A DUMMY’S GUIDE TO COAGULANTS

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

1.0 WHAT ARE COAGULANTS?

A quick look in a dictionary reveals that a *coagulant* is "an agent that induces curdling or congealing". In a water treatment sense, what we talking about is a chemical that will remove colour and turbidity present in a raw water in the form of flocs.

Coagulants are 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 appropriate. However, they can sometimes be used in combination with inorganic types, often with spectacular results. More on that later!

Here are a few Rules to remember when looking at coagulants.

RULE 1 when dosed to a raw water, inorganic coagulants decrease its alkalinity

RULE 2 as a consequence of Rule 1, the pH of the chemically dosed raw water will decrease. In some cases, this will mean that supplemental alkalinity in the form of lime, soda ash, caustic soda or some other alkali will have to be added

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) do not have as great an effect as does alum. Organic coagulants generally do not effect the raw water alkalinity and pH; which can be an advantage in some cases

RULE 4 all coagulants produce sludge in the form of the metal hydroxide together with coloured and colloidal matter removed from the raw water in the treatment process. But again, not all inorganic coagulants behave in the same way. For example, there is some anecdotal and published data suggesting ACH and PACl produce less sludge than alum when dosed at equivalent levels. Organic coagulants produce very little sludge; another factor in their favour

RULE 5 inorganic coagulants will increase the total dissolved solids (TDS) concentration of the treated water. This may be undesirable, especially when using alum, as sulphate levels in the finished water will rise

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.

$$Al_2(SO_4)_3.18H_2O \rightarrow 2Al^{3+} + 3SO_4^{2-} + 18H_2O \rightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^{2-} + 12H_2O \quad -(1)$$

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

$$Al_2(OH)_5Cl \rightarrow Al_2(OH)_5^+ + Cl^- + H_2O \rightarrow 2Al(OH)_3 + H^+ + Cl^- \quad -(2)$$

Note that from Equation (2), only one mole of hydrogen ions is produced, reflecting the hydroxylated nature of this compound.

PACl also shows similar hydrolysis as represented by Equation (3). In this reaction, three moles of H^+ are formed.

$$Al_2(OH)_3Cl_3 \rightarrow Al_2(OH)_3^{3+} + 3Cl^- + 3H_2O \rightarrow 2Al(OH)_3 + 3H^+ + 3Cl^- \quad -(3)$$

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. Within this pH, colour and colloidal matter is removed by adsorption onto/within the metal hydroxide hydrolysis products that are formed.

- if an excess of alum is added so that the dosed water Ph is less than 5.0, then the metal ions (Al^{3+}) directly eutralize 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.* This is often done to boost the removal of disinfection by-product (DBP) precursors. Obviously, coagulating at such a low Ph requires attention to potential corrosion problems, as well as the need for post-treatment Ph adjustment /alkalinity adjustment to ensure that the treated water is not corrosive.

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 typical of South Eastern Australia, pre-treatment with lime, soda ash or caustic soda will normally be required to ensure that the optimum coagulation pH is achieved.

These types of water however, also make the use of ACH possible. It is often feasible to coagulate at a relatively high pH (7.5-8.0) and so avoid the need to dose alkali for pH correction: something that is often difficult at small WTP's. Recently, ACH dosing was successfully implemented at a WTP in Eastern Victoria. Finished water residual aluminium and THM levels have both been below Australian Drinking Water Guidelines (ADWG) limits since changing over from alum to ACH, with reduced maintenance requirements.

As a rule-of-thumb, ACH doses required for a surface water will be approximately a third of those required when using alum. 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: lower sludge production, avoidance of post-treatment alkali dosing, etc.

Figure 1 summarises results obtained at a WTP operating on a variable quality and highly coloured water in Eastern Victoria. When coagulant doses are converted to the basis of mg/L aluminium dosed, there was very little difference in the performance between ACH and alum to give the same finished water quality. However, the need for post-treatment pH adjustment was avoided by using ACH.

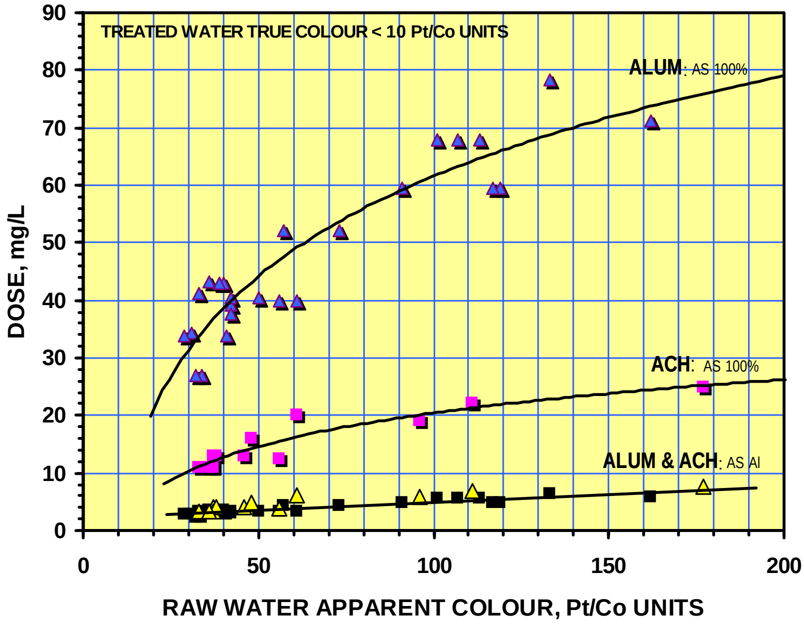

Figure 1: ***Comparison Between ACH and Alum Coagulants***

So, if you have a 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*.

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

Iron-based coagulants, such as ferric chloride, ferric sulphate and *PFS*®, are not that popular in Australia and tend be more expensive than alum on an equivalent per kg metal dosed basis. They also consume more alkalinity than alum, and hence tend to depress pH of the dosed water more dramatically. Opinions also differ as to whether they produce a fluffier floc, which is more difficult to settle. Several WTP's in NSW use *PFS*® 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 when there are chemical spills and leaks.

Table 1 summaries 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 (NOM) from water.

4.0 WHAT IS THE BEST DOSED-WATER PH?

The pH of raw water gives an indication of how acidic or alkaline it is. It is a very important parameter in water treatment, especially for 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, aluminium or DBP's may occur in the finished water. This can create problems when the raw water has a high alkalinity or pH. Very high alum doses will then be required to achieve the right dosed-water pH. The alternative is to dose acid to decease the pH to a lower value before dosing the coagulant. 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 ADWG limit of 0.2 mg/L aluminium in the finished water, as well as increasing the possibility of having floc precipitate out later in the Clearwater Storage Tank or within the reticulation system. ACH can work 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 Operator to decommission a 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 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/volume unit. This is also the same as parts per million (ppm), but only when quoted on a weight/weight basis.

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: mg/L = 10,000 X % w/w X SG.

For example, consider alum with an Al_2O_3 content of 7.5% w/w and SG 1.29. This is equivalent to 49.0% w/w strength aluminium sulphate (as $Al_2(SO4)_3.18H_2O$). Using the formula above, the concentration of the alum in mg/L, will be 10,000 X 49.0 X 1.29 = 632,000 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:

Alum dose = (150X632,000/(1000X60))/50 = 31.6 mg/L or ppm (w/w)

Or: = 1,000,000X(150/(60X1000))/50 = 50 ppm (v/v)

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

6.0 THERE SEEMS TO BE A LOT OF "NEW AGE COAGULANTS" NOW OUT THERE IN THE MARKET. AND, THEY SEEM TO COME WITH A LOT OF CONFUSING TERMS. WHAT ARE THEY, WHAT DOES IT ALL MEAN, AND WHICH IS THE BEST?

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 hydroxylated or pre-polymerised polyaluminium or polyferric coagulant. The higher the basicity of a coagulant, the lower the impact it will have on the dosed water pH. For example, aluminium chlorohydrate $Al_2(OH)_5Cl$, will have 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 polyaluminium chloride, which only has three OH ions in its structure and consequently has a typical basicity of 50-55%. 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*® from *Aluminates*) has found use in potable water treatment.

The next term to be familiar with for aluminium-based coagulants is "***percent*** $\boldsymbol{Al_2O_3}$". 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 Al_2O_3 content. For example, liquid alum is typically 7.5% w/w Al_2O_3, which is the same as 4.0% w/w aluminium (Al). For ACH and PACl coagulants, the brand name often incorporates the Al_2O_3 strength involved. As an example, *PAC-23* produced by *Aluminates*, is ACH with an Al_2O_3 content of nominally 23.5% w/w. This is equivalent to ACH with a concentration of 40.2% w/w $Al_2(OH)_5Cl$ or 12.4% w/w Al. Similarly, for *Omega Chemical's MEGAPAC 10*, this is PACl with a nominal Al_2O_3 content of 10.5% w/w. This is the same as 21.8% w/w $Al_2(OH)_3Cl_3$ or 5.6% w/w Al.

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 is commonly delivered as 7.5% w/w Al_2O_3, thus for every 100 kg of liquid chemical there are 7.5 kg of Al_2O_3 present

Another term you should understand 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 it or the 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 a given chemical, there is a direct relationship between its strength and its SG, and indeed chemical manufacturers use SG to measure the strength of a chemical during the manufacturing process. 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 $20^{o}C$.

There is only one way to determine which coagulant will work best on 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!

7.0 I'VE HEARD THAT SOMETIMES YOU CAN DOSE AN INORGANIC COAGULANT WITH AN ORGANIC ONE. PLEASE EXPLAIN.

Often when a polyDADMAC organic coagulant is used together with alum or ACH, the total chemical dose required to achieve the same finished water quality can be less than if each chemical is used on its own. Alum or ACH in combination with a cationic polyDADMAC polymer can work extremely well on highly coloured waters, which also have a low pH and alkalinity.

For example, Table 2 gives the coagulant doses determined from jar-tests using alum and a cationic polyDADMAC polymer to give the same finished water quality treating a highly coloured, soft water from Eastern Victoria.

Table 2: ***Comparison of Coagulant Doses***

ITEM	OPTION 1	OPTION 2	OPTION 3
Alum Dose, mg/L	28	0	12
PolyDADMAC dose, mg/L	0	2.3	0.3
Operating Cost, $/ML	14.3	23.0	9.1

Assuming that alum costs $250/tonne at 49% w/w strength and the polymer is $5/kg at 50% active solids, then the operating costs shown in Table 2 can be calculated. The option of using alum in combination with polymer gives the lowest chemical operating cost.
As a rule-of-thumb, when using dual-coagulants, the inorganic coagulant dose can be reduced by 50% compared to when used on its own.

However, be warned! Sometimes cationic polyDADMAC polymers don't work at all on some waters. And sometimes when you overdose with a cationic polymer you can get a phenomenon known as *restabilisation*. This is where the overall surface charge of colloidal particles present changes from negative to positive with the turbidity of the dosed water actually increasing.

There are several proprietary polyDADMAC/ACH blends available, e.g. the *Ultrion* series from *Nalco/Ondeo* and *"1190"* from *Aluminates*. *Omega Chemicals* also manufacture various polymer/ACH blends.

Generally as the proportion of polyDADMAC increases in the dual coagulant blend, the higher will be the sensitivity to getting the dose correct.

8.0 WHAT IS THE BEST WAY TO CARRY OUT A JAR-TEST?

This really is one of the most important tools a WTP Operator has for evaluating and optimising different chemical dosing regimes, as well as checking on the performance of the WTP on a regular basis. The *American Water Works Association* has updated its *M37*, which includes a very comprehensive chapter on the proper conduct of jar tests and I commend it for purchase by your Authority as an important reference (AWWA, (2000), *Operational Control of Coagulation and Filtration Processes*, M37, 2nd Edition, Manual of Water Supply Practices, Denver, CO).

There is much debate about whether the newer-style square, 2L plastic beakers give more meaningful results than when using the more traditional 600 mL round glass types. I won't buy into that argument other than to say the "Gator" jars, as they are commonly called, give the convenience of larger samples and a tap for draw off of settled samples.

One tip that you may be interested in is how to simulate the filtration step in investigating different chemical dosing regimes in the WTP lab. A cotton wool plug, 10-15 mm diameter and 50-60 mm long, is formed by rolling some cotton wool between your thumb and forefinger. This is then firmly inserted into the neck of a small plastic funnel, leaving about 10 mm proud of the stem, which is then "mushroomed" around the mouth of the stem.

Following settling, samples of the clarified water are carefully poured through the funnel, discarding the first 50 mL or so of the "filtered" water. Samples of the filtrate can then be taken for analysing parameters such as turbidity and true and apparent colour. Filtration of this sample through a 0.45-micron membrane filter then enables you to analyse for truly soluble parameters. After filtering 200-300 mL of the clarified sample, carefully pull out the cotton plug and replace it with a fresh one. You'll be able to see the penetration of filtered floc particles within the plug by a band of colour, indicating that the filtration process is working well.

An alternative, which you'll find mentioned in the textbooks, is to filter settled samples of water through *Whatman Grade 1* or *No. 1* filter paper. I've found this arrangement to be very hit and miss; you have to be very careful that you don't apply too much vacuum to the filter funnel to avoid tearing a hole in the paper and ruining the test.

9.0 IF I FIND A COAGULANT WORKS BETTER THAN THE ONE I'M USING AT THE MINUTE, WHAT'S INVOLVED IN CHANGING OVER AT MY WTP?

Conversion from one coagulant to another is generally pretty straight forward, assuming that they are both supplied in liquid form.

A couple of tips:

1. check that the coagulant dosing pumps have sufficient turn-down capability and are to able accurately dose in the range anticipated

2. check with the supplier of the new coagulant if there are any special precautions you need to carry out when changing over from one to the other. For example, in changing from alum to ACH, you must make sure that the storage tank and all dosing lines have been properly flushed out or you'll end up with a jelly-like material everywhere!

Well, this brings my guide to coagulants to an end.

Hopefully you'll find it to be of help in addressing some of the particular concerns you may have about the curious world of coagulants!

10.0 REFERENCE

(AWWA, (2000), *Operational Control of Coagulation and Filtration Processes*, M37, 2nd Edition, Manual of Water Supply Practices, Denver, CO).

Table 2: ***Commonly Available Coagulants and Details***

COMMON COAGULANT NAME[1]	TYPICAL MANUFACTURERS	CHEMICAL NAME & FORMULA	TYPICAL ANALYSIS	NOTES	INDICATIVE COST. $/tonne (as 100%)[2]
Alum	Aluminates Omega Chemicals	Aluminium sulphate $Al_2(SO_4)_3.18H_2O$	7.5-8% Al_2O_3 or 49-52% w/w $Al_2(SO_4)_3.18H_2O$ SG 1.3	Most common coagulant used in water treatment. Relatively cheap.	450
PAC 23 *MEGAPAC 23* *ALCHLOR AC* *PROFLOC A23*	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	Used in lieu of alum where raw water has low pH & alkalinity. Has little impact on pH.	2100
PAC-10 LB *MEGAPAC 10*	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	Used in lieu of alum where raw water has low pH & alkalinity. Has greater impact on pH than ACH.	2500
PAC-10 HB	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
PASS®	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! Cannot be diluted with water: forms flocs. Gippsland Water has used with success.	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	Strong alkaline coagulant. Can work on highly coloured water with low alkalinity. Used at some Tasmanian WTP's.	2200
PFS®	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	Hydroxylated ferric sulphate. Used at several WTP's in NSW.	650
Ferric Sulphate *MEGACLEAR 12*	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	Similar to *PFS*®. Has greater impact on raw water pH.	550
PROFLOC F	Orica/ Spectrum	Ferric chloride $FeCl_3$	14-15% w/w Fe(III) or 41-43% w/w $FeCl_3$ SG 1.45	Similar to other ferric coagulants. No $S0_4$ added to treated water. Very corrosive.	1400

Brand names for coagulant products are shown in italics. In general, number refers to Al_2O_3 content in % w/w e.g. *MEGAPAC **23*** is ACH with nominally **23%** w/w Al_2O_3 content.
Assumes 20 kL bulk delivery, ex works Melbourne.