

# AN OPERATOR'S GUIDE TO WATER TREATMENT COAGULANTS



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# AN OPERATOR'S GUIDE TO WATER TREATMENT COAGULANTS

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This paper is intended as a guide to using water treatment coagulants by answering a series of questions that many Water Treatment Plant (WTP) Operators have probably thought of but were too afraid to ask, or maybe didn't quite know where to look for the answers!

## 1.0 WHAT ARE COAGULANTS?

Coagulants are chemicals that are used to assist with the removal of colour and turbidity present in untreated, raw water. They do this by forming settleable particles in the form of flocs, which are then removed in downstream clarification or filtration treatment processes.

Coagulants may be classified as being inorganic or organic. Inorganic coagulants include those commonly used chemicals that rely on aluminium or iron. Organic coagulants include the so-called polyDADMAC (polydiallyldimethyl ammonium chloride) range of cationic polymers. These are special and expensive chemicals that are sometimes used in direct filtration plants when the low doses required make their use economical. However, they can sometimes be used in combination with inorganic types, often with spectacular and money-saving results!

Remember *Gebbs' Rules* when looking at coagulants and their potential applications.

- GEBBS' RULE 1* inorganic coagulants will decrease the alkalinity of a water
- GEBBS' RULE 2* as a consequence of *Gebbs' Rule 1*, the pH of the chemically dosed raw water will decrease. This often means that supplemental alkalinity in the form of lime; soda ash, or caustic soda will have to be added to maintain an acceptable dosed-water pH
- GEBBS' RULE 3* not all inorganic coagulants are created equal! Some will have a greater impact on the raw water alkalinity and pH than others. For example, *New Age Coagulants* such as aluminium chlorohydrate (ACH) and polyaluminium chloride (PACl) have less impact than alum. Organic coagulants do not affect the raw water alkalinity and pH
- GEBBS' RULE 4* all coagulants produce sludge in the form of the metal hydroxide together with the coloured and colloidal matter that is removed from the raw water. But again, not all inorganic coagulants behave in the same way. For example, ACH and PACl produce less sludge than alum when dosed at equivalent levels. Organic coagulants produce little sludge; another advantage
- GEBBS' RULE 5* inorganic coagulants will increase the total dissolved solids concentration of the treated water. This may be undesirable, especially when using alum, as sulphate levels in the finished water will increase

## 2.0 WHAT DO COAGULANTS DO?

Depending on the pH after the coagulant is added, two possible reactions are generally possible:

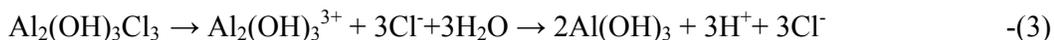
- with aluminium-based coagulants, the metal ion is hydrolysed to form aluminium hydroxide floc as well as hydrogen ions. The hydrogen ions will react with the alkalinity of the water and in the process, decrease the pH of the water as can be seen from Equation (1) for alum.



Similarly for ACH, which is described as being a pre-hydrolysed coagulant, the following reaction takes place:



Less hydrogen ions are produced with ACH, reflecting the hydroxylated nature of this compound. PACl also shows similar hydrolysis as represented by Equation (3). In this reaction, three moles of  $\text{H}^+$  are formed.



The above hydrolysis reactions typically take place at a dosed water pH in the range 5.8 to 7.5, depending on the particular coagulant. Colour and colloidal matter is removed by adsorption onto/within the metal hydroxide hydrolysis products that are formed, and is sometimes referred to as *sweep-floc coagulation*.

- if an excess of alum is added so that the dosed water pH is less than 5.0, then the metal ions ( $\text{Al}^{3+}$ ) will directly neutralize the negatively charged organic compounds and colloids in the raw water. This allows the organic molecules to contribute to floc formation and is often referred to as *enhanced coagulation* and is often done to boost the removal of disinfection by-product precursors.

## 3.0 WHICH COAGULANT SHOULD I USE; WHICH IS THE BEST?

Generally, alum is the first coagulant of choice because of its lower cost and its widespread availability. For coloured, low turbidity, low pH/alkalinity surface waters pre-treatment with lime, soda ash or caustic soda will normally be required to ensure that the optimum coagulation (dosed-water) pH is achieved.

These raw waters however, also make the use of ACH possible. It is often feasible to coagulate at a relatively high pH (7.5-8.0), avoiding the need to dose alkali for pH correction, which is often difficult at small WTP's.

As a rule-of-thumb, ACH doses required will be approximately a third of those required when using alum. But this will come with an operating cost penalty: the overall chemical cost increase when changing over to ACH from alum will be typically 15-20%. However, other benefits may still make the use of ACH attractive, including lower sludge production and the avoidance of post-treatment alkali dosing.

So, if you have untreated water with a low alkalinity and you are having difficulty treating it using alum, try one of the higher basicity coagulants e.g. ACH or PACl. Oops! I've said the "B-word"! I'll explain what that means in a minute. For smaller plants where ACH looks attractive, using a diluted form of the coagulant may be worth considering e.g. *PAC-10 HB* from *Aluminates*.

Iron-based coagulants, such as ferric chloride, ferric sulphate and *PFS*<sup>®</sup>, are not that popular in Australia and tend to be more expensive than alum on an equivalent dose basis. They also consume more alkalinity than alum, and hence tend to depress pH of the dosed water much more. Opinions also differ as to whether they produce a fluffier floc, which is more difficult to settle. Several WTP's in NSW use *PFS*<sup>®</sup> in order to meet very stringent manganese limits in the finished water, which appears possible with the use of this coagulant. Ferric-based coagulants are extremely corrosive and produce highly visible blood-/rust-coloured stains whenever there are chemical spills and leaks.

Aluminium-based coagulants are also claimed to show higher *Crypto* oocyst removal than ferric-based chemicals, which is another possible advantage.

Table 1 summarises data for the most commonly used coagulants available in Australia. It also gives important characteristics and supplier details, as well as some notes on possible applications.

Organic coagulants such as polyDADMAC liquid cationic polymers are generally only used in direct filtration WTP's where the low doses applied make their use feasible. Also, polyDADMAC's are not as good as inorganic coagulants in removing true colour and natural organic matter from water.

#### **4.0 WHAT IS THE BEST DOSED-WATER PH?**

As any competent WTP Operator knows, the pH value of a solution gives an indication of how acidic or alkaline it is. It's a very important parameter in water treatment, especially in determining effective coagulation. Each coagulant has a narrow optimum operating pH range. For example, alum tends to work best at a dosed-water pH of 5.8-6.5. If the pH is lower or higher than this optimum, then problems of high residual colour and aluminium or disinfection by-products may occur in the finished water.

This can create problems when the raw water has a high alkalinity or pH. High alum doses will then be required to achieve the right dosed-water pH. The alternative is to add acid to decrease the pH to a lower value before dosing the coagulant. Note that this is the opposite of the more common practice of dosing alkali (lime, soda ash or caustic soda) to raise the pH of low alkalinity waters.

If the pH falls outside the optimum range, you may have trouble meeting the Australian Drinking Water Guideline limit of 0.2 mg/L aluminium in the finished water, as well as increasing the possibility of having floc precipitate out later in water storages or within the reticulation system. ACH works well over a higher pH range, anywhere from 6.5 to 7.5. In some cases, this may mean that you can coagulate at a pH that avoids the need for post-treatment alkali dosing. This has been successfully implemented at a WTP located in Eastern Victoria. Changing over from alum to ACH has enabled the WTP Operator to decommission a small, "pesky" post-treatment lime dosing system.

The treated water pH is 7.0-7.2 after getting a “boost” from hypo addition for disinfection, since disinfection with sodium hypochlorite actually raises the pH of the finished water.

Ferric coagulants also work well over a wide pH range and often can be used at the higher end of the range, say from 7.5 to 8.0.

Organic polyDADMAC's work pretty well at any pH and this may prove to be an advantage in certain applications.

**5.0 THERE SEEMS TO BE A LOT OF “NEW AGE COAGULANTS” NOW IN THE MARKET. THEY SEEM TO COME WITH A LOT OF CONFUSING TERMS. PLEASE EXPLAIN!!!**

The first term you should be aware of is “basicity”. This gives a quantitative measure of how many hydroxyl ions are included in the structure of a polyaluminium or polyferric coagulant. The higher the basicity of a coagulant, the lower the impact it will have on dosed water pH. For example, ACH ( $\text{Al}_2(\text{OH})_5\text{Cl}$ ) has a basicity of 83.3%. Typically, commercially produced ACH will have a basicity of 83-85%, indicating that it will have less impact on dosed water pH than PACl, which we have noted earlier has only has three OH ions in its structure and consequently has a basicity of 50%. Alum has no OH ions in its structure and hence has zero basicity.

Whilst most hydroxylated coagulants commonly employed are aluminium-based, several ferric compounds are also commercially available. In particular, hydroxylated ferric sulphate (polyferric sulphate, PFS<sup>®</sup> from Aluminates) has found use in potable water treatment.

The next term to be familiar with for aluminium-based coagulants is “percent  $\text{Al}_2\text{O}_3$ ”. This is a common method of quoting the strength of aluminium-based coagulants on a w/w basis. Another method of referring to concentration is to state the aluminium content, which is roughly half the  $\text{Al}_2\text{O}_3$  content. For example, liquid alum is typically 7.5% w/w  $\text{Al}_2\text{O}_3$ , which is the same as 4.0% w/w aluminium (Al). For ACH and PACl coagulants, the brand name often incorporates its  $\text{Al}_2\text{O}_3$  strength. As an example, PAC-23 produced by Aluminates, is ACH with an  $\text{Al}_2\text{O}_3$  content of nominally 23% w/w. Similarly, for Omega Chemical's MEGAPAC 10, this is PACl with a nominal  $\text{Al}_2\text{O}_3$  content of 10% w/w.

The term “percent weight/weight” or “% w/w” is similar to the previous term and is the number of kilograms of active chemical per 100 kilograms of liquid chemical. For example, liquid alum at 7.5% w/w  $\text{Al}_2\text{O}_3$  has 7.5 kg of  $\text{Al}_2\text{O}_3$  in solution for every 100 kg of liquid chemical delivered.

Another important term is “*specific gravity*” or “SG”: This is the unit weight of a liquid chemical relative to water at the same temperature. Strictly speaking, SG has no units but you'll often find SG or a coagulant's density stated on laboratory reports as “g/mL” or as “kg/L”. The two are approximately the same and so in most cases can be interchanged.

For each chemical, there is a direct relationship between its strength and SG, and indeed chemical manufacturers use SG to measure the strength of a chemical during its manufacture. As an example, liquid alum (49% w/w) typically has a SG of 1.310, whilst liquid caustic soda (46% w/w) has a SG of 1.498 at 20°C.

## 6.0 HOW DO I CALCULATE COAGULANT DOSES?

When calculating coagulant doses, or any other chemical for that matter, it is important to first state on what basis the dose is to be expressed. The most commonly used unit in water treatment is “mg/L”, which is a weight per volume unit. This is also the same as parts per million (ppm), but only when quoted as ppm on a weight/weight basis, as we will shortly see!

If you state a chemical dose as “ppm” using the **volume** of chemical dosed to the **volume** of raw water, then what you have calculated is “ppm v/v” and this is **NOT** the same as mg/L!

To calculate the dose of a coagulant or other chemical in mg/L, you will need to know its % w/w strength and specific gravity.

The formula is:

$$\text{mg/L} = 10,000 \times \% \text{ w/w} \times \text{SG}$$

For example, consider alum at 49 % w/w strength aluminium sulphate (as  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) and with a SG of 1.29. Using the formula above, the concentration of the alum in mg/L, will be:  $10,000 \times 49 \times 1.29 = 632,000 \text{ mg/L}$  or 632 g/L. If you are dosing alum at a rate of 150 mL/min as found from a drop test, and the raw water flow is 50 L/s, then the alum dose will be:

$$(150 \times 632,000 / (1000 \times 60)) / 50 = 31.6 \text{ mg/L or ppm (w/w)}$$

$$\text{or: } 1,000,000 \times (150 / (60 \times 1000)) / 50 = 50 \text{ ppm (v/v)}$$

You can see from this example that the two results are quite different, so it important to understand how your coagulant dose is calculated, especially when you quote numbers to others, including your Operations Manager or Finance Comptroller!

Remember that there is only one sure way to determine which coagulant will work best for a particular raw water, and that is to carry out some jar-tests in the laboratory. In evaluating which coagulant you reckon is the best, just be careful in how you express the various chemical doses!

Well, this brings my Operator’s Guide to Water Treatment Coagulants to an end.

Hopefully you’ll find it helpful in answering some of your queries.

And...happy jar-testing!!

**Table 1: Commonly Available Coagulants and Details**

COMMON COAGULANT NAME <sup>1</sup>	TYPICAL MANUFACTURERS	CHEMICAL NAME & FORMULA	TYPICAL ANALYSIS	NOTES	INDICATIVE COST, \$/tonne (as 100%) <sup>2</sup>
Alum	Aluminates Omega Chemicals	Aluminium sulphate $Al_2(SO_4)_3 \cdot 18H_2O$	* 7.5-8% $Al_2O_3$ or 49-52% w/w $Al_2(SO_4)_3 \cdot 18H_2O$ * SG 1.3 * <b>635 g/L</b>	Most common coagulant used in water treatment. Relatively cheap.	450
<i>PAC 23</i> <i>MEGAPAC 23</i> <i>ALCHLOR AC</i>  <i>PROFLOC A23</i>	Aluminates Omega Chemicals Hardman Chemicals Orica/ Spectrum	Aluminium chlorohydrate (ACH) $Al_2(OH)_5Cl$	* 23-24% $Al_2O_3$ or 40-41% w/w ACH * SG 1.33 * 83-84% basicity * 8.5% w/w Cl * <b>535 g/L</b>	Used in lieu of alum where raw water has low pH & alkalinity. Has little impact on pH.	2100
<i>PAC-10 LB</i> <i>MEGAPAC 10</i>	Aluminates Omega Chemicals	Polyaluminium chloride (PACl) $Al_2(OH)_3Cl_3$	* 10-11% $Al_2O_3$ or 20-23% w/w PACl * SG 1.18 * 50% basicity * 10.5% w/w Cl * <b>245 g/L</b>	Used in lieu of alum where raw water has low pH & alkalinity. Has greater impact on pH than ACH.	2500
<i>PAC-10 HB</i>	Aluminates	Aluminium chlorohydrate (ACH)	* Diluted ACH. * 10% $Al_2O_3$ * 80% basicity	See ACH. Sometimes used in small WTP's.	2800
PACS	Aluminates	Polyaluminium chlorosulphate $Al_3(OH)_{4.95}Cl_{3.55}(SO_4)_{0.25}$	* 10% $Al_2O_3$ or 5.3% w/w Al * SG 1.19 * 50% basicity * 10% w/w Cl * 2% w/w $SO_4$	Aluminium-based coagulant. Not commonly used; at some NSW WTP's.	2800
<i>PASS</i> <sup>®</sup>	Aluminates	Polyaluminium silicosulphate $Al_2(OH)_{3.24}Si_{0.1}(SO_4)_{1.58}$	* 10% $Al_2O_3$ or 5.3% w/w Al * SG 1.34 * 54% basicity	Strange coagulant! Can't be diluted with water: forms flocs. Gippsland Water has used OK	2500
Sodium aluminate	Aluminates	$NaAl(OH)_4$	* 18% w/w $Al_2O_3$ or 41.7% w/w $NaAl(OH)_4$ * SG 1.47 * 12% w/w free NaOH * <b>613 g/L</b>	Strong alkaline coagulant. Can work on highly coloured water with low alkalinity. Used at some Tasmanian WTP's.	2200
<i>PFS</i> <sup>®</sup>	Aluminates	Polyferric sulphate $Fe_2(OH)_{0.6}(SO_4)_{2.7}$	* 12.2% w/w Fe(III) or 43.7% w/w $Fe_2(SO_4)_3$ * SG 1.54 * 10% basicity * <b>673 g/L</b>	Hydroxylated ferric sulphate. Used at several WTP's in NSW.	650
Ferric Sulphate <i>MEGACLEAR 12</i>	Hardman Omega Chemicals	Ferric sulphate $Fe_2(SO_4)_3$	* 12% w/w Fe(III) or 43% w/w $Fe_2(SO_4)_3$ * SG 1.50 * <b>645 g/L</b>	Similar to <i>PFS</i> <sup>®</sup> . Has greater impact on raw water pH.	550
<i>PROFLOC F</i>	Orica/ Spectrum	Ferric chloride $FeCl_3$	* 14-15% w/w Fe(III) or 41-43% w/w $FeCl_3$ * SG 1.45 * <b>609 g/L</b>	Similar to other ferric coagulants. No $SO_4$ added to treated water. Very corrosive.	1400

1. Brand names for coagulant products are shown in italics.

2. Assumes 20 kL bulk delivery, ex works Melbourne.