USING POLYALUMINIUM COAGULANTS IN WATER TREATMENT

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ABSTRACT

Polyaluminium coagulants are finding increasing use in potable water treatment plants throughout Australia, with polyaluminium chloride (PACl) in particular now having wide application. This paper reviews the properties and advantages of using these chemicals with particular reference to experience at Daylesford, the Grampians region, Swan Hill and Tidal River, all in Victoria.

KEY WORDS

Polyaluminium chloride (PACl), Aluminium chlorohydrate (ACH), Coagulants, Water Treatment

1.0 INTRODUCTION

Alum (aluminium sulphate) is the most commonly used coagulant in Australian water treatment plants, low cost being its major attraction. Alum however, has a number of disadvantages:

- limited coagulation pH range: 5.5 to 6.5,
- supplemental addition of alkalinity to the raw water is often required to achieve the optimum coagulation pH, particularly for soft, coloured surface waters that are common in Australia,
- residual aluminium levels in the treated water can often exceed acceptable limits, and
- alum floc produced is particularly fragile. This is especially important if a coagulant is required to maximise colour removal in a microfiltration-based water treatment process.

Alum reacts in water to produce aluminium hydroxide and as a by-product sulphuric acid is also formed. The metal hydroxide precipitates out of solution and entraps neutralized charged dirt particles (turbidity), as well as coagulating soluble colour and organics by adsorption.

The sulphuric acid produced reacts with alkalinity in the raw water to produce carbon dioxide, thus depressing the pH.

2.0 POLYALUMINIUM COAGULANTS

Recently, a number of alternative aluminium-based coagulants have been developed for water treatment applications.

These compounds have the general formula $(Al_n(OH)_mCl_{(3n-m)})_x$ and have a polymeric structure, totally soluble in water. The length of the polymerised chain, molecular weight and number of ionic charges is determined by the degree of polymerisation. On hydrolysis, various mono- and polymeric species are formed, with $Al_{13}O_4(OH)_{24}^{7+}$ being a particularly important cation. A less predominant species is $Al_8(OH)_{20}^{4+}$.

These highly polymerised coagulants include the following:

- polyaluminium chloride (PACl, n=2 and m=3),
- aluminium chlorohydrate (ACH, n=2 and m=5), and
- polyaluminium chlorohydrate (PACH): similar to ACH.

In practice, there is little difference between the performance of ACH and PACl in water treatment applications, even though ACH is more hydrated.

3.0 ADVANTAGES OF POLYALUMINIUM COAGULANTS

An important property of polyaluminium coagulants is their *basicity*. This is the ratio of hydroxyl to aluminium ions in the hydrated complex and in general the higher the basicity, the lower will be the consumption of alkalinity in the treatment process and hence impact on pH.

Various suppliers of ACH and PACl in Australia express the basicity of their product as a percentage e.g. Omega MEGAPAC-23 (40.2% w/w aluminium chlorohydrate) has a basicity of 82% (Omega Chemicals, 2000).

The polyaluminium coagulants in general consume considerably less alkalinity than alum.
They are effective over a broader pH range compared to alum and experience shows that PACl works satisfactorily over a pH range of 5.0 to 8.0.

Another important advantage of using polyaluminium coagulants in water treatment processes is the reduced concentration of sulphate added to the treated water. This directly affects SO_4 levels in domestic wastewater.

A raw water with a sulphate level of 3 to 5 mg/L will typically have a SO_4 concentration of 15 to 25 mg/L following treatment with alum. The amount of soluble sulphate present in domestic wastewater is now also significantly increased and this can result in elevated hydrogen sulphide production in the sewerage system, leading to odour and corrosion problems.

Table 1: ***Typical aluminium-based coagulants used in water treatment***

CHEMICAL	SYMBOL	SUPPLIER	NAME	COMPOSITION	FORMULA WT.	STRENGTH, % w/w			SG at 20°C	OTHER	TYPICAL PRICE EX WORKS MEL. $/kg		
						Al_2O_3	Al	AS IS			AS IS	100%	Al
Aluminium Chlorohydrate	ACH	OMEGA	MEGAPAC 23	$Al_2(OH)_5.Cl$	174.45	23.5	12.4	40.2	1.33	Basicity 82% Chloride 8.5% pH 3.5	1.00	2.49	8.04
Aluminium Chlorohydrate	ACH	ALUMINATES	PAC 23 (APAC 333)	$Al_2(OH)_5.Cl$	174.45	23.5	12.4	40.2	1.33-1.35	Basicity 83-85%, Cl 8.0-8.5%, pH 3.5-4.5	1.00	2.49	8.04
Polyaluminium Chloride	PACl	OMEGA	MEGAPAC 10	$Al_2(OH)_3.Cl_3$	211.33	10.5	5.6	21.8	1.18	Basicity 55% Chloride 10.5% pH 3.0	0.50	2.30	9.00
Polyaluminium Chloride	PACl	DELTREX	AC100S	$Al_2(OH)_3.Cl_3$	211.33	10.0	5.3	20.7	1.20	Sulphate 3.5% pH 3.0	0.57	2.75	10.77
Polyaluminium Chloride	PACl	DELTREX	SAB18	$Al_2(OH)_3.Cl_3$	211.33	18.0	9.5	37.3	1.38	Sulphate nil pH 3.0	0.87	2.33	9.13
Aluminium Sulphate	ALUM	ALUMINATES, OMEGA	LIQUID ALUM	$Al_2(SO_4)_3.18H_2O$	666.43	7.5	4.0	49.0	1.30	pH 2.5	0.19	0.39	4.79
Sodium Aluminate	-	ALUMINATES	-	$NaAlO_2$ ($Na_2O.Al_2O_3$)	81.97	17.8	9.4	28.6	1.50	12% NaOH 20.1% Na_2O pH 14	0.68	2.37	7.19

At one water treatment plant in the Otway region of Victoria, polyaluminium chloride replaced alum and in so doing SO_4 levels in the treated water were reduced from 27 to 4 - 5 mg/L. Previously, alum was dosed at 45 to 55 mg/L at this plant. The change to PACl had a major impact on SO_4 levels in the sewage, with reduced odour problems evident at several pump stations in the sewerage system.

Table 1 summarises principal characteristics of commercially available polyaluminium coagulants. Details for alum and sodium aluminate are also included for comparison.

Other advantages of polyaluminium coagulants include the following:

- low levels of residual aluminium in the treated water can be achieved, typically 0.01-0.05 mg/L,
- PACl and ACH work extremely well at low raw water temperatures. Flocs formed from alum at low temperatures settle very slowly, whereas flocs formed from polyaluminium coagulants tend to settle equally well at low and at normal water temperatures,
- less sludge is produced compared to alum at an equivalent dose,
- lower doses are required to give equivalent results to alum. For example, a dose of 12 mg/L PACl (as 100%) was required for treatment of a coloured, low turbidity water (Otway region, Victoria) compared to similar performance obtained when using an alum dose of 55 mg/L, and
- the increase in chloride in the treated water is much lower than the sulphate increase from alum, resulting in lower overall increases in the TDS of the treated water.

From Table 1, it will be noted that polyaluminium coagulants are typically twice the price of liquid alum on per kilogram aluminium basis. However, lower doses of the coagulant and lower pre- and post-treatment alkali doses can still make its use economical.

Polyaluminium chloride solution (10% Al_2O_3) is stable for 4 to 5 months when stored at less than 50^oC and is so ideal for bulk storage and dosing installations.

One possible disadvantage in using ACH/PACl relates to the removal of dissolved organic carbon (DOC) from water. It is well documented that effective DOC removal is possible with alum, particularly when coagulating at lower pH values using so-called “enhanced coagulation”. Alum appears to be a superior coagulant as far as removal of humic and fulvic colour constituents are concerned. A higher coagulation pH is adopted with polyaluminium coagulants and it possible that removal of THM percussors may not be as complete as with alum. The following examples illustrate that this depends on the particular raw water in question and in many cases may not be an issue.

4.0 DAYLESFORD

The Daylesford Water Filtration Plant is a new 8 ML/d in-filter/dissolved air flotation plant constructed by Vivendi Water/US Filter, with process and detailed design, engineering and procurement provided by Fisher Stewart.

The plant treats highly coloured raw water from either the Wombat or Bullarto Reservoirs.
Raw water characteristics for the supply from Wombat Reservoir are detailed in Table 2. The water is also very corrosive with a pH which can be as low as 6.4 and a calcium carbonate precipitation potential (CCPP) value of – 17.5 mg/L $CaCO_3$ (at 20^oC).

Typically this water supply has a true colour of 30 Pt/Co units and a turbidity of 2.6 NTU, although on occasions the colour can approach 100 Pt/Co units. The temperature of the raw water can be as low as 5^oC in winter months.
For raw water at 20^oC with a true colour of 60 Pt/Co units, turbidity 3.0 NTU and pH 6.7, *WaterQual* (a water treatment and quality assessment model developed by the author at Fisher Stewart) was used to compare the predicted performance of alum versus PACl. A chlorine dose of

1.5 mg/L for disinfection and a target treated water pH of 7.5 were adopted for each case.

For an alum dose of 45 mg/L and a coagulation pH of 6.9, pre- and post-treatment doses of caustic soda of 17.9 and 4.7 mg/L were required (total 22.6 mg/L).

Table 2: ***Raw Water Analysis, Wombat Reservoir at Daylesford***

	ION mg/L	**$CaCO_3$ mg/L**	EC μS/ cm		**ION mg/L**	**$CaCO_3$ mg/L**
CALCIUM	1.8	4.5	71	ALKALINITY	19.9	16.3
MAGNESIUM	2.3	9.5	pH	CHLORIDE	11.7	16.5
SODIUM	9.0	19.6	6.7	SULPHATE	1.5	1.6
POTASSIUM	0.7	0.9				

These projections compare well with the results of jar-test investigations carried out to determine the treatability of raw water supplies at Daylesford using alum (GHD 1996).

An equivalent PACl dose of 12 mg/L as 100% was adopted and used in the *WaterQual* model.

Addition of caustic soda at 3.4 mg/L was necessary to achieve a coagulation pH of 6.9. A post-treatment alkali dose of 4.7 mg/L was required in this instance (total dose 8.1 mg/L).

Characteristics of the treated water for each coagulant option determined from *WaterQual* are given in Table 3.

Table 3: ***Treated Water Quality Predicted Using WaterQual, Wombat Reservoir, Daylesford, at 20^{o}C***

COAGULANT	**LSI**	**CCPP**	**TDS**	**SO_4 (AS ION)**
ALUM	-2.2	-8.2	94	21.0
PACI	-2.2	-7.9	67	1.5

The advantages of using PACl in regard to the effect on treated water TDS and sulphate levels are apparent. Note also a small improvement in the CCPP value of the treated water when using PACl.

The chemical doses predicted from *WaterQual* when using PACl compare very well with actual requirements at the Daylesford Water Filtration Plant.

Experience at Daylesford has also confirmed the suitability of PACl, with very effective flocculation observed at the low water temperatures noted during plant start-up in July 2000 (5–10^{o}C).

Estimated chemical costs using alum amount to \$38.1/ML, compared to \$41.3/ML with PACl. For an annual treated water production of 1200 ML, this translates to a saving \$3900 per annum in favour of alum. The operational advantages of using PACl, particularly in cold months, make it an attractive coagulant for Daylesford.
The THM level in the treated water is generally 40-50 μg/L when treating raw water with a true colour of 90-100 Pt/Co units. This is well below the current AWDG recommendation of 250 µg/L. In this instance DOC removal appears to be satisfactory.

5.0 SWAN HILL

Raw water for Swan Hill is abstracted from the Murray River and has typical quality characteristics given in Table 4.

Table 4: ***Typical Raw Water Analysis at Swan Hill***

	ION mg/L	$CaCO_3$ mg/L	EC μS/cm		ION mg/L	$CaCO_3$ mg/L
CALCIUM	5.6	14.0	210	ALKALINITY	36.6	30.0
MAGNESIUM	5.4	22.2	pH	CHLORIDE	35.0	49.4
SODIUM	22.6	49.2	7.4	SULPHATE	8.0	8.3
POTASSIUM	1.9	2.4				

Alum doses in the range 30 to 60 mg/L have been used to treat this water, which has a true colour of 20-30 Pt/Co units and a turbidity of 20 to 40 NTU under normal river flow conditions.

Pre-treatment dosing with lime is only required when alum doses greater than 30 mg/L are required. The coagulation pH is usually 6.3 to 6.5 and a post-treatment dose of 10-15 mg/L lime is required to give a treated water pH of 7.1 to 7.3.

Lower Murray Water Authority has recently changed over from using liquid alum to ACH (MEGAPAC 23) at the Swan Hill Water Treatment Plant. As a consequence, the practice of pre- and post-treatment dosing with lime to adjust pH and alkalinity has now been discontinued.

Typically, ACH doses 20% of those for alum (as $Al_2(SO_4)_3.18H_2O$) are required, i.e. 6 to 12 mg/L as 100% ACH.

The raw water has a pH of 7.4 to 7.7 and following ACH addition, the coagulation pH is 7.2-7.5, reducing to 7.0 to 7.2 following chlorination (gas, 1.5 mg/L dose).

The treated water using ACH is slightly more aggressive: CCPP –10.9 to –13.3 mg/L compared to –10.7 mg/L with alum, at 20^{o}C.

By adding a small dose of lime (0.5-1.5 mg/L) at the inlet of the plant and coagulating at a slightly higher pH (7.6), the corrosivity of the treated water following chlorination can be improved to give a CCPP of –9.8 mg/L at 20^{o}C.

The changeover has allowed Lower Murray Water to defer planned capital expenditure in upgrading lime storage and dosing facilities at the Swan Hill Water Treatment Plant.

There has been no noticeable change in the level of THM's in the treated water at Swan Hill since changing over to ACH. Typically the total concentration of THM's in the treated water is 35-40 µg/L, even when treating raw water with relatively high colour levels. Further, there are no discernable levels of taste- and odour-causing compounds in the treated water (Neaves 2000).

6.0 GRAMPIANS REGION

ACH is currently being used at three of six recently constructed in-filter/DAF water treatment plants in the Grampians region of Victoria; at Birchip, Charlton and Rainbow.

Raw water to these three townships principally comes from the Wimmera-Mallee Channel system. Typically, the raw water has the following average characteristics: pH 8.5 - 8.7, TDS 500 to 600 mg/L, true colour 10 to 15 Pt/Co units and turbidity 1.5 to 2.5 NTU. The high pH and TDS levels make treatment of this particular water difficult and if alum is used, doses are higher than would be normally expected; often 60 to 100 mg/L.

For the Charlton raw water supply- pH 8.5, true colour 8 Pt/Co units and turbidity 2.5 NTU- an alum dose of 110 mg/L was required for effective treatment in laboratory jar-tests compared to 40 mg/L using PACl. The coagulation pH was 6.4 with alum and 7.2 with PACl, illustrating the reduced impact PACl has on pH. Lower residual Al levels in the treated water were also achieved using PACl (GHD 1998).

Treatment of the water supply at Murtoa (also in the Grampians region) using PACl was also found to be effective. This water supply is also largely derived from the Wimmera-Mallee Channel and has a TDS of around 550 mg/L and a pH of 8.6. Alum doses typically in the range of 50 to 70 mg/L were found to be required, with supplemental addition of sulphuric acid needed to achieve a desirable pH and so avoid excessive coagulant doses. By contrast, PACl doses required to give equivalent treatment were only 16 to 22 mg/L or a third of the alum dose required, without the need for pre-treatment pH correction (USF 1998).

The above results are consistent with actual plant operating experience at the treatment plants at Birchup, Charlton and Rainbow, where typically ACH is dosed at approximately 40 mg/L.
Sulphuric acid is used at these three sites to reduce the pH of the raw water to approximately 7.8. However, no post-treatment addition of alkali is required to correct the alkalinity of the treated water following disinfection.

The raw water quality at Rainbow is very similar to that at Birchip. The results of jar–tests (GHD 1998) and projections from *WaterQual* comparing the performance of alum and ACH at Rainbow are summarised in Table 5 for raw water with a TDS of 720 mg/L and pH 8.4, at 25^{o}C.

The coagulation pH adopted for alum was 6.7 and for ACH 7.6, whilst the target treated water pH was 7.5 in each case. A chlorine dose of 1.5 mg/L was assumed in each case for disinfection.

Using alum, the sulphate level in the treated water increases from 17.9 to 56.8 mg/L, whilst for ACH the corresponding increase is only 2.3 mg/L.

The following chemical costs (delivered to site) were used to calculate the operating cost of each treatment option:

- alum: liquid (47% w/w), $200/t
- ACH: liquid (40.2% w/w), $1100/t
- caustic soda: liquid (46% w/w), $600/t
- sulphuric acid: liquid (34% w/w), $900/t, and
- chlorine (gas): $1600/t (980 kg drums).

Table 5: ***Predicted Performance of Alum v ACH at Rainbow***

COAGULANT	DOSE (mg/L)	PRE-TREAT & DOSE[1] (mg/L)	POST-TREAT & DOSE[2] (mg/L)	TDS, (mg/L)	SO_4 (mg/L)	CCPP (mg/L $CaCO_3$)
ALUM	90	0	NaOH, 27.7	800	56.8	-6.2

ACH	20	H_2SO_4, 2.4	0	750	20.2	-6.0

1. FOR PRE-TREATMENT pH ADJUSTMENT
2. FOR POST-TREATMENT pH ADJUSTMENT TO 7.5

For the alum option, total chemical costs amount to $76.8/ML, whilst for ACH $63.5/ML; a saving of approximately 17%. This example illustrates how lower operating costs can be realized when using ACH coagulant compared to alum. Superior quality treated water is also produced with respect to TDS, CCPP and SO_4.

7.0 TIDAL RIVER

Fisher Stewart has participated in the delivery of water treatment and reticulation facilities at Tidal River, Wilson's Promontory NP through its role as consultant to Parks Victoria. Raw water supplied to Tidal River is derived from a small weir and off-take. The volume of the weir and area of the contributing catchment is relatively small and subsequently, there can be substantial changes to the raw water quality during rainfall events.

Water is treated using a 5L/s (0.4 ML/d) Aquagenics "AquaPac" packaged water treatment plant. Initially liquid alum and caustic soda were used in the treatment regime. The water was found to be difficult to treat and in an attempt to improve plant performance, PACl was trialed in lieu of alum (DELTREX AC100S).

The coagulant was found to be very effective and since changing over to PACl one of the most noticeable (and unexpected!) advantages noted has been the increased "robustness" of the water treatment process. Previously when using alum, plant performance was adversely affected after heavy rain. PACI has shown an ability to much better deal with these changes. The chemical's ability to coagulate over a wider pH range is of enormous benefit in this instance.

Another major benefit of using PACI has been a considerable reduction in the volumes of sludge trucked off-site to disposal. This has had a major impact on plant operating costs.
Pre-treatment alkalinity adjustment using caustic soda has been greatly reduced since changing over to PACl. Table 6 is a comparison between alum and PACI at Tidal River. A similar treated water quality is achieved in both instances with the CCPP higher in the case of PACl. An estimated $24/ML (or 14%) saving in total chemical costs is possible using PACl. Chemicals are delivered to site in 15 and 200L packages. This, combined with the remote location of Tidal River, explains the high cost of chemicals delivered to the site.

Table 6: ***Predicted Performance of Alum v PACl at Tidal River (at 15°C)***

COAGULANT	DOSE, mg/L	ALKALI & DOSE, mg/L		pH	CCPP	LSI	$/ML[3]
		Pre-	Post-				
Alum (as 100%)	50	NaOH[1] 18.0	0	6.6	-28.7	-3.1	174
PACI (as 100%)	17.5[2]	5.0	0	6.8	-21.1	-2.8	150

1. 48% w/w solution dosed
2. 70 ppm(v) as delivered
3. Total chemical costs include 3mg/L sodium hypochlorite dose for disinfection

Sulphate in the treated water is 6.0 down from 27.6 mg/L, reducing the potential for odour production from wastewater generated at Tidal River.

8.0 CONCLUSIONS

Polyaluminium coagulants- ACH and PACl- can often give significant advantages over alum, including:

- reduced chemical costs,

- lower residual aluminium levels in the treated water,
- improved treated water quality including lower TDS and sulphate levels and possibly higher CCPP values, and
- lower sludge production.

In many cases, post-treatment pH adjustment using an alkali is not required, reducing the overall capital cost of the plant as well as improving operator amenity and reducing maintenance requirements.

With increased competition in the marketplace, the unit cost of polyaluminium coagulants will probably decrease in the future, making conversion from alum to ACH/PACl more attractive and, more widespread in Australia.

Limited information suggests that THM formation will not be compromised when using ACH/PACl but this should be first confirmed in the laboratory with jar-tests.

And finally, a word of advice: when changing over from alum to PACl/ACH, it is important to make sure chemical storage tanks, dosing pumps and piping are all thoroughly flushed out with clean water to avoid forming an "aluminium jelly"!

9.0 REFERENCES

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10.0 NOMENCLATURE

LSI: Langelier Saturation Index
CCPP: Calcium Carbonate Precipitation Potential, mg/L $CaCO_3$
TDS: Total Dissolved Solids, mg/L

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