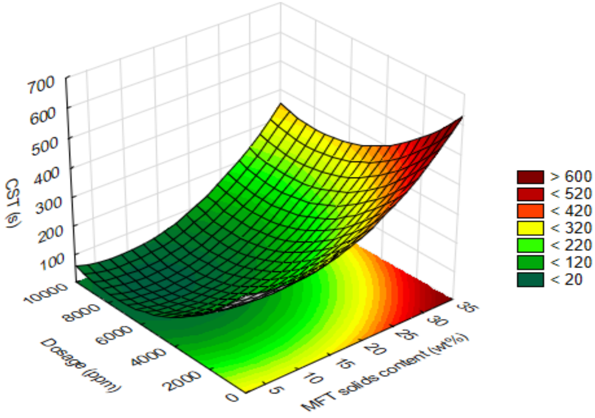


Illustration 4.2: Response surface for CST.

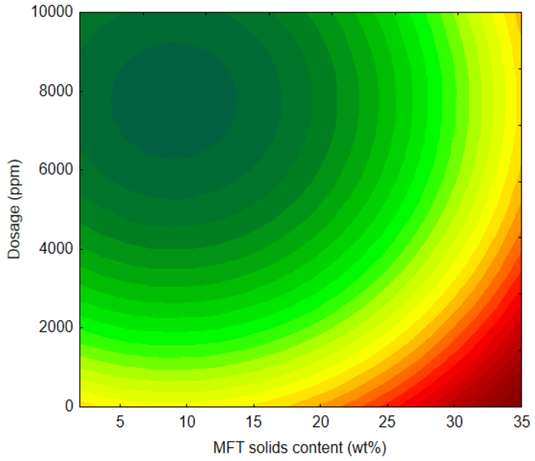


Illustration 4.1: Contour curve for normalised CST.

The software calculated the following equation for CST, where S is solids content and D is bis-amine dose on a solids basis:

$$CST\left(s\right)=74.5+151.0\cdot S+102.4\cdot S^2-193.7\cdot D+123.9\cdot D^2$$ **Equation 1**

The R^2 value for this model is 92.8%, indicating a high degree of explained variation between trials.

As expected, CST increases with solids content, and bis-amine reduces CST. The optimum dose is consistent at between 7000 and 8000 ppm solids basis for all solids content, with slightly higher doses performing better for low solids contents. This is logical, since the bis-amine will be more dilute when there is more water. Whereas previous trials showed a plateau in CST at about 2000 ppm wet basis, corresponding to about 6000 ppm solids basis, this set of trials shows that overdosing occurs only slightly beyond this range, above 7000 ppm solids basis. T very low solids concentrations, below 10%, it is not possible to achieve such low CST values. This suggests that it may be better to let tailing settle slightly rather than using bis-amine on fresh tailings.

Figures 4.3 and 4.4 represent normalised mudline after centrifugation at 910 g for 60 minutes.

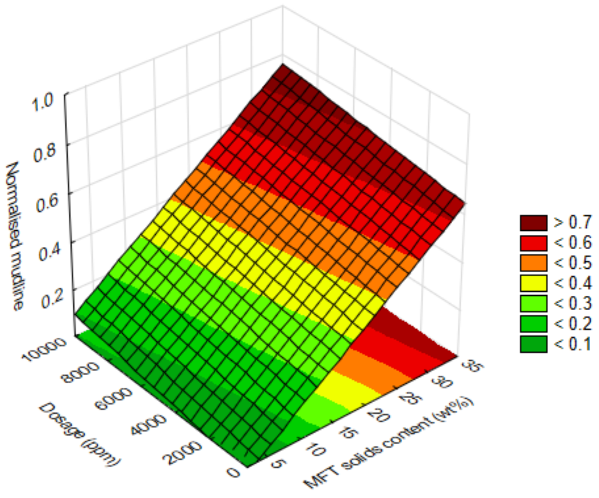


Figure 4.3: Response surface for normalised mudline.

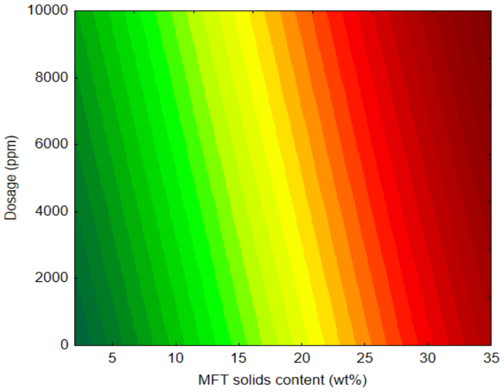


Figure 4.4: Contour curve for normalised mudline.

The equation for normalised mudline is calculated as:

$$NM = 0.33 + 0.42 \cdot S + 0.09 \cdot D$$ **Equation 2**

This explains 95.4% of the variance. The graph shows that bis-amine slightly decreases settling, which is consistent with previous results.

Figures 4.5 and 4.6 show the solids concentration factor after centrifuging, which is calculated as (solids content of sediment) / (original solids content). This represents how well each test concentrated the solids suspended in the liquid.

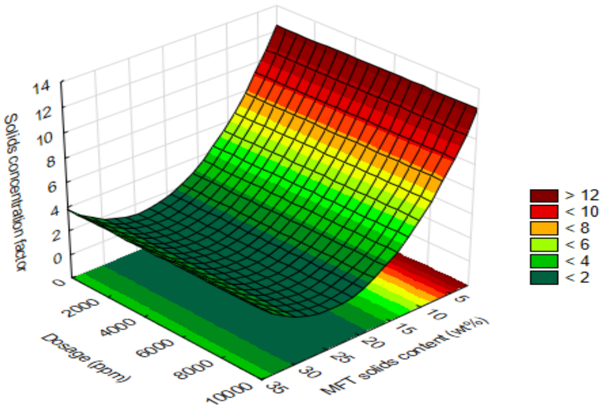


Figure 4.5: Response surface for solids concentration factor.

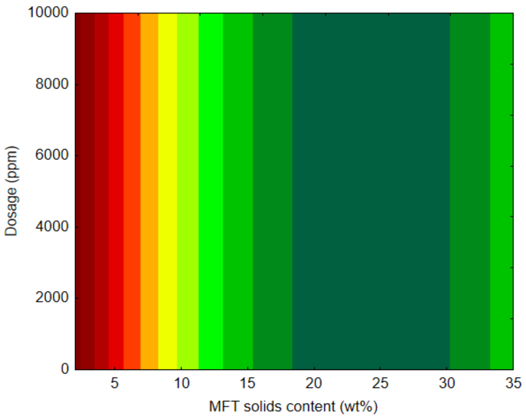


Figure 4.6: Contour curve for solids concentration factor.

The equation is:

$$SCF = 2.5 - 7.1S + 4.9S^2$$ **Equation 3**

This explains 94.2% of the variance.

The graphs show that solids concentration factor is virtually independent of bis-amine dose.

This is surprising because the previous graphs show that bis-amine has a slightly stabilising effect on the suspension. One possible explanation for this is that higher doses of bis-amine clarified the release water more: bis-amine caused more particles to separate from the water, which meant that there was more particles in the sediment, and if concentration of particles in the sediment remained the same, a greater sediment volume.

On the other hand, solids concentration factor is highly dependent on the initial solids content. At low solids contents, the concentration factor is high and increases inversely with initial solids content. This implies that low solids contents are easier to concentrate. This is logical since the repulsive forces between particles are greater when they are closer to each other. Also, we know that dilute suspensions in the form or whole tailings settle by themselves whereas MFT is stable. However, the response surface also shows a minimum for solids concentration factor at 25% solids. This implies that suspensions become easier to concentrate above this value. However, this is probably an artefact of the behaviour of MFT and the methods used to quantify it. As discussed in Section 3.2.5, MFT subjected to centrifugation develops three layers: a bottom layer with high solids content, an intermediate layer, and a top layer of relatively clean water. The intermediate layer most closely resembles the original, untreated MFT. The solids content was measured for the bottom layer, not the bottom and middle layer. In more dilute suspensions, only two layers are formed. This make the solids concentration factor appear high in those suspensions which form three layers.

Figures 4.7 and 4.8 and show the effect of MFT solids and bis-amine dose on turbidity of release water after centrifugation.

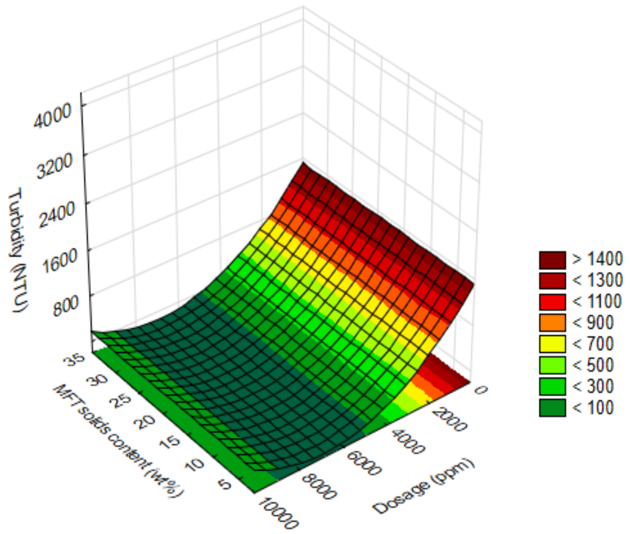


Figure 4.7: Response surface for release water turbidity.

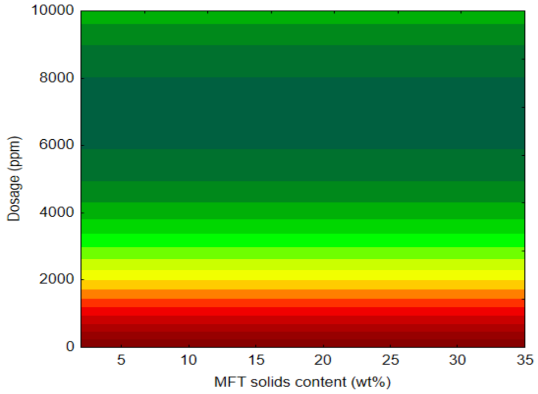


Figure 4.8: Contour curve for release water turbidity.

The equation is:

$$T(NTU) = -10.7 - 940.1 \cdot D + 853.9 \cdot D^2$$ **Equation 4**

This predicts 71.1% of the variance. This is reasonable but lower than the other outputs. The relatively low value here is probably due to machine inaccuracy.

The turbidity is highly dependent on bis-amine dose and completely independent of solids content. The turbidity was at its nadir at around 7000 ppm solids basis, which is the same as the optimum dose for CST reduction. Bis-amine is an effective treatment for reducing turbidity, a result which is in agreement with previous trials.

5 Tailings treatment using high pressure carbon dioxide

5.1 Effect of carbon dioxide, PDADMAC and modifiers

5.1.1 Supercritical carbon dioxide hypothesis

It was hypothesised that if a supercritical fluid were dissolved in MFT, it would have a similar effect to dissolving ions- and destabilise the colloid.

In order to test this hypothesis, MFT was subjected to CO_2 at around and above its critical point (31°C and 74 bar), and then tested for settling and filterability.

Since the properties of CO_2 vary markedly with pressure and temperature around its critical point, these would form two variables. Since simple organic compounds can modify the critical point of CO_2 substantially, it was decided to test supercritical CO_2 in the presence of these modifiers too. Additionally, water-soluble polymers were tested. Although these are not expected to have an interaction with supercritical CO_2, they cause a large improvement in settling and filtering behaviour and may cement any gain caused by carbon dioxide coagulation.

5.1.1.1 Methods and observations

A stirred tank autoclave was set up to put MFT into contact with carbon dioxide. The MFT and any modifiers were introduced through the open lid. Once the tank was sealed, high pressure CO_2 was injected. The internal temperature was raised through an external electrical heating jacket, and measured by an internal thermocouple. The setup is shown in Figure 5.1.

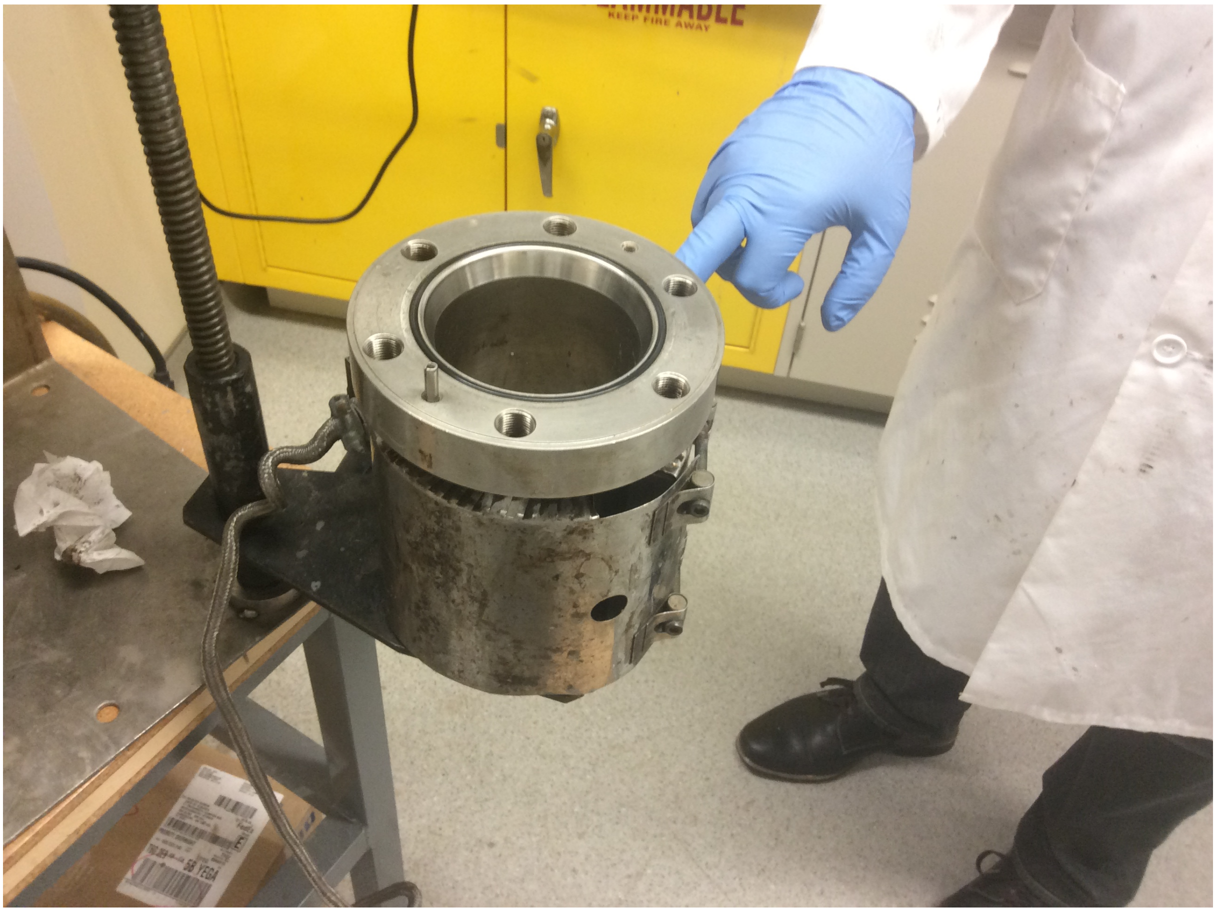


Figure 5.1 Image showing high pressure autoclave.

Tests under a variety of conditions were conducted to screen for efficacy. The tests conducted are shown in Table 6.

Table 6: Experimental conditions for carbon dioxide tests.

Test	MFT (g)	PDADMAC (ppm)	modifier?	Time (min)	Temp (c)	Pressure (bar)	Stir speed (rpm)
1	412	0	10% ethanol	60	80	70-80	300
2	1099	0	no	60	80	70	300
3	687	3600	no	60	c. 80	50-60	300
4	550	2300	no	40	70-80	60	400
5	618	800	10% ethanol	45	80	50-60	400
6	618	800	33% ethanol	60	80	94	400
7	1099	500	6% pentane	20	60	60	500
8	550	900	3% pentane	40	90	80	500
9	642	3700	6% methanol	20	gas c. 90; liquid c. 120	62-70	500
10	665	3100	1.2% methanol	20	gas c. 70-80; liquid c. 100-110	70	400
11	577	0	no	30	gas c. 70-100; liquid c. 60-100	20-30	550

Additionally, control tests were performed without CO_2 or heating:

-Control 1: Pure MFT

-Control 2: MFT with 0.5 g PDADMAC (800 ppm)

-Control 3: MFT with 2.4 g PDADMAC (3900 ppm)

After the MFT had been subjected to supercritical CO_2 for the prescribed time, the pressure release valve was opened and the contents of the tank allowed to reach atmospheric pressure. Most of the experiments lost some sample through the release valve at this point- this was not collected since it was finely divided by the high pressure gas, and dispersed. The release rate could not be finely controlled. At the time this was thought to be due to the type of valve used, but later it became apparent that it was due to the MFT foaming within the vessel and sporadically blocking the outlet.

At experiment 7, we realised that pH may play an important role in the filtering behaviour.

More acidic MFT filters more easily, and dissolved CO_2 decreases pH. We therefore measured pH after this time. All pH measurements were made at a temperature between 20 and 21ºC.

Specific notes for the individual experiments are presented in Section 5.3.

5.1.1.2 Consistency and settling

After being removed from the autoclave, the viscosity varied dramatically between the seven tests, sometimes being higher than MFT alone and sometimes lower. In some cases the material was a foam, but in others not. The degree of aeration is certainly influenced by the rate of pressure release, and the stability of the foam is affected by the presence of polymer.

All the test samples were allowed to settle overnight and some showed two distinct layers after this time, notably Test 1, with relatively clear liquid on top.

Figure 5.2: Test 1 after settling.

Figure 5.3: Test 2 after settling.

However, it is worth noting that the inside of the reactor was thickly coated with condensation after opening. The liquid being heated around the vertical face of the reactor evaporated and then condensed on the unheated and uninsulated top face. This process would continue after heating stopped, due to the large thermal mass of the liquid and heater. Therefore the clear water at the top was likely due to this condensed water not being properly mixed with the rest of the sample.

5.1.1.3 Capillary suction time

Even if there is no improvement in settling, MFT treatment technologies may still, in general, be useful if they increase the amount of moisture which can be removed through capillary action. If this is the case, the treated sludge will be more amenable to drying in a filter or when in contact with soil. Capillary Suction Time is used to measure this. A low time indicates high filterability.

The CST of the supercritical CO_2 -treated MFT was measured, and Table 7 show the average CST of the product from each of the tests conducted.

Table 7: Capillary suction time data.

Test number	Average CST (s)	Standard Deviation (s)
1	**623.8**	20.8
2	**592.8**	26.6
3	**165.3**	5.4
4	**261.0**	66.6
5	**447.0**	20.1
6	**479.2**	7.1
7	**952.2**	43.5
8	**335.4**	12.5
9	**195.2**	11.1
10	**238.1**	3.8
11	**1028.3**	21.6
Pure MFT	**1608.4**	91.9
0.5g Polymer, no CO2	**644.0**	39.7
2.4g Polymer, no CO2	**377.7**	57.7

These preliminary data can be analysed for the effect of each variable. The effect of CO_2 treatment alone is shown in Figure 5.4.

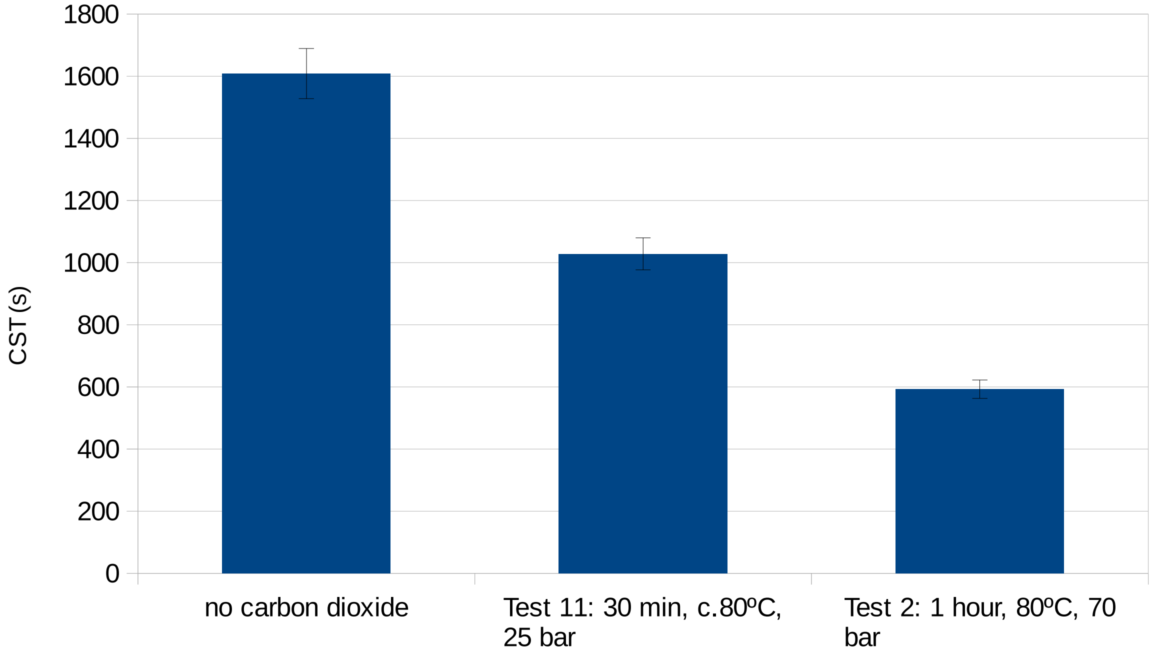


Figure 5.4 CST data showing effect of CO_2 treatment.

Clearly, CO_2 treatment reduces CST, as is expected from established industry practice and the work by Zhu et al[32]. The increased time of contact and pressure of CO_2 improves CST. This is logical because both factors would tend to increase the uptake of CO_2 by the MFT, decreasing pH and therefore CST. At this stage there is no evidence for an additional supercritical effect.

Figure 5.5 shows polymer treatment also reduces CST substantially.

Again, this is to be expected. The polymer used here, PDADMAC, is very effective in improving settling and CST in whole oil sands tailings. The same principles of its action apply in suspensions with a higher density of solids. The dose here is high, but not particularly high in proportion to the solids content of the MFT.

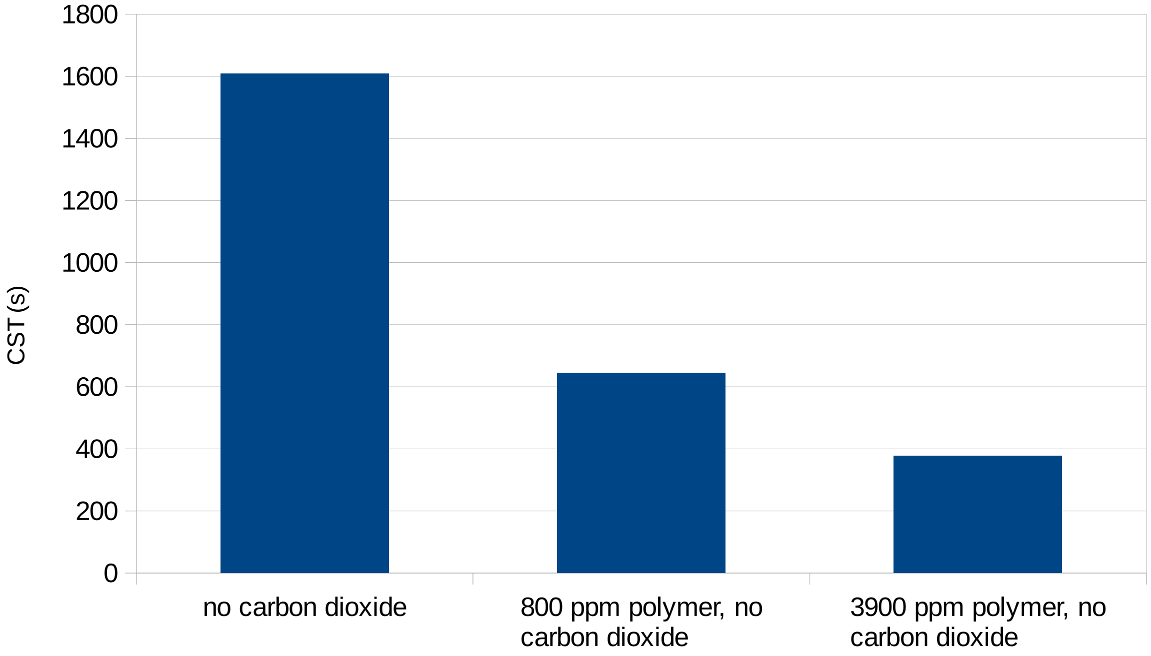


Figure 5.5: Effect of polymer addition (PDADMAC).

The effect of polymer treatment is greater than that of CO_2 treatment. When CO_2 treatment is applied in addition to polymer treatment, it produces a small additional improvement (261 s compared with 377.7 s).

Supercritical modifiers such as ethanol can affect the supercritical behaviour of CO_2 at relatively low concentrations, and it was hypothesised that they would change the effect of CO_2 treatment. The effect of adding ethanol to supercritical CO_2 appears to be negligible as demonstrated in Figure 5.6.

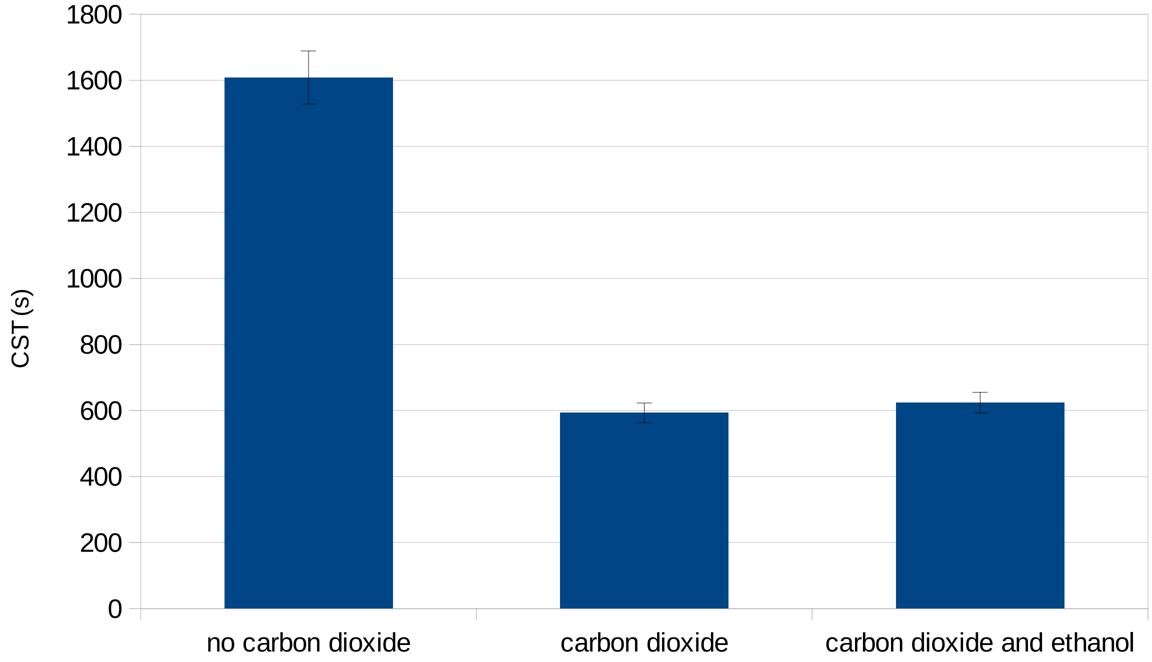


Figure 5.6: Negligible effect of ethanol.

Several tests were conducted with other supercritical modifiers in combination with polymers, since it was thought these supercritical modifiers might only exert an influence when combined with a flocculant. These tests were conducted at both high and low levels of polymer (relatively speaking). The tests involving a high level of polymer are shown in Figure 5.7.

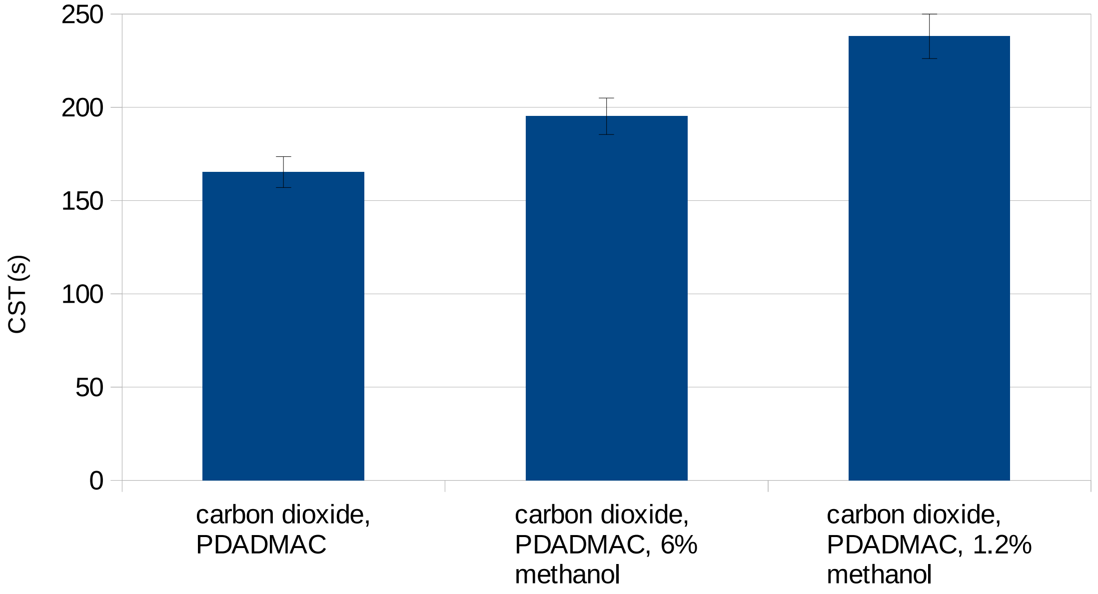


Figure 5.7 comparison of high-polymer tests (over 2000 ppm).

Addition of methanol reduced the effectiveness of polymer/CO_2 treatment, although interestingly, adding a small amount of methanol was more detrimental than adding a large amount.

Tests were also conducted at a low level of PDADMAC with ethanol and n-pentane, which results are shown in Figure 5.8.

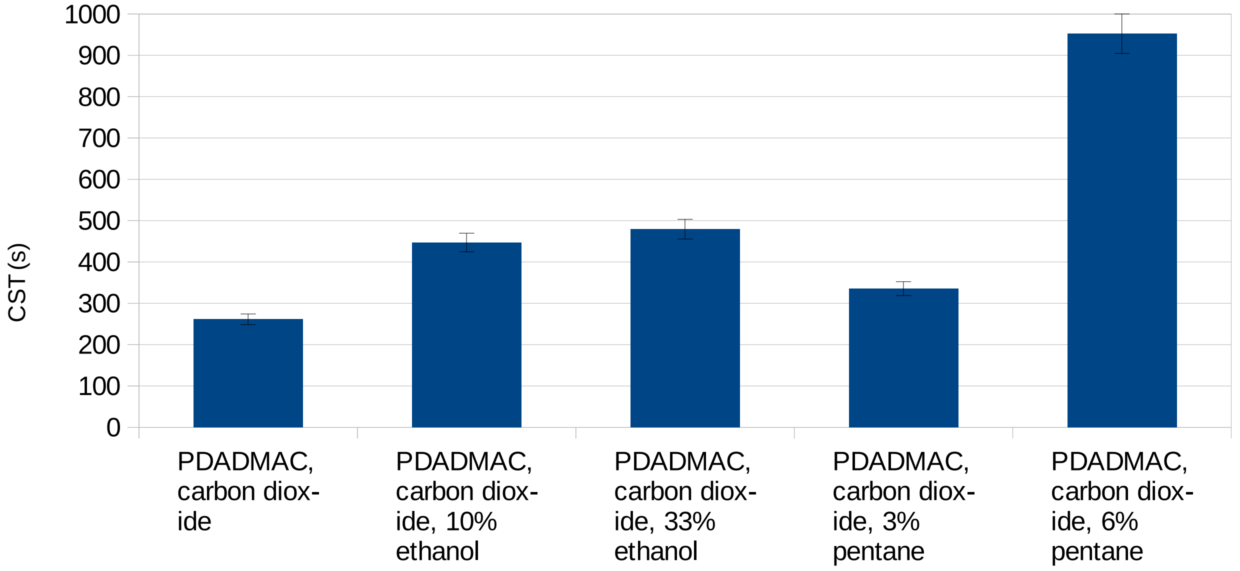


Figure 5.8 comparison of low-polymer tests (under 1000 ppm).

Again, adding modifiers reduces filterability as indicated by increased capillary suction time, although in these cases, the results show the logical consequence of increased effect at higher dosage. The effect is non-linear, but this is expected as CST is a non-linear proxy for rate of water removal.

5.1.2 Discussion of experimental data

Consideration of the experimental data reveals the following:

- CO_2 treatment improves CST. The improvement is increased with time-pressure exposure to CO_2.
- Polymer treatment reduces the CST of MFT. Increasing polymer dosage reduces CST further in the range studied.

- CO_2 and PDADMAC treatment benefits are partially additive.
- In the conditions studied, ethanol and n-pentane are detrimental to the reduction in CST during CO_2 treatment.

The hypothesis behind these experiments was that supercritical CO_2 has an independent effect on mature fine tailings which is beneficial for its remediation. Subcritical treatment with CO_2 is known to improve the settling behaviour of oilsands tailings and is already used commercially on whole tailings. To confirm this, experiments were conducted in which the pH of raw MFT was modified with hydrochloric acid or sodium hydroxide, and the CST compared with MFT modified by CO_2 treatment. Acid treatment improves CST whereas alkali treatment increases it. The results of these experiments are discussed further in Section 5.6.

At this stage, there is no evidence for an independent effect from supercritical CO_2. Test 2 and 11 used super- and sub-critical CO_2 respectively, but the improvement in CST is more easily explained by higher uptake of CO_2 for the supercritical experiment. Likewise, the improvement in the polymer+CO_2 experiments is more easily explained by the combined effect of polymer flocculation and acidity coagulation caused by CO_2 uptake. Modifiers (ethanol, methanol and pentane) have a negligible or deleterious effect on CST. The reason for this is unknown, but it is probably because ethanol, methanol and pentane cause a loss in efficacy of the polymer. This is discussed in more detail in Section 5.7.

5.2 Appendix I: Further experiments

After the preliminary experiments, we theorised that, after being subjected to supercritical CO_2 treatment, the MFT might need time, without agitation, to stabilise. We theorised that this time was necessary for particle coagulation to occur as a result of the changes in their medium brought about by the presence of a supercritical fluid.

Furthermore, it is well-known that agitating a liquid with dissolved carbon dioxide is likely to make it foam when the pressure is released. Allowing a stabilisation time would reduce the risk of foaming, and the additional agitation that brings.

Therefore, we conducted a number of tests in which the mixer was turned off, the MFT allowed to stabilise, and then the pressure released slowly.

Under this theory, it was essential that the pressure was released slowly so that the MFT was not disturbed. A number of experiments were conducted to investigate methods of doing this, but all of them suffered from the problem of "fizz" described by Zhu et al[32] when they investigated higher pressures. Although Zhu et al used much lower pressures than us, they observed that tailings subjected to CO_2 pressure above a certain point settled less readily, which they suggested was due to bubbles of CO_2 leaving solution and carrying sediment with them.

The methods attempted are described in the next sections.

5.2.1 Needle valve

A needle valve was used to finely control the rate of pressure release. The needle valve was opened slightly and the gas allowed to leak out slowly over a period of several hours. The equipment set up is illustrated in Figure 5.9.

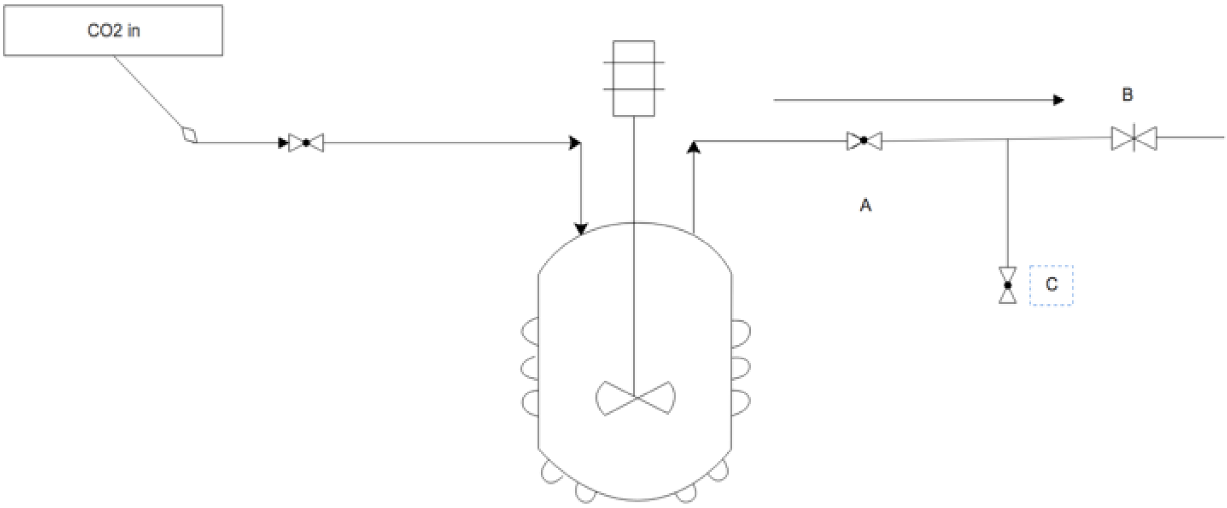


Figure 5.9 Process schematic 1.

The pressure invariably stopped falling when it reached around 30 bar. This was because MFT was forced up and into the needle valve, which became blocked. To empty the reactor the pressure had to be released in an uncontrolled manner through an alternative ball valve, which of course causes considerable agitation.

A larger needle valve was also used. This allowed the same degree of fine control but could be opened wider in case of a small droplet of MFT becoming lodged in it. However, that too became blocked.

5.2.2 Solid-liquid separator

A secondary chamber was installed between the autoclave and the release valve in an attempt to prevent any stray droplets of MFT blocking the valve, as illustrated in Figure 5.10. If this were effective, then the gas could continue to dissipate slowly even if there was a minor amount of fizz. However, the valve continued to become blocked every time the pressure dropped below about 30 bar. This suggested that a large amount of MFT was erupting from the reactor.

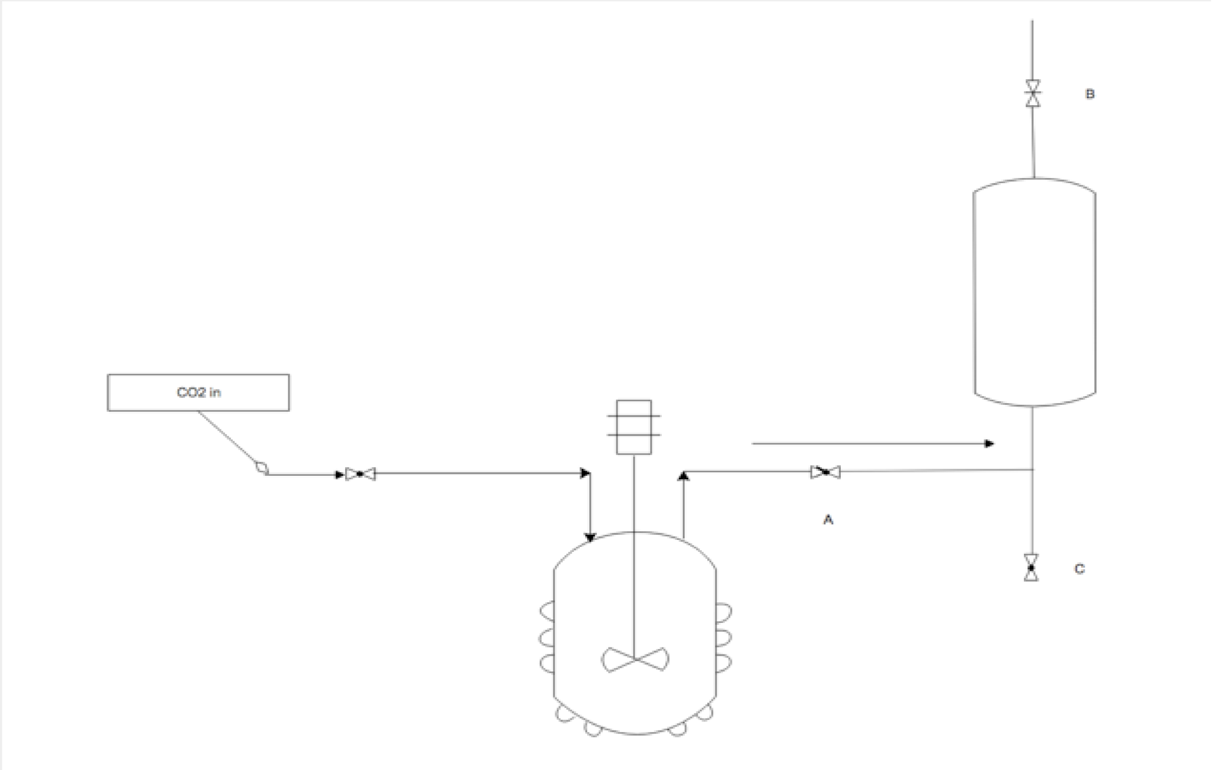


Figure 5.10 Process schematic 2.

5.2.3 Pre-pressurising release section

We thought that the MFT might erupt as soon as the ball valve A was opened, the sudden drop in pressure causing MFT to rush into the solid-liquid separator and up to the needle valve. To prevent this, we pre-pressurised the shaded area in Figure 5.11 to the same pressure as the reaction conditions. Therefore there was no sudden drop in pressure- only a slow, sustained release once the needle valve was opened.

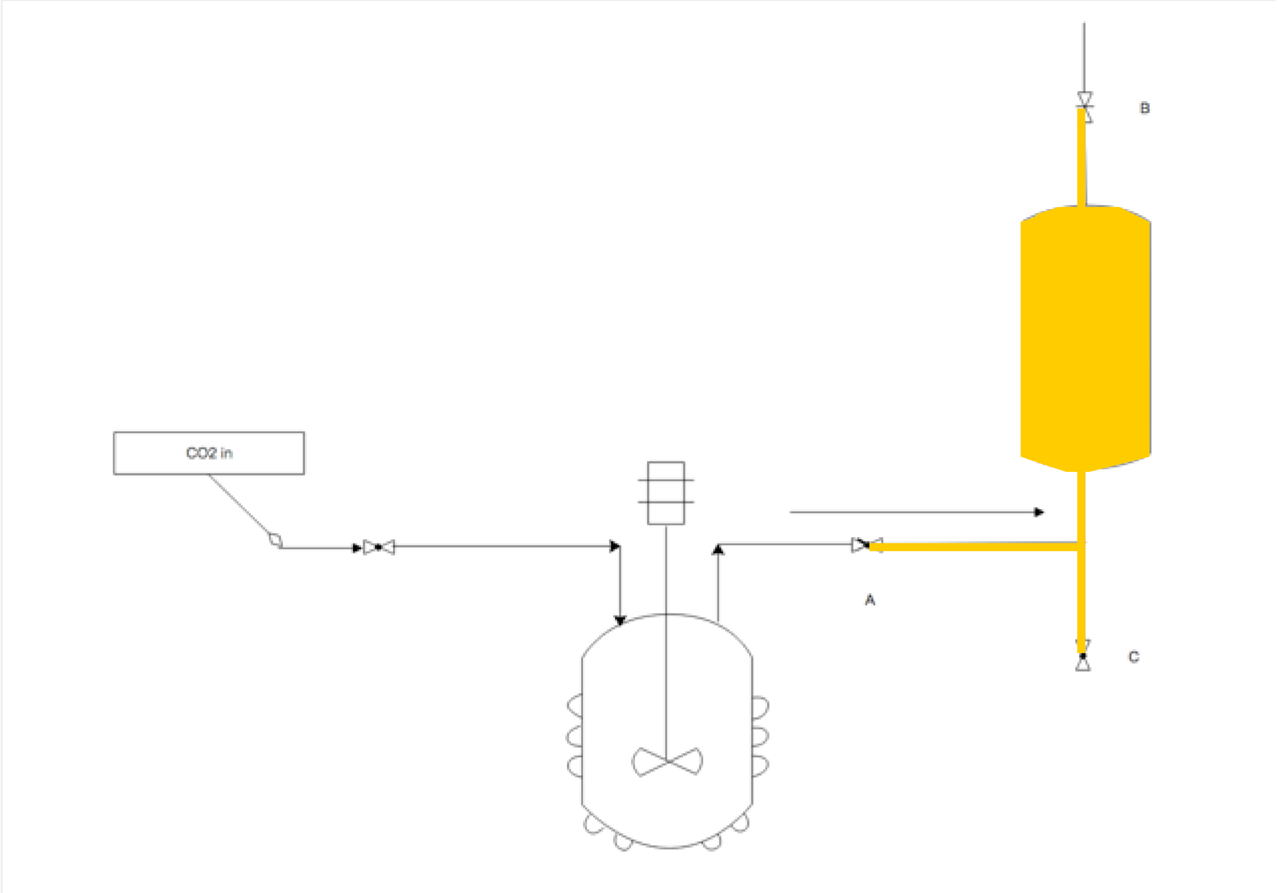


Figure 5.11: Process schematic 3.

However, this did not help either. It is thought this is because the eruption of MFT still occurred when the needle valve B was opened.

5.2.4 Packing

It was possible that that the apparently large amount of MFT which was forced into the solid liquid separator was in fact a relatively small amount of foam. We tried laying inert stone chips as packing material at the base of the solid-liquid separator in an attempt to break up the foam.

Again, the needle valve invariably became blocked.

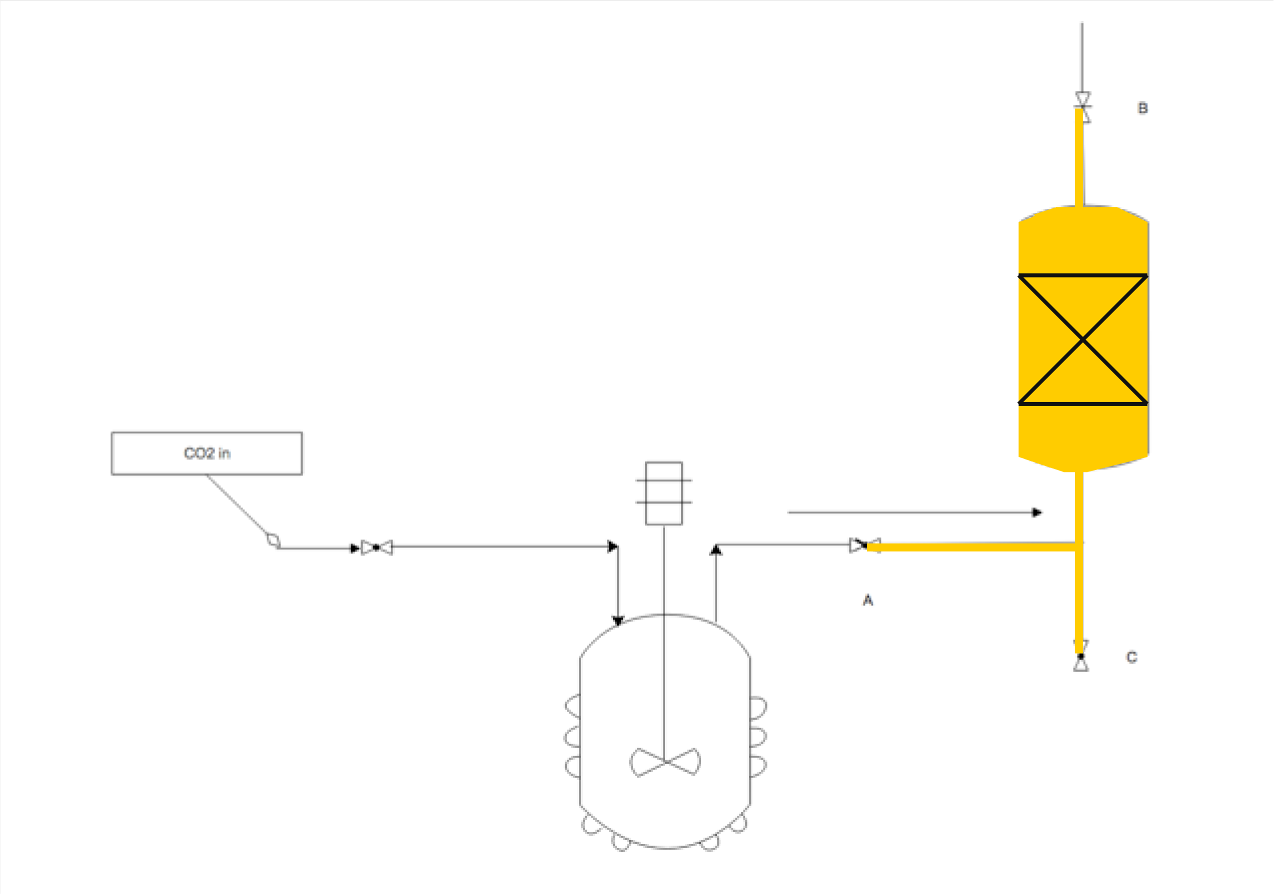


Figure 5.12 Process schematic 4.

5.2.5 Reducing MFT quantity

We thought that the reactor itself might be too full of MFT, so that its liquid contents could readily spill over into the release side. We reduced the quantity of MFT used to one third of its original level, so that the rotor was only just submerged, as shown in Figure 5.13. This prevented the needle valve becoming blocked in one test. However, around half the sample was found in the solid-liquid separator, and three subsequent tests all became blocked.

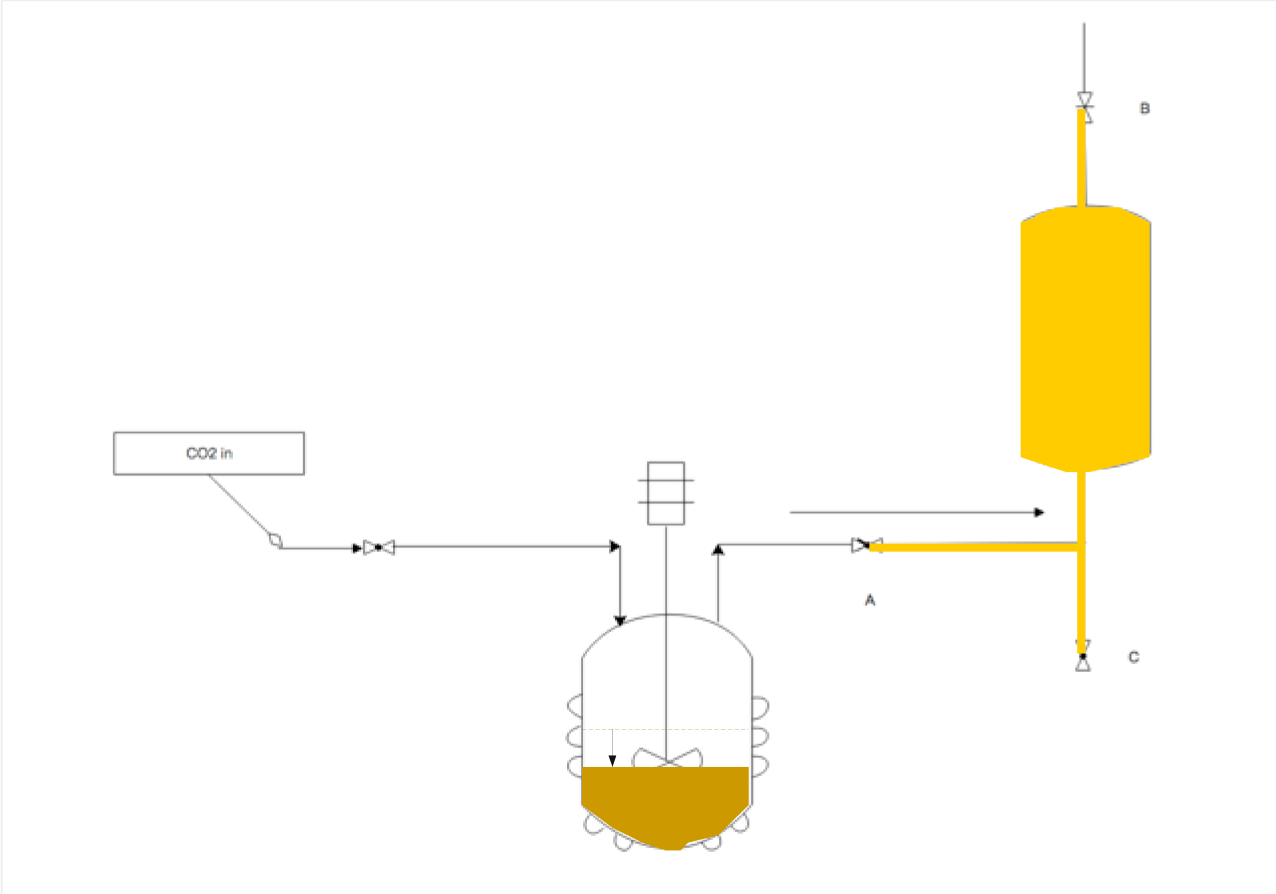


Figure 5.13: Process schematic 5.

5.2.6 Discussion

Following the preliminary experiments, we theorised that any independent supercritical effect on CST might be destroyed by the relatively uncontrolled release of pressure. I therefore tried many methods to reduce the pressure in a controlled way, which are described at length in Section 5.2. However, all the methods failed because the MFT always erupted when the pressure dropped too low.

To understand what occurs when the pressure is released in our reactor, it is helpful to think about what happens to pure water when exposed to high pressure CO_2. The water becomes saturated with CO_2 at that pressure. The liquid phase will reach saturation sooner if it is mixed, since mixing increases gas-liquid contact.

If the partial pressure of CO_2 above the CO_2-laden liquid falls below the vapour pressure of CO_2 in the liquid, CO_2 will diffuse out of the liquid phase into the gas phase. If the total gas-phase pressure falls below the vapour pressure of CO_2, there is a driving force for bubble formation. It would be possible to have such a small difference between gas-phase pressure and vapour pressure that mass transfer of CO_2 from liquid to gas phase occurs at equilibrium and only by diffusion, but this would require an extremely long time and would not be a practical way to release the pressure.

Thankfully, if we want to avoid bubble formation in our hypothetical CO_2-saturated water, it is not necessary for pressure release to occur at equilibrium, because there is an activation energy for bubble formation. The water can be supersaturated with CO_2, which means there can be a significant pressure difference between the gas phase and vapour pressure of the liquid.

Unfortunately, the MFT used in our reactor behaves differently from water. It contains many billions of clay particles. If these acted as nucleation sites for CO_2 bubble formation, it would not be possible to achieve any significant pressure difference.

It is clear from the experiments that the clay particles do indeed act as nucleation sites, since eruption of MFT occurred in all experiments and the overhead pressure could not be reduced without this happening.

Let us return to the updated hypothesis stated at the start of this chapter. It was hypothesised that supercritical CO_2 does cause coagulation (beyond that caused by the appreciable pH drop when CO_2 is dissolved in MFT) but that the coagulated particles are sensitive to agitation. This may be true, but the experiments show that it can be of no practical benefit in oil sands tailings remediation because it is impossible to release the pressure in such a way that there is no agitation. There remains a significant effect due to acidity coagulation, which occurs up to the point of CO_2 saturation, and this is can be of great benefit in MFT treatment.

5.3 Appendix II: notes on individual trials

Test number	**Notes**
3	Volume of sample after treatment approximately doubled due to aeration. Froth dissipated easily on gentle stirring.
4	Mousse-like material found on top after opening reactor, and liquid underneath. Stirred gently for CST.
5	Pressure released slowly.
7	pH at 21°C: 6.75 at top, 6.45 at bottom
8	Temp and pressure measured to be 115°C and 95 bar temporarily. This was likely a localised heating effect of the upper supercritical phase. pH at 20.5°C: 6.75
9	Consistency lumpy. pH 6.1.
10	pH 6.49 at 20.3°C
11	pH 6.24 at 20.2°C

Prior to experiment 9, only one thermocouple was employed, situated in the upper half of the reactor in the gas or supercritical phase. After this time, two thermocouples were employed, in the lower half of the autoclave and the upper.

5.4 Appendix III: capillary suction time raw data

	CST run number							
Test number	**1**	**2**	**3**	**4**	**5**	**6**	**Mean average CST (s)**	**Standard Deviation (s)**
1	599.2	602.1	612.8	636.8	657.1	635	623.8	20.8
2	631.2	587.3	613.5	556.8	575	na	592.8	26.6
3	167.9	166	169.6	171.9	158.8	157.4	165.3	5.4
4	200.4	361	229.1	201.5	346.2	227.5	261.0	66.6
5	474.3	426.7	440	na	na	na	447.0	20.1
6	477.6	475.3	494.2	479.2	476.6	472.1	479.2	7.1
7	948.2	1009.6	921.8	1008.7	893	932	952.2	43.5
Pure MFT	1542.8	1582.8	1505.6	1778	1565.5	1675.7	1608.4	91.9
0.5g Polymer, no CO2	722.5	638.7	623.1	658.7	597.3	623.6	644.0	39.7
2.4g Polymer, no CO2	317.3	336	479.2	na	355.9	400.2	377.7	57.7
8	350.2	322.6	355	326.7	327	330.9	335.4	12.5
9	202.7	180.5	207	183.1	202.7	na	195.2	11.1
10	231.8	243	237.1	239.6	235.5	241.4	238.1	3.8
11	1049.9	1006.7	na	na	na	na	1028.3	21.6

5.5 Appendix IV: underflow drainage

The gravity drainage characteristics of a sludge can also be quantified by placing the sample on a sieve and measuring the volume of water which falls through. This occurs due solely to gravity and, unlike CST, not due to capillary action. The sieves employed had mesh sizes of 250 and 500 µm. For our purposes, the ideal sludge will have self-filtering flocs which allow clear water to pass through the sieve but catch all the clay particles, leaving a dry solid in the sieve.

This test models a situation where the treated sludge is allowed to dewater on a bed of relatively coarse sand grains, or a filter with wide openings (relative to CST).

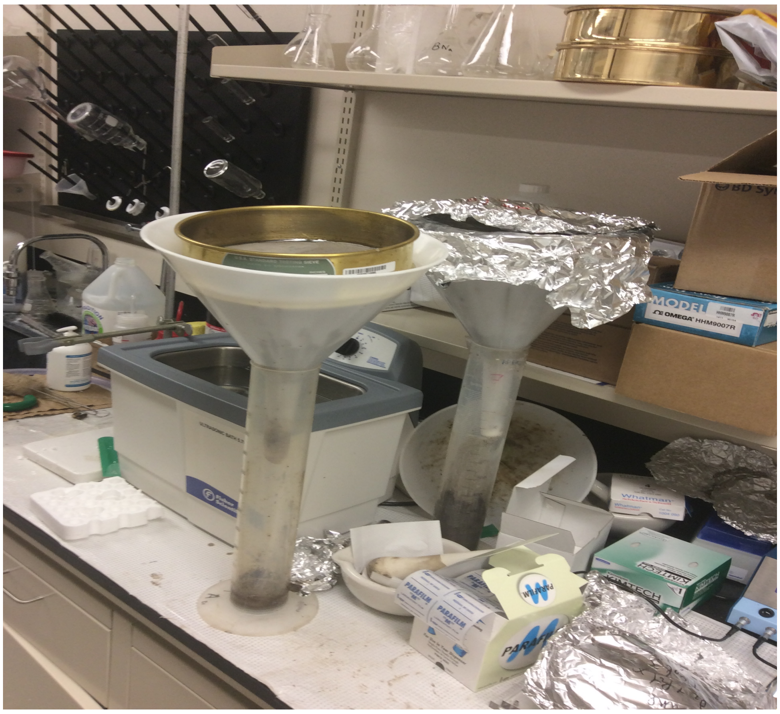


Figure 5.14: Underflow drainage test: note (from top) sieve containing treated MFT; funnel; and measuring cylinder

The tests were conducted by placing a small amount of treated MFT on the sieve and allowing the water to drain into a measuring cylinder placed underneath.

The behaviour of the sample varied markedly- the more viscous samples stayed in a small area of the sieve surface while the less viscous ones spread over the surface and were not retained at all by the sieve. Some of the samples showed release of clear water while some showed turbid filtrate.

In future tests, it is wise to continue to test different mesh sizes since the optimum size varies. The tests will also be conducted using a larger sample, such that it covers the whole surface of the sieve and there is a consistent head of pressure. There was evidence of evaporation despite the lid used. This can be controlled by wrapping in plastic film.

5.6 Appendix V: Effect of pH on CST

CO_2 treatment changes the zeta potential of the dispersed particles in MFT by reducing the pH of the liquid phase; this in turn reduces the repulsive forces between clay particles[32]. It was not initially clear whether the results obtained in this experiment are a manifestation of reduced pH or are due to an as-yet undescribed supercritical separation phenomenon. To clarify, control experiments were conducted using hydrochloric acid to acidify untreated MFT. One experiment was also conducted using sodium hydroxide to increase the alkalinity of the MFT.

Table 8: Effect of pH on CST.

test no.	conditions	Adjusted pH	CST (s)
1	200 g MFT, 2ml 37% HCl	4.46	477.7
2	212 g MFT +2ml 3.7% HCl	5.75	584.2
3	untreated MFT	7.75	1608.4
4	200 g MFT + 2 ml 5% NaOH	9.56	1956.7

After adding acid, the MFT immediately became significantly more viscous. In test 1, the pH soon after adding acid was 2.7 and in test 2 it was 5.36. The pH was increasing rapidly so the CST experiments were conducted the next day after the pH had stabilised.

The amount of acid introduced to the MFT was large- if test 1 had been conducted using distilled water instead of MFT, the pH would be 1. It is interesting that the pH increases over time to a much higher value than is expected based on an equivalent amount of acid added to distilled water. This could be due to ion exchange on the surface of the clay (for example: HCl pushes the calcium adsorption/solution equilibrium towards solution; calcium ions neutralise HCl and pH increases).

The results in the table above are shown graphically in Figure 5.15.

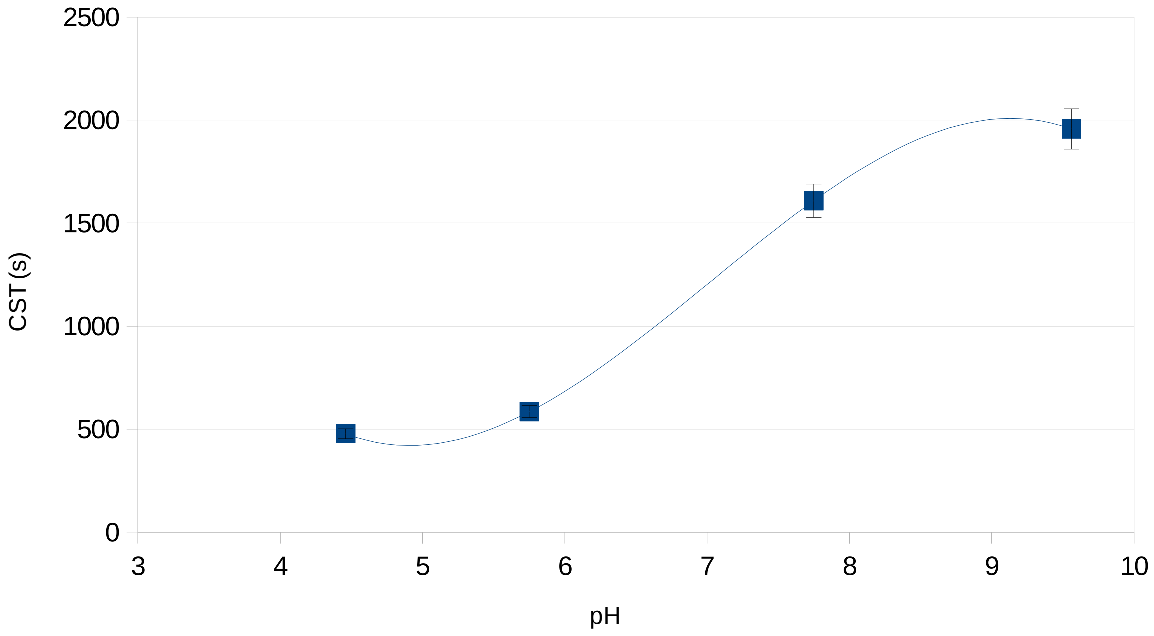


Figure 5.15: CST as a function of pH in pH-modified MFT.

It can be seen that reducing pH improves CST while increasing pH has a detrimental effect. These changes occur asymptotically to a limit of about 400 seconds at low pH and 2300 seconds at high pH.

Those tests in which pH was measured have been added to the CST/pH plot in Figure 5.16.

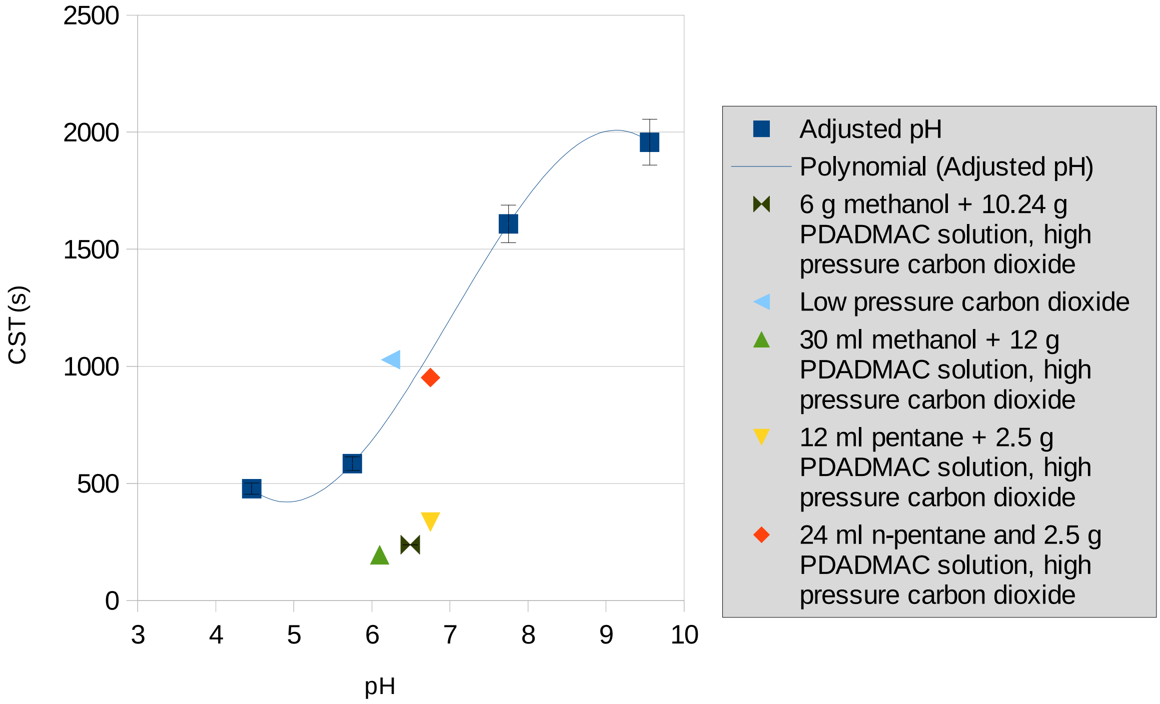


Figure 5.16: CST vs pH for MFT samples subjected to carbon dioxide treatment and simple pH modification.

The CST for the low pressure CO_2 test was slightly higher than expected. Three of the experiments' data points are below the line to a degree commensurate with the fact that they contain polymer flocculant, which reduces CST independently of pH. The point representing 12 ml n-pentane and 2.5 g polymer sits almost on the line of pH vs CST, which suggests that the effect of the polymer was negated by the pentane, or else the pentane prevented the polymer from working. This is discussed further in Section 5.7.

5.7 Appendix VI: Possible explanation of deleterious effect of supercritical modifiers

The reader will recall that ethanol had a negligibly detrimental effect on CST when combined with supercritical CO_2, as in Figure 5.17.

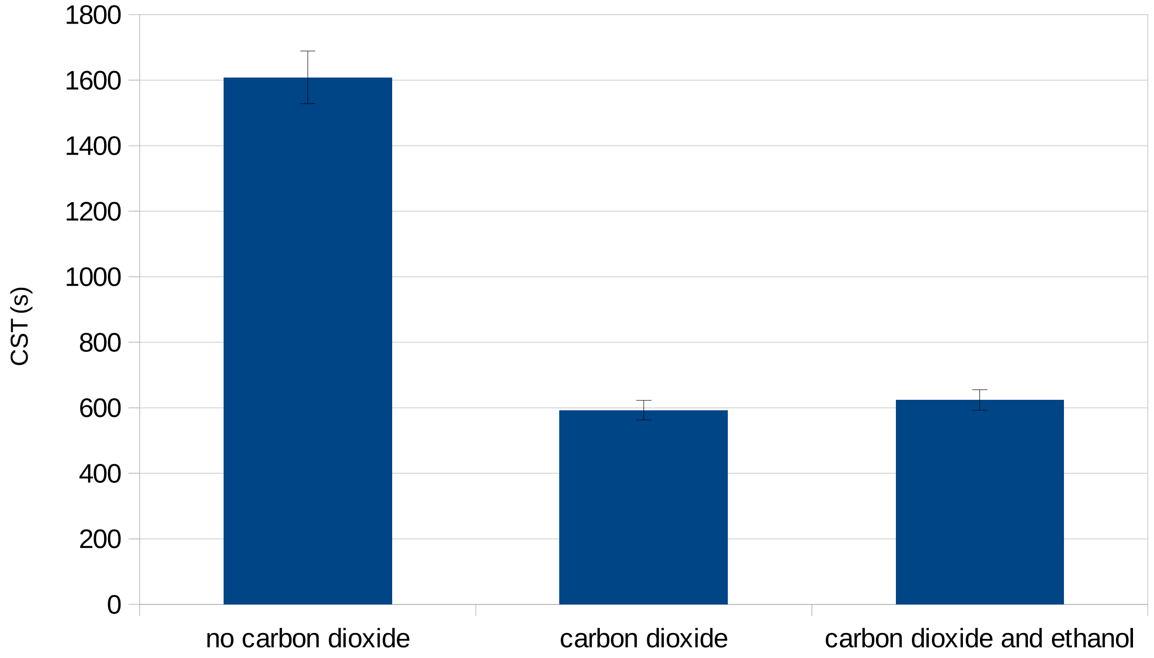


Figure 5.17: Effect of ethanol.

Methanol and n-pentane were more detrimental to performance. This is contrary to what was expected from our supercritical CO_2 theory. We expected modifiers to improve CST by increasing the supercritical effect on CST.

I hypothesised that these modifiers, and pentane in particular, reduced the effectiveness of

CO_2 treatment by reducing its partial pressure. Pentane boils at 36°C, so its vapour pressure at the reaction conditions may be a significant proportion of the total gauge pressure.

However, its vapour pressure at 60°C is only 2.2 bar, so this does not seem likely.

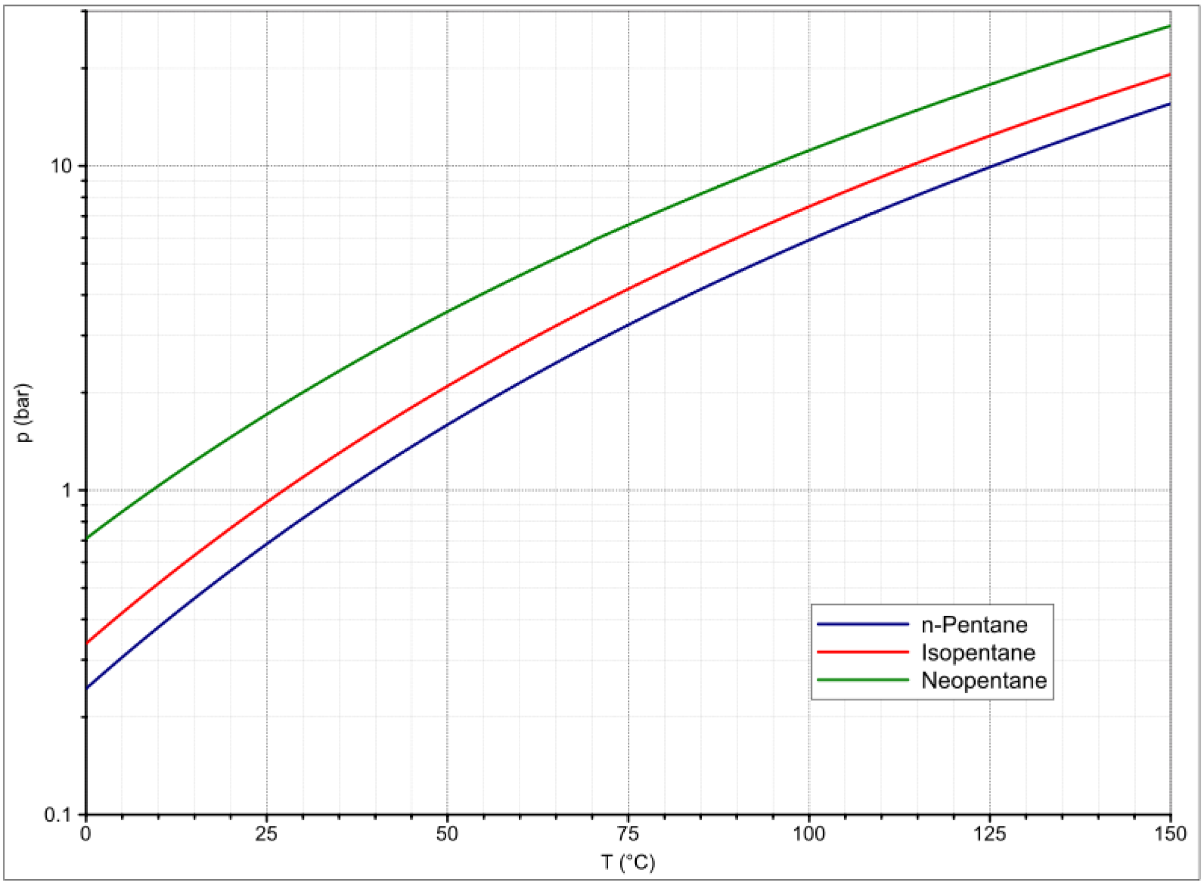


Figure 5.18 Vapour pressure of pentane isomers.

However, n-pentane is insoluble in water, so it may form a film over the interior of the reactor. In this case, its temperature would be much higher – over 100°C – because of the heating jacket. In this case, its vapour pressure would indeed be significant.

However, this does not explain the drop in efficacy of polymer/CO_2 with addition of ethanol or methanol. These alcohols have much lower vapour pressures, especially combined with water, and have no tendency to migrate to the edges.

Recall that ethanol had a negligible effect on supercritical CO_2 in the absence of polymer, but a significant effect when polymer was present. This suggests that alcohols detrimentally affect the performance of the polymer, not the CO_2. Polymer flocculants rely for their efficacy on their ability to expand in water, but coil in on themselves when bridging clay particles; that is to say, the balance of hydro- phil- and phob-icity is important. Alcohols, which exhibit hydrogen bonding at their functional group but no interaction with water at the remainder of the molecule, disturb this balance and disrupt the performance of the polymer.

6 Conclusions and recommendations

We have seen that there are alkoxysilanes which effectively treat MFT. Notably, bis-amine and hydrolysed 3-amino reduce CST, and 3-amino increases settling. Whilst carbon dioxide treatment is found to be effective, no additional supercritical effect is found.

Further research may investigate the structure of alkoxysilane oligomers and the mechanism of CST reduction. It is not yet known whether the compounds tested adhere to clay particles by silica bonding or if there is a charge neutralisation mechanism mediated by the amine group.

Although it is good at reducing turbidity, bis-amine performed poorly at flocculating the low solids suspensions we tried- this suggests that it performs badly at low solids concentrations, but well at the very low concentrations which cause turbidity. At low solids concentrations, bis-amine improves the stability of suspended clay solids and prevents settling. This limits its application to high solids wastes, such as MFT, which are both less susceptible to this effect and more likely to be usefully treated by a capillary-based process, such as belt-pressing or wick drains. There are several possible reasons for the stabilising effect which occurs at low solids concentrations. It is possible that the oligomers formed are too small to be affected by the entropic effect which causes polymers to form tight coils, therefore the clay particles are not brought into flocs large or tight enough to settle. It may also be that bis-amine is excessively hydrophilic, or that monomer units within the oligomer repel each other. Since high solids suspensions were affected less by this, it seems that the presence of clay particles offsets or cancels the effect. Further research is needed to examine the cause, since such research will help to inform the development of more effective alkoxysilane flocculants.

Nevertheless, the release water from bis-amine has particularly low turbidity. This presents something of a conundrum: bis-amine prevents settling in low-solids suspensions, but is good at removing the last trace of solids from cloudy water. Further work should evaluate its performance relative to conventional polymers. The good turbidity reduction suggests it may be useful for the final stage of waste water treatment, in oilsands or other waste waters. Since turbidity reduction is one of the main goals of most water treatment plants, it also suggests bis-amine or other alkoxysilanes may be useful in producing clean water for municipal or industrial use. Further work should explore this further.

The other alkoxysilanes tested did not significantly improve CST. This does not mean they should be ruled out, however. Alkoxysilanes with amine groups are much more prone to hydrolysis in neutral conditions than those without, and it is possible that after hydrolysis in acidic conditions, these seemingly ineffective compounds will become effective polymer flocculants. Unlike in the amino silanes, this raises the issue of introducing additional ions to process water, although this may not be a serious concern in oilsands operations under certain ranges of operating conditions.

Alkoxysilanes are a class of compounds which are as infinite and varied as the alkanes, and this thesis is merely a cursory exploration into the realm of possibility. Monomer properties such as number of siloxane bridges, type of structure (M, D, T or Q), number and size of alkyl groups and presence of functional groups will all undoubtedly play a role. On the scale of the polymers formed, molecular mass and structure will also be important, as they are in conventional polymer flocculants.

Glossary of terms

Centrate: Liquid phase above solids which have been removed in a centrifugation test.

move to the bottom of the container. Unless qualified, this refers to gravity settling.

Gravity settling: settling occurring under the action of gravity alone.

Centrifugal settling: Settling which is enhanced by the centrifugal action of a centrifuge.

Filtrate: liquid which has passed through a filter.

Release water: the aqueous phase which has been separated from a suspension, either by gravity settling or centrifugal settling.

Standard Flocculation Technique: standardised procedure followed for flocculation tests in this work (and other tests performed in the water-soluble polymers research group). Outlined in detail in section 2.2.1.

Supernatant: liquid phase above solids which have settled in a settling test.

Settling: process by which suspended particles of density greater than the surrounding medium.

References

1 Pembina Institute, 2013. Losing Ground.

2 BGC Engineering, 2010. Oilsands Tailings Technology Review.

3 Larson, R.G., 1999. *The structure and rheology of complex fluids* (Vol. 150). New York: Oxford university press.

4 Cabrera, S.M., Bryan, J., Komishke, B. and Kantzas, A., 2009. Study of the settling characteristics of tailings using nuclear magnetic resonance technique. *International Journal of Mining, Reclamation and Environment*, *23*(1), pp.33-50.

5 Sposito, G., Skipper, N.T., Sutton, R., Park, S.H., Soper, A.K. and Greathouse, J.A., 1999. Surface geochemistry of the clay minerals. *Proceedings of the National Academy of Sciences*, *96*(7), pp.3358-3364.

6 Gold, V., Loening, K.L., McNaught, A.D. and Shemi, P., 1997. Iupac compendium of chemical terminology. *Blackwell Science, Oxford*.

7 Debye, P. and Hückel, E., 1923. De la theorie des electrolytes. I. abaissement du point de congelation et phenomenes associes. *Physikalische Zeitschrift*, *24*(9), pp.185-206.

8 Levine, S., 1939. Problems of stability in hydrophobic colloidal solutions. I. On the interaction of two colloidal metallic particles. General discussion and applications. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, pp.145-164.

9 Levine, S. and Dube, G.P., 1939. Interaction between two hydrophobic colloidal particles, using the approximate Debye-Hückel theory. I. General properties. *Transactions of the Faraday Society*, *35*, pp.1125-1140.

10 Levine, S. and Dube, G.P., 1939. Interaction between two hydrophobic colloidal particles, using the approximate Debye-Hückel theory. I. General properties. *Transactions of the Faraday Society*, *35*, pp.1125-1140.

11 Derjaguin, B.V. and Landau, L., 1941. Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes. *Acta physicochim. URSS*, *14*(6), pp.633-662.

12 Laird, D.A., 1997. Bonding between polyacrylamide and clay mineral surfaces. *Soil science*,

---

162(11), pp.826-832.

13 Kitchener, J.A., 1972. Principles of action of polymeric flocculants. *British Polymer Journal*, *4*(3), pp.217-229.

14 Painter, P.C. and Coleman, M.M., 1994. *Fundamentals of polymer science: an introductory text*. Technomic.

15 Serres, A., Baudyš, M. and Kim, S.W., 1996. Temperature and pH-sensitive polymers for human calcitonin delivery. *Pharmaceutical research*, *13*(2), pp.196-201.

16 Vedoy, D.R. and Soares, J.B., 2015. Water‐soluble polymers for oil sands tailing treatment: A Review. *The Canadian Journal of Chemical Engineering*, *93*(5), pp.888-904.

17 Porterfield, W.W., 2013. *Inorganic Chemistry*. Academic press.

18 Brinker, C.J., 1988. Hydrolysis and condensation of silicates: effects on structure. *Journal of Non-Crystalline Solids*, *100*(1), pp.31-50.

19 Salon, M.C.B. and Belgacem, M.N., 2010. Competition between hydrolysis and condensation reactions of trialkoxysilanes, as a function of the amount of water and the nature of the organic group. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *366*(1), pp.147-154.

20 Arkles, B., Steinmetz, J.R., Zazyczny, J. and Mehta, P., 1992. Factors contributing to the stability of alkoxysilanes in aqueous solution. *Journal of Adhesion Science and Technology*, *6*(1), pp.193-206.

21 Plueddemann, E.P., 1991. Chemistry of silane coupling agents. In *Silane coupling agents* (pp. 31-54). Springer US.

22 Mitsukami, Y., Donovan, M.S., Lowe, A.B. and McCormick, C.L., 2001. Water-soluble polymers. 81. Direct synthesis of hydrophilic styrenic-based homopolymers and block copolymers in aqueous solution via RAFT. *Macromolecules*, *34*(7), pp.2248-2256.

23 Salon, M.C.B. and Belgacem, M.N., 2010. Competition between hydrolysis and condensation reactions of trialkoxysilanes, as a function of the amount of water and the nature of the organic group. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *366*(1), pp.147-154.

---

24 Brinker, C.J., 1988. Hydrolysis and condensation of silicates: effects on structure. *Journal of Non-Crystalline Solids*, *100*(1), pp.31-50.

25 Pingarrón Alvarez, V.I., 2006. Performance analysis of hydraulic lime grouts for masonry repair. *Theses (Historic Preservation)*, p.13.

26 Hill, C.A., Farahani, M.M. and Hale, M.D., 2004. The use of organo alkoxysilane coupling agents for wood preservation. *Holzforschung*, *58*(3), pp.316-325.

27 Plueddemann, E.P., 1991. Reminiscing on silane coupling agents. *Journal of Adhesion Science and Technology*, *5*(4), pp.261-277.

28 Xie, Y., Hill, C.A., Xiao, Z., Militz, H. and Mai, C., 2010. Silane coupling agents used for natural fiber/polymer composites: A review. *Composites Part A: Applied Science and Manufacturing*, *41*(7), pp.806-819.

29 Shang, H., Liu, J., Zheng, Y. and Wang, L., 2009. Synthesis, characterization, and flocculation properties of poly (acrylamide-methacryloxyethyltrimethyl ammonium chloride-methacryloxypropyltrimethoxy silane). *Journal of Applied Polymer Science*, *111*(3), pp.1594-1599.

30 Björkegren, S.M.S., Nordstierna, L., Törncrona, A., Persson, M.E. and Palmqvist, A.E., 2015. Surface activity and flocculation behavior of polyethylene glycol-functionalized silica nanoparticles. *Journal of colloid and interface science*, *452*, pp.215-223.

31 Fuerstenau, M.C., Jameson, G.J. and Yoon, R.H., 2007. *Froth flotation: a century of innovation*. SME.

32 Zhu, R., Liu, Q., Xu, Z., Masliyah, J.H. and Khan, A., 2011. Role of dissolving carbon dioxide in densification of oil sands tailings. *Energy & Fuels*, *25*(5), pp.2049-2057.

33 Jones, B.E. and Haynes, R.J., 2011. Bauxite processing residue: a critical review of its formation, properties, storage, and revegetation. *Critical Reviews in Environmental Science and Technology*, *41*(3), pp.271-315.

34 Banks, M.K., Waters, C.Y. and Schwab, A.P., 1994. Influence of organic acids on leaching of heavy metals from contaminated mine tailings. *Journal of Environmental Science & Health Part A*, *29*(5), pp.1045-1056.

---

35 Walter, A.L., Frind, E.O., Blowes, D.W., Ptacek, C.J. and Molson, J.W., 1994. Modeling of multicomponent reactive transport in groundwater: 1. model development and evaluation. *Water Resources Research*, *30*(11), pp.3137-3148.

36 Macur, R.E., Wheeler, J.T., McDermott, T.R. and Inskeep, W.P., 2001. Microbial populations associated with the reduction and enhanced mobilization of arsenic in mine tailings. *Environmental science & technology*, *35*(18), pp.3676-3682.

37 Han, D., Boissiere, O., Kumar, S., Tong, X., Tremblay, L. and Zhao, Y., 2012. Two-way CO2-switchable triblock copolymer hydrogels. *Macromolecules*, *45*(18), pp.7440-7445.

38 Han, D., Tong, X., Boissière, O. and Zhao, Y., 2011. General strategy for making CO2-switchable polymers. *ACS Macro Letters*, *1*(1), pp.57-61.

39 Wai, C.M. and Waller, B., 2000. Dissolution of metal species in supercritical fluids principles and applications. *Industrial & engineering chemistry research*, *39*(12), pp.4837-4841.

40 Tomioka, O., Meguro, Y., Iso, S., Yoshida, Z., Enokida, Y. and Yamamoto, I., 2001. New method for the removal of uranium from solid wastes with supercritical CO2 medium containing HNO3-TBP complex. *Journal of nuclear science and technology*, *38*(6), pp.461-462.

41 Rubin, J.B., Taylor, C.M., Paviet-Hartmann, P. and Hartmann, T., 2000. Ash Cements Stabilized by Supercritical Co2 Carbonation for Tailings Pond Overlayer. In *Turning a Problem into a Resource: Remediation and Waste Management at the Sillamäe Site, Estonia* (pp. 253-263). Springer Netherlands.

42 Wilson, S.A., Barker, S.L., Dipple, G.M. and Atudorei, V., 2010. Isotopic disequilibrium during uptake of atmospheric CO2 into mine process waters: Implications for CO2 sequestration. *Environmental science & technology*, *44*(24), pp.9522-9529.

43 Yu, W.Z., Gregory, J., Campos, L. and Li, G., 2011. The role of mixing conditions on floc growth, breakage and re-growth. *Chemical Engineering Journal*, *171*(2), pp.425-430.

44 Hudson, H.E. and Wolfner, J.P., 1967. Design of mixing and flocculating basins. *Journal (American Water Works Association)*, *59*(10), pp.1257-1267.

45 Salon, M.C.B., Bayle, P.A., Abdelmouleh, M., Boufi, S. and Belgacem, M.N., 2008. Kinetics of hydrolysis and self condensation reactions of silanes by NMR spectroscopy. *Colloids and*

Surfaces A: Physicochemical and Engineering Aspects, *312*(2), pp.83-91.

ii

46 Wang, Y., Wang, P., Kohls, D., Hamilton, W.A. and Schaefer, D.W., 2009. Water absorption and transport in bis-silane films. *Physical Chemistry Chemical Physics*, *11*(1), pp.161-166.

47 Rodrigues, M.I. and Iemma, A.F., 2014. *Experimental design and process optimization*. CRC Press.