

How to Select a Chemical Coagulant and Flocculant.

**Anthony S. Greville.
Easy Treat Environmental.**

Abstract

In many water treatment processes the selection of the chemical regime is of critical importance. The mechanical equipment will remove water contaminants to a reasonable level, but to meet the increasingly stringent Federal and Provincial licensing requirements chemical coagulation, flocculation, and disinfection are necessary. This paper will address several topics that will help the water treatment plant operator select the most appropriate chemical treatment programme for the needs of the community that the plant services.

Why do we Chemically Treat Water?

Water is essential for life as we presently know it and in North America we have become accustomed to receiving good quality water at a reasonable cost (on world wide terms Canadian drinking water is provided at an extremely low cost). In today's increasingly complex society the demands of the consumer, the medical and scientific communities, and therefore the Municipal, Provincial and Federal regulators, have caused the quality guidelines for safe drinking water to be

reviewed. In many cases what was considered acceptable by all segments of society just a decade ago would now be thought of as unsafe. In an era of changing regulations and guidelines it is difficult to define what is considered to be "good" drinking water, but reference to the *Guidelines for Canadian Drinking Water Quality* (Sixth Edition) as well as the Provincial Licensing Authority will allow for a decision to be made. At the present time it can be anticipated that changes will be made with respect to the following parameters [1];

Various pesticides, organic compounds and metals, cyanide, dioxins and furans, fluoride, nitrilotriacetic acid (NTA), total dissolved solids, trichloroacetic acid, trihalomethanes (THMs).

Once the community at large has made the decision as to the delivered quality of the finished water that will be enjoyed by the consumer, the practical considerations have to addressed.

Invariably mechanical means will be employed to help achieve the treatment objectives, but since no mechanical process is 100% efficient, chemical enhancement will often be necessary.

Another reason for appraising the utility of chemical treatment is when capital costs are being balanced against operating costs. Either the size/expense of a piece of equipment can be reduced if efficiency can be increased by implementing chemical treatment, or else physical space limitations do not allow for the installation of a large process addition and therefore optimization of existing equipment has to be considered first.

Chemicals typically find utility in the removal of suspended, colloidal and dissolved solids from water, including calcium and magnesium hardness, mineral turbidity, organic colour and other organic substances, and undesirable microbiological species that can cause

health concerns in humans. The four broad categories of chemicals used are lime for precipitation softening, coagulants and flocculants for the removal of suspended and colloidal solids, powdered activated carbon for taste and odour, and disinfectants for the removal of pathogens.

Selection of Chemical Species.

There are three fundamental variables in water treatment, all three of which will have a significant influence on the type of chemical that could be usefully employed in a particular application. The three variables are;

- 1) Raw Water Quality.
- 2) Process Equipment.
- 3) Treatment Objectives.

These three variables can be further categorized as shown in the table below;

| Raw Water Quality | Process Equipment | Treatment Objectives |
|-------------------|----------------------------|--|
| Alkalinity | Settling Lagoon | Potable Application Partial Softening Full Softening |
| pH | Direct Filtration | |
| Turbidity | Sedimentation + Filtration | |
| Colour | Solids Contact Clarifier | Industrial Application General Use Ion Exchange |
| Temperature | Dissolved Air Flotation | |
| Hardness | Mixing Intensity | |
| Taste and Odour | Sludge Disposal | |

If the above variables are reviewed prior to embarking on the coagulant and

flocculant selection process a considerable amount of time and

needless effort can be saved. An understanding of how the variables effect water chemistry will allow the operator to make sensible pre-screening decisions and let him/her focus on optimizing the process to achieve the treatment goals.

Raw Water Quality

Clearly the quality of the raw water and the contaminant classification, has to have a significant impact on the type of chemicals used for liquid-solids separation. There are however several factors to consider;

- 1) The amount of alkalinity present in the water may eliminate some coagulants from consideration.
- 2) The amount of turbidity present may only determine the amount of coagulant that may be required.

One also has to be aware of how the raw water quality will change as a function of the time of the year.

Alkalinity

Alkalinity is of critical importance when selecting a metal salt coagulant such as polyhydroxy aluminum chloride (PACl), aluminum sulphate (alum), or ferric sulphate. All these materials need some alkalinity to drive the hydrolysis reactions that allow the coagulants to function. If the water has a low alkalinity, below 50 mgL^{-1} , then the use of some of the more acidic metal salts may be precluded. In these instances there are two options, either add supplemental alkalinity (as NaOH, $\text{Ca}(\text{OH})_2$ or Na_2CO_3), or use a

high basicity coagulant (>50% basicity) such as PACl or ACH. If the water to be treated carries a very low alkalinity loading then the use of artificial alkalinity will always be necessary. In such a case it might be useful to try a combination of acidic and basic aluminum salts, PACl, ACH or alum, together with sodium aluminate. Should the alkalinity be $>50 \text{ mgL}^{-1}$ then, in general, there will be sufficient present to drive most coagulation reactions. However, if the coagulant dosage has to be higher (by a factor of two) than the raw water alkalinity it may be necessary add some alkalinity to drive the hydrolysis reactions to completion.

pH

The pH of the water could also determine/eliminate many treatment options. If the pH is higher than 8.5 and Dissolved Organic Carbon (DOC), often referred to as colour, has to be removed a highly acidic coagulant that will drive the pH down to ± 7.0 will have to be considered. It may be necessary to add some soda ash in order to bring the Langlier Stability Index back to zero after such treatment. If the pH is acidic great care will have to be taken to ensure that the chemical reactions occur as desired and that the finished water is stable, removal of colour will be easy. Ferric salts often perform well in acidic conditions. The most challenging conditions occur when colour has to be removed from a water that has a high pH and a low alkalinity. Careful depression of pH without alkalinity destruction can be realized if gaseous CO_2 and $\text{Ca}(\text{OH})_2$ are added together. The choice of coagulant will determine the extent to which pH has

to be depressed. This is a somewhat sophisticated approach and would not be recommended for a smaller community with a restricted capital budget.

Turbidity

The precipitation of mineral turbidity by the classic coagulation and flocculation process is well defined and reasonably straight forward. Turbidity can be classified as being anionically charged silica particles. Often the effect that turbidity has is dependent on the amount present rather than the classification. In low turbidity waters (<10 NTU) an organic polyelectrolyte should not be considered. The choice of inorganic coagulant should be one that quickly generates the $Al(OH)_3$ sweep floc and will form a stable sludge bed. In moderate turbidity waters (<100 NTU) the use of a general purpose inorganic salt is preferred, and most will be successful if the other conditions are right. In high turbidity situations, or in those instances where surface water turbidity can increase very rapidly, a PACI blended with a polyepiamine is often the best choice. Sludge bed height, sludge volume, dewatering efficiency, and pH depression are all reasons to consider the PACI blend over large additions of alum or ferric sulphate. Organic polyelectrolyte on its own will be effective, but the cost is high, and there is the potential to blind downstream filters with a high dosage of epiamine or pDADMAC (> 4.0 mgL⁻¹).

Colour

Dissolved Organic Carbon, DOC, colour, is the parameter around which a chemical treatment regime is built. Hydrophillic colour is invariably more difficult to separate from water than is hydrophobic mineral turbidity. The complexing of colour is dependent on the pH of the water, the classification of the colour colloid, and the ability of the coagulant to break the hydrogen bonds present. The choice of chemicals must be one that will create a water in which the colour will be least stable (usually at a pH between 5.5 and 7.0), the alkalinity will be preserved for turbidity precipitation, and the finished water will be neither corrosive or scaling.

In many applications it is difficult for one material to be completely successful by itself, especially the inorganic metal salts. In these instances cost performance economics dictate that a small amount of an organic short chain polymer, usually from the pDADMAC family be utilized. If alum or ferric sulphate is the primary coagulant, then the supplemental addition of pDADMAC will have to be via a separate feed system. If any of the PACI preparations are used, a one product blend can be selected.

Temperature

Temperature can affect the performance of the inorganic metal salts that rely on a chemical reaction. The colder temperatures (<5^o C) have a profound effect on alum and iron salts to the extent that performance is often unacceptable during the winter. It is not unusual for a water plant to have to heat the raw water to a minimum of 8^o C in winter to maintain adequate finished water quality. In

industrial applications carryover of alumina or iron flocs can cause process non-conformities and off specification production. The non-sulphated polyhydroxy aluminum chloride choice does not appear to be as temperature sensitive and is therefore a good first choice coagulant for cold water applications. Almost all the coagulants will perform well in warmer waters, $10^{\circ} \text{C} \leq T \leq 25^{\circ} \text{C}$.

Hardness

Calcium and magnesium hardness are present in all waters to some degree or another. The amount of CaH and the end use of the water will determine the strategy required to handle the presence of these minerals. Typically lime is added to allow for the precipitation softening process to take place. Lime sludges are dense and will tend to settle, however, it is recommended that 10 mgL^{-1} of an alumina coagulant be added to capture the lime fines. It should be stressed that the coagulant is present only to capture the lime fines and not to coagulate raw water turbidity. Lime sludges cannot be returned to the environment, so dewatering or lagoon storage is required, all coagulants should be evaluated with respect to their ability to dewater on the equipment in the water plant.

The major criteria for efficient lime softening is pH control, pH should be maintained at 10.0 ± 0.2 . A metal based coagulant will consume alkalinity, especially in a well buffered high pH water, which could compromise the softening process. The best coagulant is

therefore a pre-hydrolysed species with a high basicity. PACI has been found to be very suitable for lime softening applications. A flocculant is seldom needed, but filtering is always recommended.

The only major problem encountered with a lime softening programme is if there is a need

to soften at a high pH and remove organic colour at a low pH. The only real solution is to make a capital investment in two clarifiers, arranged in series. Initially the raw water is treated in a conventional way, at pH 7.0, a low basicity coagulant should be added to ensure that a good sludge bed is maintained for the straining and filtering action. This is followed, in a separate clarifier, by the lime softening step, at pH 10.0 with a high basicity coagulant.

In municipal applications, where the requirement is to reduce hardness to $<100 \text{ mgL}^{-1}$ flocculants are not recommended, however the water should always be filtered. In those industrial applications where the water is sent to an ion exchange stage, hardness is reduced to $\sim 40 \text{ mgL}^{-1}$ and a flocculant is always used. Filtering is still required prior to the ion exchange equipment. The advantage of a low basicity coagulant is even more pronounced in full softening applications, and the non-sulphated PACI is the coagulant of choice.

Taste and Odour

Taste and odour can be controlled in a variety of ways, but one of the most common is with the addition of powdered activated carbon, (PAC). PAC generates

fine particles that have to be well coagulated. Most of the coagulants will settle PAC/organic particles, however because of the very fine nature of the species it is better to choose a coagulant that generates the densest sludge. The correct choice will result in minimal pin floc carryover, while the incorrect choice will be characterized by a low consistency sludge bed and observable pin floc carryover.

Process Equipment

The process equipment does have some impact on the choice of coagulant and flocculant, however the raw water quality is the predominant factor.

Settling Lagoon

The presence of a pretreatment settling lagoon will allow the water plant to maintain, on a year round basis, a consistent and much better quality of raw water. A settling lagoon will enable the water plant to let any temporary poor quality surface water by-pass the plant in-take, while concurrently permitting all the settleable solids to be naturally precipitated from the raw water prior to treatment. The choice of chemical treatment should therefore be consistent on a year round basis, as should be the overall treatment regime. A chemical programme can be tailored to meet specific needs and can be far less forgiving than programmes that have to satisfy fluctuating raw water quality situations.

Direct Filtration

A direct filtration plant will require a coagulant/flocculant combination that will readily generate a robust yet filterable floc with the raw water contaminants. The first inclination is to believe that the larger the floc the better, but this is often not the case. A large floc will be easily filtered from the water but all the filtering action will take place on the top of the filter bed, leaving the majority of the media unused. A smaller, denser, and more robust floc will also filter well but will use a greater percentage of the filter bed resulting in an improved quality of finished water and longer run lengths before breakthrough. Those coagulants that hydrolyze quickly to form a sweep floc will show up well in a jar test, however the sweep floc is very fragile and may easily break up into fines that will be difficult to filter. The prepolymerized inorganic metal salts are the best option in direct filtration units.

There will be a temptation to consider the use of organic polyelectrolytes as filter aids, especially the pDADMAC's if there is colour to remove. The use of these products can be beneficial, but only as an aid to the primary coagulant. Should the dosage of these materials be above 4.0 mgL^{-1} there will be a very real tendency to cause filter blinding and large "mud balls".

Sedimentation and Filtration

The configuration of the settling basin process will have to be considered, especially the chemical feed point and the intensity of the flocculators. If there are good flocculators, or mixing chambers, with several minutes detention time (>5 minutes) then the best choice is a non catalyzed prepolymerized metal salt. Such a chemical regime will generate a

dense floc that will expel water naturally. This floc will settle well, and depending on the retention time in the main settling basin may or may not require a flocculant. If the mixing energy or detention time is insufficient, the best option is to consider a sulphated alumina salt since the catalyzing characteristic of the sulphate will allow for reasonable results. Since a sweep floc will surface adsorb the raw water contaminants without any real coagulation there will always be a need for an organic polymer flocculant and carryover may become a concern.

Again there may be a temptation to consider the use of either a pDADMAC or a polyepiamine, they will show well in a jar test. As with the direct filtration process care has to be taken since if any unreacted short chain polymer is carried over to the filter plant, mud balls and filter blinding could result. There is also the possibility that the cationic solution polymers may cause an overdose of positive charge that may result in poor settling and extra loading on the filters.

Solids Contact Clarifier

A well designed and operated solids contact clarifier followed by a properly sized filter plant will present few challenges to any one chemical treatment regime that it will not present to another. There is typically good mixing time and intensity in the centrewell, where there is also the opportunity for floc collisions and growth. A "good" sludge bed will provide a straining and filtering medium, which can be complimented by the inclined baffle

plates that many clarifiers are now equipped with. If there is any unacceptable carryover, the filter plant will usually separate the pin floc from the water.

There are several process variables that can enhance or detract from the performance of a chemical treatment programme. Raw water temperature, chemical feed point(s), turbine speed, sludge bed height, and clarifier blowdown can all be adjusted so as to optimize the performance. All chemical treatment programmes, if it is the correct choice for the raw water and the treatment goals, should be able to be optimized in a solids contact clarifier.

Dissolved Air Flotation

Dissolved Air Flotation (DAF) Units are becoming increasingly common in water treatment. In DAF units coagulant is added to the raw water or wastewater just before the flocculators. A robust floc has to be formed quickly since upon entering the DAF unit the raw water is mixed with an air pressurized stream of effluent water. The drop in pressure allows the air to be released and the bubbles float to the surface of the flocculator/clarifier. The coagulated particles absorb/adsorb/entrap the air bubbles and also float to the top of the vessel. A thickened sludge forms at the top which is periodically removed.

The coagulant has to be able to form a very robust sludge that will resist fracture in the flocculating chamber. A limitation of the DAF unit is that any sludge particles that fracture will form a very

small, almost colloidal, particle that will pass through the filters and reduce the quality of the finished water. For this reason it has been found that the prepolymerized coagulants, that are held together with chemical bonds, provide the best sludge particle and give the best finished water quality. The alum sludges, that rely on floc collisions to build a settleable sludge tend to fracture easily. For a DAF unit, a sludge stability test is the best indicator of performance. Do not be fooled by large fluffy flocs that look good in a jar test. Prepolymerized salts are often the best choice and should be screened first.

Mixing Intensity

The mixing intensity or available mixing time will have a greater effect on the performance of the chemical rather than on the choice. However, if there is insufficient mixing to optimize the coagulation process it is recommended that a sulphated aluminum or polyaluminum salt be considered. A sweep floc of aluminum hydroxide will be generated that will allow for chemical enmeshment of colloidal particles. While a true coagulation process will not have taken place, with the aid of a good flocculant, the solids should be separated from the water. If the mixing regime is satisfactory it is better to move away from the catalyzed materials and rely on hydrolysis to generate the cationic species required for coagulation and particle collisions for flocculation. Chemical efficiency will be much improved and there may not be a need for a flocculant.

Sludge Disposal

Sludge disposal is becoming a very important operating parameter for many utilities. In some jurisdictions it is still possible to return aluminum sludges to a receiving water, including those that have undergone pH adjustment with Na_2CO_3 or $\text{Ca}(\text{OH})_2$. However, lime softening sludges that contain increased $\text{Ca}(\text{OH})_2$ concentrations and all iron based sludges have to be dewatered and sent to a land fill site. Settling lagoons and dredging or else the transfer to a municipal wastewater plant are also options for these more hazardous sludges. The type of equipment available to the utility operator, or else the capital monies allocated to plant improvement will have a significant impact on the coagulant choice.

Treatment Objective

The treatment objective will obviously have an impact on the type of treatment regime that is considered. While the processes available to all water plant owners are the same there is a difference in operating philosophy between a municipal supplier and an industrial facility. In the municipal segment the water plant serves the need to produce quality water as an end in itself. Due to public health concerns the municipal water plant operator will always strive to supply the best quality water possible.

An industrial facility will often treat water for use in the process of the plant. Quality is determined by the needs of the process only and not by public health concerns. Economics play a very significant role in the selection of a treatment regime since water treatment is considered a cost of business. To confuse the issue, an industrial facility that only has to meet process quality guidelines may not be able to live with poor quality water for long due to the potential to manufacture off-specification product.

In summary, a municipal water plant is often run to meet regulations and community standards while an industrial process facility is run by economics (an industrial potable water plant has to meet all the government regulations).

If a water treatment plant operator is planning to optimize the coagulation and flocculation functions within the plant the first option is to consider all the fixed parameters, as shown above. It is quite possible that by understanding the process and the chemicals available that many options will be eliminated and that a few will stand out as being good selections. A relatively easy process to select the best from all the good options can then be initiated.

consideration. In most cases there are several parameters that have to be considered. Following the same process outlined to select the most likely coagulant will also give a good indication as to the analytical requirements. Raw water quality, process equipment and treatment objective will determine the important operating parameters and also identify the parameters that need to be considered in the laboratory.

While each situation is different, there are a number of consistencies throughout the industry. The following list of analytical procedures should always be considered before beginning an evaluation procedure. Without familiarity with the necessary procedures and equipment required in order to obtain accurate and meaningful results, time spent on jar testing would be worthless.

| | |
|----------------------|---|
| Alkalinity | (measured in mgL ⁻¹) |
| pH | (measured in pH units) |
| Turbidity | (measured in NTU) |
| True Colour | (measured in TCU) |
| Total Organic Carbon | (measured as UV absorbance or mgL ⁻¹ TOC) |
| Temperature | (measured in degrees Celsius) |
| Hardness | (measured in mgL ⁻¹ as CaCO ₃) |
| Taste and Odour | (subjective test) |
| Aluminum | (measured in mgL ⁻¹) |
| Iron | (measured in mgL ⁻¹) |
| % Reduction Rates | (measured in %) |
| Filter Requirements | |

Determination of Analytical Requirements

When evaluating a potential chemical treatment programme it is essential that there be a method to measure the performance of the regime under

Assembly of Required Equipment

The most common test method used is the jar test. This concept has been available to water plant operators for approximately 50 years and has proven to be reliable. Jar tests will tell an operator which products or combination of products will work satisfactorily and give some indication of the approximate dosage (order of magnitude) required. Once a programme has been selected and optimized in-plant the jar test can provide some guidelines for operational changes to respond to a change in prevailing raw water conditions. The usefulness of the jar test procedure is dependent on the protocol used during the test, therefore it is important that the test be designed with the plant and the treatment objectives in mind. Before a meaningful series of jar tests can be conducted the following planning steps must be addressed;

- 1) Selection of equipment.
- 2) Preparation of reagents.
- 3) Preliminary test protocol compatibility study.
- 4) Development of final test procedure.
- 5) Determination of data requirements and necessary calculations.

Selection of Equipment

The most important piece of equipment in a jar test procedure is the physical jar itself. Other equipment considerations will be the drive mechanism of the stirrer, the design of the impeller, the presence of a water bath, analytical equipment, and general supplies.

Type of Jar

There are several types of jar available but perhaps the two most common are the 1 litre circular jar and the 2 litre square jar. The 1 litre circular jar is more popular, however it is the least efficient and representative of all the jar options and should be avoided if possible, [2]. The 2 litre square jar with a sampling port 10 cm from the water line is the best choice and of course the most expensive!

The limitations with the 1 litre circular jar include the following observations;

- i/ Small volume of water increases the margin of error when scaling up to full plant scale.
- ii/ The water will rotate with the paddle in the jar reducing the effective rate of mixing.
- iii/ It is very difficult to develop good settling data in a 1 litre jar.
- iv/ Very little supernatant water to analyze if several tests are required.

If a circular jar is to be used then a 2 litre capacity jar with stators should be considered. Figure 1 below shows an arrangement that allows for good mixing, settling and sample extraction. This design is often referred to as the Hudson Jar. The 2 litre square jar (sometimes called the Gator Jar) (Figure 2) with a sampling port 10 cm below the water line is the best choice as it offers several advantages that address the concerns above;

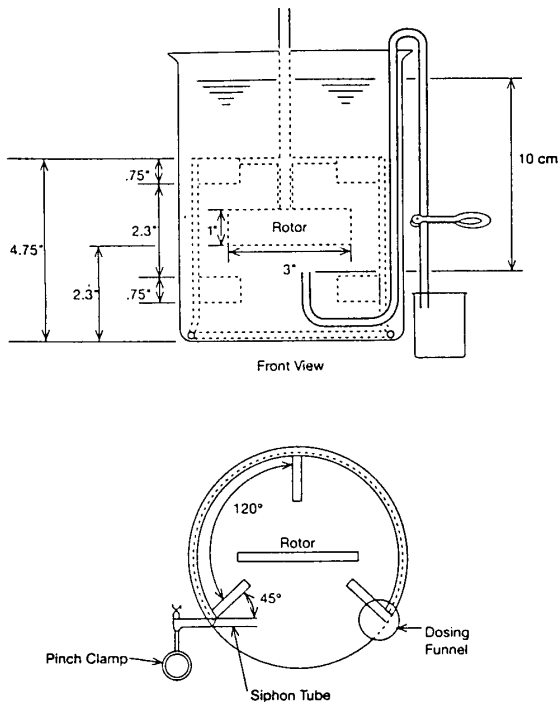


Figure 1
Hudson Jar

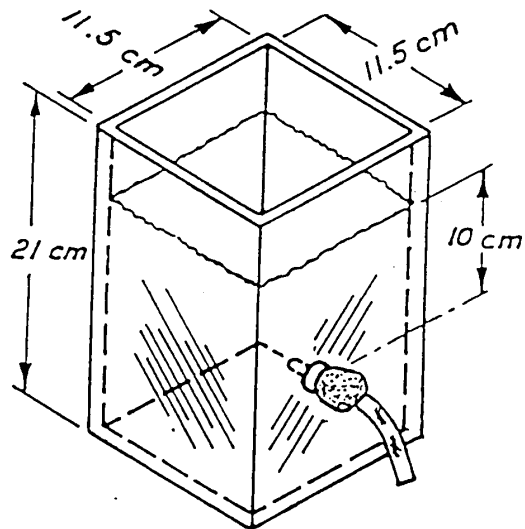


Figure 2
Gator Jar

- ii/ Larger volume reduces the margins of error.
- iii/ Square walls reduce water rotation making stators unnecessary.
- iii/ Settling velocity can be easily developed with the 10 cm sampling port configuration.
- iv/ Plenty of supernatant for analytical work.
- iv/ Thicker walls and lower thermal conductivity will reduce temperature changes during the testing period.

Stirrer Drive Mechanism

There are two basic types of stirrer drive mechanism that can be used to turn the impeller. The gear driven unit will have 4 or 6 impeller shafts run off a single variable speed motor. The impellers therefore all turn at the same speed during a jar test sequence. The speed can typically be varied between 5 and 250 rpm.

The second option is the magnetic stirrer option. The advantages the magnetic stirrer offers is extra space at the top of the jar is available for coagulant addition and the stirrers can be operated

independently of each other. In this way it is possible to determine the effect of varying mixing intensities in a side by side comparison.

A modification to the magnetic stirrer concept is a recent development that allows for paddles to be electrically operated independently of each other. This allows for variations in both mixing intensities and durations. Since each paddle can be activated on its own, mixing can begin concurrently with treatment chemical addition rather than trying to add six different chemicals at the same time. A major improvement with just one limitation, at present this design is only available for the 1 litre circular jars, and not for the 2 litre Gator Jars.

Impeller Design

There are several impeller designs available, the most common being the flat paddle, magnetic stir bar and a marine turbine. Each design offers different characteristics, the most important of which is the mixing energy, or velocity gradient, G . In general the flat impeller offers the highest velocity gradient, in a 2 litre square jar a G of 350 S^{-1} can be obtained with 200 rpm of the paddle. This is sufficient to duplicate most treatment plant conditions. The magnetic stirrer is less intense, up to 200 S^{-1} can be obtained with 200 rpm. The marine paddle (shaped like a ship's propeller blade) is the least efficient, at 200 rpm a velocity gradient of 70 S^{-1} can be generated in a 2 litre Gator Jar. This

makes a marine paddle unsuitable for most water treatment applications.

Water Bath

A water bath is recommended when cold water ($<10^{\circ} \text{ C}$) is to be evaluated. Many chemical treatment programmes are temperature sensitive, and fluctuations of $5 - 10^{\circ} \text{ C}$ in temperature, when the raw water temperature is $< 2^{\circ} \text{ C}$ are unacceptable. The best way to determine if a water bath is required is to run a quick jar test with raw water at ambient temperature. Put another sample aside and let it warm up 10° C and run an identical test. If there is a difference in floc formation rates and size, then a cold water bath is necessary.

The best design is to fabricate a clear bath that will contain all the jars to about their mid-point height. A sample of raw water at ambient temperature should be allowed to flow through the bath keeping the water temperature in the sample jars constant. This flow should be maintained throughout the test period, including the settling time.

Analytical Equipment and General Supplies

There should always be a good supply of beakers, syringes, pipettes, filter papers and all the analytical equipment required to be most efficient. Without the necessary tools to properly perform the test and to accurately assess the results the time and effort spent will be wasted.

Determination of Jar Test Protocol

The most important variable in the jar test is the actual test protocol used to perform the evaluation. A proper procedure will allow for good and meaningful results, an inappropriate procedure will render the results meaningless. Each plant will of course have a different protocol, and it may take some time to design the best procedure, however it should be remembered that the test protocol only has to be defined once!

Preparation of Stock Solutions

The preparation of the stock solutions used for evaluation of course has a significant bearing on the outcome of the test. In general coagulants and flocculants are diluted for test work for three reasons;

- 1) Ease of handling.
- 2) Ensure good mixing in the jar.
- 3) In the case of flocculants, to allow for activation.

There has been a suggestion that the use of microsyringes (no preparation by dilution of stock solutions is required) offer advantages over dilution and standard syringes. The main difference is that the charged coagulants can begin to lose their effectiveness once they have been diluted. To a degree this is true, however, if the coagulant stock solution is discarded after 2 hours there appears to be no significant reduction in efficiency. PAM based flocculants, when diluted to 1% maintain their charge for at least 24 hours, allowing for a full day's

work.

If dilution is required it is best to prepare 1% solution of coagulant and 0.1% of flocculant. A complete outline of the procedures involved in the preparation of stock solutions is presented in *Calculation of Chemicals Dosages for Water and Wastewater Treatment* [3], prepared by Easy Treat Environmental. A brief summary is presented below;

Example 1. Coagulants and Solution Polymers.

For products such as alum, PACl, ferric and ferrous salts, lime, NaOH and the solution cationic polymers, simple dilutions are all that will be required to permit accurate delivery of product. Solution strength and relative density should always be factored into you dilution calculations.

In general it is recommended that a 1% solution (by weight) of coagulant be prepared. This will allow for accurate delivery, good mixing and reasonable volumes to handle.

A 1% solution is defined as being 1% by weight, i.e 1g (or 1000 mg) of chemical in 99g (or 99 ml) of water for a total of 100g. 1 ml of this 1% solution will contain

$$\frac{1}{100} \times 1000 \text{ mg} = 10 \text{ mg}$$

This added to 1 litre is 10 mg per litre, or 10 mgL⁻¹ (or 10 ppm)

If you add 1 ml of a 1% solution to a test volume of 1 litre, the added dosage is 10 mgL⁻¹.

If you add 1 ml of a 1% solution to a test volume of 2 litres, the added dosage is 5 mgL⁻¹.

How is a 1% solution prepared? In simple terms, a 1% solution is prepared by adding 1g of chemical to 99 ml of water. Therefore, since it is easy to measure 99 ml of water, the only real source of potential error is in measuring 1g of chemical, especially if the relative density is different from 1.0.

Polyhydroxy Aluminum Chloride

To prepare a 1% solution of PACl one has to consider the relative density. 18% PACl has a relative density of 1.37. This means that 1 ml will weigh 1.37g.

$$\text{Thus } 1\text{g} = \frac{1}{1.37} \text{ ml} = 0.73 \text{ ml.}$$

So a 1% solution of PACl can be prepared by adding 0.73 ml of neat chemical to 99 ml of water.

Aluminium Sulphate

To prepare a 1% solution of alum (dry basis) one has to consider both relative density and solids content. Typically alum has a relative density of 1.34, and a solids content of 48.5%.

$$\text{Thus } 1\text{g} = \frac{1}{1.34} \text{ ml} = 0.746 \text{ ml}$$

0.746 ml will weigh 1g. However, since alum is 48.5% active content, 1g of solution will contain only 0.485g of alum.

Therefore
1g of dry alum
 $= 0.746 \times \frac{1}{0.485} = 1.54 \text{ ml}$

So a 1% solution of alum (dry basis) can be prepared by adding 1.54 ml of liquid alum (48.5%) to 99 ml of water.

Example 2 **High Molecular Weight Emulsion** **Polymers.**

For high molecular weight emulsion polymers, dilution before use serves two purposes, activation of the chemical and accurate delivery during evaluation.

A 1% solution, that is reasonable for the coagulants or solution polymers, is not practical for the emulsion polymers, the solution would be too viscous to handle, making it difficult to perform good jar tests. Typically a 0.1% or 0.2% solution is prepared in two steps. First a 0.5% - 1.0% solution is prepared to allow for activation, then a second dilution to 0.1% - 0.2% is made to allow for ease of handling and accurate delivery.

To Prepare a 0.5% Solution : **For Activation of the Polymer.**

Dry Powder

Weight accurately 0.5g and dissolve in 99.5 ml of water.

Emulsion:

Measure

0.5 ml and dissolve in 99.5 ml of water.

Density

**To prepare a 0.1% Solution :
For Ease of Handling.**

Once activation/dissolution is complete, dilute by volume 20 ml of the 0.5% solution to 100 ml. That is add 20 ml of 0.5% solution to 80 ml of water to generate 100 ml of 0.1% solution.

[Since the polymer has a relative density of 1.02 and 0.5g has been added to 99.5 ml of water, with a relative density of 1.00, it is reasonable to assume that the 0.5% solution has a relative density of 1.00.]

If you remember that for the coagulants, 1 ml of a 1% solution added to 1 litre gave a 10 mgL⁻¹ dosage, then it follows that:

If you add 0.5 ml of a 0.1% solution to a test volume of 1 litre, the added dosage is 0.5 mgL⁻¹.

If you add 1 ml of a 0.1% solution to a test volume of 1 litre, the added dosage is 1.0 mgL⁻¹.

If you add 0.5 ml of a 0.1% solution to a test volume of 2 litres, the added dosage is 0.25 mgL⁻¹.

Determination of Test Protocol

The actual test procedure has to be carefully determined, to be representative of the plant and so yield meaningful results. There are several critical parameters that have to be considered before a preliminary test can be performed. Three important considerations are mixing intensity, mixing duration and settling time. If one is attempting to duplicate the actions of a clarifier, the critical operating parameters include;

- 1) Velocity Gradient.
- 2) Flocculator Detention Time.
- 3) Settling Time.
- 4) Selection of Filter Medium.
- 5) Preliminary Test Protocol Compatibility Study.

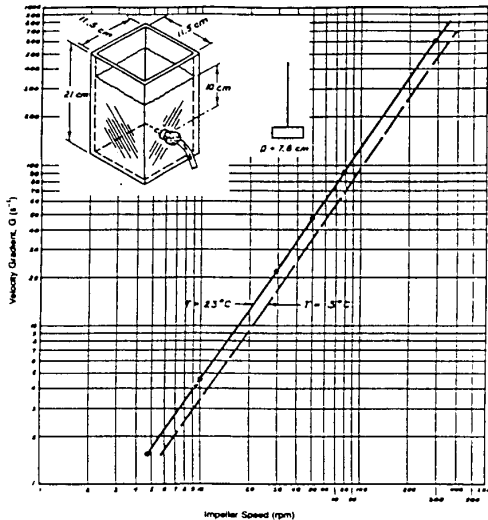
Velocity Gradient

The Velocity Gradient (G measured in S⁻¹) is a measure of the mixing energy that is present during both the flash mix and the flocculation stages of water treatment. In a jar test, velocity gradient corresponds to the fast mix and the slow mix. The higher the velocity gradient the more intense the mixing. The best way to determine the velocity gradient is to refer to the operations manual or consult with the design engineer or the manufacturer. G is a calculated number, the calculation of which is beyond the scope of this paper. For more information on how to determine G please refer to [4] and [5].

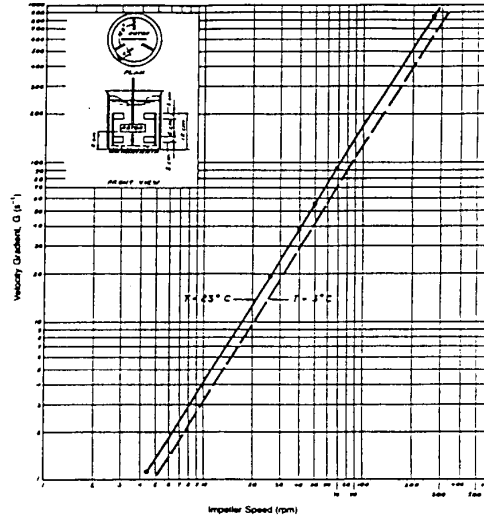
Once the velocity gradient has been

determined the important step is to duplicate the same mixing intensity in the

jar test. In general the rapid mix G is 200



Source: Cornwell and Bishop (1983).



Source: Cornwell and Bishop (1983).

Figure 3
Velocity Gradient for a Gator Jar

- 300 S⁻¹ while the slow mix is at the lower end of the 15 - 150 S⁻¹ range, 40 S⁻¹ being typical. When the jars to be used in the jar test apparatus evaluation are purchased it is normal to find a chart that correlates impeller speed, impeller design and velocity gradient for the jar. The diagrams for the flat paddle impeller in the 2 litre Gator Jar (Figure 3) and a Hudson Jar (Figure 4) are shown below. It is straight forward to determine the rpm of the paddles once the G forces experienced at various locations within the plant are known.

Flocculator Detention Time

The calculation of detention time is at once very simple, yet an accurate time is

Figure 4
Velocity Gradient for a Hudson Jar

almost impossible to determine. Detention time is calculated using a simple formula;

$$T_d = V/Q$$

where

T_d = Theoretical Detention Time (in minutes)

V = Tank Volume (in cubic meters)

Q = Flow Rate (in cubic meters per minute)

The problem lies in the fact that almost every system has some sort of short circuiting inherent in it. It is quite possible that the real detention time could be as much as 50% lower than the theoretical. The only way to verify the

real detention time is to run some tracer tests in the plant. Of course this only need be done once, when the operator is satisfied that the hydraulics of the plant are understood the all jar tests can be tailored to the real conditions.

In general, rapid mix is designed for 20 seconds to a minute (normally reasonable) while flocculation is designed for 30 minutes (the source of most errors).

Please note that the velocity gradient and the detention time for both the rapid mix and the flocculation stage have to be determined, there should be 4 numbers on which to base the development of the jar test protocol.

Settling Time

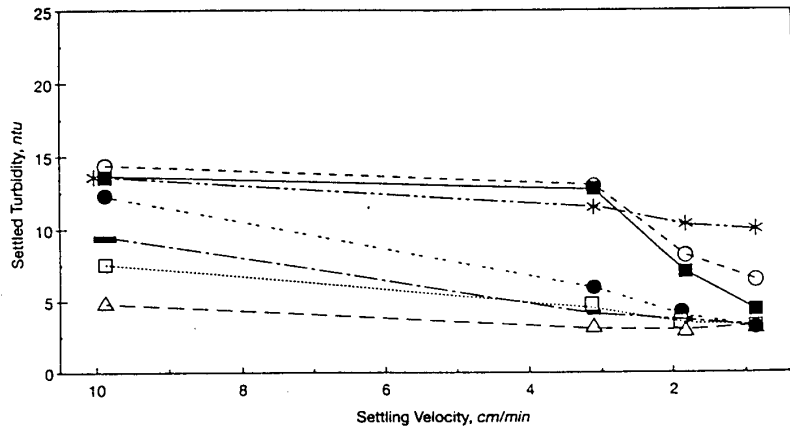
Settling time is one of the greatest sources of error when running a jar test. The main error arises because the settling time is often too long. While a long settling time gives very good results, they are often not very meaningful. Given time, all coagulated and flocculated particles will settle to the bottom of a motionless jar. The objective is to duplicate the plant process and be able to determine differences between chemical treatment regimes. Settling time is therefore an operating parameter that has to be measured carefully.

An example of how extended settling

times can obscure any meaningful comparison between treatment regimes is demonstrated in the graph below (Figure 5). If a sample is drawn from the jar after 3 minutes (3 on the Settling Velocity axis) there are discernable differences between the treatment regimes. If, however, settling is allowed to continue for 30 minutes (0.3 on the Settling Velocity axis) then there are no differences at all, the lines converge. The test results provide no meaningful relationship that will allow for comparison between treatment regimes.

The best method to duplicate settling time is to determine how long it takes for a particle to settle 10 cm in the clarifier. This can be done by calculation and verified by physical examination. Once the time taken for a flocculated particle to settle 10 cm has been determined the settling time in the jar has also been determined. The 2 litre Gator Jars, with a tap 10 cm from the water line are very useful, and far more reliable than the circular jar that demands water be syringed from the surface.

To calculate settling time one has to determine the Surface Loading of the clarifier or sedimentation basin. Once the surface loading is known the settling velocity can be determined, and then it is straight forward to calculate the time it will take to settle 10 cm. The table below outlines settling velocity and time to settle 10 cm.



Test Conditions:
 Alum = 25 mg/L
 Polymer = 1 mg/L
 pH Adjustment = Lime
 Rapid Mix = 14 s @ 400 1/s
 Flocculation = 14.7 min @ 18 1/s
 Raw Turbidity = 11.3 NTU
 Raw pH = 7.2
 Settled pH = 7.0

Figure 5 Settling Velocity and Sampling Time

| Surface Loading Rate <i>gpd/ft²</i> | <i>m/h</i> | Settling Velocity <i>cm/min</i> | Sampling Time for 10 cm <i>mins</i> |
|---|------------|------------------------------------|--|
| 180 | 0.3 | 0.5 | 20 |
| 360 | 0.6 | 1.0 | 10 |
| 720 | 1.2 | 2.0 | 5 |
| 1440 | 2.4 | 4.0 | 2.5 |
| 3600 | 6.0 | 10.0 | 1 |

Note : 1 gpm/ft² = 1440 gpd/ft² = 2.4 m/h is equivalent to a settling velocity of 4 cm/min.

The calculation for settling time can be verified by extracting a sample of water for the clarifier and measuring the time it takes for 80% of the particles to fall 10

cm. In general this estimated settling time will be close to the calculated sampling time and can be used as a guideline in the jar test.

Selection of Filter Medium

In almost all instances the settled water is passed through a filter before it is sent to the distribution system.. It therefore makes sense that there should be a filtering step in the jar test procedure. If the jar test has been well run, filtering the settled sample, drawn from 10 cm down, will provide interesting results. The most obvious is a distinction between true and apparent colour. Recently the concept of "filterability" has been gaining attention, alumina may be intentionally precipitated after coagulation in order to filter it out to reduce residual. Modern DAF units are also looking at using the filter plant more efficiently.

There are a large number of filters papers available from which to chose. Which one should be chosen for chemical treatment evaluation? As before, the best advice is to obtain a filter paper that best mimics the filter plant. This is easier said than done, similarities between the laboratory bench and the full scale plant are few.

The selection of a specific filter and method of use depends on the information required and the ability of the method to reproduce a filtered water quality that is similar to the full scale plant. A guide to filter performance is tabulated below.

| Selected Filter | Efficiency | Practical Use |
|----------------------------|--|--|
| 0.45 µm membrane filter | Natural organics must be dissolved to pass through | True vs Apparent Colour Reduction in DOC |
| 1.0 µm glass fibre filter | General Purpose Filter for Water Treatment Plants | Colour & TOC Reduction, Chlorine Demand Studies |
| 8.0 µm (Whatman 40) filter | Open filter that allows for broad comparisons | Direct Filtration Plants and comparison of Filter Aids |

Preliminary Test Protocol Compatibility Study

Once the test parameters are known, mixing intensity and duration for both the rapid mix and the flocculation mix, and the settling time have been calculated, a preliminary procedure can be written. At this time it is best to perform a compatibility study that compares the results from the jar test with the full scale application in the plant.

Aliquots of plant settled water and jar test water are collected and analyzed for the primary operational parameters of concern. Always analyze for turbidity, colour and pH, as well as any other tests deemed important. A simple bar chart should be drawn that compares the full scale plant results with the jar test results. A correlation of greater than 85% should be experienced on all parameters before the preliminary test protocol can be finalized. Should there be inconsistencies the items to review are velocity gradients and detention time calculations. Do not make the mistake of adjusting the jar test procedure based simply on differences between turbidity results in the jar and the plant. Figure 6 below shows an example of a typical compatibility graph. The selection of the filter can also be analyzed in a similar fashion.

Selection of Chemical Treatment Regime

The hard work has been done! By following the process outlined above, much of the frustration with jar tests has been eliminated.

- 1) The operation of the plant is well understood.
- 2) Coagulants have been pre-screened to select only those that will perform well.
- 3) Analytical requirements have been defined and prepared for.
- 4) Laboratory equipment has been selected.
- 5) A jar test protocol that gives meaningful results has been developed.
- 6) A filter protocol has been defined.
- 7) A compatibility study has shown that everything above is in order.

There are now only three questions remaining;

- 1) Which coagulant/flocculant combination provides the best results?
- 2) How much has to be added?
- 3) How much will it cost?

The first two questions can be answered relatively easily.

Selection of Coagulant

The first step is to select the coagulant of choice and make an estimation of the optimum dosage.

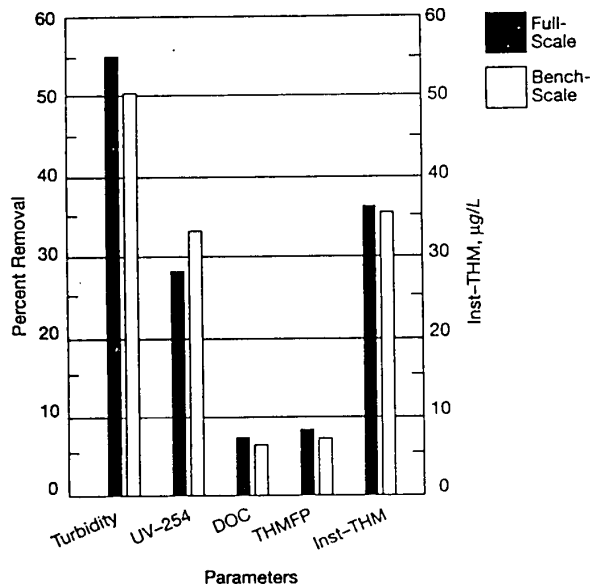


Figure 6
Preliminary Jar Test Protocol
Compatibility Study

The selection of a coagulant and its optimum dosage is made by a combination of observations and measurements. The objective is to generate a "pin-floc" that coagulates the hydrophobic mineral turbidity and the hydrophilic organic colour. The DOC loading is often the determining factor with respect to both coagulant choice and dosage [1] [6]. A good starting point is to consider 5 mgL⁻¹ of Al₂O₃ or 2 mgL⁻¹ of Fe³⁺ for every 1.0 mgL⁻¹ of DOC. pH depression should also be factored into the initial thoughts.

A suggested procedure is as follows:

- 1) Set the paddles to 10 rpm.
- 2) Add any oxidants as required.
- 3) Add the coagulant under consideration at the required dosage.
- 4) Add any pH adjustment chemicals as required.
- 5) Set the impeller speed to the required rpm for rapid mix and continue for the predetermined duration.
- 6) *Observe the performance of the coagulant to reduce colour during the flash mix stage.*
- 7) Set the impeller speed to the required rpm for flocculation and continue for the predetermined duration.

- 8) *Observe the formation of pin flocs, and record the time for development.*
- 9) *Continue to observe the flocs and record any developmental milestones.*
- 10) *Make a note if the flocs develop very quickly but fail to grow after the initial formation.*
- 11) *Look for the colour of the water between the flocs and record the observation.*
- 12) *Look for the presence of any floating materials in the jar.*
- 13) *Set the impeller speed to zero and remove from the jar. Begin the settling period.*
- 14) *Classify the flocs with respect to size.*
- 15) *Classify the flocs with respect to settling rate.*
- 16) *Observe and record if any flocs float to the surface.*
- 17) *Record if the temperature rises and causes a release of oxygen.*
- 18) *Observe and record if there are any flocs that "hang-up" in the centre of the jar.*
- 19) *After the predetermined time withdraw samples at 10 cm from the water line.*
- 20) *Perform all the required analytical tests on the samples.*
- 21) *Return to the jar and look for sign of continued "hang-up".*
- 22) *Slowly switch on the impeller and increase rpm until the sludge bed lifts, record rpm for each chemical regime.*
- 23) *Turn-off the impeller and observe the settling rate of the sludge bed.*

- 24) *If an analysis for a contact-time-dependent reaction, such as the formation of THMs, is required, it may be necessary to set aside the samples and let sit for the total detention time within the plant, most likely several hours. Under these circumstances several 500 ml beakers will be required.*
- 25) *Select the best coagulant at it's optimum dosage.*

Selection of a Flocculant

A flocculant may or may not be required. Once the coagulant and it's optimum dosage have been determined the same procedure outlined above can be followed to determine whether or not a flocculant shows some benefits.

Selection of Final Programme

Once the chemical treatment programme has been selected a final set of tests should be performed to determine the benefits of the flocculant. A series of eight tests should be performed as follows;

- 1) *Settled water from the plant.*
- 2) *Settled water from the jar without flocculant.*
- 3) *Settled water from the jar with flocculant.*
- 4) *Settled water from the jar using*

- | | |
|--|--|
| incumbent chemical treatment programme. | achieve the objectives. Having taken the time to prepare properly, the jar test can provide the following information; |
| 5) Filtered water from the plant. | 1) Which coagulants will work in the plant. |
| 6) Filtered water from the plant without flocculant. | 2) Which coagulants are unsuitable. |
| 7) Filtered water from the jar with flocculant. | 3) A ranking of the coagulant efficiencies. |
| 8) Filtered water from the jar using incumbent chemical treatment programme. | 4) An indication as to the order of magnitude for the required dosage to meet the treatment objectives. |
| At this stage you are ready to make you decision as to a chemical treatment programme. | 5) A reasonable expectation of anticipated results. |

The jar test is a very useful tool if the approach is correct. The key is to think about what your objectives are and develop a protocol that will allow you to

It should be emphasised, however, that there is only one jar test that really counts and that is in the large jar on the operating floor!

References

- 1] *Water Treatment Principles and Applications. A Manual for the Production of Drinking Water.* Canadian Water and Wastewater Association, 1993.
- 2] *Operational Control of Coagulation and Filtration Processes, M37.* American Water Works Association, 1992.
- 3] *Calculation of Chemical Dosages for Water and Wastewater Treatment.* Easy Treat Corporation, Calgary, Alberta. 1997.
- 4] Cornwall, D. A. and Bishop, M. M. *Determining Velocity Gradients in Laboratory and Full Scale Systems.* Jour. AWWA, 75:9:470-475. 1983.
- 5] Fair, G. M., Geyer, J. C. and Okun, D. A.. *Water and Wastewater Engineering.* John Wiley and Sons, New York, 1968.
- 6] Greville, A. S. and Nalezty, J. A. *Polyhydroxy Aluminum Chloride - The "Hi-Tech"*

Alberta Water & Wastewater Operators Association
22th Annual Seminar March 11- 14, 1997

Coagulant with a Future. Alberta Water and Wastewater Operators Association
Seminar Proceedings, 1994.

© Easy Treat Corporation
March 1997.