Coagulant Overview

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Outline

- Coagulation Overview
  - Purpose of Coagulation
  - 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

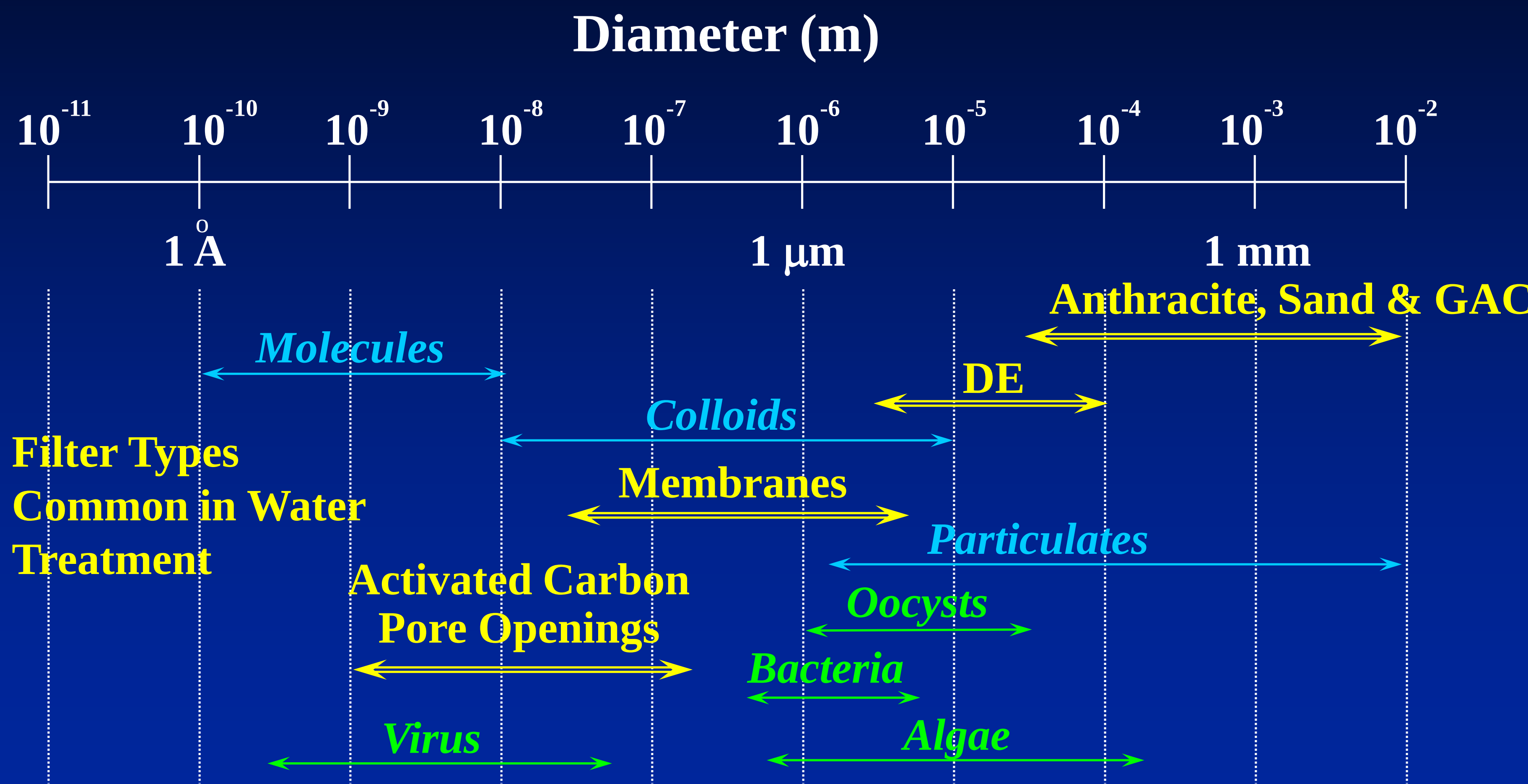
- One objective of water treatment is to manage the removal of the water-borne solids whose presence makes the water unsuitable for its intended use.

- 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.

- Removing solids by coagulation and filtration significantly reduces the disinfectant demand. In turn, this reduces the formation of DBPs.

Sizes of Solids Involved in Water Treatment



Coagulation Overview

- As the graph demonstrates, in the absence of coagulation, many solids are too small to be directly removed by filtration.
- Colloidal material (d < 10 μ) typically represents a significant fraction of the solids to be removed and can have a rather insignificant effect on raw turbidities.
- 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.

Coagulation Demand

- "Approximate" coagulant demand for low turbidity raw waters:
  - 0.61 mg of Al^{+3}/mg of raw water DOC
  - 1.26 mg of Fe^{+3}/mg of raw water DOC
  - This translates to:
    - 6.8 ppm of alum (db)/ppm of raw water TOC
    - 5.0 ppm of ACH (neat basis)/ppm of raw water TOC
    - 12.6 ppm of 50% LFS (neat basis)/ppm of raw water TOC
    - 9.3 ppm of $FeCl_3$ (neat basis)/ppm of raw water TOC

Coagulant Demand--Example

	May 30, 2007	July 2, 2007
Raw Water Turbidity	45 NTU	48 NTU
Raw Water pH	7.7	7.65
Raw Water Alkalinity	95 ppm	100 ppm
Coagulant Dosage	40 ppm	60 ppm

Coagulant Demand--Example

	May 30, 2007	July 2, 2007
Raw Water Turbidity	45 NTU	48 NTU
Raw Water pH	7.7	7.65
Raw Water Alkalinity	95 ppm	100 ppm
Coagulant Dosage	40 ppm	60 ppm
UV-254 Absorbance	**0.40**	**0.60**

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.

Cation Comparison

Valence is the charge on an ion in solution.

Cation	Valence	Coagulation Efficiency	Floc Formation	Unit Cost
Na^{+1}	+1	Poor	Extremely Poor	Moderate
Ca^{+2}	+2	Fair	Poor	Moderate
Al^{+3}	+3	Very Good	Very Good	Low
Fe^{+3}	+3	Very Good	Very Good	Low
Zr^{+4}	+4	Excellent	Very Good	Very High

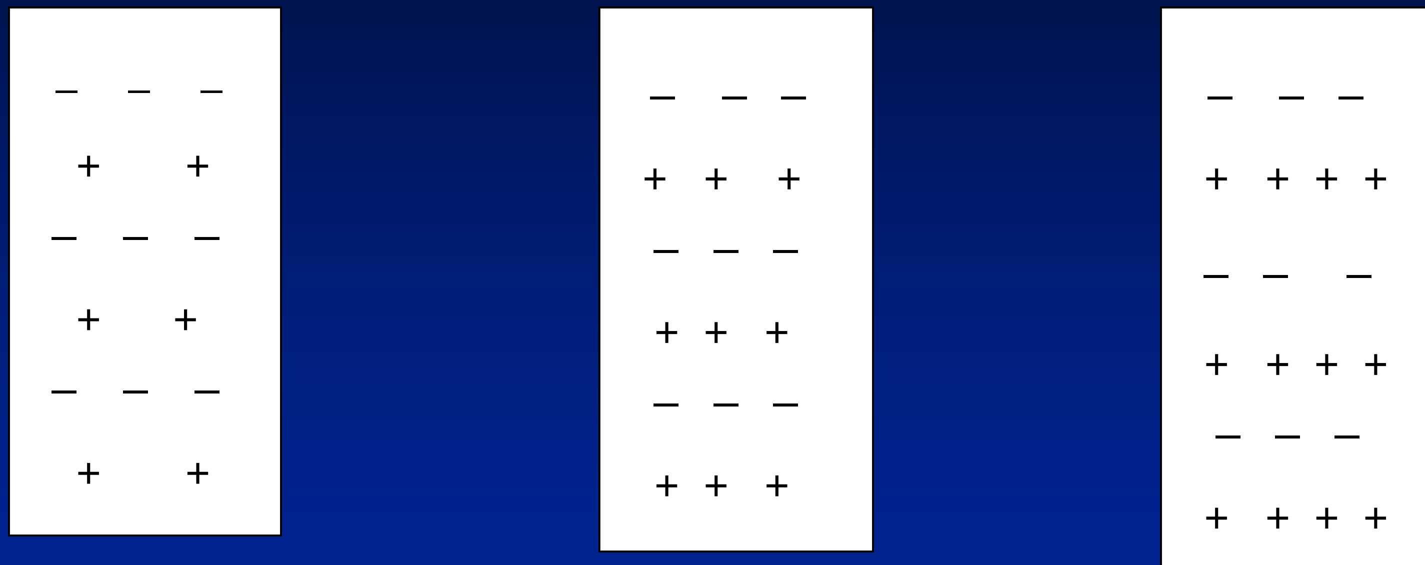
Coagulant Mechanisms

- Step 1: Charge neutralization significantly reduces the electrical charge repulsion between particles, allowing them to come together.
- Step 2: Metal hydrolysis forms floc particles.
- Step 3: Adsorption of neutralized particles onto floc particles.
- Step 4: Particles grow larger due to flocculation
- Step 5: Particles settle. Small particles are adsorbed onto settling particles (“floc sweep”).

Coagulant Mechanisms

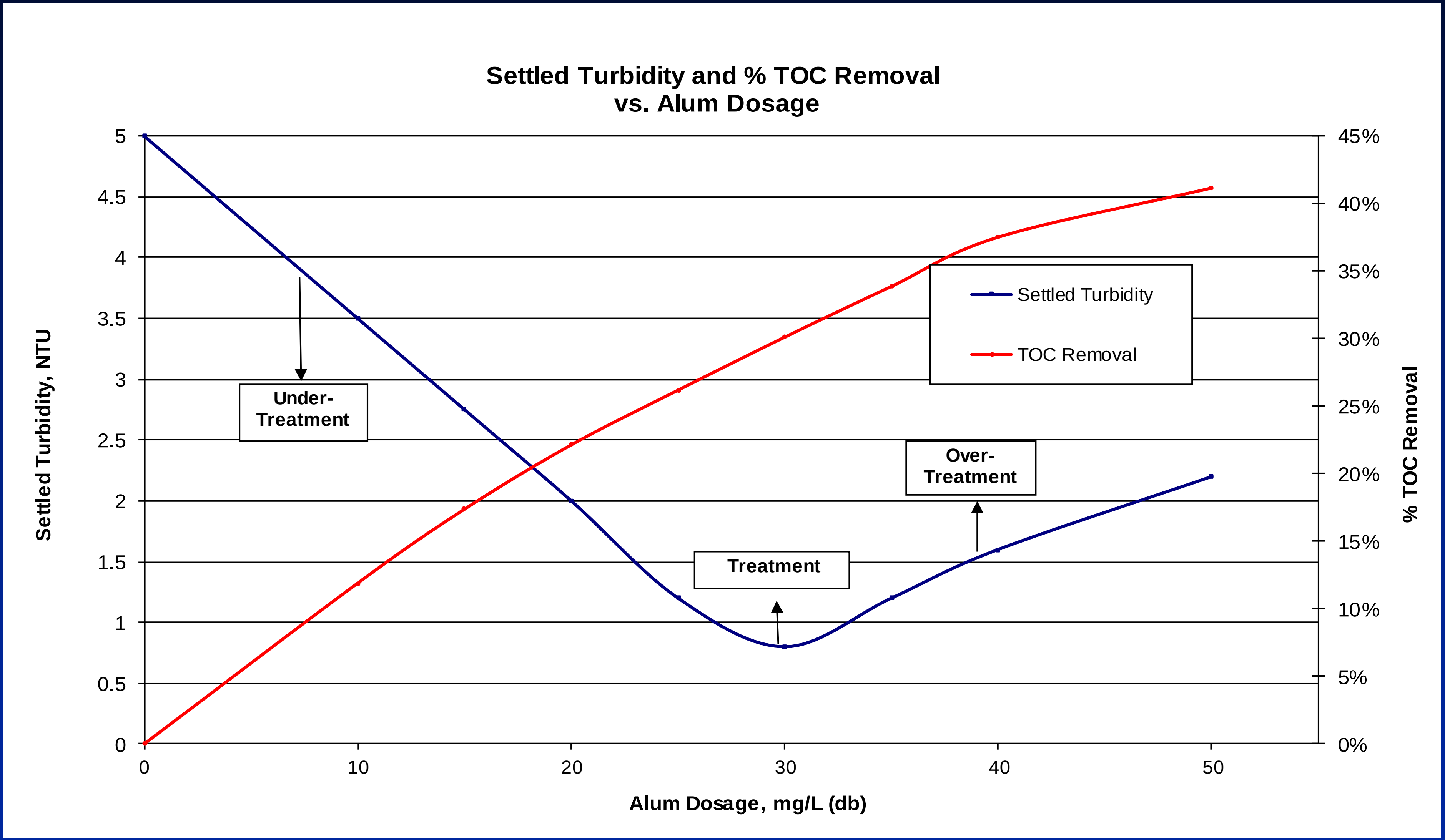
- Charge neutralization occurs on an atomic “scale”. Thus, in the early stages of treatment, the number of charges delivered by the coagulant is more important than the weight of the metal.
- The number of metal atoms delivered by the coagulant also affects the number of floc particles created.
- Thus, the concentration of atomic units of M^{+3} delivered affects 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”).

Charge Neutralization



Under-Treatment Treatment Over-Treatment

Performance vs. Alum Dosage



Most Commonly-Used Inorganic Coagulants

- "Simple Coagulants": Bulk solution contains only "hydrated" metal ions
  - Aluminum Sulfate (Alum)
  - Ferric Sulfate (LFS)
  - Ferric Chloride
- "Polymeric Coagulants": Bulk solution contains "polymeric Al species"
  - Polyaluminum Chlorides (PACls and ACH)

Equal Metal Dosage Conversions

Product	% Metal	Specific Gravity	Equal Metals Molar Dosage ppm (liquid basis)
39% Ferric Chloride	13.4	1.418	67 (27 db)
60% Ferric Sulfate	12.0	1.580	75 (45 db)
50% Ferric Sulfate	10.0	1.435	90 (45 db)
Liquid Alum	4.34	1.335	100 (48.5 db)
ACH	12.17	1.34	36
PACS	5.71	1.24	76

Metal Equivalent Dosages

- 100 mg/L ("liquid" basis) of liquid alum
  - 100 mg/L x (0.0434 mg of Al/mg of alum) x (1 mmole of Al/27 mg of Al) = **0.1607 mmole/L of Al**

- 50% LFS
  - **0.1607** mmole/L of Fe x (55.8 mg of Fe/mmole of Fe) x (1 mg of 50% LFS/0.1 mg of Fe) = **89.7 mg/l of 50% LFS** ("liquid" basis).

Organic Coagulants

- DADMAC
- EPI / DMA
- Polymer-Inorganic Coagulant Blends
  - 2 % by weight to 50 % by weight
- 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.

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

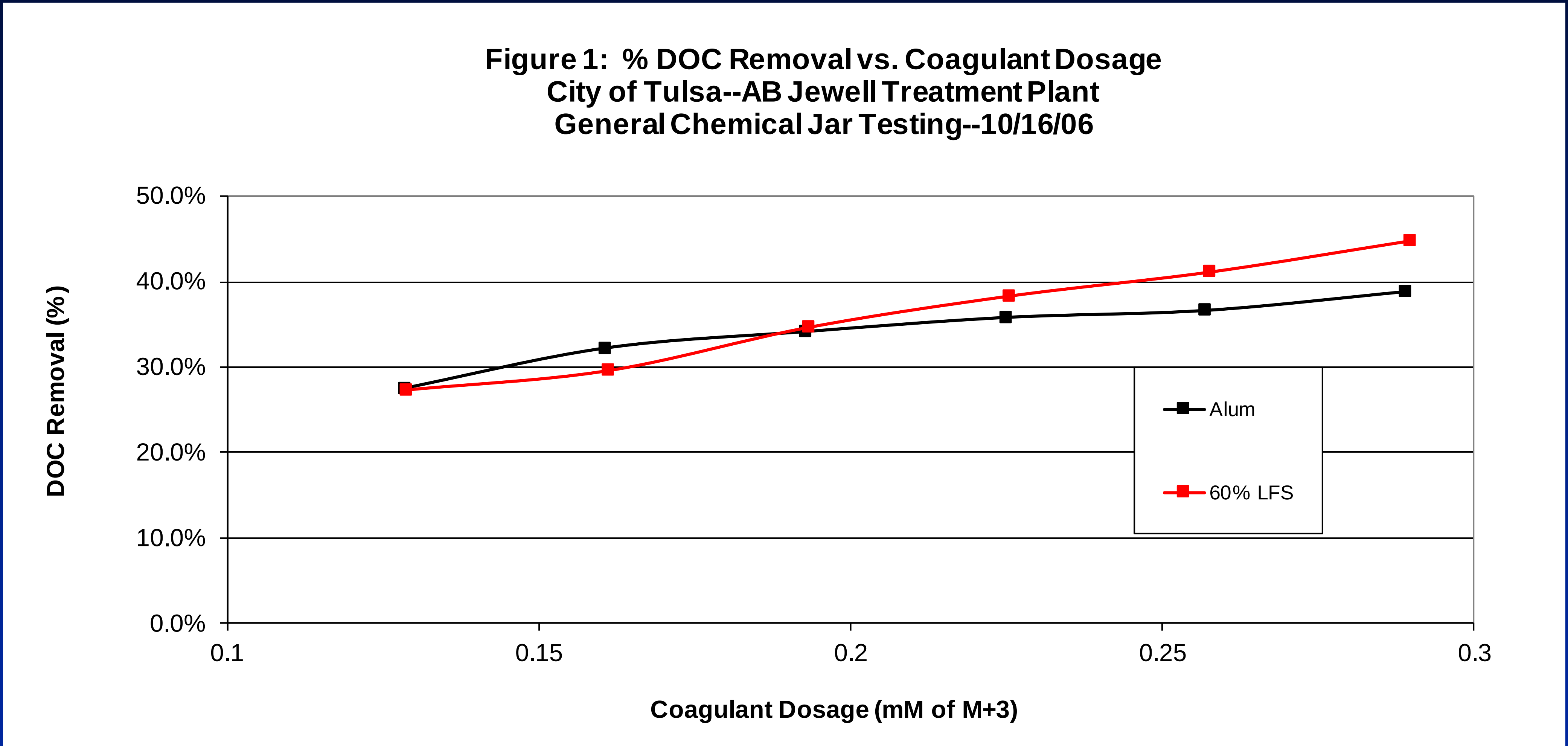
- Hydrolysis reaction: **$M^{+3} + 3\,H_2O \Rightarrow M(OH)_3 + 3\,H^+$**

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

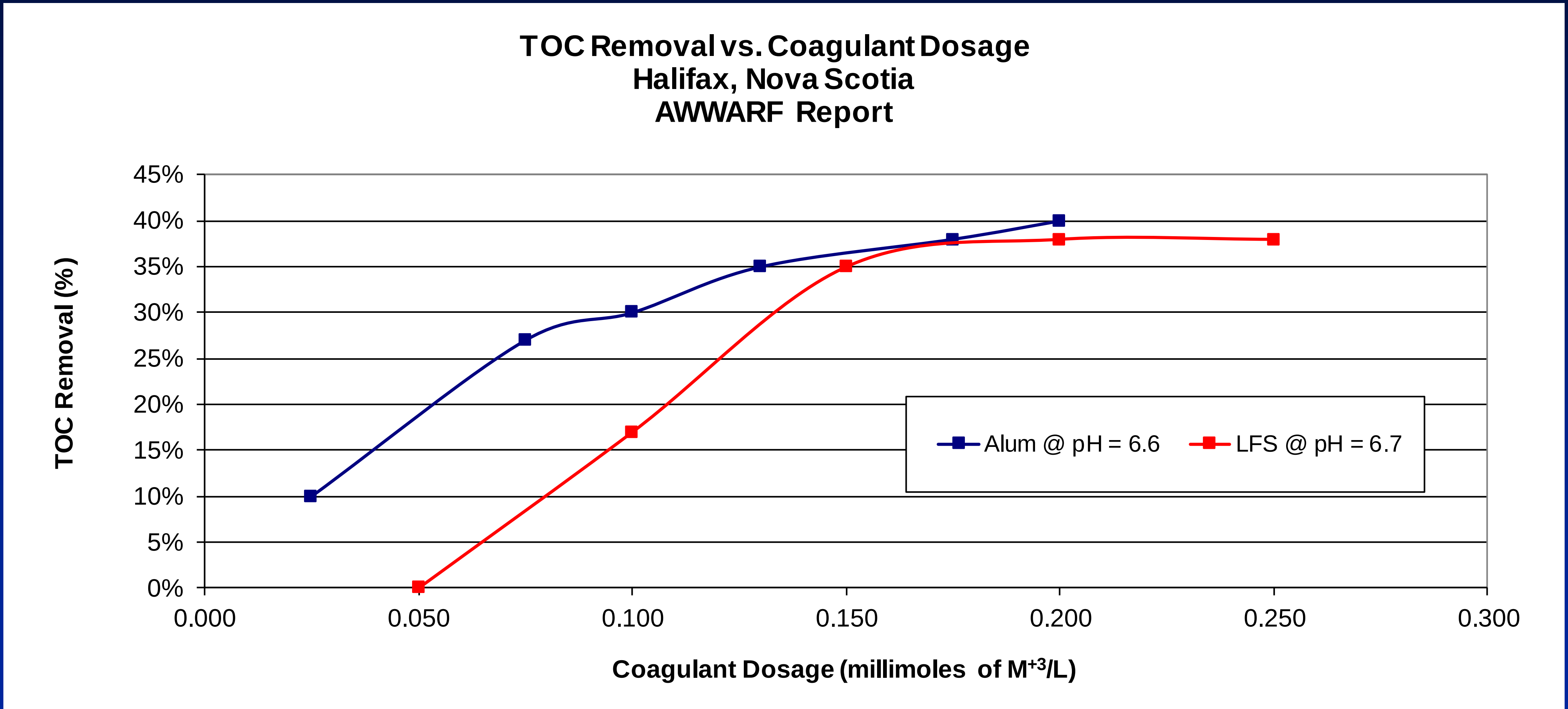
Alum - Ferric Dosage Conversions

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 **hydrolysis reaction of an ACH having a basicity of 83%:**

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

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.

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		

QUESTIONS??