Coagulant Options

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Outline

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  - Coagulant types and characteristics
- Coagulant Options
  - Understanding the role of Coagulation
  - Optimizing existing treatment programs
  - Modifying coagulant treatment programs
    - Switching coagulants
    - Co-coagulant programs

Coagulation Overview

Coagulation Overview

- One objective of water treatment is to manage the removal of the water-borne <u>solids</u> whose presence makes the water unsuitable for its intended use.
- Many of these solids are too small to settle out on their own and are stabilized by surface charges that resist their agglomeration. These surface charges are generally negative.
- The purpose of inorganic coagulants is to destabilize solids and increase their size to facilitate their removal by settling and filtration processes.

Coagulation Overview

- Colloidal material (d < 10 μ) typically represents a significant fraction of the solids to be removed and can have a rather insignificant effect on turbidity.

- In many cases, a significant fraction of the TOC is colloidal.

- For many systems, the required coagulant dosage is controlled by the amount of charge required to neutralize the surface charges on the colloidal particles.

Characteristics of Inorganic Coagulants

- Have large positive valence (for charge neutralization). Coagulant efficiency significantly increases with its valence. (Schulze-Hardy Rule)

- Form insoluble precipitates in water (for adsorption and sedimentation).

- Are inexpensive.

- Aluminum and Ferric-based salts meet these criteria and are almost universally used.

Coagulant Mechanisms

- Coagulants initially work on an atomic "scale".
- Thus, the concentration of atomic units of M^{+3} delivered effects coagulant performance more than the weight of M^{+3} . (Useful to remember when comparing the performance of alum and ferric salts).
- It's also possible that some coagulants are more effective on an "equal molar" basis than others (that is, "simple coagulants" vs. "polymeric inorganic coagulants").

Coagulant Types

Aluminum-Based Inorganic Coagulants

- "Simple Coagulants": Bulk solution contains Al^{+3} $(H2O)_6$
  - ↗ Aluminum Sulfate (Alum)
  - ↗ Aluminum Chloride

- "Polymeric Coagulants": Bulk solution contains "polymeric Al species"
  - ↗ Polyaluminum Chlorides (PACls)
  - ↗ Polyaluminum sulfates
  - ↗ Polyaluminum silicate sulfates

Ferric-Based Inorganic Coagulants

- “Simple Coagulants”: Bulk solution contains Fe^{+3} $(H2O)_n$
  - ↗Ferric Chloride
  - ↗Ferric Sulfate
  - ↗Ferric Chloride/Sulfate blends

- “Polymeric Coagulants”: Bulk solution contains “polymeric Fe species”
  - ↗Poly-Ferric Sulfate

Characteristics of "Simple" Coagulants

- To a first approximation, simple coagulants tend to exhibit comparable performance when dosed on an "equal (molar) metals basis".

- Coagulant species are "simple" metal-hydroxy ions, e.g. $Al(OH)_2^+$

- Since speciation is pH-dependent, optimal performance is generally pH-dependent. The optimal pHs for TOC removal are generally considered to be:
  - ↗ For simple Al salts: 6.4 – 7.0
  - ↗ For simple Fe^{+3} salts: < 6.0

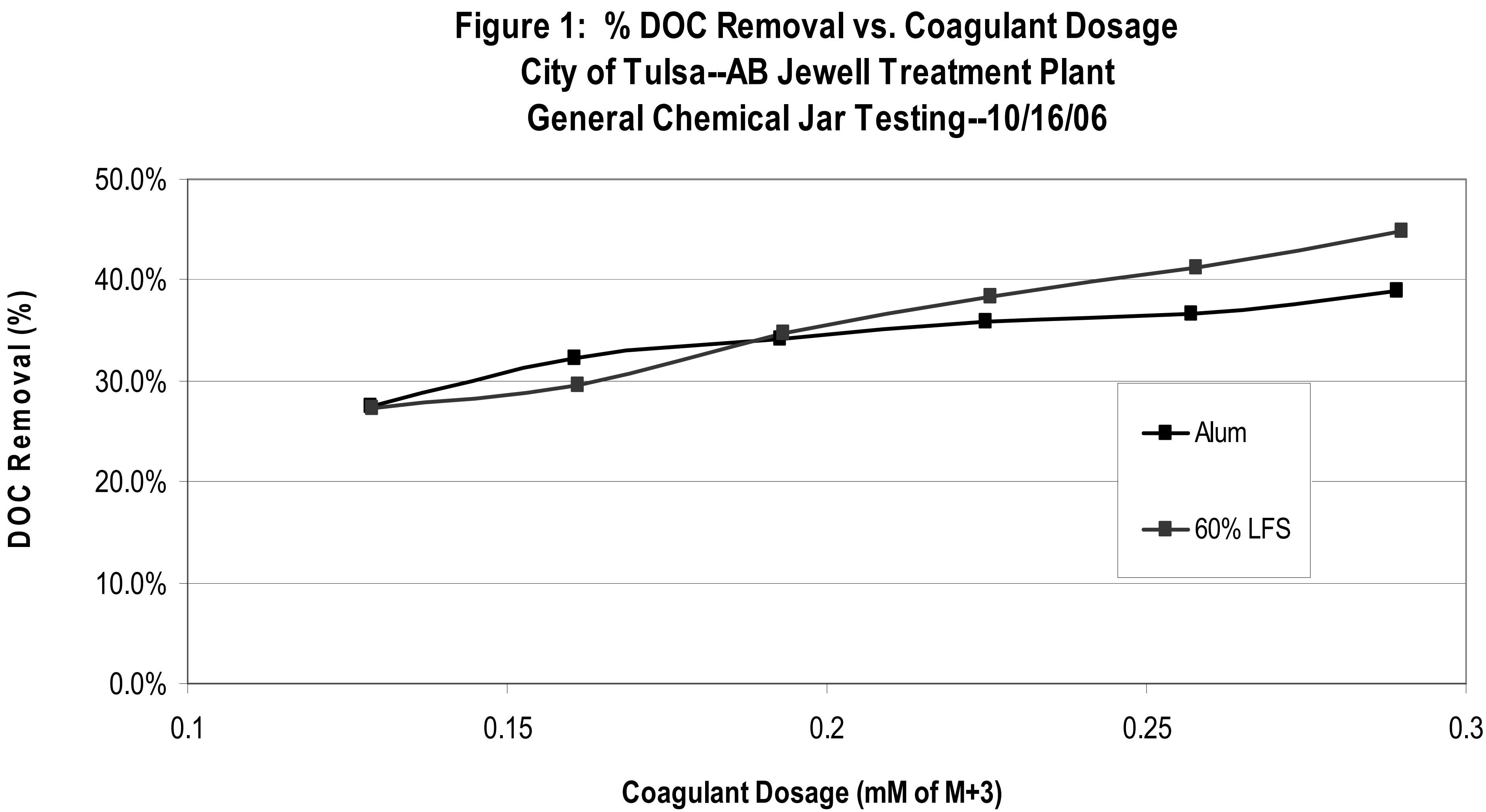
- Hydrolysis reaction: $\mathbf{M^{+3} + 3\ H_2O \Rightarrow M(OH)_3 + 3\ H^+}$

  Note: 1 mole of metal releases 3 moles of acid. This correlates with the post-treatment alkali requirement.

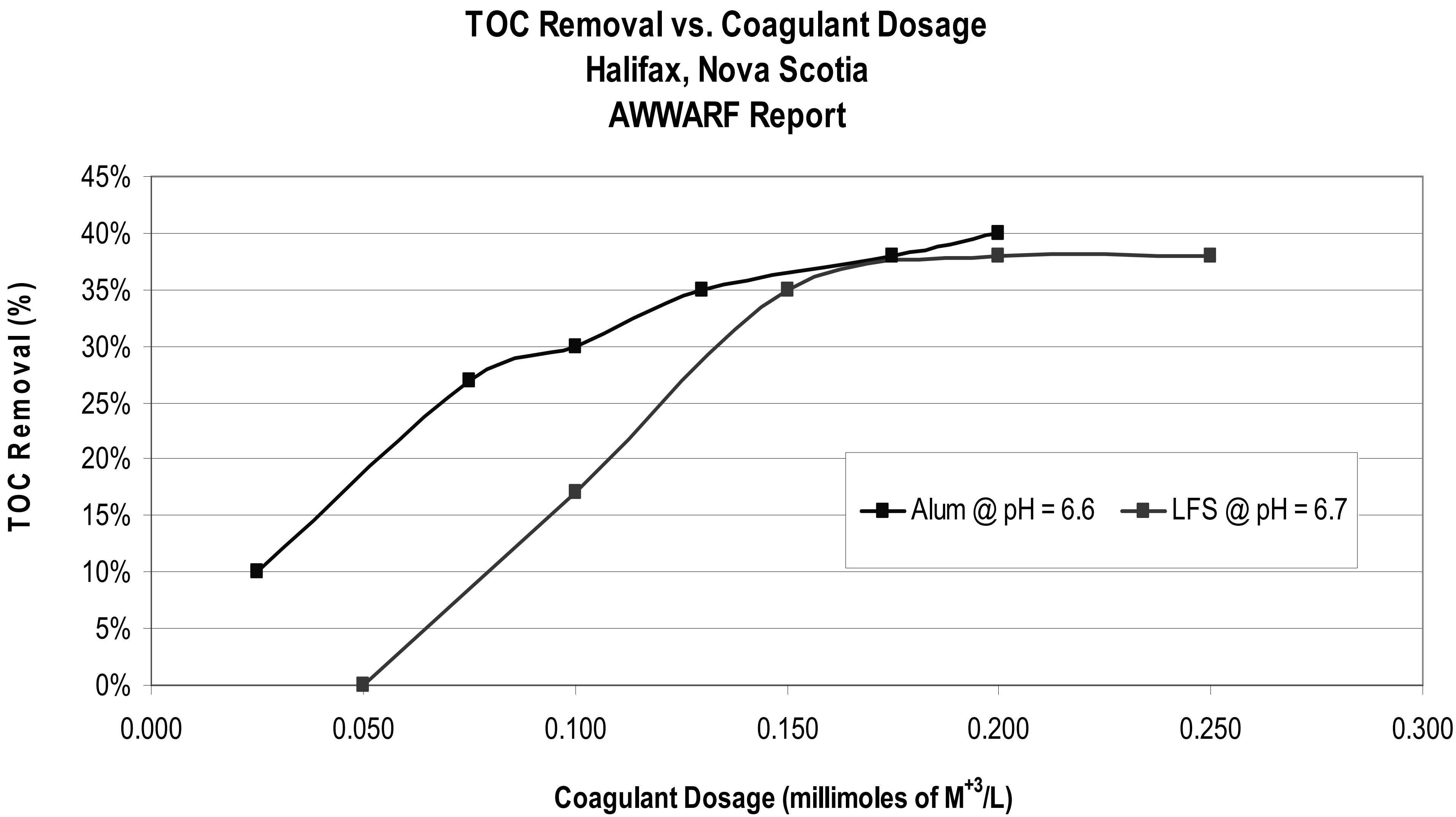
Alum - Ferric Dosage Conversions

Product	% Metal	Specific Gravity	Equal Metals Molar Dosage ppm (liquid basis)
39 % Ferric Chloride	13.4	1.418	67
“60 %” Ferric Sulfate	12.0	1.580	75
“50 %” Ferric Sulfate	10.0	1.435	90
Liquid Alum	4.34	1.335	100 (48.5 DB)

TOC Removal Data



TOC Removal Data (2)



Polyaluminum Coagulants

- "Polyaluminum" coagulants are Al-based products having OH groups incorporated into their structure.
- Types of polyaluminum coagulants include the following empirical formulas:

$Al_2(OH)_{6-x}Cl_x$	**Polyaluminum Chloride** = PACl
$Al_2(SO_4)_z(OH)_{(6-(x+2z))}Cl_x$	**Polyaluminum Chlorosulfate = PACS**
$Al_2(OH)_{(6-2z)}(SO_4)_z$	**Polyaluminum Sulfate** = PAS
$Al_2(OH)_{(6-2(z+w))}(SiO_x)_w(SO_4)_z$	**Polyaluminum Silicate Sulfate =** PASS

Polyaluminum Coagulants

- "Polyaluminum" coagulants can be considered to be partially "pre-hydrolyzed". The degree of "pre-hydrolysis" varies with the product, and is defined as the product's Basicity:

% Basicity = 100% x $[OH^-]$ / {3 x $[Al^{+3}]$ }

where

the species concentrations are in mole/liters

- The basicity represents the percentage of the product's Al valence that is associated with OH groups.

- Thus, each polyaluminum coagulant type represents a unique "family" of coagulants, with each family member having a different basicity (and treating characteristics).

Polyaluminum Coagulants

$$\text{Basicity (\%)} = \frac{[OH^-]}{3[Al^{+3}]} \times 100$$

- Low Basicity = 10 - 33 %
- Middle Basicity = 34 - 67 %
- High Basicity = 68 - 83 %

Polyaluminum Chlorides

- Basicities can range from 10 - 83%
- Al content can increase with increasing Basicity (the basicity stabilizes the product).
- The amount of polymeric species increases with increasing basicity.
- Products having Basicities > 70% contain polymeric species possessing high cationic charge and are very efficient coagulants. These products are called aluminum chlorohydrates (ACHs).

Polymeric Aluminum Species

- Polymeric species include:
  - $Al_2(OH)_2(H2O)_8^{+4}$
  - $Al_6(OH)_{12}(H2O)_{12}^{+6}$
  - $AlO_4Al_{12}(OH)_{24}(H2O)_{12}^{+7}$

  Due to their higher valence, these species are much more effective coagulants than +3 valence species.

- The proportion of high valence species increases with increasing Basicity.

Characteristics of “Polymeric” Coagulants

- Generally contain “inorganic polymeric” species that are more efficient than “simple metal-hydroxy” species.

- Effect of increasing basicity:
  - ↗ Coagulant performance becomes less pH-dependent.
  - ↗ Coagulant’s alkalinity consumption decreases (i.e. less pH suppression). In turn, this means less post-treatment alkali demand. For example, consider the h**ydrolysis reaction of an ACH having a basicity of 83%:**

$$\mathbf{Al_2(OH)_5^{+1} + 1\ H_2O \Rightarrow 2\ Al(OH)_3 + 1\ H^+}$$

Note: 2 moles of metal ions releases 1 mole of acid. Thus, using these products significantly reduces the post-treatment alkali requirement.

Characteristics of Simple vs. Polymer Coagulants

- Alkalinity consumption:

  ACH ≈ PASS < PACl < PAS < Alum ≈ LFS < $FeCl_3$

- Coagulant (Dosage) Efficiency:

  ACH > PACl ≥ PAS = PASS > Alum = LFS = $FeCl_3$

- Ease of Use: Alum = LFS = $FeCl_3$ > PAS = PASS > PACL > ACH (Based on "width of dosage treatment window").

- Unit Pricing: ACH > PACl > PASS > PAS > Alum ≈ LFS ≈ $FeCl_3$

Note: Alkalinity consumption, coagulant efficiency, and unit pricing comparisons are on a "molar basis".

Characteristics of Al vs. Fe-based Coagulants

- Filtration characteristics
  - For alum, filter runlengths are generally limited by turbidity breakthrough.
  - For Fe^{+3} salts, filter runlengths are generally limited by headloss. Inadequate filtration can cause colored water issues.
- Ferric salts are more shear-resistant than alum.
- $FeCl_3$ is significantly more corrosive than alum or LFS.
- Sludge issues
  - Alum will invariably generate fewer pounds of chemical sludge than Fe^{+3} salts.
  - Fe^{+3} salts generated-sludge may dewater more easily than Al-generated sludge.

Organic Coagulants

- DADMAC
- EPI / DMA
- Polymer-Inorganic Coagulant Blends
  - **2 % by weight to 50 % by weight**
  - Blends are more likely to be made with alum and PACLs.
- Generally speaking, polymer type is more important than polymer MW—that is, some waters are more “responsive” to one polymer type that the other.

Settling Aids

- High molecular weight polymers
  - Dry
  - Emulsion
  - Either type requires a properly designed addition system to function properly. Emulsions are typically easier to use.

- Characterized by MW and charge (anionic vs. non-ionic). Performance may be controlled by MW more than charge.

- Typically used at dosages of 0.03 – 0.3 mg/l “active basis”. Dosage is limited to avoid possible filter issues.

Drinking Water Application Matrix

	Alum	Alum/Polymer	Acid Alums	Acid Alum/Polymer	PAS	PASS	PACS	PACL	PACL/Polymer	ACH	ACH/Polymer	LFS	LFS/Polymer	Acid Ferrics
TOC/DBP Reduction	X		X	X								X		X
Cold Water Performance					X	X	X	X	X	X	X			
Low Turbidity Raw Water							X		X		X			
Reduced NaOH Consumption		X				X	X	X	X	X	X			
Sludge Reduction		X						X	X	X	X			
Low Alklalinty Raw Water								X	X	X	X			
Turbidity Reduction		X		X				X	X	X	X	X	X	
Ease of Use	X	X										X	X	
Variable Raw Water Quality	X	X										X	X	
High pH Raw Water										X	X	X	X	
Lime Softening												X		
Arsenic Removal	X							X		X		X		

Coagulant Options

Factors Motivating Interest in Different Treatment Programs

- Implementation of the Stage 2 DBP Rule
- Cost of treatment chemicals
- Filtration Issues
  - Increased focus on filtered water quality
  - Partnership for Safe Drinking Water
  - Particle counting
- Population growth and water shortages
- Sludge disposal issues
- Corrosion by-product issues (lead and copper)

Best Coagulant Program

- The "best" coagulant program is that which robustly achieves all critical treatment objectives at the minimum overall treatment cost.

- The "best" program depends on the following factors:
  - ↗ Specific raw water quality
  - ↗ Plant design
  - ↗ Specific logisitical issues (e.g. sludge disposal, etc).

Thus, identifying the "best" program needs to be done on a "case-by-case" basis.

Understanding the Role of Coagulants

- Coagulants are meant to work in conjunction with good plant design. There is a limit to the extent that coagulants can overcome poor plant design.

- TOC/DBP Rule Compliance
  - ↗ The USEPA envisioned that complying with TOC/DBP Rules would be achieved by the combined action of improved coagulation and disinfection practices.

  - ↗ Singer has demonstrated that, in general, the most readily-removed TOC species are also the ones that generate the most DBPs. Thus, after complying with the TOC rule, modifying disinfectant practices will generally be more effective in further reducing DBP formation than will achieving additional TOC removal.

Optimizing Existing Programs

- Since colloidal charge and TOC content significantly impact coagulant dosage, there is an opportunity to optimize coagulant usage by the improved monitoring of these two parameters.

- Optimization techniques based on this concept include:
  - Online streaming current and zeta potential instruments
  - Online TOC and UV-254 instruments
  - Closed-loop coagulant dosage control based on statistical correlation of historical plant performance data coupled with real-time analytical results of relevant parameters.

Optimizing Existing Programs

- Optimize coagulant performance by pH adjustment. For TOC removal:
  - ↗ For simple Al salts: 6.5 – 7.0
  - ↗ For simple Fe^{+3} salts: < 6.0.

  Methods of pH adjustment:
  - ↗ Acid addition
  - ↗ Lime or NaOH addition
  - ↗ Use of acidified coagulants

Options for Changing Coagulant Treatments

- A total year-round conversion to a different coagulant
  - Likely returns the greatest reward
  - Likely involves the most risk
  - Requires the most time and effort to implement
- A seasonal switch to a different coagulant
  - Relatively easy to accomplish
  - Less risk and less effort
  - Less reward

Options for Changing Coagulant Treatments

- A co-coagulant conversion
  - Returns less reward than a complete switch
  - Is least risky option
  - Requires more storage capabilities
  - Can be a transition to a total switch
  - Can involve either inorganic and/or organic products
    - LFS + ACH/polymer blend
    - Alum + ACH + anionic settling aid
    - Alum + polyDADMAC

Changing Treatment Programs

- Identify and prioritize treatment goals. Quantify required levels of improvement. If vendors are involved, clearly communicate this info to them.

- **Establish an acceptable treatment balance**.

- Use the Drinking Water Application Matrix as a guide for selecting candidate products.

Changing Primary Coagulants

- Jar testing: Probably the initial stage of coagulant screening
  - ↗ Insure that test procedure is consistent with the guidelines presented in AWWA Manual M37: "Operational Control of Coagulation and Filtration Processes".
  - ↗ Testing doesn't need to include all treatment chemicals. Chemicals such as PAC and $KMnO_4$ generally effect the performance of all coagulants to the same extent.
  - ↗ Initially perform "screening" tests to identify candidates capable of complying with "regulatory issues" (e.g. TOC removal).
  - ↗ Minor settling issues can often be resolving by adding organic polymers (either co-coagulants or settling aids).
  - ↗ Review results quantitatively.

Changing Primary Coagulants

- Pilot testing:
  - Has marginal value over jar testing if the pilot unit is not "scaled" consistently with the plant.
  - An important advantage of a pilot unit is the ability of determining the filtration performance associated with alternate treatments (assuming that the pilot unit has filters).
  - If the unit has filters, the test duration should be long enough to determine the steady-state consequence of the treatment change (for example, the steady-state filter runlength).

Summary

- Successfully improving the performance of treatment programs involves:
  - ↗ Understanding the limitations of coagulants.
  - ↗ Prioritizing the treatment goals to be improved.
  - ↗ Matching candidate coagulants with the critical treatment goals.
  - ↗ Utilizing a systematic and disciplined approach to evaluate the various options available.

- Improving coagulant performance doesn’t necessarily mean changing primary coagulants. Other options include:
  - ↗ Optimizing the performance of the existing coagulant
  - ↗ Co-coagulant programs
  - ↗ Season-specific programs.

QUESTIONS??