REMOVAL OF COLOUR AND SOLIDS FROM QAL SEA WATER NEUTRALISATION EFFLUENT USING VEOLIA ACTIFLO HIGH RATE CLARIFIER

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Abstract

Colour, solids and pH are important parameters in seawater neutralised effluent discharge quality.

Coagulants such as ferric chloride, ferrous and ferric chloride, activated carbon, magnesium sulphate are known to remove colour and solids, however they exhibit poor settling rates resulting in 'cloudy' solutions. The addition of microsand in combination with coagulants and flocculants in the patented Veolia Actiflo process enhances flocculation and settling to give improved removal rates of colour and solids.

Laboratory simulations of the Veolia Actiflo system were performed on clarifier overflow and decant pond overflow using combinations of inorganic coagulants (ferric chloride, aluminium chlorohydrate (ACH), polyaluminium chloride (PAC)), organic coagulants including polyDADMAC (polydiallyldimethyl ammonium chloride) range of cationic polymers, together with a number of powder flocculants from different suppliers.

Removal rates of up to 96% of colour and 90% of solids have been achieved. Impacts were observed on pH, TIC and TOC.

Based on the results of the laboratory tests, a trial of the Actiflo process has been performed at a pilot plant scale.

Design data obtained from the laboratory and pilot plant trials resulted in a preliminary design for sizing and costing of a potential full scale plant.

Notation and units

Terms:

Apparent Colour – Measured using HACH DR2000 Spectrophotometer @ 455 nm, expressed in PtCo units. The measurement is made on an unfiltered sample and includes the contribution from dissolved and suspended matter.
True Colour – Measured after filtration through 0.45 disposable filter.
TSS - Total Suspended Solids are solid materials (including organic and inorganic) suspended in water expressed as mg/L.
TIC – Total Inorganic carbon expressed as mg/L C.
TOC – Total Organic Carbon expressed as mg/L C.

1. Introduction

The Queensland Alumina Ltd refinery located in Gladstone, Queensland, Australia utilises a seawater neutralisation process to neutralise liquor and solid phase alkalinity in plant waste streams. Partially seawater neutralised waste streams from the refinery are pumped to a neutralisation facility at the Residue Disposal Area (RDA). Additional seawater is added to complete the neutralisation process in a mixing tank before separation of the mud and depleted seawater using an Outotec clarifier. The overflow from the clarifier flows across the surface of Residue Disposal Area 2 (RDA2) into a decant pond. The discharge from the decant pond flows via a gabion to a labyrinth designed to settle solids. The discharge from the labyrinth flows into an open discharge channel from where it is discharged via a submerged pipe into an estuary.

Profiling across the RDA has identified that the major source of both colour and dissolved organics (TOC) is from plant liquor. A typical profile for colour and TIC/TOC is shown in Figure 1 Profile of Colour across RDA1 and Figure 2 TIC/TOC Profile across RDA2 respectively.

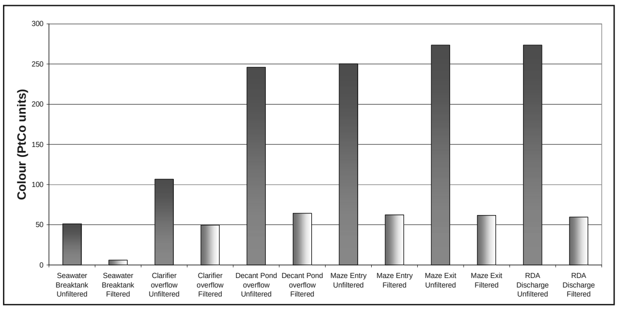

Figure 1 Profile of Colour across RDA

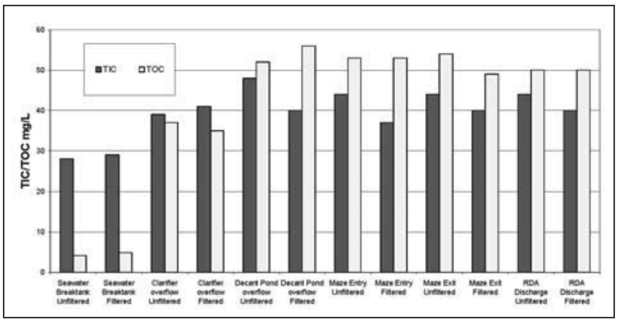

Figure 2 TIC/TOC Profile across RDA

Colour in clarifier overflow is from dissolved organics, red mud and other suspended particles. In the decant pond, colour originated from dissolved organics, red mud particles and biomass generated during degradation of organics. Filtration of decant overflow or clarifier overflow is an effective way to remove colour, however the sheer volume to be filtered makes this method expensive and impractical.

Coagulants such as ferrous (II) sulphate, ferric (III) chloride, magnesium chloride, aluminium sulphate and activated carbon, have been used successfully in wastewater treatment in the removal of colour, solids and organic matter. When used in a seawater situation, the effectiveness of these coagulants is impacted by their inability to settle quickly resulting in high measured apparent (unfiltered) colour. True (filtered) colour measurements show that a number of these coagulants are capable of removing colour but to be effective in a removal process will require filtration or some flocculant addition to aid (rapid) settling and give good overflow clarity.

2. Veolia Aciflo Process

The Actiflo process is a compact, conventional–type water clarification system that utilises microsand as a seed for flocculant formation. The microsand provides surface area that enhances flocculation and also acts as a ballast or weight. The settling characteristics of the resulting sand ballasted flocculant allow for a clarifier design with high overflow rates and short retention times and also a smaller system footprint.

A diagrammatic System Flow of the Veolia Actiflo is shown in Figure 3 Diagrammatic System Flow of Veolia Actiflo3.

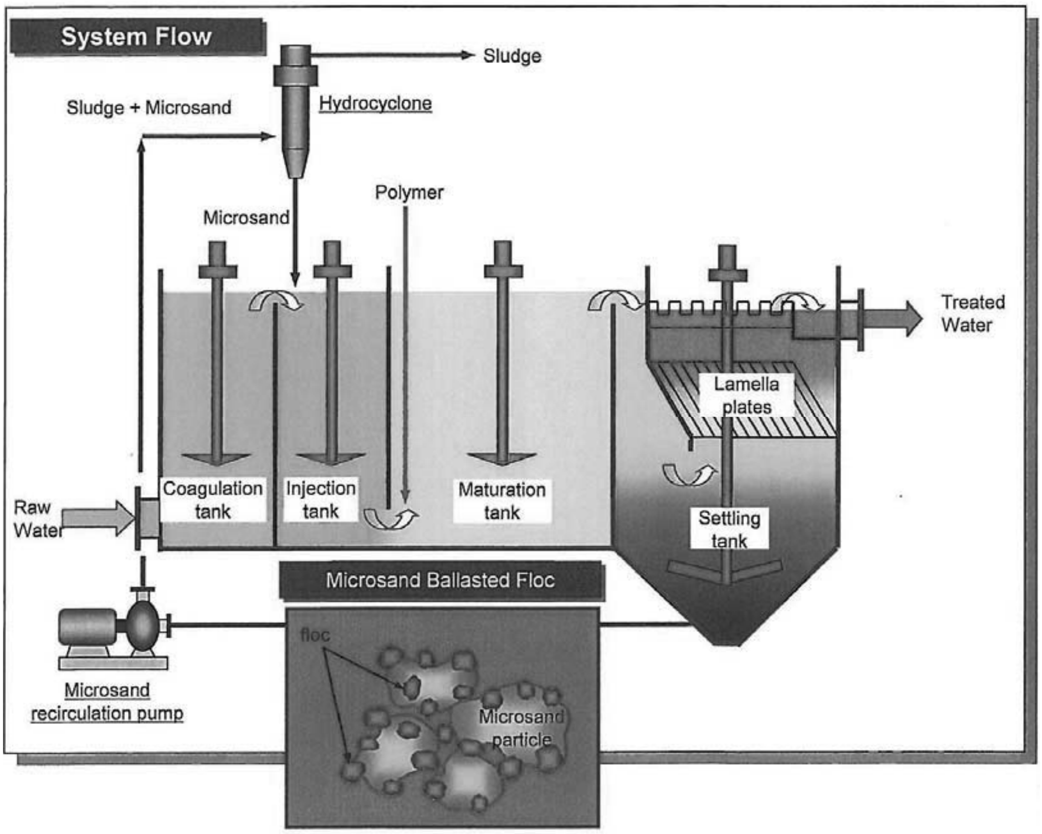

Figure 3 Diagrammatic System Flow of Veolia Actiflo

In the Actiflo plant, a coagulant (such as ferric chloride) is first added to the influent stream where a part of the dissolved matter is converted to an insoluble solids substance in the form of a colloid. These colloids (partly from chemical precipitation and partly from the influent) can coagulate to larger primary particles. These precipitation and coagulation processes occur simultaneously and are very rapid processes. The influent stream is then fed into an injection tank where microsand is added and mixed well.

As water flows from the injection tank to the maturation tank, a flocculant is added (such as Nalco Optimer 83372, BASF Magnafloc LT25 or SNF AN 913VHM). Gentle mixing occurs in the maturation tank allowing the formation of flocculant bridges between the microsand and destabilised particles forming large settable flocculant particles. The large surface area of the microsand further improves the process.

After flocculation, the water is admitted to the lamellar separators where the flocculants settle quickly and the treated water leaves through the effluent channels. The precipitated sludge and microsand are extracted from the bottom of the lamella separator and pumped to the hydrocyclone. The re-circulated flow makes up 3-4% of the influent depending on the concentration of suspended solids in the influent.

3. Laboratory Simulation of Veolia Actiflo Process

3.1 Selection of Coagulants and Flocculants

Ferric chloride was selected for initial testwork. Samples of RDA clarifier overflow and decant pond overflow were sent to Veolia Water Systems for initial tests using a jar test procedure to simulate the Actiflo process. The results are shown in Figure 4 Removal Performed by Veolia using Actiflo Process Simulation using Micosand, Ferric Chloride and Flocculant on A) Clarifier Overflow and B) Decant Pond Overflow4.

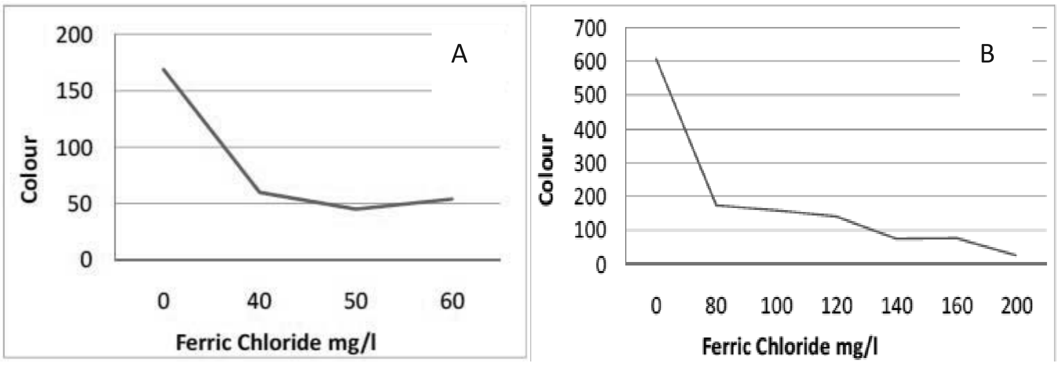

Figure 4 Removal Performed by Veolia using Actiflo Process Simulation using Micosand, Ferric Chloride and Flocculant on A) Clarifier Overflow and B) Decant Pond Overflow

Additional analyses were performed to measure apparent and true colour, solids and TIC/TOC. The results are shown in Table 1.

Table 1 Colour (Apparent and True), pH, Solids and TIC/TOC Analyses

	PtCo (Apparent)	PtCo (True)	pH	Solids mg/L	TIC mg/L	TOC mg/L
Clarifier O/F Untreated	146	77	8.46	21	21	87
Clarifier O/F Treated	53	26	6.77	17	16	75
Decant O/F Untreated	576	35	8.19	75	42	45
Decant O/F Treated	33	3	5.82	24	11	27
Clarifier % Removal	64	66		19	24	14
Decant % Removal	94	91		68	74	40

In terms of percentage removal, the decant pond overflow showed higher results for colour, solids, TIC and TOC. The use of ferric chloride has significant impacts on pH, TIC and TOC. The impact on pH limits the maximum dose of ferric chloride that can be used.

After preliminary screening of coagulants and flocculants using a jar test procedure, additional Veolia Actiflo simulations were performed using a Boltac gang stirrer containing six stirrers to simulate mixing of microsand, coagulant(s) and a number of different flocculants. Ferric chloride was tested by itself as well as co-dosing with other coagulants. These other coagulants included BASF Magnasol 572, BASF Magnafloc 1610, Aluminium chlorohydrate (ACH), Polyaluminium chlorohydrate (PAC) and SNF Dryfloc SU 25E. A trial Nalco product TX15339 was also tested by itself as it was known to contain ferric chloride blended with other inorganic salts. In combination with these coagulants a number of flocculants were tested. Nalco Optimer 83372 and 83376, BASF Magnafloc LT20, LT25 and LT27 and SNF AN 913 VHM were all evaluated as potential flocculants.

Using the Boltac gang stirrer, coagulants was added with microsand (10g/L) and mixed at 300 rpm for three minutes. After this time flocculant (1 ppm) was added and stirred for a further two minutes. After this period, the stirrers stopped and the solution was allowed to settle for fifteen minutes after which a 25 ml syringe sample (at a constant depth from each square cell) was taken for measurement of colour and other properties.

A typical set of the results achieved with different combination of coagulants and flocculants on clarifier overflow is shown Figure 5.

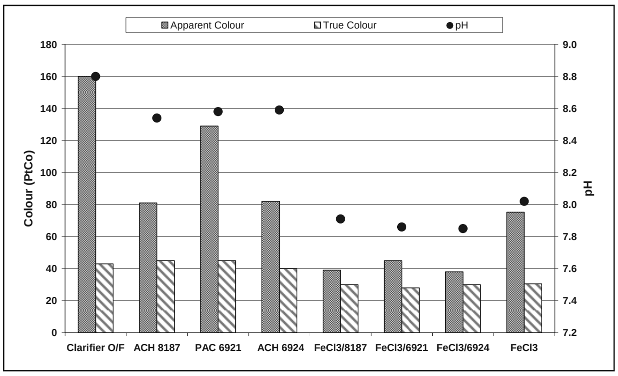

Figure 5 Clarifier Overflow: 20 ppm PAC/ACH and 30 ppm Ferric Chloride and 1 ppm Nalco 833722

Summarising the results of the laboratory trials:

Ferric chloride has been shown to work by itself as a coagulant for the removal of colour with doses between 30 and 200 ppm. Higher doses of ferric chloride adversely lower pH.

Mixed coagulant dosing using ferric chloride with other suppliers coagulants has resulted in synergistic effects, where the combined performance is better than the performance of the individuals.

From the coagulants and flocculant supplied by BASF, coagulant Magnasol 572 performed better than Magnafloc 1610. From the flocculants supplied, Magnafloc LT25 and Magnafloc LT27 performed about the same with both better than Magnafloc LT20. The combination of Magnasol 572 and Magnafloc LT25 was chosen for further test work with the Veolia Actiflo Plant trial.

At the same dose concentration of 30 ppm, ACH performs as well as ferric chloride, without the impact on pH. The synergistic impact of both coagulants is better than the impacts of the individual coagulants. Increasing the concentration of ACH above 50 ppm produces a cloudy non-settling solution. This is unlike ferric chloride where increasing the concentration up to 100 ppm results in better colour removal.

Nalco TX15339 is a robust coagulant mixture that performs over a wide range of conditions at the RDA. The limitation for using Nalco TX15339 is the impact on pH and doses will need to be optimised with respect to its impact on pH.

A comparison of either Nalco 83372 or SNF AN913 VHM flocculants with ferric chloride shows both to perform equally as well in the removal of colour. The critical component in colour removal is dependent on the coagulant used whereas the flocculant is critical for the settling influencing overflow clarity.

3.2 Order of Addition

From communications with Veolia Water Solutions and Technologies, it was observed the order of addition of coagulants impacted colour removal with decant pond overflow.

As a follow up on these results, additional laboratory Actiflo tests were performed with the order of coagulants changed and compared against the addition of both coagulants together. A decant pond overflow sample was tested with ACH and ferric chloride. The results of adding ACH first, ferric chloride first and adding together are shown in Table 2.

Table 2 Impact of the Order of Coagulant Addition on Decant Pond Overflow

Coagulant#1	[Coagulant1] pm	Coagulant #2	[Coagulant2] ppm	Colour Apparent	Colour True	Solids mg/L
ACH	20	$FeCl_3$	30	37	18	31.7
$FeCl_3$	30	ACH	20	71	17	26.7
ACH/$FeCl_3$ together	20	$FeCl_3$	30	187	16	20.0
Untreated				97	21	48.3

([#]Actiflo running conditions: Coagulant 1 added and mixed for 20 seconds, then coagulant 2 added – mixed for total time of 3 minutes before flocculant addition and stirred for further 2 minutes – then 15 minutes for settling)

It can be seen with the addition of ACH first followed by ferric chloride, the resulting colour is lower. The addition of both coagulants together has resulted in an increased colour due to a non-settling fluffy solids observed. In a second series of tests, increasing the mixing time for the addition of the first coagulant to 60 seconds before adding the second coagulant only improved the colour removal slightly. The order of addition would appear to be more important than the time of mixing.

The order of coagulant addition was also tested for clarifier overflow. The combinations tested were ACH and ferric chloride with Nalco Optimer 83372 and Magnasol 572 and ferric chloride with Magnafloc LT25. The results are shown in Table 3.

Table 3 Impact of Order of Coagulant Addition on Clarifier Overflow

Coagulant #1	[Coagulant1] ppm	Coagulant #2	[Coagulant2] ppm	Colour Apparent	Colour True	Solids mg/L
Untreated				132	76	60.0
ACH	20	$FeCl_3$	30	67	46	16.7
$FeCl_3$	30	ACH	20	67	52	75.0
ACH/$FeCl_3$ together	20	$FeCl_3$	30	81	51	46.7
Magnasol 572	20	$FeCl_3$	30	62	44	0
$FeCl_3$	30	Magnasol 572	20	89	46	23.3
572/$FeCl_3$ together	20	$FeCl_3$	30	80	47	0

The order of addition for ACH and ferric chloride is not critical with both giving the same apparent colour removal – however both perform better individually than when added together.

For the BASF products, the addition of Magnasol 572 first, followed by ferric chloride removed more apparent colour than the reversed order or the addition of the two products together.

3.3 Aluminium

As both ACH and PAC are based on an aluminium backbone, the impact of these chemicals on aluminium levels was measured and compared to the Clarifier overflow as a baseline. The results of these analyses are shown in Figure 6.

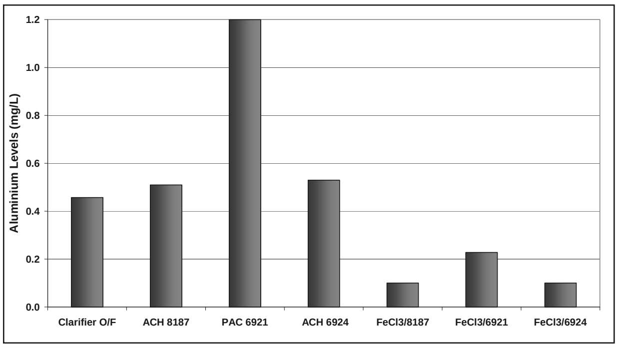

Figure 6 ICP Analyses for Aluminium – Impact of ACH and PAC on Clarifier Overflow

It can be seen that PAC has increased the level of aluminium in solution by a factor of 2.6 whilst the aluminium levels have remained the same using either ACH coagulant. Interestingly, the use of ferric chloride in combination with both types of aluminium based coagulants has reduced aluminium levels.

4. Plant Trial

The Veolia Actiflo pilot plant was located near the RDA clarifier. Phase 1 of the trial was run using clarifier overflow supplied via a sump pump submerged in the clarifier. Phase 2 was run using decant pond overflow which was collected by a water tanker and pumped into a ~ 30 000 L tank. The same sump pump was used to supply feed to the Actiflo unit. The normal flow rate through the Actiflo unit was $10 m^3/h$. Figure 7 shows the location of the Veolia Actiflo Unit at the RDA clarifier.

Figure 7 Actiflo Pilot Plant

4.1 Clarifier Overflow

A typical set of results for a clarifier overflow run on the Veolia Actiflo Unit is shown in Figure 8Figure 8 % Removal of Colour, Turbidity and Solids: Varying FeCl3 with Nalco Optimer 83372 (1ppm)librium at each point on the curve is achieved in 20 to 30 minutes.

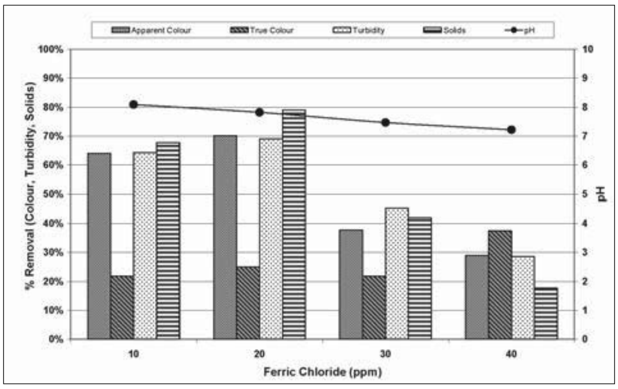

Figure 8 % Removal of Colour, Turbidity and Solids: Varying FeCl3 with Nalco Optimer 83372 (1ppm)

At a dose of 20 ppm, all chemical combinations showed greater than 60% removal of apparent colour.

In terms of the greatest apparent colour removal, this was observed at 91% using ferric chloride with Nalco Optimer 83372. The optimum dose addition appears to be between 20 to 30 ppm for the different coagulant - flocculant combinations. The next best performing combination involved ferric chloride and SNF AN 913 VHM (89% removal). This is not surprising as no real difference was observed using either flocculant in laboratory tests. Combinations of ACH and ferric chloride with Nalco Optimer 83372 and BASF Magnasol 572 and BASF Magnafloc LT25 performed equally as well and were the next best performing for colour removal followed by ACH with Nalco Optimer 83372.

The same trends were observed for percentage turbidity removal.

Where the trends change is when we examine the percentage solids removal. ACH and SNF AN 913VHM show the best solids removal at 92%.

Even with the pH above 10, 86% of solids removal occurred for ACH and SNF AN 913VHM. In the plant, above pH 10, Nalco Optimer 83372 (the current flocculant used at the RDA) does not perform and settles poorly giving high overflow solids.

For all the combinations of coagulants containing ferric chloride, the pH was maintained above 7, providing the dosages were 30 ppm or less.

Operating above pH's of 10, ACH solubilizes aluminium and increases its concentration in solution. At normal pH's around 8.5, aluminium is removed from solution. The operating conditions can become important if ACH was used as a coagulant.

Interestingly, the greatest removal of TOC was observed when only the flocculant was added. Nalco Optimer 83372 showed removal of 23% of TOC and 22% of TIC. The level of TOC removal was observed to decrease with increased amounts of ferric chloride to 30 ppm. Above this level, TOC was observed to increase with this combination of coagulant and flocculant. TOC removal in most cases were low, however with Magnasol 572/ Magnafloc LT25, the TOC levels were seen to increase. Magnasol 572 is a combination of ACH and poly DADMAC. Poly DADMAC is a cationic organic coagulant so will be soluble in water. The increase in TOC observed with Magnasol 572 is thought to be due to the poly DADMAC component of this coagulant. Similar results showing an increase in TOC were also observed for the coagulant combination of ferric chloride (30 ppm) and Magnasol 572 for all dosages.

Due to the acidic nature of ferric chloride, it comes as no surprise that the TIC removal increased with increased dosage. With levels of ferric chloride less than 10 ppm, the TIC has been observed to increase and this is thought to be due to the turbulent mixing nature in the Actiflo unit leading to carbonation. Above 10ppm ferric chloride, the TIC levels start to decrease. 40% TIC removal is observed for Magnasol 572 with Magnafloc LT25 at 10 ppm of the coagulant.

4.2 Decant Pond Overflow

A typical set of results for a decant pond overflow run on the Veolia Actiflo Unit using ferric chloride as the coagulant is shown in Figure 9.

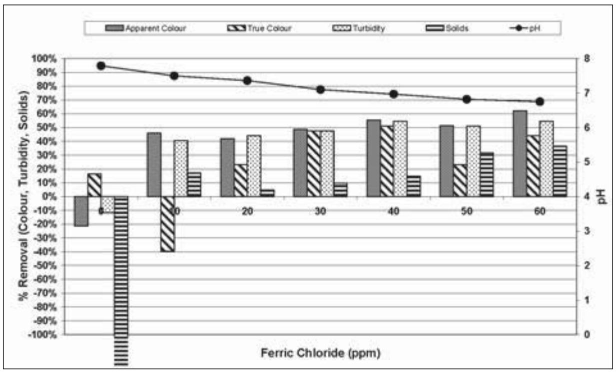

Figure 9. % Removal of Colour, Turbidity and Solids: Impact of Ferric Chloride with Nalco Optimer 83372 (1ppm)

Comparing all the combinations of coagulant and flocculants used on the decant pond overflow, ACH and SNF AN 913VHM performed the best with 70 % removal of colour. The percentage removal of solids was lower compared to the clarifier overflow – this was explained as being due to no /or lower mud solids present in the decant pond overflow.

Ferric chloride with Nalco Optimer 83372 and the combination of ferric chloride and ACH performed the next best. The same trend for colour was also observed for turbidity.

As seen above with the clarifier overflow, the best colour and turbidity removal did not mean the best removal of suspended solids. The combination of 20 ppm ferric chloride with ACH and Nalco Optimer 83372 showed the greatest removal with up to 50% removal of suspended solids. It was also observed that the solids increased with ACH and Nalco 83372 – this is thought to be due to the extraction of soluble organics from solution. TOC data shows removal of organics from the decant pond overflow and again provides some support for this theory (in laboratory experiments using poly-Dadmac type flocculants it has been observed that there is a correlation between removal of soluble organics and increased solids).

For all the combinations of coagulant and flocculants tested on the decant overflow, pH remained between 7 and 8 at lower doses and only at dosages of ferric chloride above 30 ppm was observed to drop below 7.

The highest TOC removal was observed for 40 ppm ACH with Nalco Optimer 83372. The increase in solids at 40 ppm ACH corresponds very well with the TOC removed. However, this is the only data that supports extraction of soluble organics from solution. While TOC is removed from the decant overflow, there is no information whether the organics are destroyed or extracted from solution. However, the percentage of TOC removal in the decant samples is low.

As observed with the Clarifier samples, an increase in the concentration of ferric chloride addition has resulted in the expected decrease in TIC. This is also observed when co-dosing coagulants with ferric chloride. As mentioned previously, the acidic nature of ferric chloride reacts with carbonate and decreases its level.

Comparison of both TOC and TIC data for both the Clarifier overflow and the decant pond overflow show the Veolia Actiflo process can remove at best about 22% of the TOC. Slightly higher levels of removal are observed for TIC when using an acidic coagulant such as ferric chloride.

5. Options for Full Scale Plant

Based on the results of the pilot trial, a configuration of 8 Veolia Actiflo ACP2-75 Units capable of treating 170ML/d flow is suggested.

These units, when equipped with a HCS (High Concentration Sludge) recirculation loop, enable sludge concentrations to be increased by up to 10 times significantly reducing sludge volumes. Sludge concentrations up to 3% can be achieved.

Disposal options for sludge include:

- Pumping at ~ 2-3% w/w solids to RDA
- Thickening to high solids slurry (25 to 50% w/w)
- Production of a dry cake for transport to land fill

Sludge thickening can be achieved by the use of a high rate thickener (HRT) to dewater sludge discharge from Actiflo.

Sludge dewatering can be achieved using a pressure filter fed with thickened sludge. This can produce a cake of spadeable quality for landfill.

6. Conclusions

Laboratory testing identified and short listed potential coagulant – flocculant combinations for testing on a pilot plant trial scale. Operation of the Veolia Actiflo Pilot Unit showed the limitation of the laboratory batch tests in simulating plant performance and the importance of pilot plant testing before implementation to full scale.

Based on the results achieved on the Veolia Actiflo Pilot Plant, colour and solids removal from both clarifier overflow and decant pond streams can be achieved using economic dose rates of coagulant and flocculant. Whilst optimum conditions for treating clarifier overflow were identified during the plant trial, additional work would need to be performed to optimise Actiflo operating parameters for the treatment of decant pond overflow.