STUDIES OF ANODISING SLUDGE AND ITS USES

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Abstract

Anodising is an important finishing technique used to produce controlled oxide coating on aluminium extrusions which impart aesthetic finish, longer life and resistance to corrosion and abrasion. The anodising process however leads to generation of significant amounts of acid and alkaline waste containing mainly aluminium. Normally these wastes are neutralised producing aluminium hydroxide sludge the disposal of which is problematic.

Finex is New Zealand's most recently developed anodising plant established in Hamilton in 2004. During the first period of operation the company was faced with a costly sludge disposal problem. The present project was devised to study their production plant and wastewater treatment plant. A brief study of the sludge showed that even under optimum conditions and with use of polyelectrolyte, gravity settling produced excessive volumes of sludge. The decision was made to install a plate and frame filter press.

With the reduction of its bulk by dewatering, the problem of sludge disposal was essentially solved. However the 12 tonnes per week of dewatered sludge production still posed the challenge of devising a way of using the material beneficially. The characteristics of the sludge were determined and routes to commodity products were investigated.

Commodity alum was produced in good yield at 4°C by treatment of the sludge with sulphuric acid followed by crystallisation with anhydrous potassium sulphate. The product was very similar to the commercial product. Under basic conditions, sodium aluminate was produced by adding stoichiometric amount of OH^-. Under acid conditions at the $H^+/Al(OH)_3$ stoichiometric ratio of 3, 95% of the aluminium was recovered as aluminium salt solution. When acid addition was less than the stoichiometric ratio of 3, the polyelectrolyte containing sludge showed little tendency to re-suspend. A variety of mechanical and thermal methods was used in an attempt to disaggregate and re-suspend the sludge. These included ultrasonic treatment at 80°C at frequency 14 kHz for 6 hours, autoclaving the sludge in electrical furnace at 150°C for 6 hours, homogenisation at 3000 rpm for 30 minutes at 20°C and mechanical grinding using mortar and pestle at 20°C. The

ultrasonic treatment was effective in re-suspending 30% of the sludge. The other treatments were largely ineffective.

On comparing the heavy metal concentration present in the original anodising sludge with the heavy metal concentration in the recovered commodity products, it was found that heavy metal content reduction was achieved with the alum crystallisation process. On producing aluminate, Cd, Mg and Ni were reduced through the removal of insoluble hydroxides. Minimal reduction of heavy metal content was achieved in the acidic aluminium chloride solution.

The acidic and alkaline products prepared from anodising sludge were tested for their usefulness as coagulation agents. Critical coagulation concentrations for kaolin suspensions for all products were determined to be 5 mg/L. For all systems except the ultrasonic re-suspended sludge, clear solutions of low turbidity resulted after 1 hour standing.

An analysis of the cost recovery of various commodity products from waste sludge indicated that recovery of acid aluminium chloride solution was most cost effective while the recovery of alum produces the purest product. Assuming that the acid aluminium chloride solution could be substituted for and sold at the same per kg of aluminium price as polyaluminium chloride, a 52% margin over consumables cost allows the possibility of a modest profit. The main benefit to Finex from proceeding with a sludge recovery program however is likely to be enhancement of the companies green credentials.

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I have many people to thank for the assistance and support that I have gained throughout the duration of my study.

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1 General Introduction

1.1 Background

In recent years usage of aluminium has significantly increased in all segments of the world economy, with principal uses in transportation, construction, electrical applications, consumer durables, and mechanical equipment (Frei 1972; Nethercot 2002; Xie, *et al.* 2006). A number of unique and attractive properties of aluminium account for its engineering significance. These include its workability, light weight, corrosion resistance, good electrical and thermal conductivity, optical reflectivity, and ease of recycling (Fariaut, *et al.* 2001). Along with increased usage of aluminium, there has been a necessity increased for coating facilities to add protective and decorative finishes to the aluminium surface. Anodising is an electrochemical treatment method which results in aluminium alloys being coated with varying thicknesses of a controlled oxide coating (Blawert, *et al.* 2006). Such surface finish results in longer life of the aluminium metal by making it hard and corrosion and abrasion resistant. In addition it also improves surface appearance, reflectivity and several other features (Grubbs 2002).

In 1946 Southern Aluminium Finishing in United States initiated work on commercial anodising (Graves 2003). The global anodising industry has grown very rapidly since then. The anodising process generates significant effluent which must be treated before discharge to sewer systems in order to comply with local authority effluent discharge limits. Thus the reduction and recycling of anodising wastes has gathered much attention and has become a priority for both environmental regulatory agencies and the anodising industry.

The Finex anodising plant in Hamilton, New Zealand was established in 2004 and is engaged in protective oxide coating of aluminium extrusions. The majority of the trade waste generated at the Finex site is derived from alkaline and acid treatment stages. The alkaline rinse wastewater is neutralised with the spent acid anodising solutions producing voluminous aluminium hydroxide sludge contaminated with other metals in the aluminium alloy or used as part of the

anodising process (Tulyaganov, *et al*. 2002). This sludge imposes cost burdens to Finex due to its high water content and volume resulting in high transportation and disposal costs. Thus an initial objective of the present work was to investigate methods for reducing its volume by dewatering. A second general objective was to investigate possibility of developing beneficial uses for the sludge as an alternative to dumping it in landfill. Possible beneficial uses might include production of alum or dissolution and/or re-suspension for use as a coagulant.

1.2 The Finex plant

Finex is New Zealand's most modern anodising plant. It is an independent anodising operation producing high quality anodic surface finishes for the architectural, engineering and fabrication industries.

Typically an anodised extrusion at Finex goes through various immersion tanks during its treatment which deposits and seals a tough oxide layer on it. The extrusions are placed on an appropriate rack by which they are transported by crane through the various process treatment tanks. Some process solution is always left on the extrusions and it is necessary to drain and rinse it from the metal surface to prevent contamination of succeeding process bath solutions. At Finex there are water rinse tanks between each process stage. The plant operates a counter flow rinsing system to minimise the amount of water usage during anodising process. In this system rinse water overflows from the clean rinse tank to the next rinse tank which is discharged constantly to the waste treatment plant facility where the pH is adjusted to meet wastewater discharge limits. The alkali waste stream is neutralised with spent anodising acid to precipitate aluminium hydroxide which is allowed to settle. The flow in each rinse water tank is restricted by a flow regulator to minimise the direct usage of raw water and so reduce the total waste volume. Figure 1.1 presents the operational steps that are employed at Finex anodising facility.

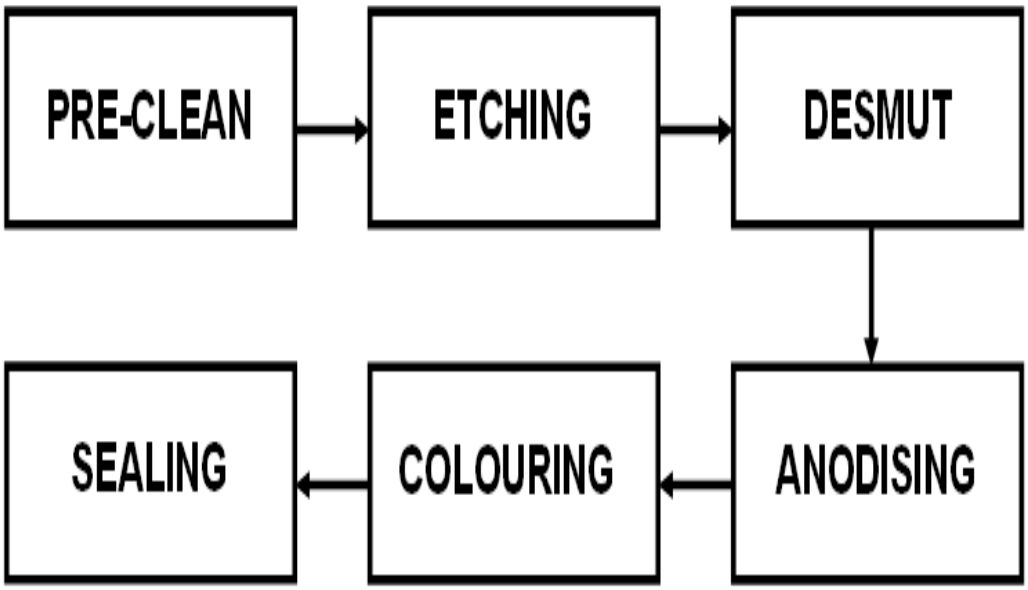

Figure 1. 1 Process operational steps at Finex (Silverton 2008)

1.3 Waste disposal at Finex

During the aluminium anodising process carried out at Finex, two types of effluents are produced: spent acidic solutions from the anodising baths and alkaline rinsing wastewater. These solutions are highly contaminated and cannot be discharged directly into the sewer. They are therefore diverted to the company's wastewater treatment plant for further treatment. Finex follows a typical trade waste treatment including the neutralisation of acidic and alkaline waste streams followed by metal hydroxide precipitation using polyelectrolyte and gravity settling of the sludge and finally dumping the gravity settled sludge to the landfill. It may be possible to reduce the volume of the gravity settled sludge by optimisation of the settling process. Alternatively, dewatering technologies might be used.

1.4 Technologies for dewatering of sludge

Dilute sludge can be dewatered by several dewatering technologies. These include rotary vacuum filtration, filter pressing and centrifugation.

1.4.1 Rotary vacuum filtration

As shown in Figure 1.2 rotary vacuum filtration consists of a cylindrical drum covered with the porous filter cloth. When the drum is slowly rotated through the slurry, the solids from the slurry are separated by the filter cloth with vacuum applied from the inner surface. A scraper is used to shave the dewatered cake from the surface of the filter cloth. The filtrate is collected in the horizontal pipes connected directly to the central drain shaft. The filter cloth is washed by a water sprayer before starting the next batch (Cheremisinoff 1995). The advantages include low capital cost compared to other dewatering technologies. The disadvantages include low dewatering capacity, low life of the filter cloth, cake build up and eventual clogging of the filter cloth (Theodore & Jornitz 1998). Large drums are required taking up large floor space areas to collect the dewatered cake. Close monitoring of operating parameters is essential for good operation (Saravanamuthu & Ben-Aim 1989).

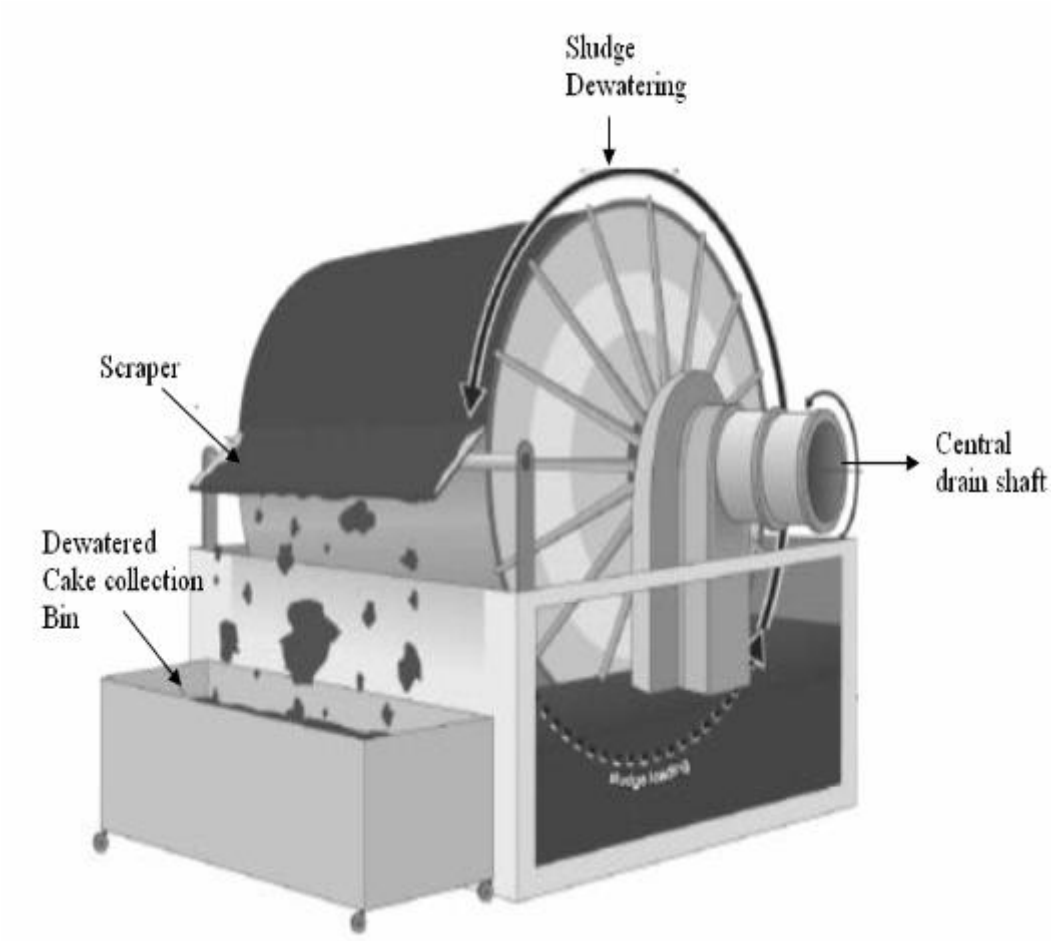

Figure 1. 2 Typical rotary vacuum filter (Barash, *et al*. 2003)

1.4.2 Filter presses

Plate and frame filter press

A typical plate and frame filter press (See Figure 1.3) consists of sequence of square vertically arranged parallel plates with cavities between the plates pressed together by a hydraulic ram pump. The filter plates are covered with filter cloths and are concave on each side to form a cavity. When the cycle starts the sludge slurry is pumped into the central cavities of the filter plates and on other side the hydraulic ram pump tightly squeezes the filter plates. The filtrate from the plates escape through the common drain outlets moulded in the filter plates and is transported to the drain point via a common filtrate pipe. The filter press uses high pressure to maximise the rate of filtration and produce highly dewatered solids. This process of pumping sludge slurry into the plates is continued until the cavities in the filter plates are filled with sludge. The pressure is then released to separate the plates and a densely formed cake easily falls in the discharging bin (Darby 2001). The advantages of the plate and frame filter press include lower capital cost, low noise; small space requirements, less tendency towards leakage, low maintenance and operating cost. The disadvantages include the short life of filter cloths and the batch operation mode (Noyes 1993).

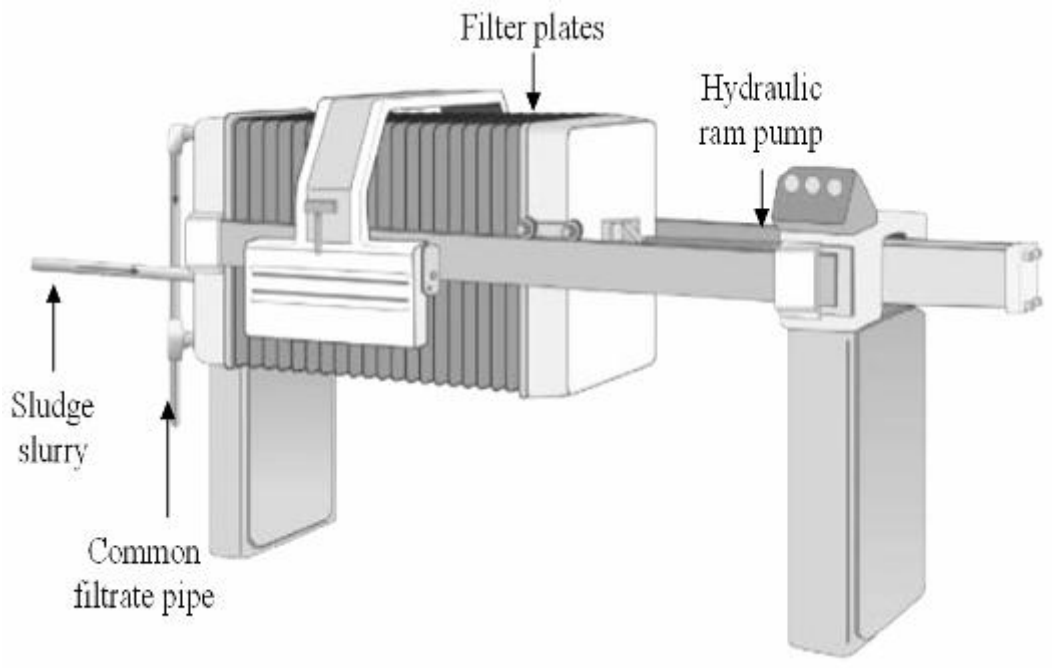

Figure 1. 3 Typical plate and frame filter press (Barash, *et al.* 2003)

Belt filter press

A typical belt filter press has the two set of belts arranged one above the other to dewater solids (See Figure 1.4). According to Alley (2000) dewatering of solids in belt filter press is carried in three operational zones:

- **Chemical conditioning zone**: The sludge is mixed with the polyelectrolyte for better flocculation of the solids. This mixing is carried either in the belt press or in the chemical conditioning tank prior to belt filter press.
- **Gravity drainage zone**: Polyelectrolyte flocculated solids enters the gravity drainage zone, where sedimentation of solids is carried out by the force of gravity. Solids free supernatant water leaves the gravity zone into drain system.
- **Compression zone:** Concentrated solids leaves the gravity drainage zone and enters the compression zone where dewatering of solids is carried out by squeezing the solids between two belts and by applying pressure to the sludge by means of drive rollers that are in contact with the belt. Now sludge enters the shear stage where the high pressure shear force is applied to bring about the final dewatering by releasing some of the bound water within the sludge. Finally the dewatered cake is removed by a scraper.

Belt filter pressing is a continuous operation with low power consumption and vibration problems. The disadvantages include higher capital cost, lower dewatering ability and short operating life of the belt caused by wear during scraping of the dewatered cake (Spellman 1997).

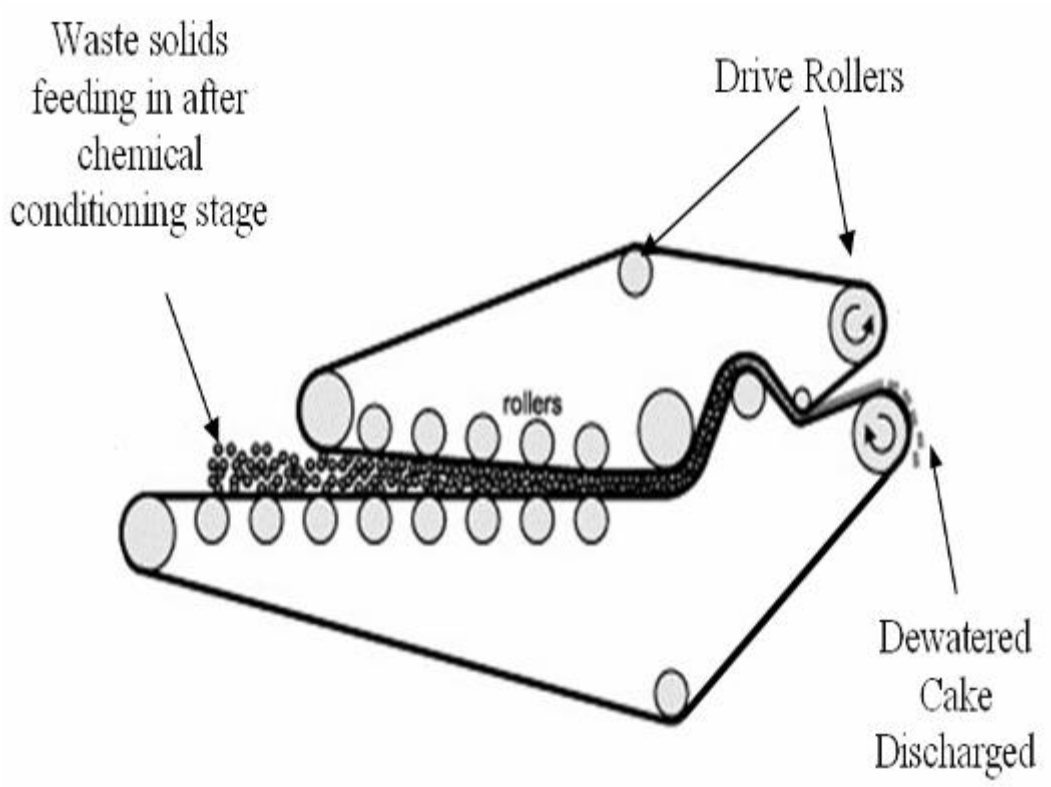

Figure 1. 4 Schematic representation of typical belt filter press (Wakeman 2007)

1.4.3 Centrifugation

Centrifugation is a solid liquid separation technology carried out by using centrifugal force. The sludge is fed into a cone shaped drum. The drum is rotated by a screw conveyor to generate a centrifugal force which allows the solids to concentrate on the wall of the drum (See Figure 1.5). This concentrate solid is continuously separated by an auger. The advantages of this device are that it does not occupy a large space, it can be operated in both batch and continuous modes and it quickly thickens large amounts of high water content slurries. Its disadvantages include the high free flowing suspended solids in the supernatant water, very noisy when operated at high speeds and high maintenance costs (Cheremisinoff 1998; Wakeman & Tarleton 1998).

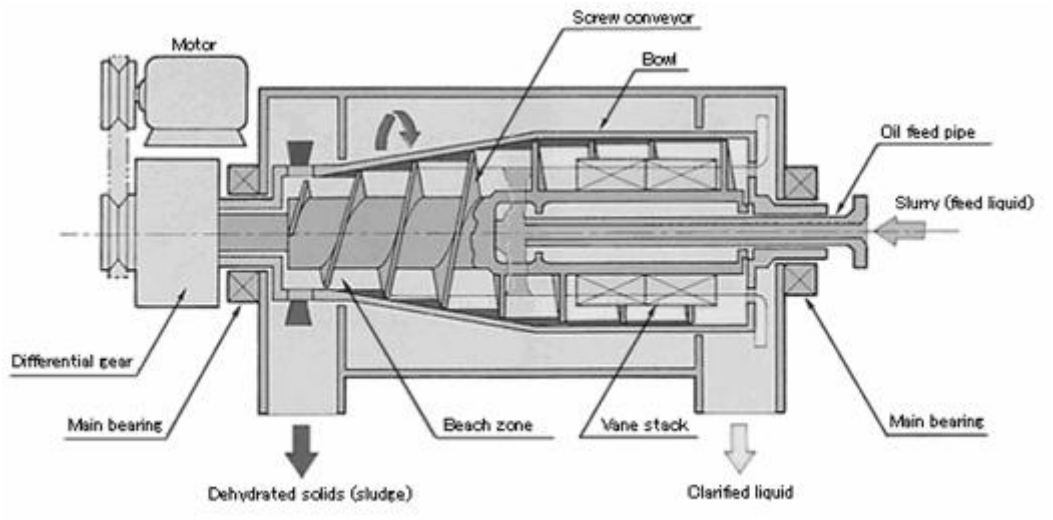

Figure 1. 5 Schematic representation showing essential features of centrifuge (Mitsubishi 2008)

1.5 Recovery of spent chemicals

The anodising process generates large quantities of wastewater from the alkaline etching and acid anodising operations carrying high concentrations of dissolved aluminium (Ferreira & Olhero 2002). Reclamation of such wastewaters and recovery of aluminium is important from both ecological and economic points of view. Etching is caused by reaction of aluminium and caustic soda which produces sodium aluminate and hydrogen gas. Complexing agents are added to the etch tank to prevent precipitation as aluminium hydroxide. If complexing agents are not used hard rock scale of aluminium hydroxide is formed in the etch tank (Wukasch & Dalton 1993).

Caustic soda and dissolved aluminium from the etching tank may be reclaimed by caustic regeneration system (See Figure 1.6). Etch solution is continuously pumped into the top of a crystalliser tank containing a slurry of aluminium hydroxide. This acts as a crystallisation generator which continuously precipitates dissolved aluminium as aluminium hydroxide crystals. These settles at the bottom of the crystalliser tank and are periodically withdrawn and dewatered by a centrifuge for ultimate disposal or sale. Regenerated etch solution with reduced aluminium and high caustic soda content is pumped back into the etch bath directly from top of the crystalliser (Anon 1983; Brown 1982; Dejak 1984; Verheul 1999).

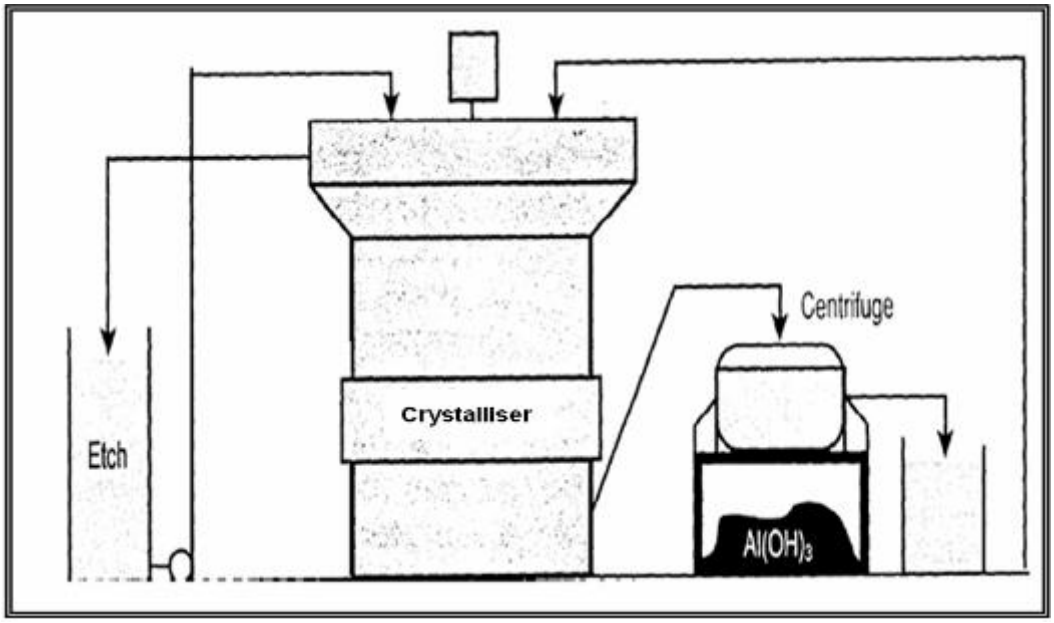

Figure 1. 6 Schematic representation of the caustic soda and aluminium recovery system (Brown 1986; Strazzi & Bellei 2002; Munns 1991)

A drawback to this type of recovery process is the fact that it is possible only if the aluminium sequestering additives are not added to the etch tank solution and limited concentration of aluminium should be present in the etching bath solution. Running the etch bath at low concentration of aluminium and without sequestering additive affects the final quality finish of the aluminium extrusions to a considerable extent (Strazzi & Bellei 2002).

The feasibility of aluminium recovery from spent acid anodising solution by ion exchange was studied by (Brown, *et al.* 1979). This technique, commercially known as APU®, uses proprietary ion exchange resins which selectively absorb the acid component from acid solutions of dissolved metal salts (Sheedy 1997). The acid purification unit includes two main operational steps: sorption and desorption. In the sorption step contaminated anodising acid is pumped into the bottom of the resin column resulting in sorption of the acid by the resin and rejection of aluminium salt solution which passes through the resin column. During the desorption step water is pumped from the top of the column desorbing acid from the resin and the recovered acid product is collected from the bottom of the resin column. This cycle is repeated continuously by automatically opening and closing a series of valves (Barash, *et al*. 2003). Figure 1.7 shows the typical process flows of acid purification system.

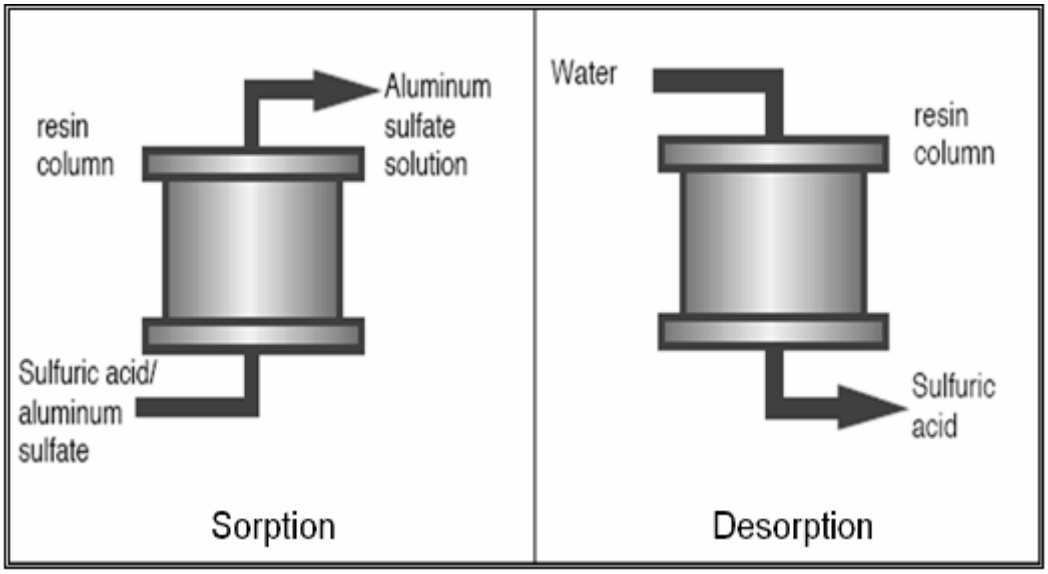

Figure 1. 7 Schematic diagram showing operating cycles of acid purification unit (Pajunen & Harrison 1997)

One drawback to this type of recovery process is the fact that the acid removal rates per pass can be as low as 25%. The reason for such low recovery is due to entrapment of aluminium in the resin bed columns (Bailey 1998).

Further studies have used diffusion dialysis technology to recycle spent anodising acid and aluminium (Jeong, *et al.* 2005). Diffusion dialysis is a membrane separation process in which an anion exchange membrane acts as a semi permeable barrier between flowing deionised water and aluminium contaminated acid solution (See Figure 1.8). The anion exchange membrane has the positive charge which will attract and diffuse the sulphate ion through its surface. According to the physical law of diffusion and electroneutrality substance of high concentration must flow to low concentration without imbalance in electrical charge. So to satisfy law of electroneutrality and to stop creating any imbalance on other side of membrane every sulphate ion that passes through the membrane carries two positively charged hydrogen ions (Lin & Lo 1998).

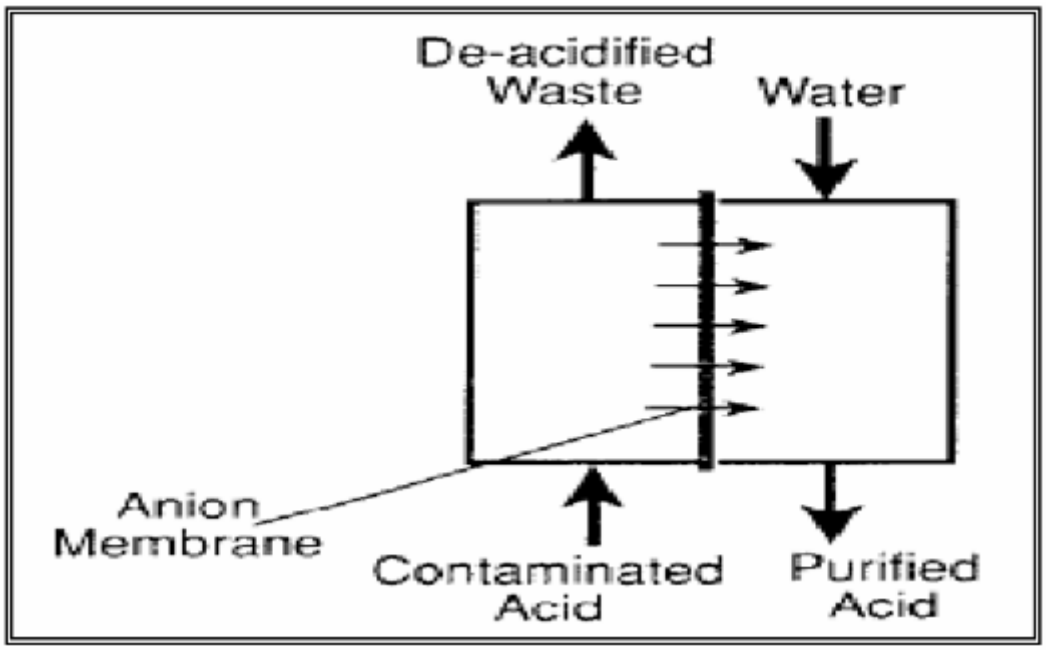

Figure 1. 8 Schematic diagram showing working of diffusion dialysis (Munns 1991)

The hydrogen ions present in the acid solution will cross the membrane due to their high concentration in the acid, small size relative to aluminium and their high mobility (Barash, *et al.* 2003). Aluminium's passage across the membrane is inhibited due to charge repulsion and the selectivity of membrane. The net effect will be a higher rate of diffusion of acid through the membrane than dissolved aluminium. The concentration gradient is maintained by flow of acid in the opposite direction to the flow of water. Water entering the diffusion dialysis system exits as reclaimed metal depleted purified acid solution and the contaminated acid entering the diffusion dialysis system exits as an acid solution contaminated with high metal content (Franken 2003; Smith & Means 1994).

The major drawbacks of these systems are their very high capital and maintenance cost and the considerable amount of aluminium and process chemicals lost as a reject waste and drag out waste from the rinse tanks.

An alternative strategy for reclaiming useful materials from anodising waste is to generate aluminium commodities from the sludge when the waste streams are neutralised prior to disposal. The aqueous chemistry of Aluminium(III) indicates several possibilities.

1.6 Aqueous chemistry of Aluminium(III)

The Al^{+3} ions formed by the dissolution of aluminium salts in water undergo hydration to form a primary hydrated shell with six octahedrally co-ordinated water molecules to form the species $Al^{+3}_{(aq)}$ (Jiang & Graham 1998). Hydrolysis of such ions results in serial loss of protons.

$$Al^{+3}_{(aq)} \underset{pK_1}{\leftrightarrow} AlOH^{2+}_{(aq)} \underset{pK_2}{\leftrightarrow} Al(OH)_2{}^{+}_{(aq)} \underset{pK_3}{\leftrightarrow} Al(OH)_{3(s)} \underset{pK_4}{\leftrightarrow} Al(OH)_4{}^{-}_{(aq)} \qquad (1.1)$$

Where the pK values for the equilibria are summarised in Table 1.1.

Table 1. 1 Hydrolysis and solubility constants for Al^{+3} for zero ionic strength at 25 °C (Sposito 1996; Sarpola 2007)

pK_1	pK_2	pK_3	pK_4
4.95	5.6	6.7	7.5

In the above equation 1.1, each individual step involves deprotonation which causes the equilibria to be shifted to the right. At intermediate pHs, fresh amorphous aluminium hydroxide is precipitated. Aluminium hydroxide is colourless gel, amphoteric in nature and insoluble in water (Harding, *et al.* 2002). On ignition at about 500°C aluminium hydroxide is converted into aluminium oxide (Al_2O_3) or alumina (Baynes 1888; Bokhonov, *et al.* 1995). The calculated variation of soluble species with pHs is shown in the Figure 1.9.

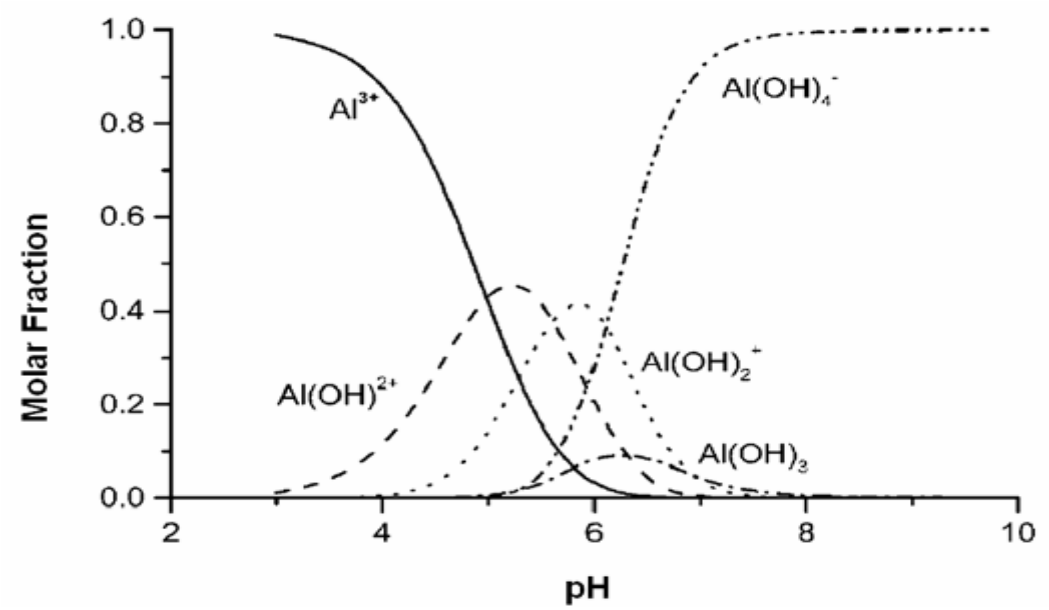

Figure 1. 9 Distribution of Al hydrolysis products as a function of pH (Gregory & Duan 2001)

The above Figure 1.9 illustrates that at pHs between 5 to 8 $Al(OH)_3$ is formed. At pHs above 8, $Al(OH)_3$ should form soluble $Al(OH)_4^-$ and below 5, $Al(OH)_3$ should form soluble species of Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$ (Gitelman 1989). Thus providing equilibrium is reached it should be possible to dissolve precipitated $Al(OH)_3$ by either raising the pH above 8 or lowering the pH below pH 5.

1.7 History of reclamation of anodising sludge

The successful use of sodium aluminate generated as a waste from alkaline etching solution from aluminium finishing industries was reported by Shut'ko & Butchenko (1987). Recently a study was conducted to regenerate concentrated free caustic by precipitating the aluminium from the etching solution with precipitating agents (Barakat, *et al.* 2005). Four different precipitating agents were hydrated lime [$Ca(OH)_2$], hydrogen peroxide (H_2O_2), $H_2O_2/Ca(OH)_2$ mixture, and dry lime (CaO). It was concluded that CaO was most efficient. The production of various types of zeolites for industrial use from residual effluents of aluminium industries was investigated by La Iglesia, *et al.* (2002). They concluded that zeolites 4A and 13X, could be synthesised from acid anodising effluent and zeolites Y and ZSM-5 could be synthesised from alkaline aluminium extrusion effluents. In a further study, alkali waste solution was reacted with sodium silicate to remove the aluminium as zeolite and unreacted alkali was recovered (Saito, *et al*. 1985).

While the processes described above have the advantage of reclaiming waste aluminium from anodising effluents in presence of sequestering agents they have not been implemented because of cost and the absence of a commercial market for the grade of zeolite product produced.

Several studies report on the use of anodising sludge directly as a coagulant to aid in phosphorus removal at municipal wastewater treatment plants. Spent aluminium sludge proved to be an effective coagulant for the removal of phosphorus, turbidity and COD (Panswad & Chamnan 1992; Georgantas & Grigoropoulou 2005).

A successful study was carried out on aluminium rich anodising sludges to produce high-alumina refractory ceramics by calcining the sludge at up to 800 °C (Ferreira & Olhero 2002). The production of cordierite-based materials and diatomite from industrial anodising sludge was investigated by using dry pressing and extrusion as a shaping method (Tulyaganov, *et al.* 2002; Labrincha, *et al.* 2006). However a major drawback is the fact that anodising sludge cannot be directly used in the production of alumina rich ceramic products without costly drying.

The conclusion drawn from the literature is that there remains a need for a simple, technically and commercially feasible technique which would allow extraction of aluminium from anodising sludge in a form that could be beneficially used. Use as a coagulant is a possibility.

1.8 Coagulant characterisation

The removal of particles from water is often achieved by coagulation. Coagulation is a well known process for solid liquid separation and removal of turbidity present in the wastewater. Colloidal suspensions in aqueous media appear to be very cloudy and the observed turbidity directly depends on two factors mass concentration and the particle size distribution. Particles are capable of remaining in the suspension for long periods of time. Coagulation can be described as the process that brings about aggregation of small particles that are suspended in the liquid medium (Correia, *et al.* 2005). Cationic coagulants act by compression of diffuse layer, charge neutralisation of negatively charged colloids and absorption of impurities in the amorphous precipitate of metal hydroxide formed during the coagulation process (O' Melia & Amritharajah 1990).

The most common chemicals used in the coagulation process at wastewater treatment plants are Al(III) species, such as aluminium sulphate, polyaluminium chloride and sodium aluminate (Edzwald 1993). The main advantages of using Al^{+3} salt coagulants is their improved floc formation, remarkable ability to entrap suspended solids and lower sludge volume (Delgado, *et al*. 2003). In recent years polymerised forms of aluminium coagulants have been used.

1.8.1 Potassium aluminium sulphate (alum)

In 1830, Sprengel was the first chemist to propose the extraction of potassium aluminium sulphate (alum) from minerals. In 1842, Turner patented Sprangel process (Ronalds 1855). The general formula of double salt alums is $M^{+}M^{3+}(SO_4)_2.12H_2O$, where M^{+} is the univalent cation commonly (Na^{+}, K^{+}, Ti^{+}, NH_4^{+}, or Ag^{+}); M^{3+} is a trivalent cation commonly Al^{3+}, Cr^{3+}, Ti^{3+}, or Co^{3+}. Potassium alum is favoured because it can be easily precipitated by evaporation from the aqueous solutions of potassium sulphate and aluminium sulphate (Holden 1961). The most common method of alum synthesis is by treating bauxite ore with sulphuric acid. Powdered bauxite is digested with sulphuric acid. It is then treated with barium sulphide to reduce Fe^{+3} to Fe^{+2}, and the solution is filtered. The filtrate is then mixed with calculated amount of potassium sulphate and the solution is allowed to cool. Regular octahedral shaped crystals of potash alum separate out (Jain 2000).

Potash alum consists of 18.34% sulphate of potash, 36.20% sulphate of alumina and 45.46% water (Ure 1846). It is soluble in from 16 to 20 times its weight of cold water and slightly more than its own weight of boiling water (Bristow 1861). On heating, it melts at 92.5°C in its own water of crystallisation (Jain 2000). For many years alum has been widely used as a mordant in dyeing, as a tanning agent, as a cement hardener, as a precipitant for wastewater treatment, for purification of drinking water, as a food additive and even as an astringent to stop bleeding (Emsley 1999). The solubility of potassium alum at various temperatures is shown in the following Table 1.2 according to Graham (1858):

Table 1. 2 Solubility of potassium alum at various temperatures

Temperature(°C)	g Alum/100g of water
0°C	3.20
10°C	9.52
30°C	22.00
60°C	31.00
70°C	90.00
100°C	357.00

From the above table 1.2 it is clear that the solubility of potassium alum is very temperature dependent.

1.8.2 Polyaluminium chloride

In 1960s, research into inorganic coagulants led to the development of partially hydrolysed polymerised aluminium salts. These are the inorganic polymers with high molecular weight. These polymers have a number of advantages including faster floc formation, lower dose rate, savings in pH adjustment chemicals and greater effectiveness at lower temperature (Smethurst 1979). Polyaluminium chloride is produced by forcing hydrolysis of simple coagulants like alum or aluminium chloride through the addition of base. The degree of neutralisation generally expressed as the mole ratio of neutralisation denoted as 'r'.

$$r = (\text{moles } OH^-) / (\text{moles } Al^{+3}) \quad (1.2)$$

In commercial polyaluminium chloride solutions the degree of neutralisation (r) is 2.46 (Hahn, *et al.* 2002). The species in polyaluminium chloride (PAC) are of three types: Al_a (mononuclear Al, including Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$), Al_b (medium polymer species), and Al_c (larger polynuclears and/or $Al(OH)_3$) (Bottero, *et al.* 1980; He, *et al.* 2005).

Among the Al_b species, Al_{13} ($[AlO_4Al_{12}(OH)_{(24+n)}(H_2O)_{(12-n)}]^{(7-n)+}$) has been detected in freshly prepared solutions (Akitt, *et al.* 1972). Al_b is considered to be one of the more efficient species of PAC and is also regarded as helpful in improving the performance of PAC due to its high positive charge and stability.

1.8.3 Sodium aluminate

Sodium aluminate is a widely known commercial inorganic coagulant. It is prepared by treating aluminium oxide with caustic soda. Sodium aluminate is highly alkaline, viscous and corrosive compound. It is available in anhydrous and liquid form. It differs from alum as a coagulant as it is very alkaline in its reactions compared to acidic alum. It is sometimes used in conjunction with alum as a coagulant to get special results. For example coagulating highly coloured water with alum lowers pH and results in undesired levels of soluble aluminium. This can be precipitated by adding sodium aluminate which raises the pH. Thus

sodium aluminate is substituted for part of alum dosage. It is used in several other applications such as in paper industry, as concrete solidifier, in brick production (Bratby 2006; Elliott 1998; Scholz 2006). It is also used in lime softening which by formation of insoluble calcium aluminate flocculates precipitated calcium carbonate and magnesium hydroxide (Twort, *et al.* 2000).

1.9 Objectives of the present study

Considering the literature related to the anodising industry and bearing in mind what is known about the chemistry of aluminium, the following specific objectives were recognised as being worthy for investigation:

- A study of the Finex site and their current waste treatment system to allow a better understanding of where waste is generated and how it might be minimised. This will also involve a detailed characterisation of the amount and nature of sludge currently being produced.
- An evaluation of dewatering technologies with the view of adopting a cost effective technology to reduce the volume of the material currently disposed of to landfill. This will also involve characterisation of the dewatered sludge once a dewatering technology is installed.
- An investigation on beneficial uses of the sludge produced at the Finex site. The aluminium literature suggests three processes might be possible. These include the production of commercial grade anhydrous potassium aluminium sulphate (alum), production of an acidic dissolved aluminium or acidic re-suspended colloidal solution of aluminium cations or hydrolysis products resembling commercial coagulant (polyaluminium chloride) and production of alkaline coagulant resembling the commercial coagulant (sodium aluminate).

2 Materials and methods

2.1 Introduction

The methods used to collect and characterise the aluminium hydroxide sludge, identify products formed during the recovery experiments and test the effectiveness of the recovered aluminium products for water treatment applications will be described.

2.2 Characterisation of sludge

2.2.1 Preparation and settling of gravity settled sludge

Gravity settled sludge (GSS), was the sludge settled by gravity after mixing the alkaline wastewater from etch rinse with the spent anodising acid.

To prepare the GSS, 20 L liquid samples of the acid and alkaline waste solution were collected in clean, sealable, dried plastic containers, pre-rinsed by the waste solution before collection. These liquid samples were transported to the laboratory and stored at 20°C and used for the preparation of sludge and other work. The acid and alkaline waste liquids were reacted with each other to give a range of final pH values (CyberScan 2500 pH meter calibrated at pH 4.0 and 7.0 before use).

The sludge suspensions were allowed to settle for 10 days in a 1 L graduated measuring cylinder. The settled sludge volume was measured at appropriate intervals of each day to determine the settling rate.

To determine the effect of polyelectrolyte addition on the settling rate and properties of the sludge, the preparation was repeated at the pH of optimum settling with the addition of 0.2% anionic polyelectrolyte (Acefloc 903L) provided by Ace Water Treatment Limited, Christchurch.

2.2.2 Filter press sludge

A composite sample of filter press sludge (FPS) was collected for a week from all sides of the waste discharge bin immediately after pressing and was stored in an air tight snap locked polyethylene bag.

2.2.3 Water and non-volatile solids content of the sludge

In order to determine sludge water content, a weighed amount of the GSS and FPS was transferred in a dry porcelain dish, which had been pre-heated for 1 hour at 105°C, stored in a desiccator and weighed before use. After transferring the sludge to the porcelain dish it was weighed again and placed in the oven set at 105°C for 24 hours. After cooling in the dessicator, the sample was weighed again. This cycle of drying, cooling, desiccating and weighing was repeated for 72 hours.

To measure the amount of non-volatile solids present, the sludge dried at 105°C for 72 hours was further heated at 500°C for 4 hours which was sufficient to achieve constant weight (APHA, *et al.* 2005).

The non volatile solids content was determined by the equation:

$$\textit{Non-volatile solids content (\%)} = \frac{(A-B)\times 100}{(A-C)} \qquad (2.1)$$

A = Weight of the porcelain dish + sludge (before heating at 500°C), g
B = Weight of the porcelain dish + sludge (after heating at 500°C), g
C = Weight of the porcelain dish, g

2.2.4 XRD analysis

X-ray diffraction analysis (XRD) (Philips X'pert instrument with 2Θ ranging from 20° to 100° at intervals of 0.03°) was carried out to determine crystallinity of the fresh FPS, the FPS dried at 105°C and FPS dried at 500°C. The heated samples were prepared by crushing and grinding to a fine powder using a mortar and pestle.

XRD analyses were also used to confirm the preparation of alum by comparison of the diffraction patterns of the prepared crystals with that of a commercial sample of potassium alum.

2.2.5 XRF analysis

The elemental content of the dried (105°C) FPS was determined by using X-ray fluorescence (XRF) spectroscopy. The sludge was ground to fine powder by using mortar and pestle. Nine grams of $Li_2B_4O_7$ was added to 1 g of sample and fused into a glass bead. Element analyses were performed on the fused bead using a Specrto X-lab 2000.

2.2.6 SEM/EDXS analysis

Scanning Electron Microscopy–Energy Dispersive X-ray Spectrometry (SEM-EDXS) analysis (Hitachi S4100) was carried out to investigate the microstructure and morphology of the fresh and heated (105°C) FPS at low and high magnifications. To determine elemental analysis at higher magnification a small amount of the fresh FPS sample was crushed and transferred to a microscope stubb, coated with platinum by ion sputtering (to make the sample conducting) and was stored in a vacuum dessicator before examination.

Similarly, SEM-EDXS analysis was carried out on the prepared crystals.

2.2.7 Metal analysis by ICP-OES

Samples were stored in 30 mL plastic specimen bottle and 1 mL of conc. HNO_3 was carefully added to them. Samples were then stored in a refrigerator at 4°C until analysed. All sample bottles used were first cleaned using the following procedure: (1) degreasing with clean soapy water, (2) washing with acetone, (3) soaking in warm (40°C–50°C) 2 Molar HNO_3, (4) rinsing with Milli-Q water.

Analysis for aluminium and heavy metal contamination was carried out by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a GBC Integra ICP Spectrometer. The instrument was optimised using a multi element standard containing Al, Mg, Cd, Ni, Pb, Sn, Fe and Zn. This was used to find the most sensitive wavelength and the wavelength which would have the least

interference. Parameters such as power, viewing height were adjusted until the maximum and most stable signal was observed from each element (APHA, *et al.* 2005). For the metal determinations the instrument was calibrated using a standard solution containing 5 mg/L Al, Mg, Cd, Ni, Pb, Sn, Fe and Zn prepared by adding 5 mL of 1000 mg/L stock solution to a 100 mL deionised water. The 1000 mg/L stock solutions of Al, Mg, Cd, Ni, Pb, Sn, Fe and Zn were prepared according to protocols used in the Department of Chemistry (Barker 2008).

Milli-Q water with 2 mL of concentrated HNO_3/L of Milli-Q water was used for the blank. The typical calibration curves of Al, Mg, Cd, Ni, Pb, Sn, Fe and Zn are shown in appendix-A.

2.3 Jar testing of recovered aluminium coagulants

The effectiveness of recovered acidic aluminium chloride solution, alkaline aluminate solution, ultrasonic re-suspended sludge solution and alum was tested in coagulation trial using a jar tester (Boltac Industries, Hamilton) and kaolin suspensions. Synthetic turbid water was prepared by mixing 50 g of laboratory grade kaolin powder into 1 L distilled water. The suspension was stirred slowly at 30 rpm for 3 hours in the jar test apparatus to produce a uniform dispersion of kaolin particles. The suspension was then allowed to stand for 24 hours for complete hydration of kaolin. This kaolin suspension was used as a stock solution for preparation of water samples of same turbidity for coagulation tests. Six 1 L beakers were filled with 1 L tap water and the turbidity of each beaker was adjusted to 30 NTU by drop wise addition of kaolin stock solution. The pH of all six jar test beakers were adjusted to the desired pH by using 0.1 mol/L NaOH or 0.1 mol/L HCl followed by addition of appropriate volumes of recovered aluminium solution to give concentration ranging from 1 to 6 mg/L. The pH was re-adjusted to the desired value. The suspension was allowed to mix slowly at 20 rpm for 10 minutes followed by rapid mixing at 60 rpm. The rapid stirring was carried out for 30 minutes followed by 60 minutes settling period. After settling, turbidity of the supernatant was measured by turbidity meter (HACH 2100P). The experiment was repeated at six different pH values ranging between 5 and 7.5.

3 Studies of the anodising process at Finex

3.1 Introduction

This chapter summarises details of the processes used at the Finex site. A process flow diagram was constructed. Effluent generated from each process was determined and the characteristics of the sludge produced were investigated with the aim of reducing disposal costs.

3.2 Processing operations at Finex

Initially the extrusion is degreased in the hot (60°C) pre-cleaning solution for thoroughly cleaning the extrusion marks, body oils, greases and other surface contamination. After rinsing with water the metal is etched in hot (60°C - 65°C) strong caustic soda solution to remove the existing natural oxide layer and to remove minor imperfection like machining defects that may exist on the metal surface. It is then rinsed twice. After etching operation the smut of residual metallic alloying materials remaining on the metal surface is removed by desmutting at ambient temperature in a dilute nitric acid solution followed by the two rinses. Now the metal is ready for anodising. This is achieved by immersion in an electrolyte of sulphuric acid at 18°C - 20°C. Electrical current of up to 10000 amps at 15 to 20 volts is applied at the current density of 1.6 amp/decimetre^2 between the aluminium metal anodes and the cathodes along the sides of the tank. The resulting electric circuit creates an oxidation process at the anode and hence the metal develops an oxide coating. The metal is then rinsed three times. For satin anodising the metal is carried to the seal stage. If colour is required the metal precedes to the 2- step electrolytic colouring bath. At this stage there is a combination of an inorganic metal salt and electrical AC/DC current at 20°C - 25°C. A current of about 4000 to 5500 amp is applied which deposits the inorganic metal salt in the base of pores. The colour is determined by the thickness of the deposit. The work is then sealed at 85°C in a thermo chemical process. Finally the metal is rinsed in hot deionised water at 64°C.

Figure 3. 1 Aluminium extrusions being lifted out of a chemical process tank at Finex

Table 3. 1 Process baths chemicals and operating conditions at Finex

No	Tank	Chemicals & concentration	Temp	Time	Agitation
1	Pre-cleaner	5% -10% by volume of inhibited immersion alkaline detergent and surfactant.	60ºC	2 to 10 minutes depends on the contamination	No air agitation
2	Rinse	Tap water	Ambient	30 seconds	Mild air agitation
3	Etch	5%-10% by weight of active NaOH and proprietary additives used to reduce fumes, improve etching, improve rinsing, and promote uniform finish on the surface.	60ºC to 65ºC	13 minutes	Mild air agitation
4	Rinse	Tap water	Ambient	30 seconds	Mild air agitation
5	Rinse	Tap water	Ambient	30 seconds	No air agitation
6	Desmut	Mixtures of 0.5% by volume nitric acid and proprietary chemicals	Ambient	3 minutes	Mild air agitation

7	Rinse	Tap water	Ambient	30 seconds	Mild air agitation
8	Rinse	Tap water	Ambient	30 seconds	No air agitation
9	Anodising –I	15% sulphuric acid by weight	18ºC to 20ºC	23-55 minutes	Mild air agitation
10	Rinse	Demineralised water	Ambient	30 seconds	Mild air agitation
11	Anodising – II	15% sulphuric acid by weight	18ºC to 20ºC	23-55 minutes	Mild air agitation
12	Rinse	Demineralised water	Ambient	30 seconds	Mild air agitation
13	Colouring	Tin sulphate, sulphuric acid along with proprietary stabiliser for better throwing power	20ºC to 25ºC	1-30 minutes	Mechani-cal agitation
14	Rinse	Demineralised water	Ambient	30 seconds	No air agitation
15	Rinse	Demineralised water	Ambient	60 seconds	Mild air agitation
16	Seal	2% to 2.5% of nickel acetate by volume plus wetting agent in deionised water	85ºC	15-30 minutes	No air agitation
17	Rinse	Demineralised water	64ºC	4 minutes	No air agitation

3.3 Process effluent from Finex

Finex effluents are derived from pre-clean, etching, desmut, anodising, colouring and seal stages.

3.3.1 Pre-clean (Degrease)

The pre-cleaner is a non-etching alkaline soak. Degreasing solution contains proprietary surfactants which enhance degreasing by facilitating penetration and loosening of contaminants on the surface of aluminium. The aqueous degreasing solution saponifies oil and greases and thus makes them soluble in water. Degreasing solutions have a long life and do not generate significant waste. The rinse water tank after the degreasing stage is diverted to the final discharge after pH adjustment.

3.3.2 Etching

The etch solution used at Finex is caustic soda with the added proprietary sequestering agents. Etching removes approximately 60 to 70 g of aluminium per square metre of aluminium being processed. As etching proceeds dissolved aluminium builds up rapidly in the etching tank and is removed drag out. Drag out is a form of continuous dumping into the following water rinse tank. The aluminium level in the rinse tank is controlled by continuous discharge into the wastewater treatment plant by the counter flow rinsing system.

3.3.3 Desmutting

The desmut bath is made up of dilute nitric acid with proprietary chemicals added. The solution has a long life and is usually replenished with make up solution to replace drag out losses. After desmutting the work is rinsed in the counter current rinse stream.

3.3.4 Anodising

The electrochemical anodising process is carried out in a sulphuric acid electrolyte. During the anodising process some aluminium is dissolved into the electrolyte and the aluminium concentration is controlled to below the maximum limit of 15 g/L by periodic dumping of part of the anodising solution into the spent acid storage tank. The post anodising rinsing is performed in a rinse tank that is part of the counter current rinse system.

3.3.5 Colouring

Electrolytic solution of tin sulphate is used to give matt tin plating shell on the metal. The main consumption of chemicals is by drag out into the following rinse tank that is part of the rinse system.

3.3.6 Sealing

The final hydrothermal sealing process uses a solution containing low concentration of nickel salts and surfactants. The sealing solution has a long life and does not produce any waste. The solution lost by drag out is replenished with the new solution. The hot deionised water rinse is diverted directly to final discharge after pH adjustments.

3.4 Major waste streams

At Finex the two main waste streams, spent anodising acid and alkaline wastewater solutions are neutralised in underground tank 1, U/G # 1 (See Figure 3.4). Alkaline water is continuously discharged to the U/G # 1. Spent acid is manually transferred from the spent acid storage tank to the U/G # 1 by a separate pipe. After pH adjustments the combined acid and alkali wastewater is pumped into the continuous precipitation chamber by a suction pump at the flow rate of 3 m^3/hour.

The composition of the waste streams was determined by taking composite samples as described in section 2.2.1 and analysing aluminium content as described in section 2.2.7. Representative flow data were obtained by measuring the time required to fill a 5 L sampling container. Data are summarised below:

Spent Anodising Electrolyte

Volume:	Approximately 7 m^3/week
Average aluminium content:	Approximately 15 g/L
Average weight of aluminium in spent acid:	105 kg/week as aluminium

Spent Etch water Solution

Volume:	Approximately 80 m^3/week
Average aluminium content:	Approximately 50 g/L
Average weight of aluminium in spent etch:	4000 kg/week as aluminium
Average amount of aluminium neutralised:	4105 kg/ week

3.5 The continuous precipitation system (CPS)

The CPS consists of the following stages:

- Acid reaction chamber 1 and alkali reaction chamber 2,
- Floc chamber,
- Clarifier chamber,
- Two sludge thickening chambers, and
- Supernatant chamber.

Figure 3. 2 CPS unit for trade waste treatment at Finex

Influent wastewater from U/G #1 is pumped into the CPS unit and enters the acid stirred reaction chamber 1. Concentrated hydrochloric acid is added via metering pumps to influent wastewater based on the pH requirement. The acid addition is relatively controlled by a programmable logic controller. The effluent flows from the acid reaction chamber 1 into the alkali reaction chamber 2 by gravity. It is a stirred tank chamber for uniform mixing of the wastewater and pre-clarification pH adjustment using 50% w/w caustic soda solution. Acid and alkali reagents are added to each stage by dosing pumps. After alkali stage wastewater overflows into the floc chamber by gravity.

The floc chamber is designed as a stirred tank reactor for flocculation of the precipitates with a low-shear paddle wheel mixer. Polyelectrolyte is added via a metering pump to encourage flocculation of precipitates. The precipitates from the floc chamber flows by gravity into the clarifier chamber.

The clarifier chamber is designed as an up-flow inclined tube type clarifier which provides a better settling surface area for the flocs and creates the laminar flow environment necessary for effective clarification. The flocs enter the clarifier chamber, settle as sludge and then pumped to the sludge thickening chambers by a sludge pump (USFilter 2000).

The solids free clear supernatant flows from the top of the clarifier chamber through a set of gravity force and flows to the sewer system. The settled sludge from both the sludge thickening chambers is diverted by gravity into a settled sludge holding underground tank 2 (U/G # 2) which overflows to underground tank 3 (U/G # 3). Further gravity thickening occurs in both underground tanks. These tanks have the capacity sufficient for approximately 3 days production. After 3 days the compact gravity settled sludge from U/G # 2 and U/G # 3 is disposed to the landfill by an approved contractor.

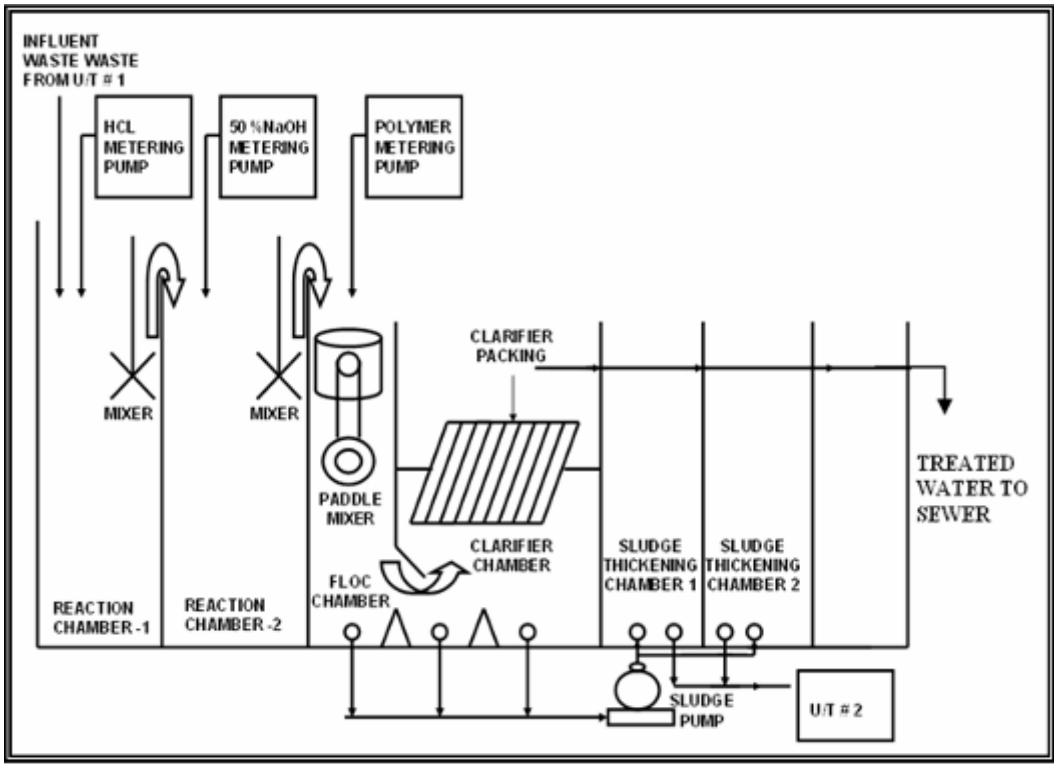

Figure 3. 3 Detailed schematic diagram of CPS unit at Finex (USFilter 2000)

3.6 Process flow diagram at Finex

The various processing operation, as at the beginning of the project and as described above are summarised in the process flow diagram (Figure 3.4). It shows that the aluminium extrusion goes through 17 process tanks out of which 7 tanks are chemical process tanks and remaining 10 tanks between each process tanks are water rinse tanks. These rinse tanks are continuously flushed with fresh water to prevent contamination of next process solution. The wastewater of tanks 2, 7, 10, 14 and 17 as part of counter current rinsing system are discharged directly to sewer after pH adjustment since these rinse waters do not contain metal concentrations that need to be regulated under the plant discharge limits. Wastewater from tank 4 is discharged to U/G #1 at the wastewater treatment plant facility for treatment. The details of wastewater treatment were described in section 3.4 and section 3.5.

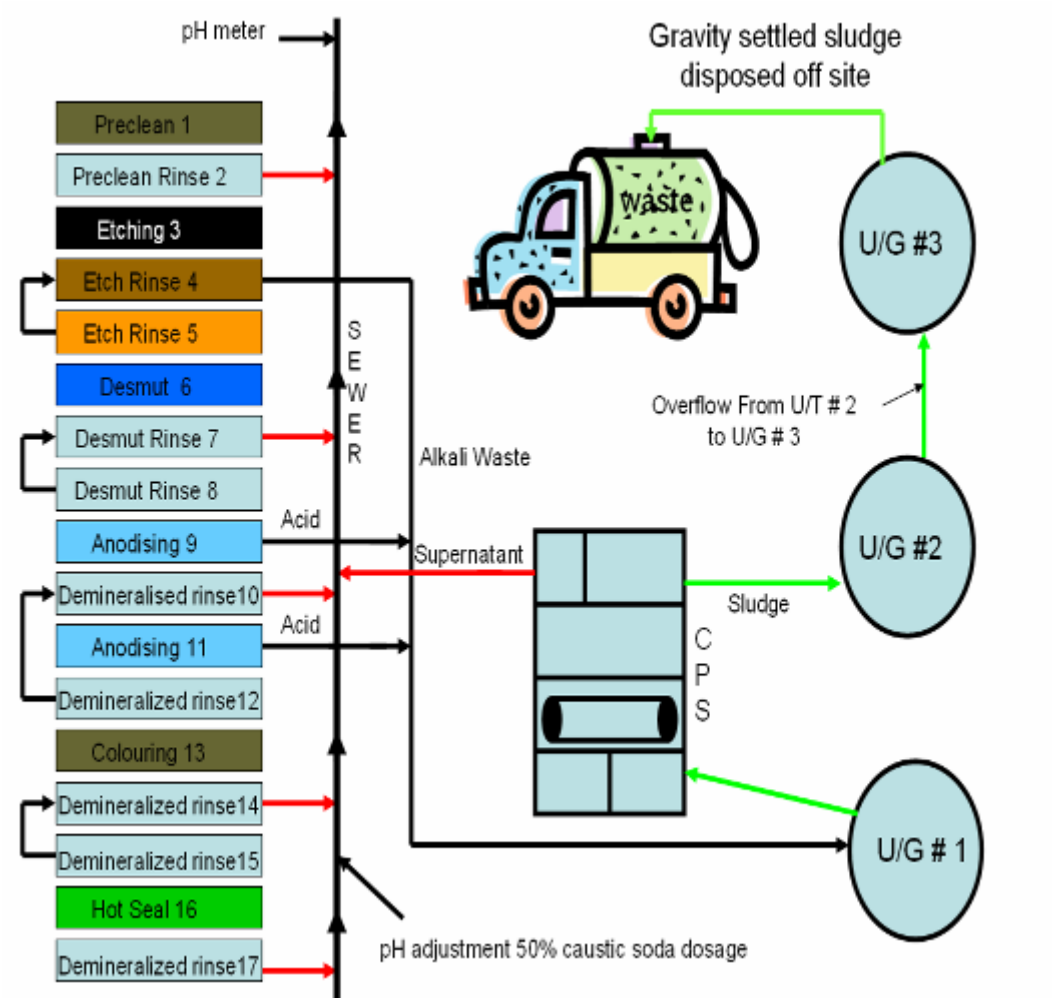

Figure 3. 4 Detailed process flow diagram of Finex anodising facility

3.7 Characteristics of settled sludge

The aluminium content of the sludge produced in one week was approximately 4000 kg and its weight was approximately 115 tonnes. Most of the weight of the sludge is water. Sludge disposal costs could be reduced by reducing water content. Attempts were made to reduce sludge volume by varying pH, settling time and polyelectrolyte addition to optimise gravity sedimentation.

3.7.1 Effects of pH and settling time on sludge volume

pH and settling time are influential factors determining settled sludge volume. An experiment was performed to determine the effect of pH on the volume of 1 L of sludge formed after settling times varying from 2 to 8 hours typical of factory operation.

Settled sludge volume data are summarised in Table 3.2 and the data showing settled sludge volume % of initial neutralised waste stream volume at various pH after 8 hour of settling are plotted in Figure 3.5.

Table 3. 2 Settling under gravity of 1 L of sludge at various reaction pHs

pH	2 hr (mL/L)	4 hr (mL/L)	6 hr (mL/L)	8 hr (mL/L)
4	927	910	905	900
4.5	930	918	900	895
5	864	855	843	838
5.5	534	505	492	485
6	455	442	435	420
6.5	330	300	240	210
7	360	345	338	325
7.5	448	432	425	410
8	530	510	495	488
8.5	645	633	617	605
9	784	763	744	732

From the experimental results shown below in Figure 3.5, it is clear that at the optimum pH value of 6.5 the settled sludge volume was approximately 21% of the initial volume after 8 hours. The solid settled with a clear boundary between the

supernatant and settled solids. However the settling rate was too slow to be used at the Finex site. The most likely explanation for the effect of pH is that at high and low pHs (above and below the isoelectric point) the aluminium hydroxide sludge will acquire +ve or –ve charge so that compaction is prevented by charge repulsion.

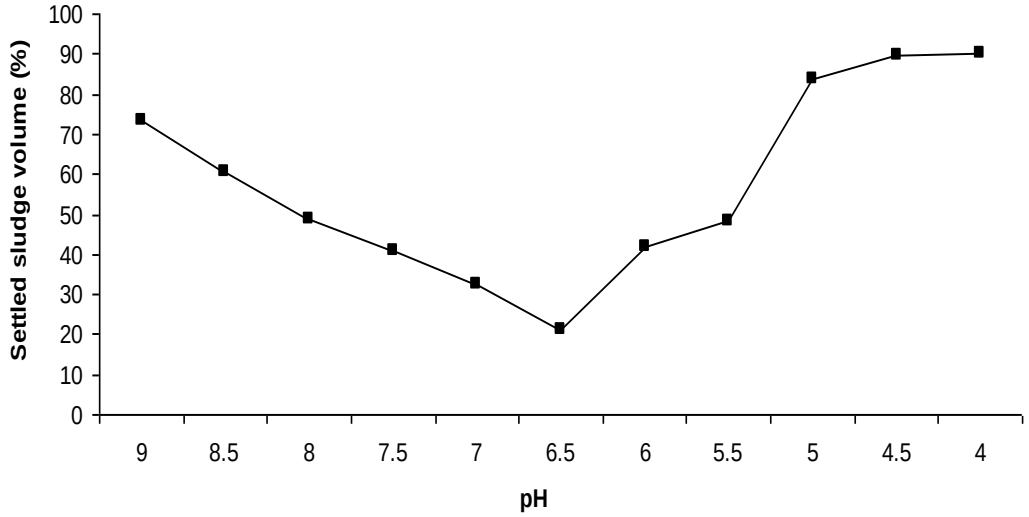

Figure 3. 5 Volume % of sludge (relative to initial volume) as a function of pH after 8 hr gravity settling

When the system at pH 6.5 was allowed to settle for a prolonged period, settling continued until about day 7 when the settled sludge volume was 5% of the original volume. After this very little further settling was observed. (See Figure 3.6).

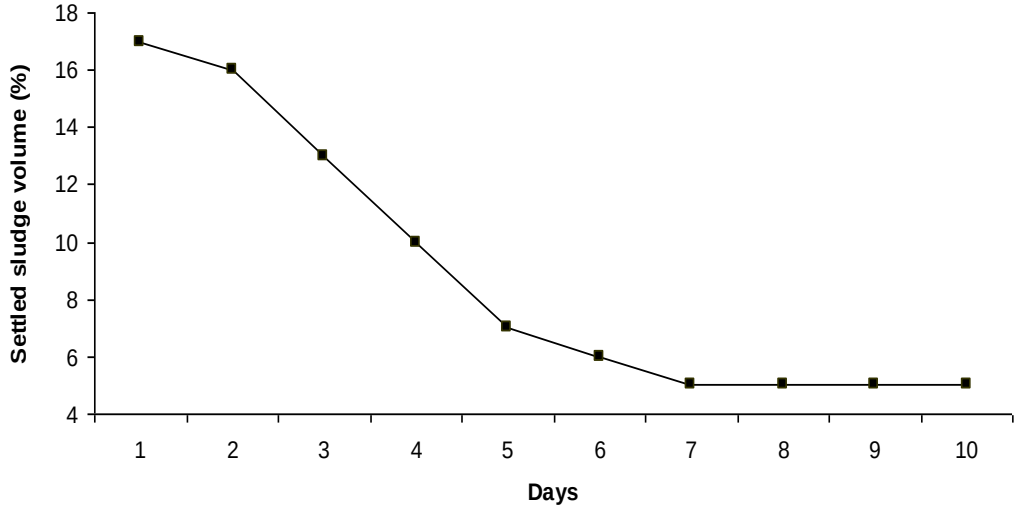

Figure 3. 6 Variation of gravity settled sludge volume % with time at pH 6.5

3.7.2 The effect of polyelectrolyte addition

The settling experiment was repeated after adding 0.2% of an anionic polyelectrolyte. Data for a range of pHs after 10 minutes of settling are summarised in Figure 3.7. Again the minimum settled sludge volume (12% of original volume) was observed at pH 6.5. Little further sludge volume reduction occurred on settling the system for a further 8 hours (See Figure 3.8).

The effectiveness of polyelectrolyte addition is demonstrated by the fact that the volume percentage of settled sludge after 10 minutes was less than that of the original sludge after 8 hours settling. However, unlike the polyelectrolyte free sludge, little further compaction occurred after prolonged settling.

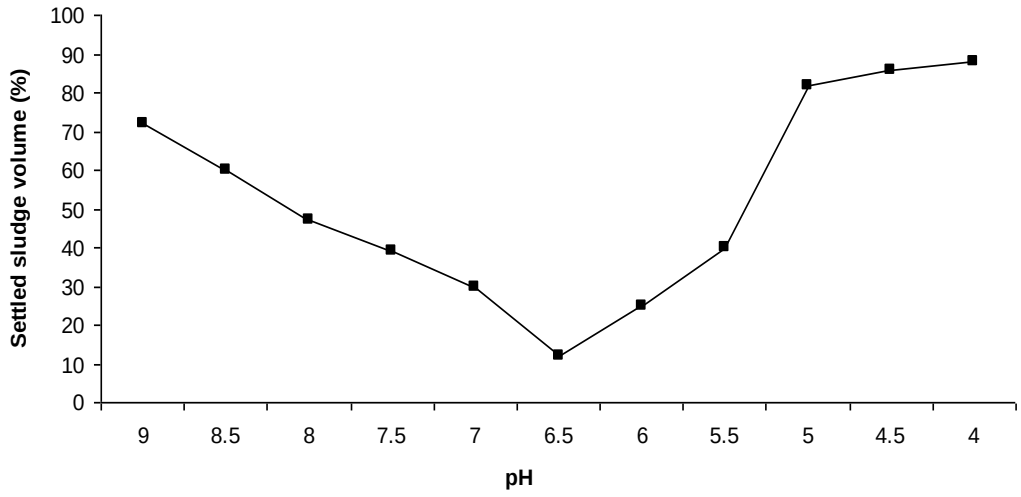

Figure 3. 7 Volume % of sludge as a function of pH after 10 minutes gravity settling after polyelectrolyte addition

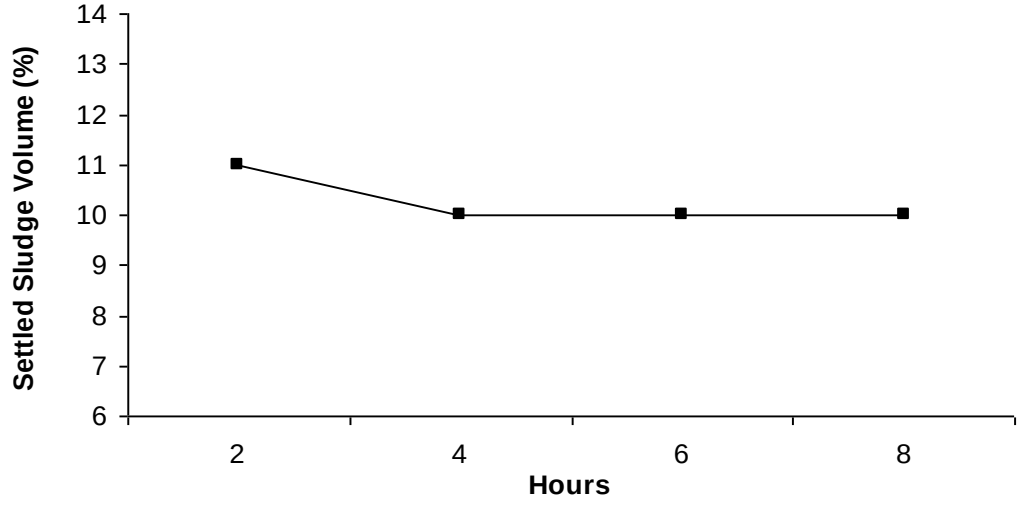

Figure 3. 8 Volume % of sludge at pH 6.5 after 8 h gravity settling after polyelectrolyte addition

3.7.3 Water and non-volatile solids content

The water and non volatile solids content of the polyelectrolyte flocculated sludge gravity settled for 10 minutes was determined. The method for this experiment is described in Section 2.2.3. Result are summarised in Tables 3.3 and 3.4. After heating the sludge for 72 hours at 105°C most of the free water had been lost. The total weight of the water was determined from total weight loss after heating at 500°C for 4 hours. The non-volatile components of the gravity settled sludge was only about 2% of its wet weight.

Table 3. 3 Water loss from gravity settled sludge flocculated with polyelectrolyte

No	Initial sludge (g)	24 hr at 105°C (g)	48 hr at 105°C (g)	72 hr at 105°C (g)	4 hr at 500°C (g)
1	418.62	25.27	18.89	17.64	8.97
2	384.96	23.45	21.86	15.63	5.44
3	359.44	21.59	15.89	14.89	8.1
4	368.79	22.95	15.97	14.43	8.73
5	289.63	17.76	12.78	11.22	4.42
6	254.76	15.88	11.57	10.65	6.33

Table 3. 4 Water and non-volatile solids content of gravity settled sludge after polyelectrolyte addition

No	Total weight (g) of GSS	Total water lost (g)	Weight of solids after water loss (g)	Water content (% of initial GSS)	Non-volatile Solids (% of initial GSS)
1	418.62	409.65	8.97	97.86	2.14
2	384.96	379.52	5.44	98.59	1.41
3	359.44	351.34	8.1	97.75	2.25
4	368.79	360.06	8.73	97.63	2.37
5	289.63	285.21	4.42	98.47	1.53
6	254.76	248.43	6.33	97.52	2.48
Mean	-	-	-	97.97	2.03

3.8 Summary

The study of the wastewater treatment system at Finex revealed that the site produced 115 tonnes per week (6 days) of high water content sludge, the disposal

of which cost approximately $2000. This volume can be reduced by using polyelectrolyte and or prolonged settling times. However even then the water content of the sludge was found to be about 98%. The cost of disposal of this sludge is directly related to amount of water retained by it. Thus there is an economic incentive to reduce retained water.

According to the literature (See Section 1.4), mechanical dewatering of anodising sludge is a routine operation. The issue addressed in the next chapter was the acquisition of an appropriate dewatering technology for the Finex site.

4 Acquisition of dewatering technology

4.1 Introduction

This chapter summarises the factors that led to the acquisition of the Amston plate and frame filter press at Finex. The performance of the press was evaluated and the characteristics of the dewatered sludge were determined.

4.2 Selection of a dewatering technology for Finex

A dewatering process that leads to low water contents and low suspended solids was sought. The belt press and centrifugation technologies are continuous but belt press leaves high suspended solid content in the supernatant water, has high maintenance and is prone to frequent stoppages and centrifugation is noisy and expensive to maintain (Silverton 2008). Plate and frame filter presses, while not continuous; have an established reputation in the industry (Retter 1997). Easy installation, low maintenance and operating cost, simple solids dumping procedure and highest cake solids concentration compared to other mechanical dewatering equipment are attractive features of this technology (Higgins 1995).

These considerations were the major factors that led to the decision in to purchase of an Amston plate and frame filter press. The plant process flow diagram showing the incorporation of the filter press is shown in Figure 4.1. The press was installed to be able to take sludge from U/G #2 and U/G #3. Dewatered sludge after mechanical pressing was disposed to landfill.

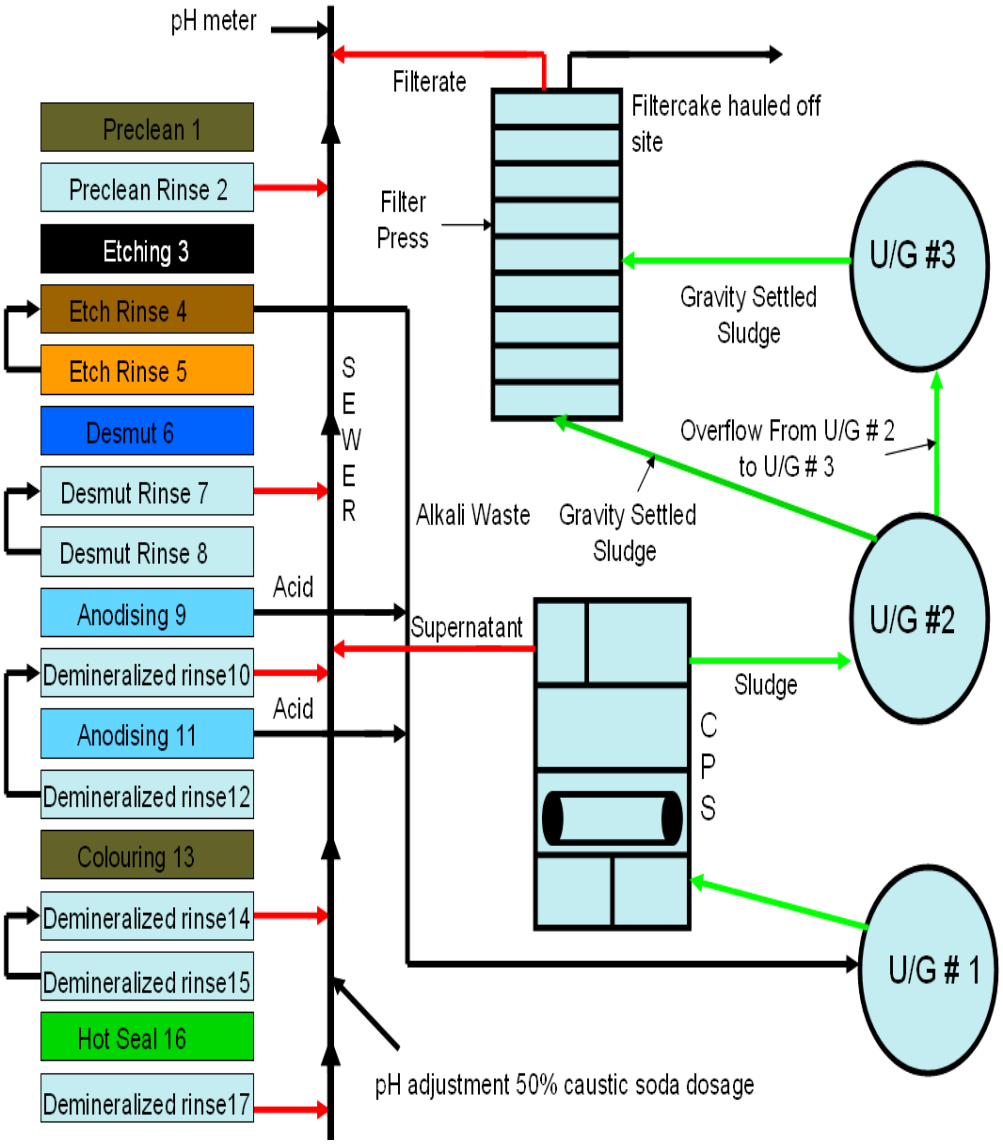

Figure 4. 1 Finex plant process flow diagram after incorporation of the filter press

The Amston filter press is a plate and frame hydraulic filter press with 46 filter plates (See Figure 4.2). Each plate is coated with polypropylene filter cloths. The cloths are made up of monofilament fibres. The smooth surface characteristics of monofilament fibres facilitate cake release properties (Silverton 2008). As the cycle starts the dilute sludge slurry is pumped by 2 inch air operated diaphragm pump from one end and 100 psi pressure is applied by hydraulic pump from the other end to hold the compressed plates and maximise the rate of dewatering. As filtration proceeds the plate chambers will be packed by dewatered cake. The filtrate water drains off the dewatered cake and is discharged to wastewater system through drain pipes. When the filtrate water stops draining this indicates that the plate chambers are full and the press is ready for dump.

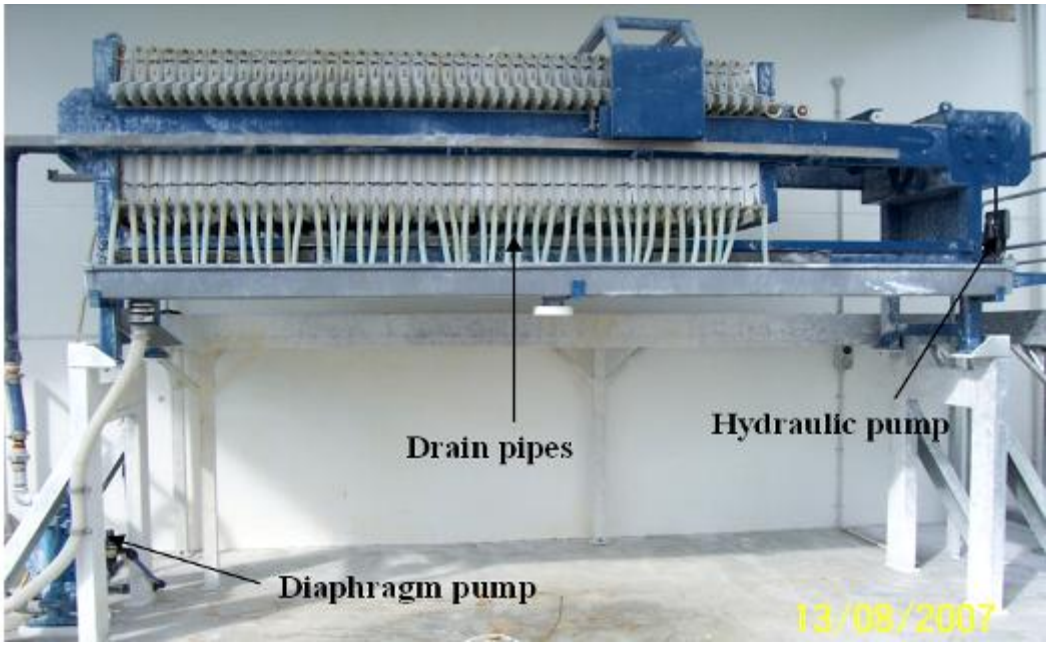

Figure 4. 2 Amston plate and frame filter press unit used for dewatering of sludge at Finex

4.2.1 Performance characteristic of filter press

Apart from one change of the filter cloths after 8 months, the Amston plate and frame filter press has given 11 months of consistent and trouble free operation. It has coped well during periods of high production. Typically it takes 4 hours of cycle time to fill the plate chambers. When the plate chambers have reached their holding capacity the feed valve is closed and plates are separated. The dewatered trapped solids dumping procedure is very simple and requires 10 minutes to start the new cycle.

Prior to the acquisition of press Finex was producing 115 tonnes of sludge per week (6 days). In the 11 months since the press was acquired 12 tonnes of sludge is disposed per week (6 days). This represent the net saving over that period of $70,000 which has covered 70% cost of acquisition.

4.3 Dewatered sludge characteristics

4.3.1 Water and non-volatile solids content

Experiments (See Section 2.2.3) were conducted to determine the water and non-volatile solids content of the dewatered sludge generated from Finex filter press. Data are presented in Tables 4.1 and 4.2. After heating for 72 hours at 105°C most of the free water had been lost. The total weight of water was determined from the

total weight loss after heating at 500°C for 4 hours. Using the 500°C result the mean non-volatile solids content for 6 trials was 18.73%. This is slightly less than the specified 20% dry solids claimed for the device.

Table 4. 1 Water loss from dewatered filter press sludge

No	Initial Sludge (g)	24 hr at 105°C (g)	48 hr at 105°C (g)	72 hr at 105°C (g)	4 hr at 500°C (g)
1	121.73	34.08	26.17	25.58	22.83
2	95.84	24.91	21.37	20.70	17.22
3	79.61	20.58	16.65	15.94	14.83
4	65.49	16.63	14.49	13.48	12.79
5	98.72	23.65	21.67	20.87	19.19
6	75.85	18.20	16.80	15.46	13.69

Table 4. 2 Water and non-volatile solids content of dewatered filter press sludge

No	Total weight (g) of FPS	Total water lost (g)	Weight of solids after water loss (g)	Water Content (% of initial FPS)	Non-volatile Solids (% of initial FPS)
1	121.73	98.9	22.83	81.25	18.75
2	95.84	78.62	17.22	82.03	17.97
3	79.61	64.78	14.83	81.37	18.63
4	65.49	52.7	12.79	80.47	19.53
5	98.72	79.53	19.19	80.56	19.44
6	75.85	62.16	13.69	81.95	18.05
Mean	-	-	-	81.27	18.73

4.3.2 Elemental analysis of FPS

Elemental analysis of the 105°C dried FPS was determined by X-Ray fluorescence (See Section 2.2.5). Data are presented in Table 3.6. The aluminium content in the sludge solids dried at 105°C was 35.2% which is close to the theoretical value of 34.6%.for $Al(OH)_3$.

Table 4. 3 Metal content (% by weight percent) of FPS dried at 105°C

Sample	Al	Mg	Cd	Ni	Pb	Sn	Fe	Zn
1	35.1	0.01	0.01	0.14	0.01	0.19	0.48	0.09
2	35.3	0.02	0.01	0.20	0.01	0.15	0.52	0.10
Mean	35.2	0.015	0.01	0.17	0.01	0.17	0.5	0.09

4.3.3 XRD of FPS

Crystalline forms of dewatered sludge before and after heating (105℃ and 500°C) were analysed by XRD. XRD powder patterns are given in Figure 4.3, Figure 4.4 and Figure 4.5. The lack of peaks for the fresh sludge and the broad peaks over the 2Ɵ range from 20°-100° for the sludge dried at 105℃ and 500°C indicate that the material was amorphous in the fresh state and poorly crystalline in the dried and calcined states. The main mineralogical constituent detected in the sludge dried at105℃ was $Al(OH)_3$ and in sludge dried at (500°C) was alumina (Al_2O_3).

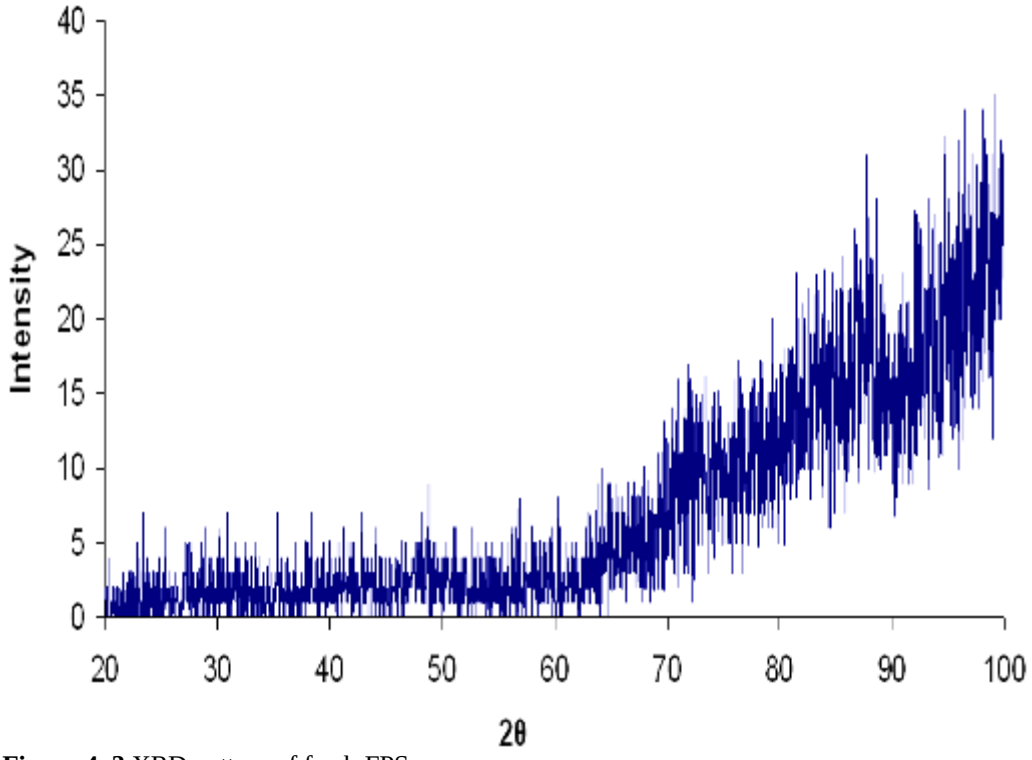

Figure 4. 3 XRD pattern of fresh FPS

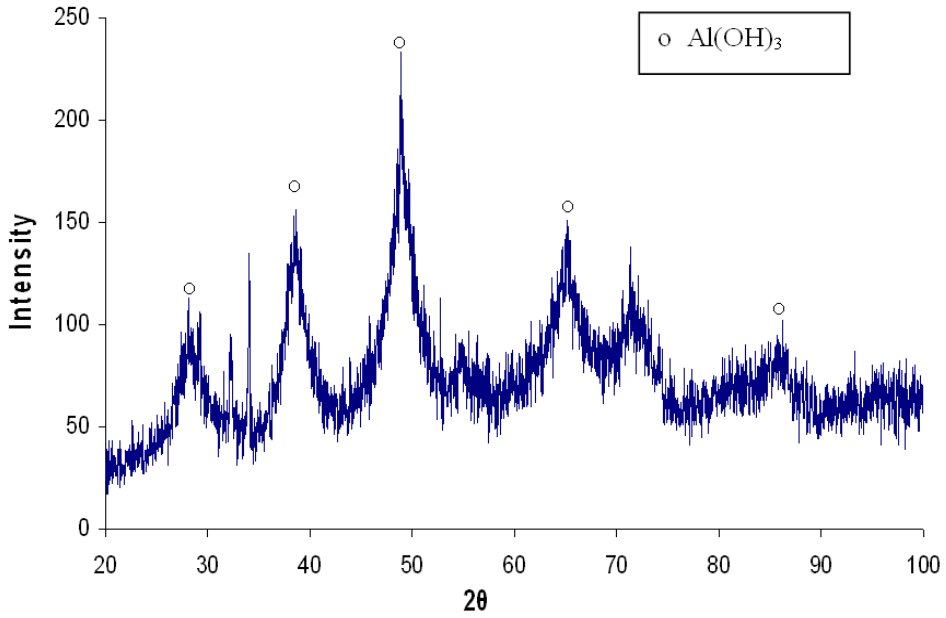

Figure 4. 4 XRD pattern of FPS dried at 105°C

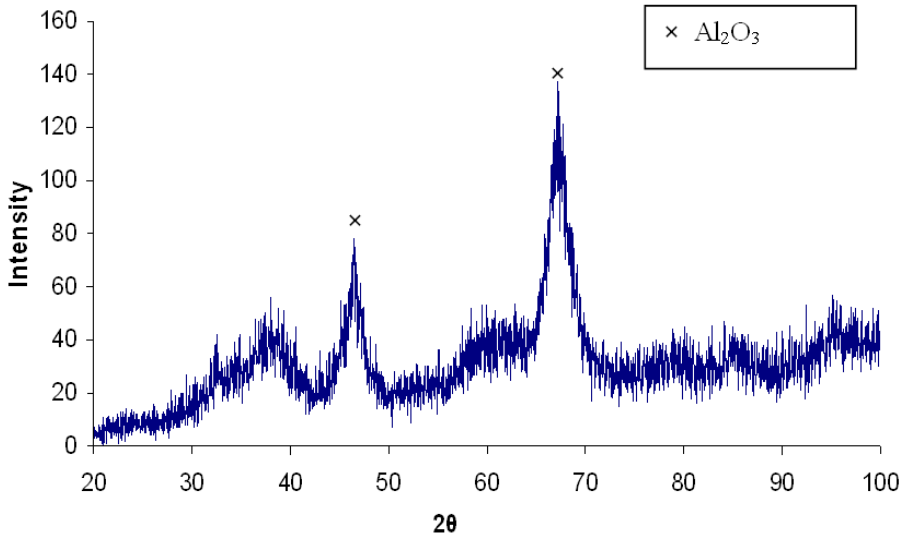

Figure 4. 5 XRD pattern of FPS dried at 500°C

4.3.4 SEM/EDXS analysis of FPS

Solid state speciation of the dewatered sludge was further probed by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectrometry (EDXS). The fresh sludge has a flaky appearance at low magnification and when viewed at high magnification it appears to be made of aggregates of small primary particles of approximately 1 µm diameter. After heating at 105°C, the

micrographs show much less evidence of the 1 µm colloid particles. Instead the material appears to have coalesced consistent with partial crystallisation to form $Al(OH)_3$ (See Figure 4.6).

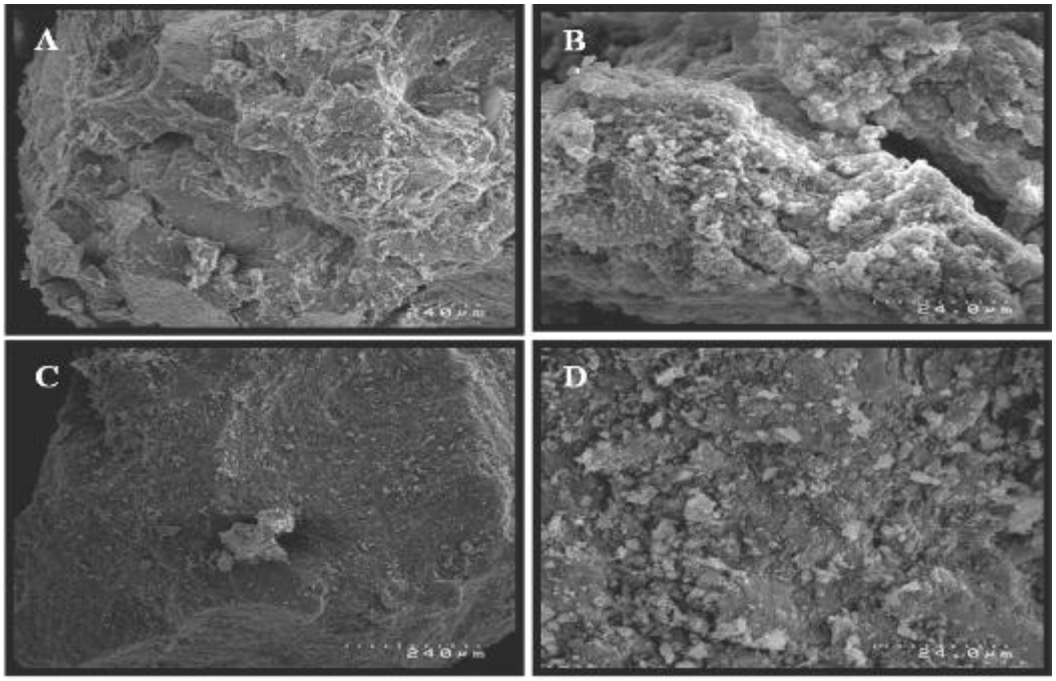

Figure 4. 6 SEM images of the fresh FPS sludge (A and B) and FPS dried at 105°C (C and D)

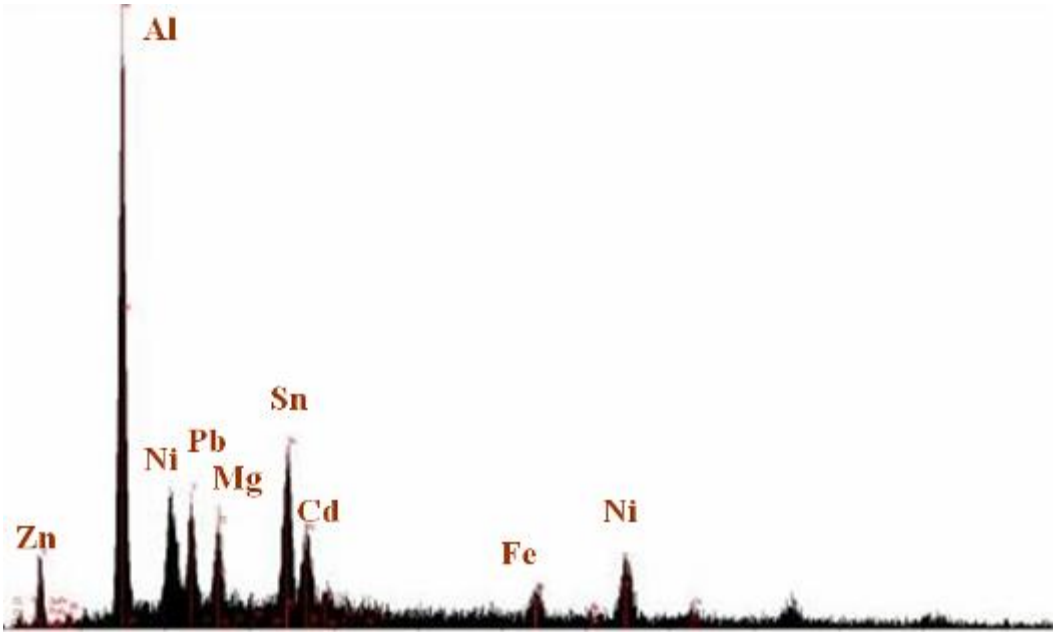

Figure 4. 7 EDXS spectral analysis of fresh FPS

The EDXS spectra of the fresh dewatered sludge sample (See Figure 4.7) gave strong signals for Al and weaker signals for Sn, Ni, Fe, Cd, Pb, Zn and Mg.

4.4 Summary

The acquisition of an Amston plate and frame filter press allowed the volume of sludge produced at the Finex site to be reduced from 115 tonnes of 2% solids per week (6 days) to 12 tonnes of 19% solids per week (6 days). This represented a savings of $1400 per week.

A study of the dewatered FPS indicated that in its fresh state it was x-ray amorphous and consisted of aggregates of colloidal particles of approximately 1 µm in diameter. On drying at 105°C, water was lost and poorly crystallised $Al(OH)_3$ was formed. Heating to 500°C resulted in further loss of water the formation of poorly crystallised gibbsite.

With the reduction of its bulk by dewatering, the cost of sludge disposal was reduced by more than 70%. However the 12 tonnes per week of dewatered sludge production still presented the challenge of devising a way of using the material beneficially and further reducing disposal costs. This formed a third major objective of the current investigation.

5 Beneficial uses of aluminium hydroxide sludge

5.1 Introduction

The possibilities for beneficial use of the waste aluminium hydroxide recovered as dewatered sludge have been described in section 1.9. There it was decided that the three most promising possibilities were to (1) dissolve the sludge in acid and precipitate the commodity chemical alum, (2) dissolve the sludge in sodium hydroxide to produce the chemical commodity sodium aluminate solution, (3) dissolve or re-suspend the sludge in acid as a concentrated dissolved or colloidal solution of aluminium cations or hydrolysis products. All these materials could find applications as coagulating agents. The alum would also find other applications where a pure aluminium salt is required.

5.2 Preparation of alum

5.2.1 Acid dissolution of the sludge

The acidic dissolution of the fresh dewatered sludge was carried out by addition of analytical reagent grade 98% sulphuric acid. The quantity of acid required to extract all the available aluminium in the sludge was calculated from the equation given below:

$$\underset{\text{(Sludge)}}{A1(OH)_{3(s)}} + \underset{\text{(Acid)}}{3H^{+}_{(aq)}} \rightarrow A1^{3+}_{(aq)} + 3H_2O \qquad (5.1)$$

From above stoichiometric equation (5.1) 3 moles of sulphuric acid will be required to dissolve 1 mole of the aluminium in the sludge. The aluminium content of dewatered sludge was found to be 35.2% by weight of aluminium hydroxide (See Section 4.3.2). The complete dissolution should require 5.44 g of 98% sulphuric acid per g of aluminium contained in the sludge.

Experimental

The apparatus used is shown in Figure 5.1. Details of the composition of the sludge and reagents used are summarised in Table 5.1.

A weighed amount of sludge FPS was added to the beaker, heated to 90°C and the appropriate amount of 98% sulphuric acid was added drop wise with periodic stirring at 90 rpm to break up the sludge. Stirring was continued for 1 hour after the acid addition. The content of the beaker was then filtered through the 0.45µm membrane filter paper to remove the minor amount of undissolved material remaining. The pH of the filtrate was determined and a sample was taken for analysis of aluminium content by the ICP-OES method (See Section 2.2.7). The concentration of aluminium obtained was consistent with dissolution of virtually all the initial sludge (See Table 5.1).

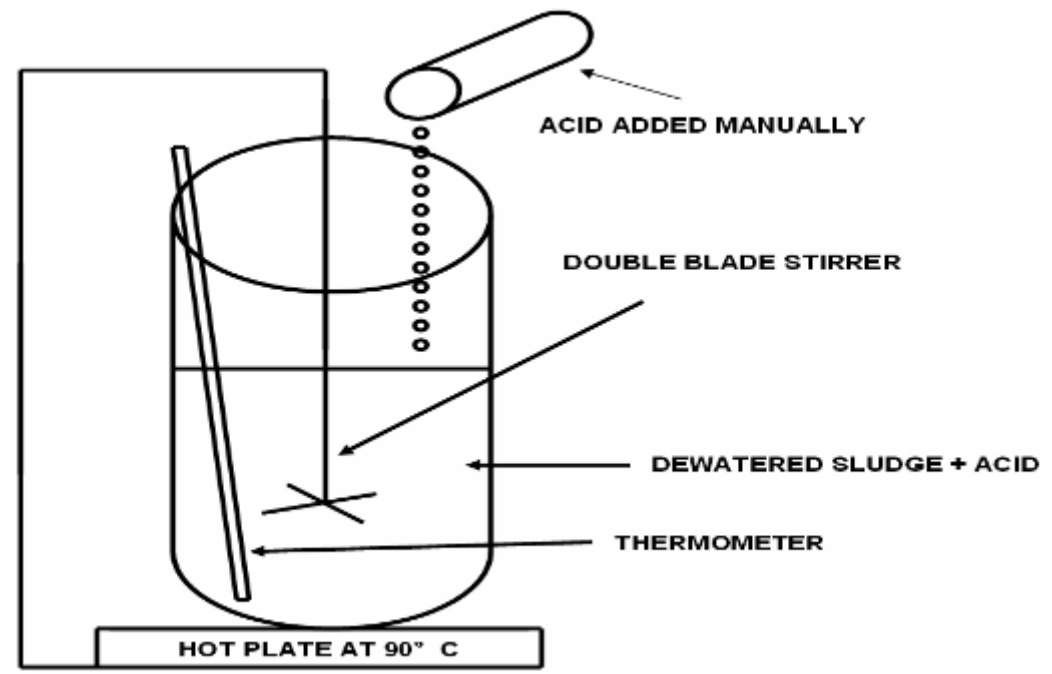

Figure 5. 1 Schematic diagram representing acid dissolution of sludge

Table 5. 1 Experimental details for acid dissolution of sludge

Mass of the Sludge (g)	17.25
Non-volatile solids content (g)	3.23
Aluminium content in sludge (g)	1.13
Sulphuric acid addition to sludge (g)	6.14
Aluminium content in sludge (moles)	0.041
Sulphuric acid addition to sludge (moles)	0.062
$H^+/Al(OH)_3$	3
Final pH	2.0
Recovered aluminium (moles)	0.040
Recovered aluminium (percent)	96

5.2.2 Crystallisation of alum

The Al^{+3} solution prepared above was used in an attempt to crystallise alum according to chemical equation given below:

$$K^{+}_{(aq)} + Al^{3+}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 12H_2O_{(liq)} \rightarrow KAl(SO_4)_2.12H_2O_{(s)} \quad (5.2)$$

Equation 5.2 indicates that an equimolar amount potassium sulphate needs to be added to the aluminium sulphate (i.e. 1 g Al will require 3.2g K_2SO_4).

The filtrate solution after acidic dissolution was reacted by slowly adding the mole equivalent amount of anhydrous potassium sulphate. The solution was warmed and stirred at 30°C for 15 minutes to dissolve the white gelatinous precipitates formed while addition of potassium sulphate. The experiment was repeated 4 times and the solution was allowed to crystallise at 4°C, 20°C, 30°C and 60°C for 7 days.

Finally the crystals formed were separated from mother liquor by filtration through a piece of clean filter paper. They were thoroughly washed with ethanol and were dried at 30°C in an oven for 1 hour. The dried potassium alum crystals were used to calculate the percentage yields and were stored in a desiccator until further use.

The well formed crystals produced at a yield of 92.6% were characterised by XRD and SEM-EDXS analysis (See Section 2.2.4 & 2.2.6).

5.2.3 Effects of crystallisation temperature on potash alum yield

As described in Section1.8.1, potassium alum solubility is highly temperature dependent. The results given in Table 5.2 for experiments at different crystallisation temperatures indicate that 92.6% of alum was recovered at 4°C, 80.2% at 20°C, 73.1% at 30°C and 65.3% at 60°C. These results are consistent with alum solubility at the respective temperatures and indicate that virtually all the aluminium in the sludge was dissolved.

Table 5. 2 Crystallisation of alum at various temperatures

Sludge (g)	Al in sludge (Moles)	H_2SO_4 Added to sludge (Moles)	Al recovery (Moles)	Potassium added (Moles)	Temp (°C)	Alum produced (Moles)	Yield (%)
45.57	0.11	0.16	0.10	0.10	4	0.092	92.6
32.56	0.08	0.12	0.07	0.07	20	0.056	80.2
24.45	0.06	0.09	0.05	0.05	30	0.036	73.1
31.63	0.08	0.11	0.07	0.07	60	0.045	65.3

The effect of crystallisation temperature on yield is also shown in Figure 5.2 along with the yield expected from solubility considerations (See Section 1.8.1).

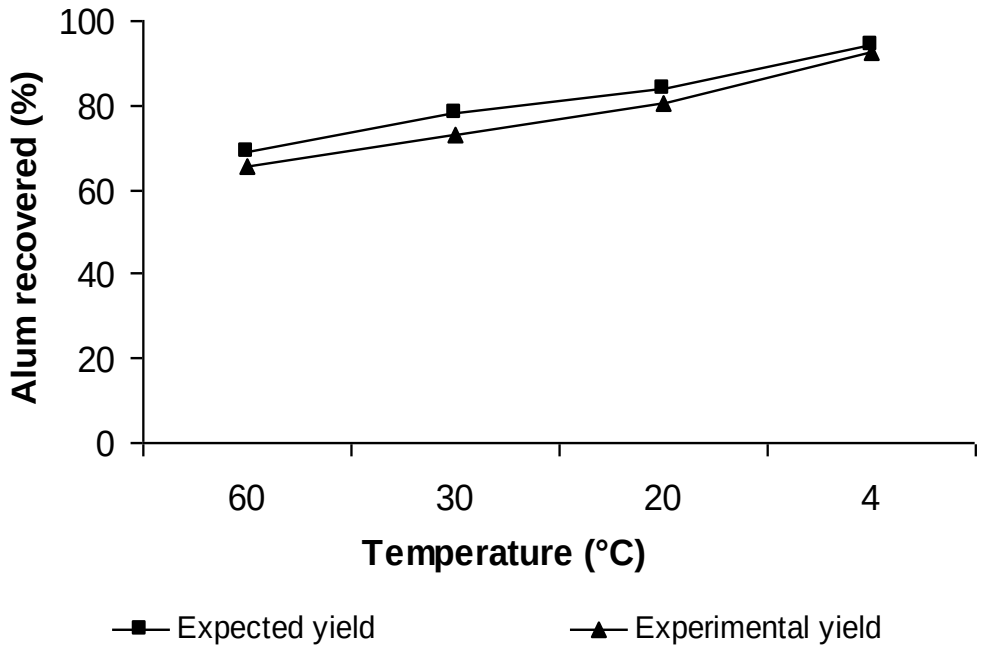

Figure 5. 2 Comparison between experimental and expected yield of potassium alum crystals at various temperatures

Microscopic examination of the crystals (magnification 13X) showed clumps of fairly poorly formed crystals of irregular size and shape (See Figure 5.3).

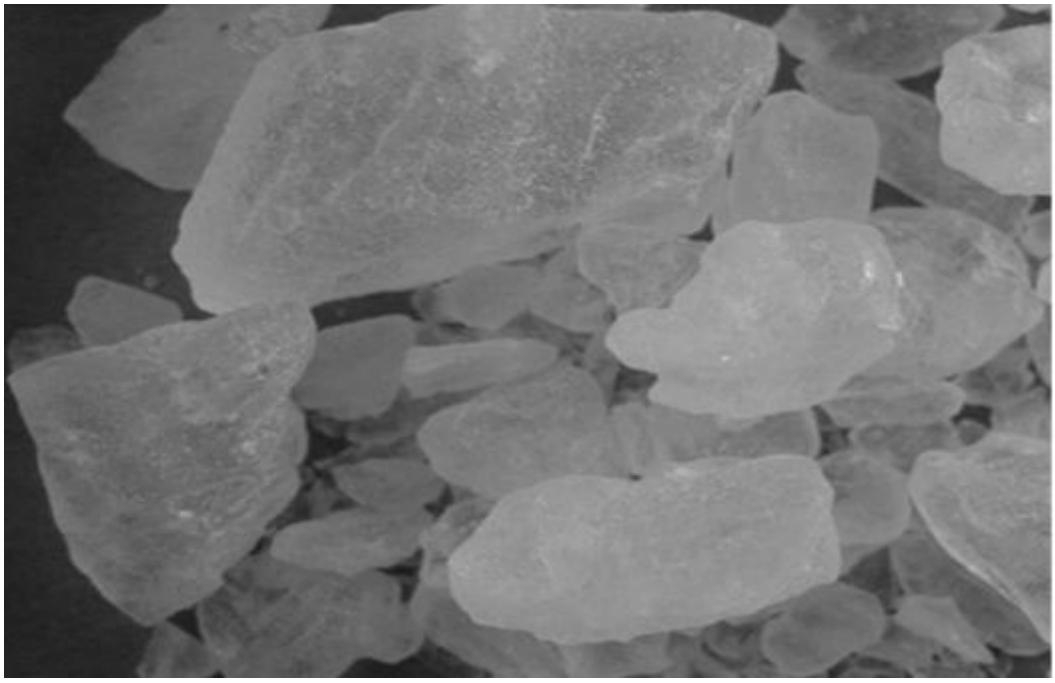

Figure 5. 3 Microscopic picture of alum crystals recovered from anodising sludge

5.2.4 Characterisation of the alum

SEM images of the prepared crystals confirmed the irregularity observed with the light microscope. A minority of the crystals however had the characteristic octahedral form observed in a commercial sample (See Figure 5.4).

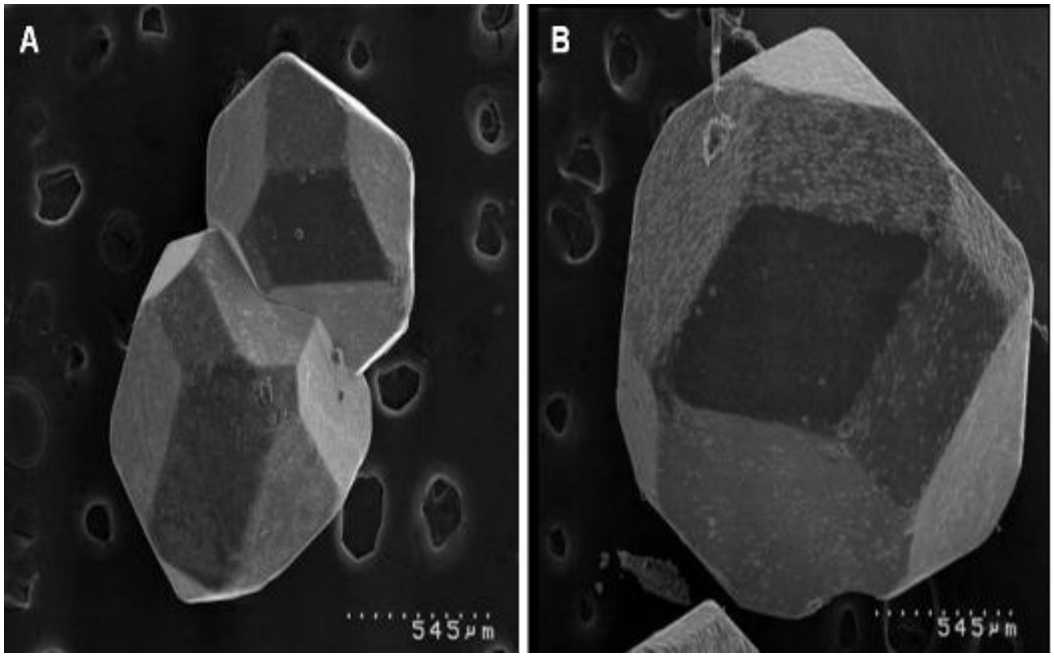

Figure 5. 4 SEM images of selected alum crystals recovered from anodising sludge

XRD traces as shown in Figure 5.5 confirmed that the product formed was potassium alum. The diffraction angles and relative intensities of all major lines are closely similar to commercial sample of potassium alum.

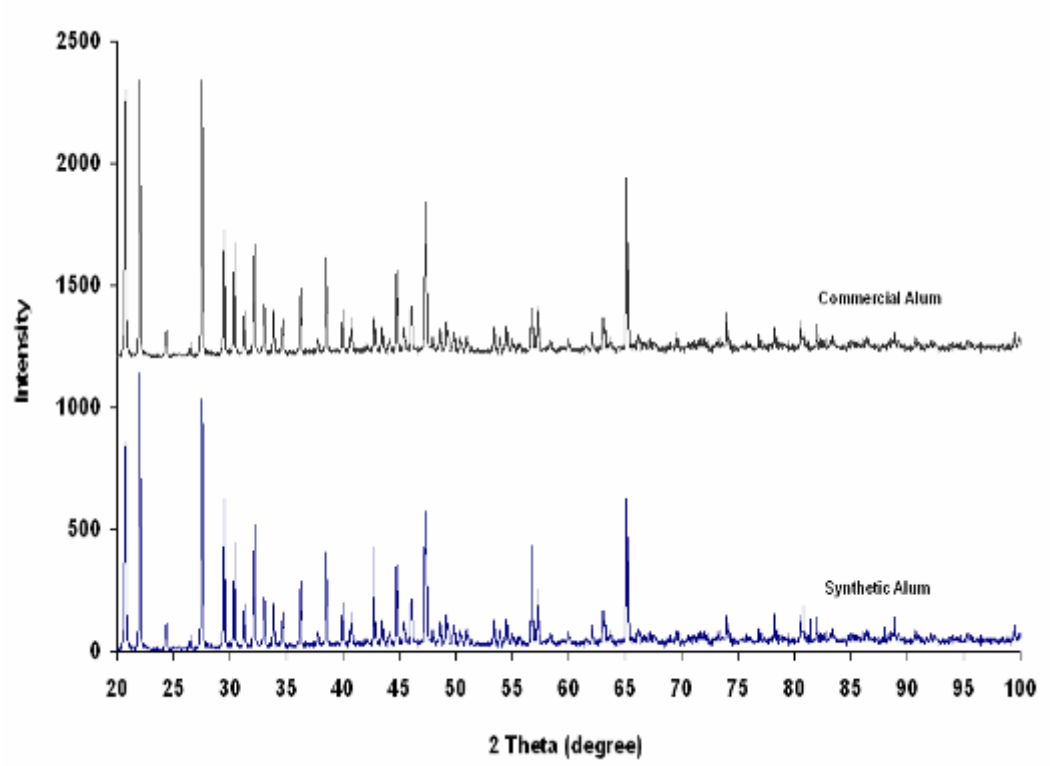

Figure 5. 5 Comparison of XRD images of commercial potassium alum and alum recovered from anodising sludge

An indication of the purity of the product was obtained using the EDXS facility of the scanning electron microscope. The EDXS trace is shown in Figure 5.6. The strong signals of Al, K, S and O were identified. A small Pt peaks were also observed due to sputtering effect but there was no evidence of Mg, Cd, Ni, Pb, Sn, Fe or Zn, the heavy metals known to be present in the original sludge. The sensitivity of the EDXS experiment is such that the absence of a line indicates the concentration of the metal was below 50 ppm.

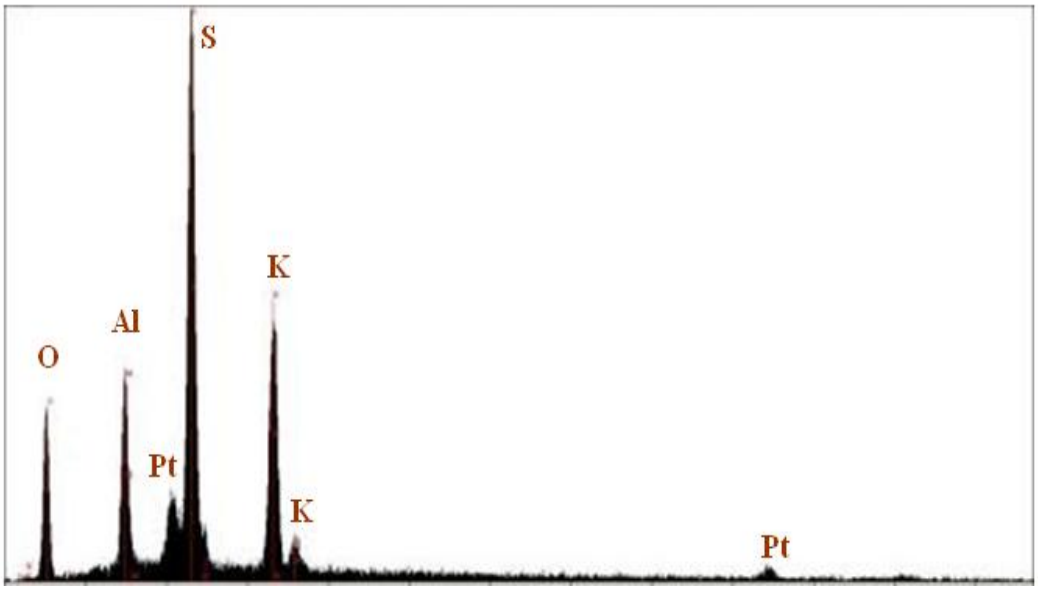

Figure 5. 6 EDXS spectral analysis of synthetic crystal

The absence of significant amounts of heavy metals in the alum product was confirmed by ICP-OES method analysis. Data are summarised in Table 5.3.

Table 5. 3 Metal content of recovered alum produced from aluminium anodising sludge

Metal (mg/L)	**Commercial standard grade Alum**	**Expected heavy metal content present in sludge**	**Recovered Alum**
Total Cadmium	0.4	68	0.2
Total Nickel	39	251	44
Total lead	4	78	2
Total Zinc	9	133	4
Total Iron	675	154	18
Total Tin	28	297	34
Total Magnesium	6	435	3

The content of the expected heavy metals were all similar or less than the values in the commercial product and lower than the values in the sludge by up to an order of magnitude.

From the results of these studies it is clear that alum in good yield and of commodity quality can be obtained from dewatered anodising sludge after a single crystallisation step. If a higher quality material was required, this could be obtained by further crystallisation steps.

5.3 Preparation of aluminate

5.3.1 Alkali dissolution of the sludge

The quantity of sodium hydroxide required to solubilise the sludge as aluminate can be calculated from the stoichiometry of the reaction given below:

$$\underset{\text{(Sludge)}}{Al(OH)_{3(s)}} + \underset{\text{(Alkali)}}{OH^-_{(aq)}} \rightarrow \quad Al(OH)_4^-{}_{(aq)} \qquad (5.3)$$

Every mole of aluminium in the sludge will require 1 mole of sodium hydroxide to form sodium aluminate (i.e 1 g Al requires 1.48 g of NaOH).

An experimental procedure similar to that described in Section 5.3.1 was used except that 50% by weight sodium hydroxide was added instead of acid. Details are summarised in Table 5.4.

The reaction mixture remained cloudy until approximately the equivalence point of OH^- addition, whereupon it became substantially clear. Further addition produced no change in the appearance of the system which remained slightly cloudy.

Table 5. 4 Experimental details for alkali dissolution of sludge

Mass of the Sludge (g)	14.32
Non-volatile solids content (g)	2.68
Aluminium content in sludge (g)	0.94
Sodium hydroxide addition to sludge (g)	1.39
Aluminium content in sludge (moles)	0.034
Sodium hydroxide addition to sludge (moles)	0.034
$OH^-/Al(OH)_3$	1
Final pH	11.6
Recovered aluminium (moles)	0.031
Recovered aluminium (percent)	92%

The product at the equivalence point was filtered through 0.45 µm filter and the filtrate was analysed by ICP-OES. Results are summarised in Table 5.5.

Table 5. 5 Metal content of recovered alkaline aluminate product produced from aluminium anodising sludge

Metal analysed (mg/L)	Expected heavy metal content present in sludge	Alkaline aluminate product content	Corrected sludge content*
Total Cadmium	68	15	54.4
Total Nickel	251	136	200.8
Total lead	78	41	62.4
Total Zinc	133	105	106.4
Total Iron	154	122	123.2
Total Tin	297	246	237.6
Total Magnesium	435	147	348

*The corrected sludge content was calculated from the original sludge using an approximate dilution factor of 20%.

Given that the volume of the system was increased by approximately 20% due to the addition of the sodium hydroxide solution a similar percent decrease in metal content can be expected. The reductions of Cd, Mg and Ni were greater than 20% indicating the removal of insoluble hydroxides. Surprisingly, very little Fe was removed even though Fe(III) is not soluble in alkaline solutions. Little removal of Sn, Pb and Zn was observed as can be explained by the formation of soluble stannate, plumbate and zincate anions in the alkaline solution of the experiment.

5.4 Preparation of concentrated colloidal systems

In section 1.9 the possibility of re-suspending the aluminium hydroxide as concentrated colloidal solution was discussed.

5.4.1 Preliminary experiment

In a preliminary experiment to test the possibility of recovering soluble or suspended aluminium species from freshly precipitated $Al(OH)_3$, 20 mL of 0.1 mol/L $AlCl_3$ was titrated against 0.1 mol/L NaOH until all the aluminium had precipitated as $Al(OH)_3$. The precipitate formed was reacted with further NaOH until all the aluminium dissolved. The pH (CyberScan 2500 pH meter) and

turbidity (HACH 2100P) were recorded at regular intervals during the titration. Data are summarised in Figure 5.7.

During the addition of the alkali, after an initial steep rise in pH to approximately 3.5 the pH stayed relatively constant and the solution remained essential clear until the ratio of OH^-/Al^{+3} reached approximately 2.5 whereupon the pH and turbidity both rose steeply. A visible precipitate was first formed at the OH^-/Al^{+3} ratio of approximately 3. Upon further addition of alkali, the pH rose steeply and turbidity decreased steeply. Visible precipitates were seen until OH^-/Al^{+3} of 4. The solution became clear at OH^-/Al^{+3} ratio of 4.3 at a pH of 12.24.

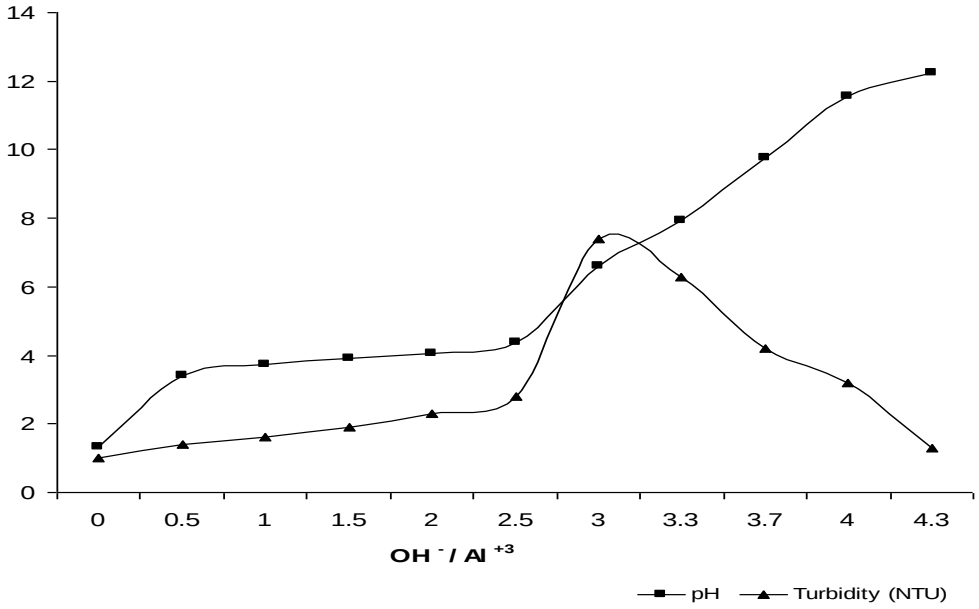

Figure 5. 7 Variation of pH and turbidity with OH^-/Al^{+3} ratio of added reagents in the neutralisation of 0.1 mol/L $AlCl_3$ with 0.1 mol/L NaOH

In a second experiment to determine the degree of re-suspension of freshly precipitated $Al(OH)_3$, 20 mL of 0.1 mol/L $AlCl_3$ was titrated against 0.1 mol/L NaOH until all the aluminium had precipitated as $Al(OH)_3$. The precipitate was then titrated with 0.1 mol/L HCl at H^+ to $Al(OH)_3$ ratios of 0.5, 1, 1.5, 2, 2.5 and 3. The pH and turbidity of these solutions were recorded after each addition. Data are summarised in Figure 5.8. The pH and turbidity were observed to drop, slowly at first and then more rapidly when the mole ratio of $H^+/Al(OH)_3$ reached approximately 1.5. The solution became essentially clear at a mole ratio of approximately 2.5 indicating the dissolution of the suspended aluminium colloids or polycations to form cationic species.

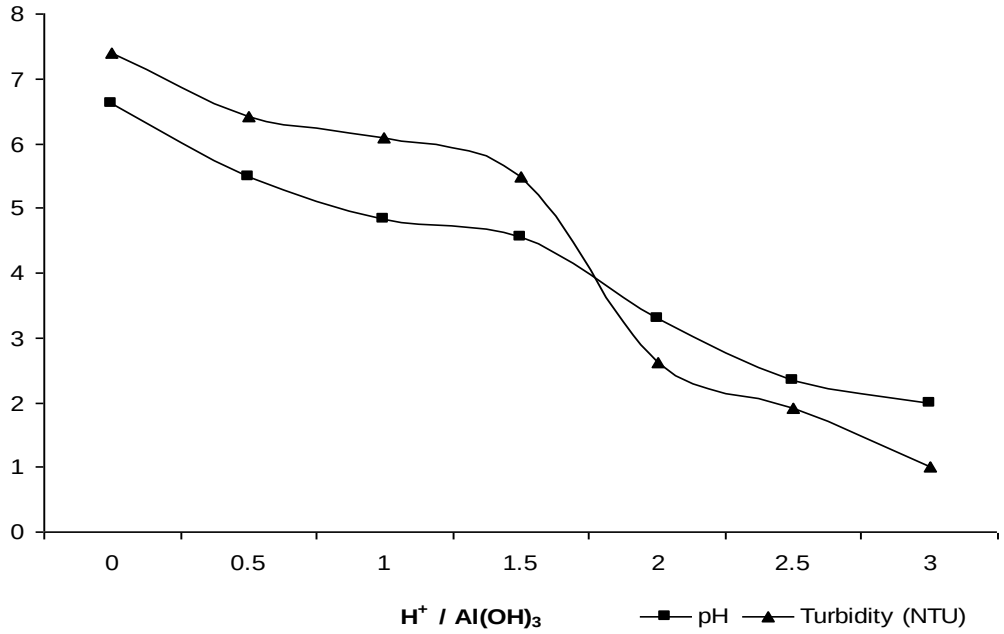

Figure 5. 8 Variation of pH and turbidity with $H^+/Al(OH)_3$ ratio of added reagents in the dissolution/re-suspension of freshly precipitated $Al(OH)_3$ with 0.1 mol/L HCl

5.4.2 Acidic dissolution of the FPS by hydrochloric acid

In an attempt to prepare acidic re-suspended coagulant from the dewatered sludge, HCl was added at the $H^+/Al(OH)_3$ ratios of 0.3, 0.5, 1, 1.2, 2, 2.5 and 3. An experimental procedure similar to that described in Section 5.2.1 was used except analytical reagent grade 36% HCl was used instead of 98% sulphuric acid. Data are summarised in Table 5.6.

Table 5. 6 Experimental details of acid digestion experiments

Experimental runs	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Mass of the Sludge(g)	12.75	11.39	14.25	16.35	14.82	17.65	13.57
Non-volatile solids content (g)	2.39	2.13	2.67	3.06	2.78	3.31	2.54
Aluminium content (moles)	0.031	0.028	0.035	0.040	0.036	0.043	0.033
Hydrochloric acid addition (moles)	0.010	0.014	0.035	0.048	0.072	0.108	0.099
$H^+/Al(OH)_3$	0.3	0.5	1	1.2	2	2.5	3
Final pH	7.6	6.1	4.9	4.5	3.6	2.7	2
Re-suspended aluminium (moles)	0.001	0.003	0.010	0.014	0.018	0.033	0.031
Re-suspended aluminium (percent)	4	12	28	35	52	68	95

The product at the equivalence point ($H^+/Al(OH)_3$ ratio of 3) was filtered through 0.45 µm filter and the filtrate aluminium and heavy metal content was determined. Results are summarised in Table 5.7.

Table 5. 7 Metal content of re-suspended aluminium prepared from aluminium anodising sludge

Metal analysed (mg/L)	**Expected heavy metal present in sludge**	**Acidic aluminium chloride product content**
Total Cadmium	68	65
Total Nickel	251	249
Total lead	78	76
Total Zinc	133	128
Total Iron	154	148
Total Tin	297	297
Total Magnesium	435	434

As expected there was very little removal of Cd, Ni, Pb, Zn, Fe, Sn and Mg. All the metal will be soluble in the acid condition used to recover the aluminium.

Dissolved/re-suspended aluminium contents and pHs for the systems formed at $H^+/Al(OH)_3$ ratios of 0.3, 0.5, 1, 1.2, 2, 2.5, 3 were determined initially and after 39 days of aging. Results are summarised in Figures 5.9 and 5.10. They show that 95% percent of aluminium was recovered from the sludge by adding the stoichiometric amount of acid resulting in a pH of 2, while at $H^+/Al(OH)_3$ ratios of 0.3, 0.5, 1, 1.2, 2, 2.5 the aluminium recovery increased roughly in proportion with the acid added. Little change occurred on aging for 39 days. The re-suspension behaviour of the sludge contrasts strongly with the re-suspension of the freshly precipitated $Al(OH)_3$ system as shown in Figure 5.9.

It is clear from this experiment that the properties of the dewatered sludge differ significantly from the properties of freshly precipitated $Al(OH)_3$ system. While the variation of pH with added acid was approximately similar for the two systems (See Figure 5.10), the re-suspended aluminium was much higher in the freshly precipitated aluminium system. It can thus be inferred that while the acid is reacting with hydroxyl groups of the $Al(OH)_3$ in the FPS sludge, the aluminium species formed remain aggregated. A possible reason for this could be the binding

effect of the polyelectrolyte which strengthens the floc structure against the destabilising effect of increasing cationic charge that must occur as more H^+ ions with hydroxyl groups of the $Al(OH)_3$.

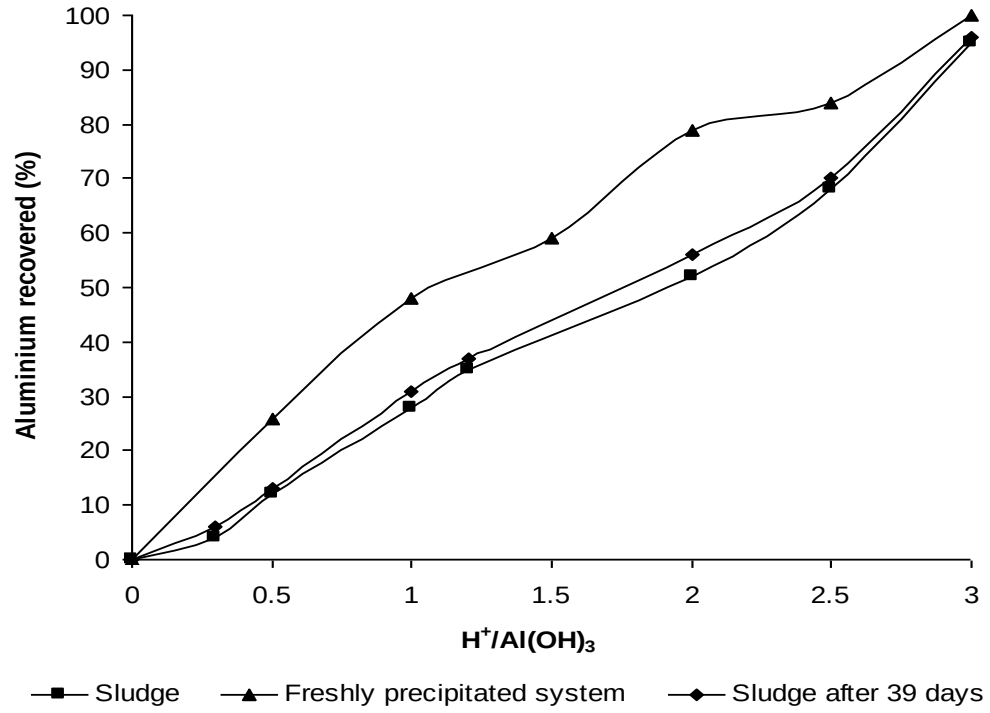

Figure 5. 9 Comparison of aluminium recovered between sludge, freshly precipitated $Al(OH)_3$ and sludge after 39 days of aging at various $H^+/Al(OH)_3$ ratios

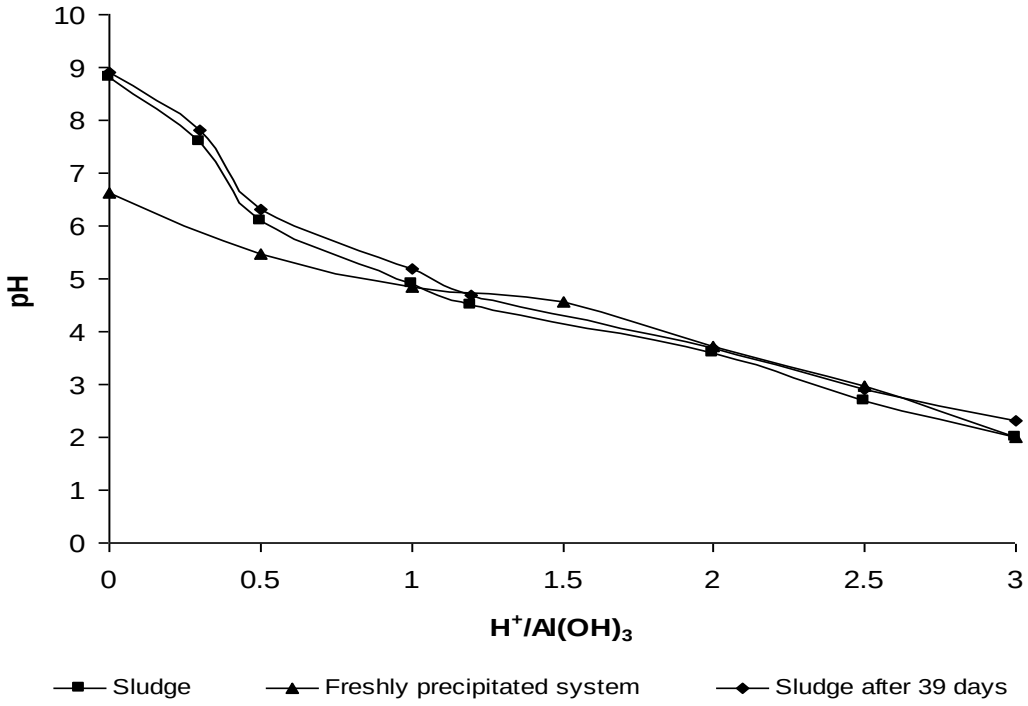

Figure 5. 10 Comparison of pH between sludge, freshly precipitated $Al(OH)_3$ and sludge after 39 days aging at various $H^+/Al(OH)_3$ ratios

5.4.3 Acid digestion of FPS under forcing conditions

The possibility that re-suspension of the dewatered sludge was inhibited by the polyelectrolyte used in the flocculation of this material suggested that re-suspension might be achieved by a more aggressive environments. A series of experiments was designed in an attempt to disaggregate the surfactant containing flocs. These included autoclaving at 150°C, rapid homogenisation at 3000 rpm, ultrasonic treatment at 80°C and mechanical grinding using mortar and pestle.

A weighed amount of dewatered sludge was reacted with the appropriate amount of analytical reagent grade of 36% HCl at the ratio $H^+/Al(OH)_3$ of 2 by an experimental procedure similar to that described in Section 5.2.1. The acidified semisolid sludge was divided into four parts and was transferred into four clean test tubes for the following experiments.

1. Batch autoclave

One test tube was placed in the inner volume of the batch autoclave and heated at 150°C for 6 hours.

2. Ultrasonic treatment

The second test tube was sonicated in the ultrasonic treatment bath (Transonic-700H type, Hitachi Co., Tokyo, Japan) pre-heated at 80°C and ultrasonic vibration at the frequency of 14 kHz was applied for 6 hours.

3 Rapid homogenisation

The third sample was transferred to a beaker and stirred at 3000 rpm for 30 minutes at 20°C.

4. Mechanical grinding

The known amount of wet acidic sludge was ground using a mortar and pestle for 20 minutes at 20°C.

Each treated sludge was transferred to a clean test tube with equivalent volume of water, agitated vigorously for 20 minutes and settled for 72 hours.

A photograph of the tubes after 72 hours is given in Figure 5.11. It is clear that the ultrasonic treatment had most effect on the sludge. The supernatant solution has a milky appearance and the volume of solid sludge appears significantly less than other treated system. All the other supernatants remained clear with very little change in sludge volume except for the autoclave sample where a noticeable decrease in volume is apparent.

Data for supernatant aluminium concentrations for the different mechanical and thermal treatments are given in Figure 5.12. They show that ultrasonic treatment had most effect resulting in re-suspension of approximately 30% of the sludge. The other treatments all caused some re-suspension but this was less than 10% for all except the rapid homogenisation which caused 12% re-suspension.

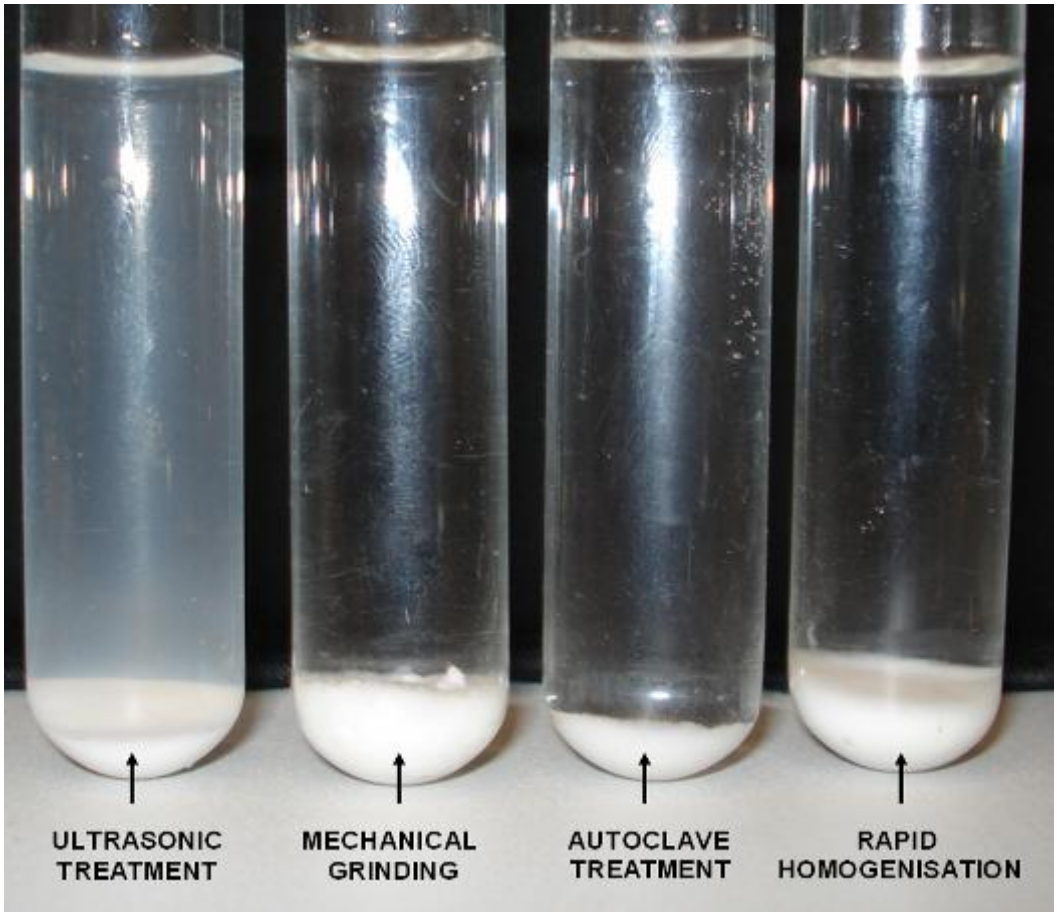

Figure 5. 11 Photograph of sludge systems after various mechanical and thermal treatments

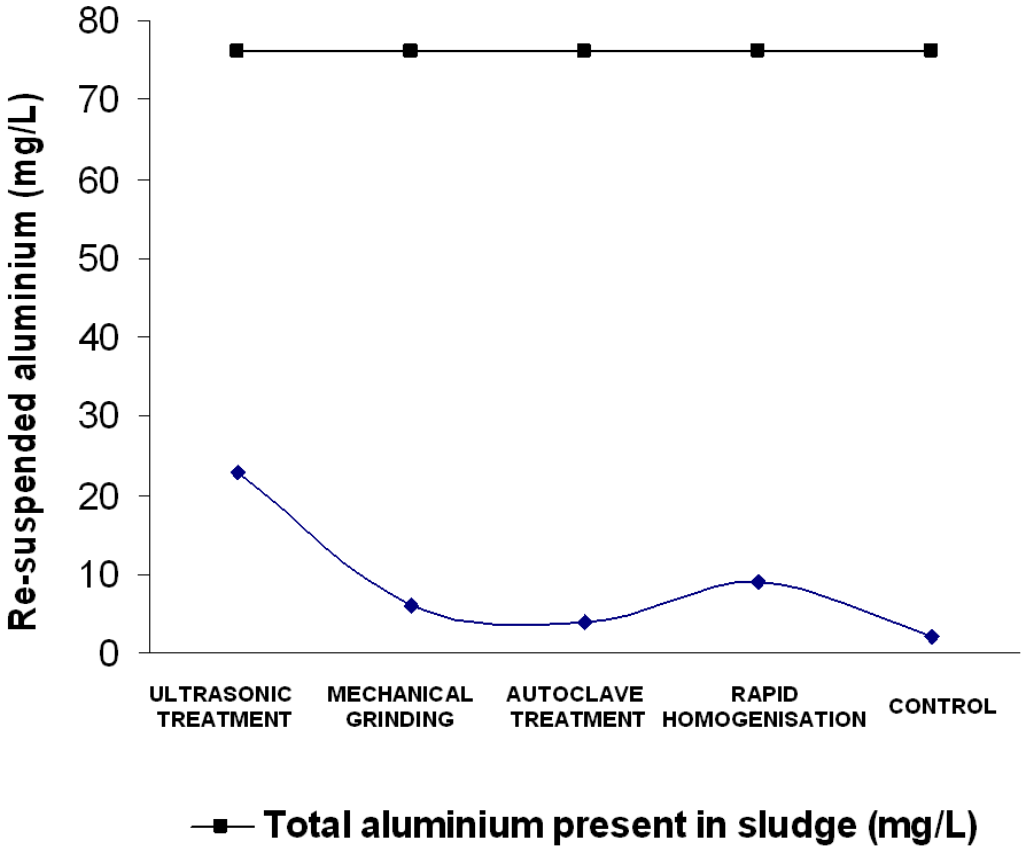

Figure 5. 12 The effect of mechanical and thermal treatment on acid sludge re-suspension

5.5 Coagulation testing

The effectiveness of recovered acidic aluminium solution ($H^+/Al(OH)_3$ = 3), alkaline aluminate solution ($OH^-/Al(OH)_3$ = 1), ultrasonically re-suspended acid sludge solution ($H^+/Al(OH)_3$ = 2) and alum solution was tested by jar testing. Experimental details are described in Section 2.3. The data is presented in appendix B. Most efficient coagulation occurred at pH 6.5. The critical coagulation concentrations for all systems were found to be approximately 5 mg/L. For all systems except the ultrasonic re-suspended sludge, clear solution of low turbidity resulted after 1 hour standing.

5.6 Cost effectiveness of recovered aluminium as a coagulant

An analysis of the consumables cost (Tandt 2008) for recovery of aluminium species from 1000 kg of FPS sludge according to various procedures described above is summarised in Table 5.8.

Table 5. 8 Consumables cost for recovery of aluminium species from anodising sludge

PRODUCTION OF POTASSIUM ALUM COAGULANT		
98% sulphuric acid	195 L	$185
99.9% anhydrous potassium sulphate	203 kg	$406
Weight of potassium alum produced	967 kg	$591
Cost per kg of alum produced	1 kg	$0.6
Weight of aluminium recovered	63.2 kg	$591
Cost per kg of aluminium recovered	1 kg	$9.3
Market value per kg of aluminium in alum	1 kg	$11.5
PRODUCTION OF ALUMINIUM CHLORIDE COAGULANT		
36% hydrochloric acid	226 L	$203
Acidic aluminium chloride coagulant produced	271 L	$203
Weight of aluminium recovered	62.6 kg	$203
Cost per kg of aluminium recovered	1 kg	$3.3
Market value per kg of aluminium in polyaluminium chloride	1 kg	$5
PRODUCTION OF POLYALUMINIUM CHLORIDE COAGULANT		
50% w/w sodium hydroxide	150 L	$375
Polyaluminium chloride coagulant produced	451 L	$578
Weight of aluminium recovered	62.6 kg	$578
Cost per kg of aluminium recovered	1 kg	$9.2
Market value per kg of aluminium in polyaluminium chloride	1 kg	$5
PRODUCTION OF ALKALINE COAGULANT		
50% w/w sodium hydroxide	67 L	$167
Alkaline coagulant produced	81 L	$167
Weight of aluminium recovered	60.6 kg	$167
Cost per kg of aluminium recovered	1 kg	$2.75
Market value per kg of aluminium in sodium aluminate	1 kg	$2.60

The margins (the difference between market value and consumables cost of production expressed as a percentage of the materials cost of production) available for plant and labour are small being 24% for alum, 52% for acidic aluminium chloride solution (assuming the solution can be sold for its aluminium content at the same per mole price as polyaluminium chloride) and -6% for sodium

aluminate solution. If the acid aluminium chloride solution was partially neutralised to produce polyaluminium chloride (OH^-/Al^{+3} = 2.46) the margin would be -46%. Negative margins indicate that these options are not viable.

The data of table 5.8 indicate that the most advantageous product to market is acid aluminium chloride solution. Unfortunately it is likely that a market for this product would have to be established from users who would have to be convinced to pay a price similar to that of polyaluminium chloride. With a margin of 24% the production of alum appears to be financially feasible providing the processing, marketing etc costs can be contained.

Figures 5.13 and 5.14 are process flow diagrams indicating the essential processing steps for the recovery of the aluminium in its various forms.

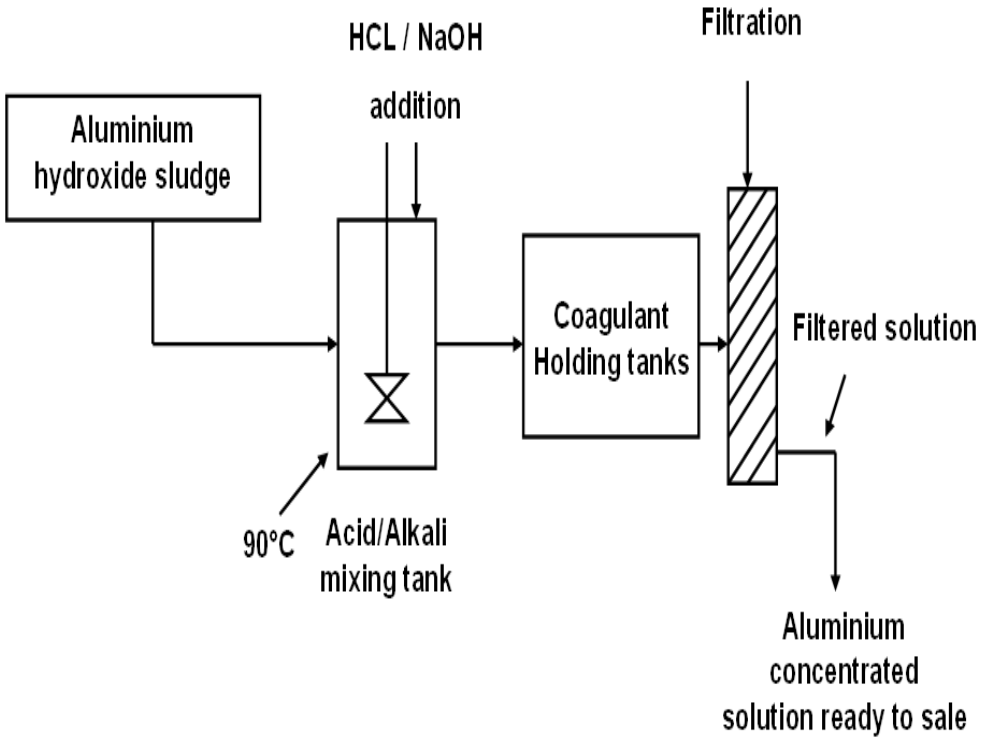

Figure 5. 13 Schematic diagram for recovery of alkaline aluminate and acidic aluminium chloride solutions from anodising sludge

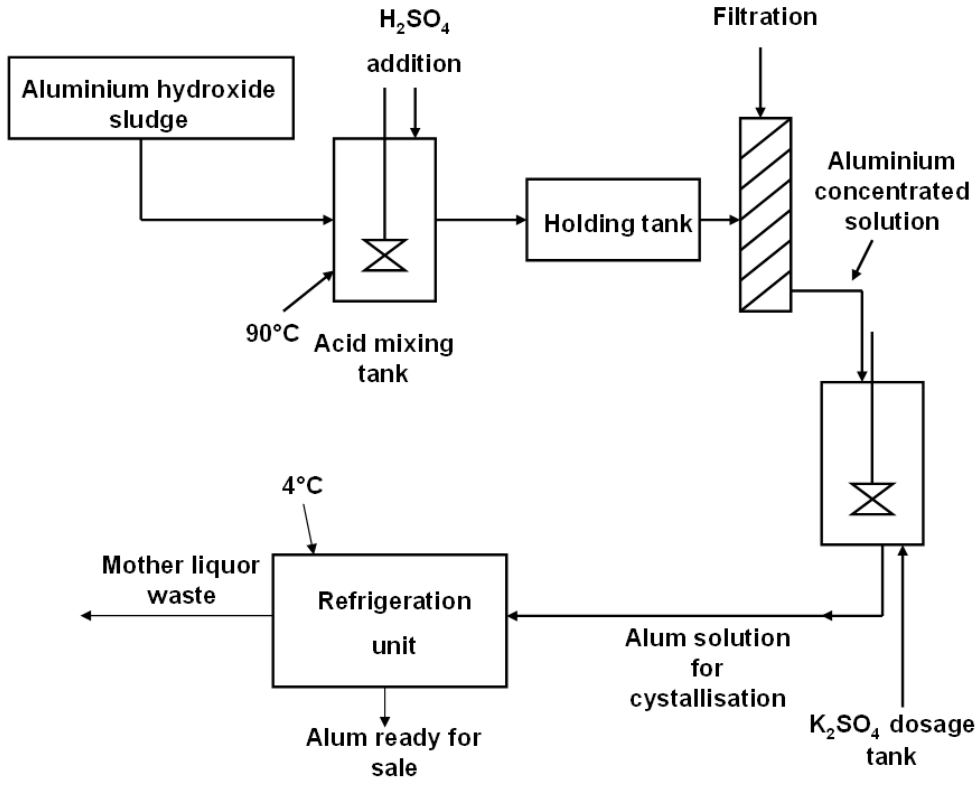

Figure 5. 14 Schematic diagram for recovery of crystal alum from anodising sludge

For alum precipitation the same processing equipment could be used for the initial sludge solubilisation and product filtration. Further steps for potassium sulphate addition and refrigerated alum crystallisation would be needed. For polyaluminium chloride production an addition step for sodium hydroxide addition would be required.

It is clear from cost considerations that while significant cash flow could be generated from the recovery of the sludge; the profit is likely to be modest at today's prices of sludge disposal. The main benefit to Finex from proceeding with a sludge recovery program however is likely to be enhancement of the companies green credentials.

6 Discussion and conclusion

6.1 General discussion

Finex is New Zealand's most recently developed anodising plant established in Hamilton in 2004. During the first period of operation the company was faced with a costly sludge disposal problem. In order to reduce the volume of the anodising sludge produced at Finex prolonged settling and polyelectrolyte addition experiments were conducted. It was found that flocculation by polyelectrolyte at optimum pH of 6.5 resulted in faster settling to 12% to the sludge's original volume. Prolonged settling times without polyelectrolyte addition gave better volume reductions but were too long to be able to cope with current production. A literature research was carried out on dewatering technologies. A plate and frame filter press was chosen as the most appropriate dewatering technology for the Finex site.

With the reduction of its bulk by dewatering, the problem of sludge disposal was essentially solved. However the 12 tonnes per week of dewatered sludge production still posed a challenge to devise a way of using the material beneficially. The characteristics of the filter press sludge such as water content, non-volatile solids content, morphological characteristics by XRD, elemental analysis by SEM-EDXS methods were determined.

Commodity alum was produced in good yield at 4°C by treatment of the sludge with sulphuric acid followed by crystallisation with anhydrous potassium sulphate. The product was very similar to the commercial product. Under basic conditions, sodium aluminate was produced by adding stoichiometric amount of OH^-. Under acid conditions at the $H^+/Al(OH)_3$ stoichiometric ratio of 3, 95% of the aluminium was recovered as aluminium salt solution. When acid addition was less than the stoichiometric amount, the polyelectrolyte containing sludge showed little tendency to re-suspend. A variety of mechanical and thermal methods was used in an attempt to disaggregate and re-suspend the sludge. These included ultrasonic treatment at 80°C at frequency 14 kHz for 6 hours, autoclaving the sludge in electrical furnace at 150°C for 6 hours, homogenisation at 3000 rpm for 30

minutes at 20°C and mechanical grinding using mortar and pestle at 20°C. The ultrasonic treatment was effective in re-suspending 30% of the sludge. The other treatments were largely ineffective.

The acidic and alkaline commodity products prepared from anodising sludge were tested for their usefulness as coagulation agents. Critical coagulation concentrations for kaolin suspensions were found to be 5 mg/L, for all systems. In all cases except the ultrasonic re-suspended sludge, clear solution of low turbidity resulted after 1 hour standing.

Good heavy metal reduction was achieved by the alum crystallisation process. In the case of aluminate production Cd, Mg and Ni were reduced by greater than the expected 20% dilution factor through the removal of insoluble hydroxides. As expected minimal reduction of heavy metal content was achieved in the acidic aluminium chloride solution. Heavy metal content might preclude the possibility of the use of recovered aluminium in certain applications. However for typical water treatment coagulation where aluminium is used in 0 to 10 mg/L range the level of added heavy metals is unlikely to be a problem (< 1 ng/L).

An analysis of the cost of recovery of various aluminium commodity products from waste sludge indicated that recovery of acid aluminium solution was most cost effective while the recovery of alum produces the purest product. Assuming that the acid aluminium chloride solution could be substituted for and sold at the same per kg of aluminium price as polyaluminium chloride, a 52% margin over consumables cost seems possible which allows a modest profit. The main benefit to Finex from proceeding with a sludge recovery program however is likely to be enhancement of the companies green credentials.

6.2 Conclusion

Studies of the waste management system at the Finex anodising plant have led to the following outcomes:

1. An initial study of the Finex site and their current waste treatment system allowed the drawing of a detailed process flow diagram. Detailed characterisation of the amount and nature of sludge being produced indicated that gravity settled sludge contained high water content and large savings in disposal costs could be achieved by efficient dewatering.

2. An evaluation of dewatering technologies was performed. It was concluded that plate and frame filter press was a cost effective technology to reduce the volume of the sludge currently disposed of to landfill.

3. From an investigation of possible beneficial uses of the sludge produced at the Finex site, the production of alum, alkaline sodium aluminate solution and acidic aluminium chloride solution were all found to be possible. The most cost effective process was found to be the production of acidic aluminium chloride solution. While the heavy metal content of this product was higher than that of crystallised alum, this is unlikely to be an issue if acidic aluminium chloride solution is used as a coagulant in the 0 to 10 mg/L concentration range typical of water treatment processes.

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Appendix-A: Calibration curves for measurements of metal ions

Metal ion measurement by ICP-OES

Typical calibration curves of aluminium, magnesium, cadmium, nickel, lead, tin, iron and zinc are shown in the following.

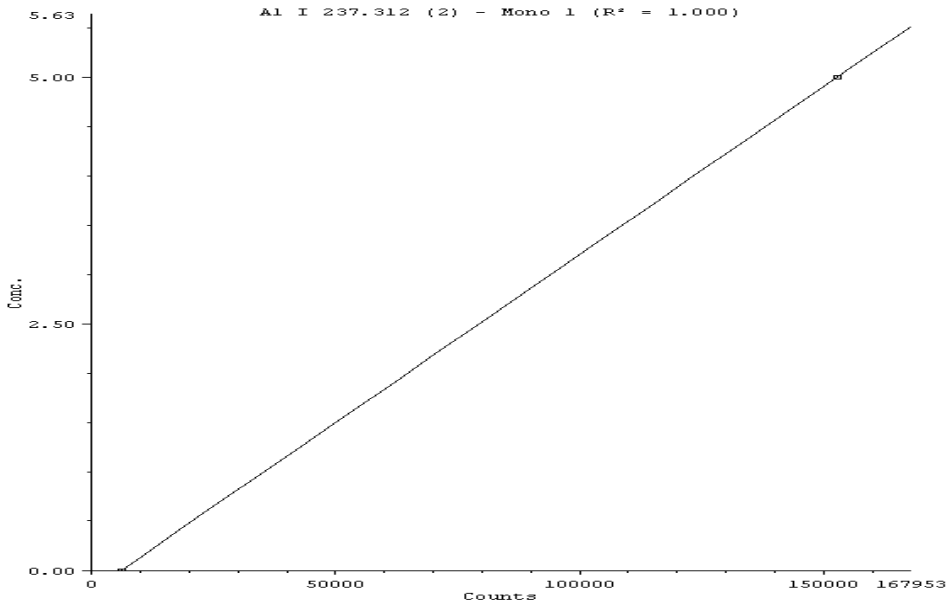

Figure A. 1 Aluminium calibration curve

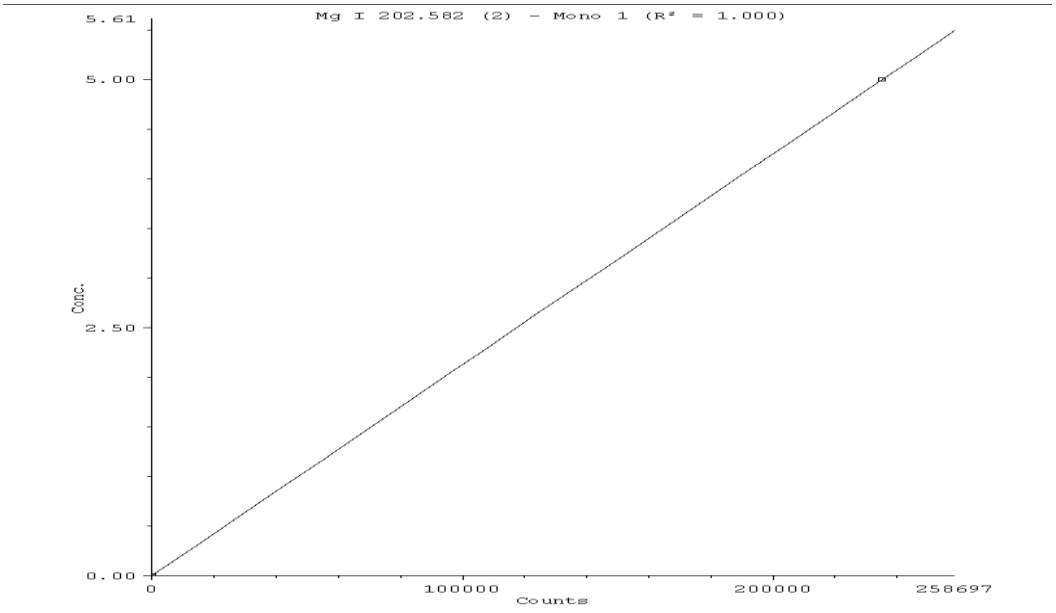

Figure A. 2 Magnesium calibration curve

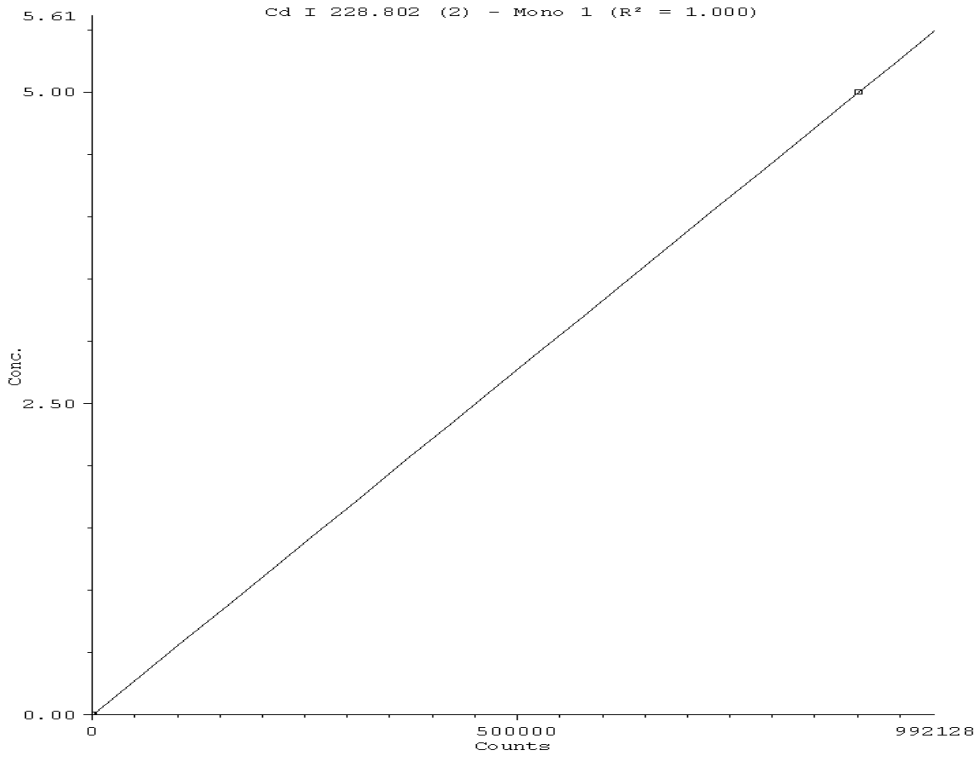

Figure A. 3 Cadmium calibration curve

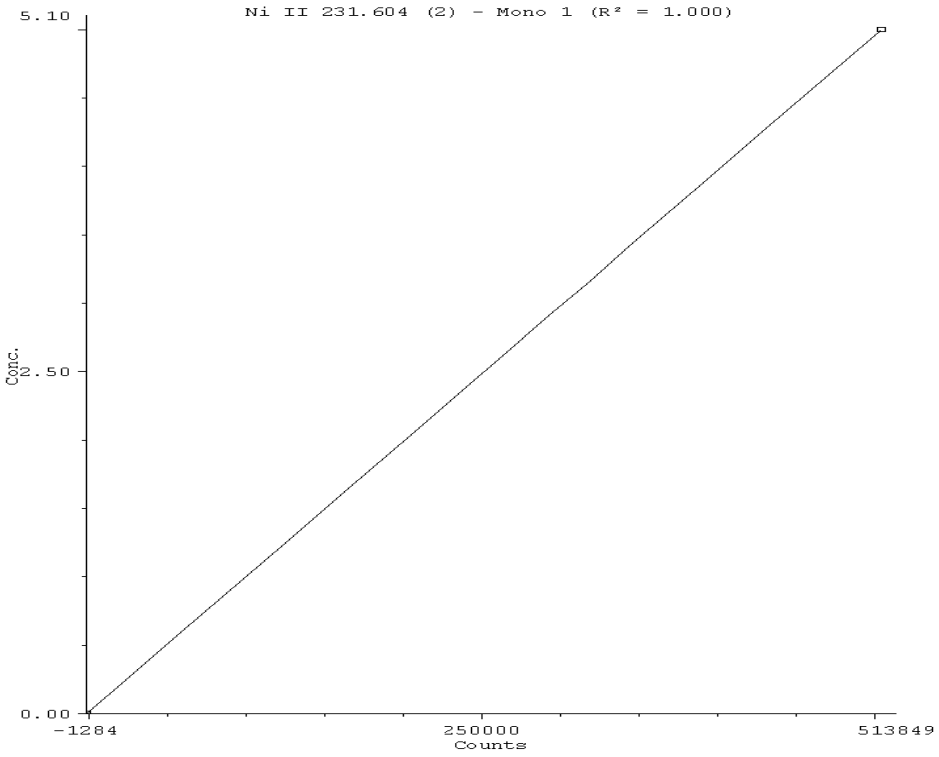

Figure A. 4 Nickel calibration curve

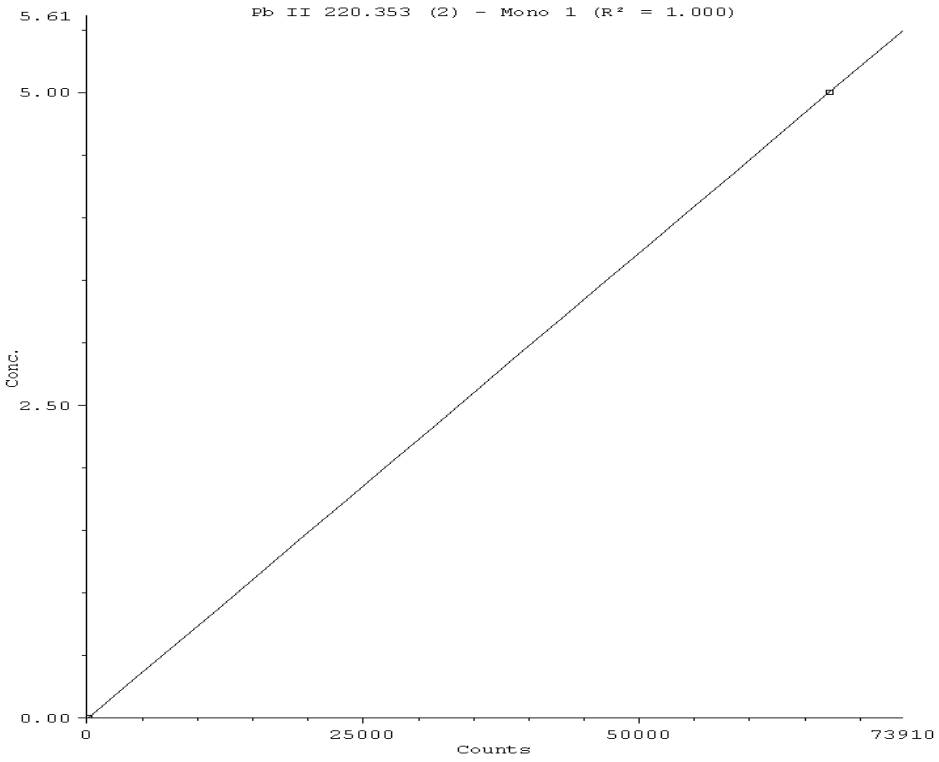

Figure A. 5 Lead calibration curve

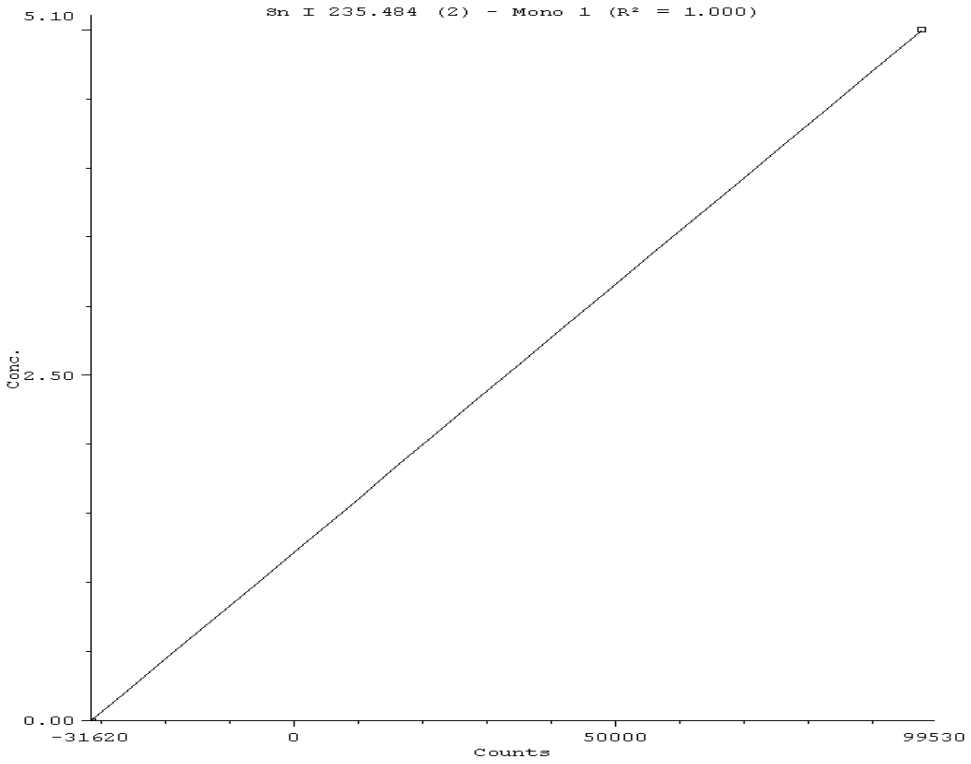

Figure A. 6 Tin calibration curve

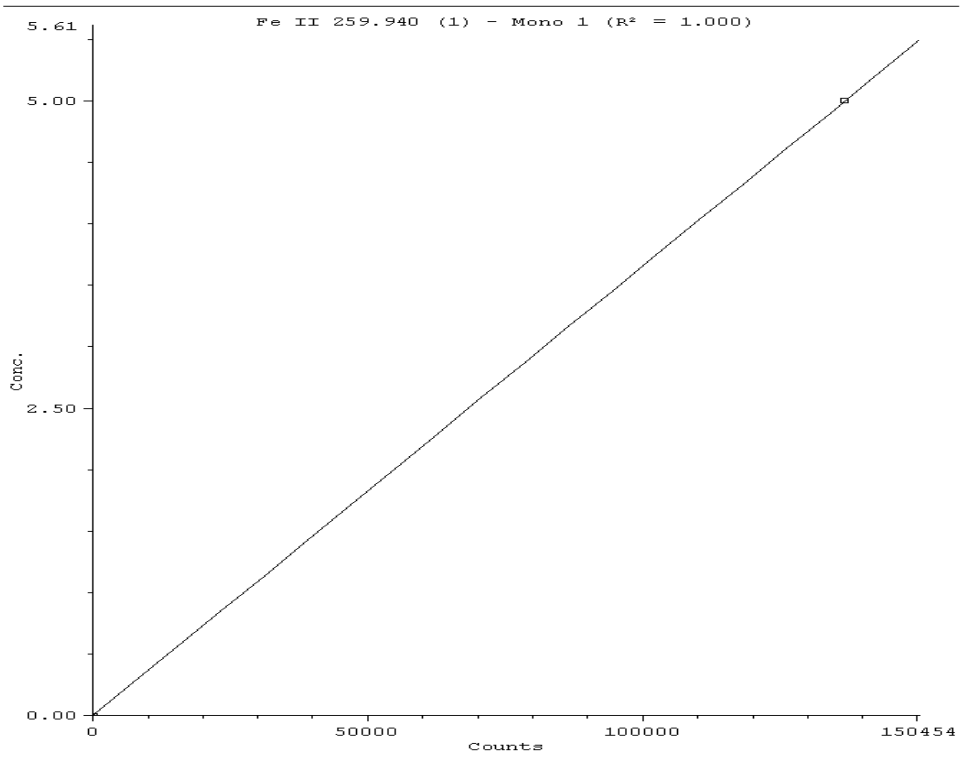

Figure A. 7 Iron calibration curve

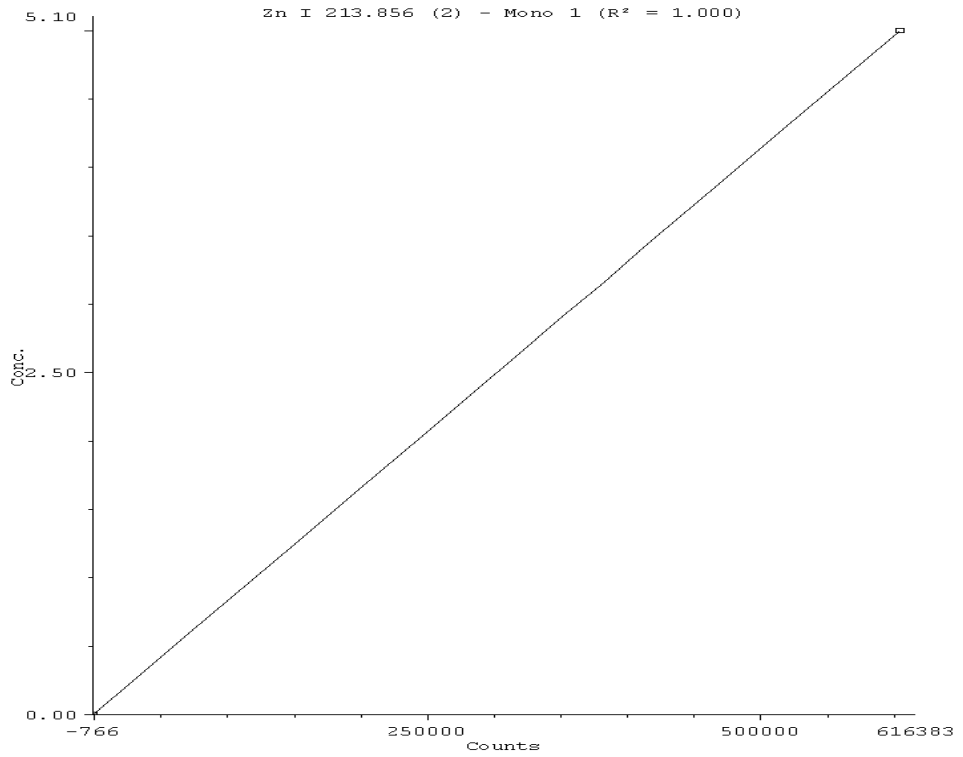

Figure A. 8 Zinc calibration curve

Appendix-B: Performance of recycled coagulants

Table B. 1 Jar test data of acidic aluminium chloride solution with synthetic kaolin water

No	Volume (mL) of acidic aluminium chloride solution added to 1 L kaolin water	Concentration (mg/L of $Al^{+3)}$ in water sample (dosage)	pH	Residual Turbidity (NTU)
1	1.2	1	5	28
1	2.4	2	5	27
1	3.6	3	5	26
1	4.8	4	5	25
1	6.0	5	5	28
1	7.2	6	5	28
2	1.2	1	5.5	28
2	2.4	2	5.5	27
2	3.6	3	5.5	26
2	4.8	4	5.5	27
2	6.0	5	5.5	25
2	7.2	6	5.5	26
3	1.2	1	6	27
3	2.4	2	6	25
3	3.6	3	6	21
3	4.8	4	6	22
3	6.0	5	6	25
3	7.2	6	6	26
4	1.2	1	6.5	24
4	2.4	2	6.5	21
4	3.6	3	6.5	18
4	4.8	4	6.5	11
4	**6.0**	**5**	**6.5**	**6**
4	7.2	6	6.5	15
5	1.2	1	7	24
5	2.4	2	7	22
5	3.6	3	7	22
5	4.8	4	7	16
5	6.0	5	7	11
5	7.2	6	7	18
6	1.2	1	7.5	26
6	2.4	2	7.5	29
6	3.6	3	7.5	29
6	4.8	4	7.5	28
6	6.0	5	7.5	28
6	7.2	6	7.5	28

Note: The aluminium content in acidic aluminium chloride solution was 837 mg/L

Table B. 2 Jar test data of alkaline aluminate solution with synthetic kaolin water

No	Volume (mL) of alkaline aluminate solution added to 1 L kaolin water	Concentration (mg/L of Al^{+3}) in water sample (dosage)	pH	Residual Turbidity (NTU)
1	1.3	1	5	29
1	2.6	2	5	28
1	3.9	3	5	27
1	5.2	4	5	28
1	6.5	5	5	28
1	7.8	6	5	29
2	1.3	1	5.5	28
2	2.6	2	5.5	27
2	3.9	3	5.5	27
2	5.2	4	5.5	28
2	6.5	5	5.5	28
2	7.8	6	5.5	29
3	1.3	1	6	27
3	2.6	2	6	26
3	3.9	3	6	28
3	5.2	4	6	28
3	6.5	5	6	28
3	7.8	6	6	30
4	1.3	1	6.5	24
4	2.6	2	6.5	22
4	3.9	3	6.5	21
4	5.2	4	6.5	18
4	**6.5**	**5**	**6.5**	**9**
4	7.8	6	6.5	15
5	1.3	1	7	21
5	2.6	2	7	23
5	3.9	3	7	25
5	5.2	4	7	27
5	6.5	5	7	28
5	7.8	6	7	28
6	1.3	1	7.5	28
6	2.6	2	7.5	26
6	3.9	3	7.5	25
6	5.2	4	7.5	24
6	6.5	5	7.5	28
6	7.8	6	7.5	29

Note: The aluminium content in alkaline aluminate solution was 769 mg/L

Table B. 3 Jar test data of ultrasonic re-suspended sludge solution with synthetic kaolin water

No	Volume (mL) of ultrasonic re-suspended sludge solution added to 1 L kaolin water	Concentration (mg/L of $Al^{+3)}$ in water sample (dosage)	pH	Residual Turbidity (NTU)
1	1.4	1	5	>30
1	2.8	2	5	>30
1	4.2	3	5	>30
1	5.6	4	5	>30
1	7.0	5	5	>30
1	8.4	6	5	>30
2	1.4	1	5.5	>30
2	2.8	2	5.5	>30
2	4.2	3	5.5	>30
2	5.6	4	5.5	>30
2	7.0	5	5.5	>30
2	8.4	6	5.5	>30
3	1.4	1	6	>30
3	2.8	2	6	>30
3	4.2	3	6	>30
3	5.6	4	6	>30
3	7.0	5	6	>30
3	8.4	6	6	>30
4	1.4	1	6.5	>30
4	2.8	2	6.5	>30
4	4.2	3	6.5	29
4	5.6	4	6.5	29
4	**7.0**	**5**	**6.5**	**26**
4	8.4	6	6.5	>30
5	1.4	1	7	>30
5	2.8	2	7	>30
5	4.2	3	7	>30
5	5.6	4	7	>30
5	7.0	5	7	>30
5	8.4	6	7	>30
6	1.4	1	7.5	>30
6	2.8	2	7.5	>30
6	4.2	3	7.5	>30
6	5.6	4	7.5	>30
6	7.0	5	7.5	>30
6	8.4	6	7.5	>30

The aluminium content in the ultrasonic re-suspended sludge was 716 mg/L

Table B. 4 Jar test data of alum solution with synthetic kaolin water

No	Volume (mL) of alum solution added to 1 L kaolin water	Concentration (mg/L of $Al^{+3)}$ in water sample (dosage)	pH	Residual Turbidity (NTU)
1	2.1	1	5	28
1	4.2	2	5	28
1	6.3	3	5	26
1	8.4	4	5	24
1	10.5	5	5	27
1	12.6	6	5	28
2	2.1	1	5.5	28
2	4.2	2	5.5	26
2	6.3	3	5.5	24
2	8.4	4	5.5	27
2	10.5	5	5.5	25
2	12.6	6	5.5	25
3	2.1	1	6	27
3	4.2	2	6	25
3	6.3	3	6	21
3	8.4	4	6	20
3	10.5	5	6	23
3	12.6	6	6	26
4	2.1	1	6.5	23
4	4.2	2	6.5	21
4	6.3	3	6.5	19
4	8.4	4	6.5	9
4	**10.5**	**5**	**6.5**	**4**
4	12.6	6	6.5	11
5	2.1	1	7	23
5	4.2	2	7	21
5	6.3	3	7	22
5	8.4	4	7	18
5	10.5	5	7	19
5	12.6	6	7	21
6	2.1	1	7.5	26
6	4.2	2	7.5	27
6	6.3	3	7.5	27
6	8.4	4	7.5	28
6	10.5	5	7.5	29
6	12.6	6	7.5	29

The aluminium content in the alum solution was 478 mg/L