Determining an Effective Coagulant Dosage

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The material in this talk is from:


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The focus of this talk:

- A method* for:
  - selecting the coagulant type
  - estimating the coagulant dosage
  - estimating acid or base requirements, if any

- Hydrolyzing metal salt coagulants
- Removal of NOM (natural organic material)

*Evaluating design alternatives and estimating treatment costs
The method uses:

- The “effective acid content” of hydrolyzing metal salt (HMS) coagulants.
- An understanding of the effect of pH on the solubility of the metal hydroxide precipitate [Al(OH)$_3$ and Fe(OH)$_3$].
- A simple relationship between the initial NOM concentration (TOC) and the HMS dosage.
- Equilibrium chemistry calculations that relate alkalinity – pH – total inorganic carbon conc.
Effective Acid Content of Hydrolyzing Metal Salt Coagulants
Hydrolysis of Al (and Fe)

Aluminum ion $\leftrightarrow$ Aluminum hydrolysis product $\leftrightarrow$ Hydrogen ion

$$\text{Al}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Al}^{2+} + 2\text{H}_3\text{O}^+$$

Bicarbonate ion $\leftrightarrow$ Carbon dioxide $\leftrightarrow$ Hydrogen ion

$$2\text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{H}_2\text{CO}_3 (\text{CO}_2 + \text{H}_2\text{O}) + \text{H}^+$$

Alkalinity and pH decrease
Hydrolysis of Al (and Fe)

\[
\begin{align*}
&\text{Al}(\text{H}_2\text{O})^{3+}_6 \quad \text{aquo aluminum ion} \\
&\text{Al}(\text{OH})(\text{H}_2\text{O})^{2+}_5 \quad \text{mononuclear species} \\
&\text{Al}_{13}\text{O}_4(\text{OH})^{7+}_{24} \quad \text{polynuclear species} \\
&\text{Al(OH)}_3(s) \quad \text{aluminum hydroxide precipitate} \\
&\text{Al(OH)}_4^- \quad \text{aluminate ion species}
\end{align*}
\]

Low pH

High pH
Calculating the Effective Acid Content

Prehydrolyzed product solutions

Effective acid content (meq/mg metal) = \( \frac{300 - 3B}{100(\text{AW})} \)

B = basicity of the product (0 to < 83%)

A W = atomic weight of the metal (Al, AW = 27 g and Fe, AW = 55.9 g)
Calculating the Effective Acid Content

Acidified (acid supplemented) product solutions

Effective acid content (meq/mg metal) = \frac{300}{100(AW)} + \frac{A}{EW(M)}

A = weight percent of pure acid (H$_2$SO$_4$ or HCl)

EW = equivalent weight of the acid (H$_2$SO$_4$, EW = 49 g/eq and HCl, EW = 36.5 g/eq)

AW = atomic weight of the metal (Al, AW = 27 g and Fe, AW = 55.9 g)

M = metal content (weight % Al or Fe) of the coagulant product solution
Example calculation of the effective acid content using numbers from product data sheets
Product Data Sheet Example

Product A

CHARACTERISTICS
Liquid Alum is a clear, light green or yellow to colorless solution. It is a cationic inorganic coagulant and flocculant suitable for industrial and municipal water and wastewater treatment applications.

NSF/ANSI Standard 60: Drinking Water Chemicals - Health Effects; Certified

TYPICAL PROPERTIES
Formula: Aqueous solution of aluminum sulfate
C.A.S. 10043-01-3 (Aluminum sulfate)
pH (neat) 2.0 - 2.4
Specific Gravity @ 70°F (21°C) 1.335
Freezing Point 4°F (-16°C)
Density, lbs/gal., U.S. 11.14
Aluminum as Al, % 4.2 - 4.4
Aluminum as Al₂O₃, % 8.0 - 8.4
Aluminum as Al₂(SO₄)₃•14H₂O (Dry Alum), % 46 - 49
Effective acid content = \( \frac{300 - 3B}{100(AW)} = \frac{300 - 3(0)}{100(27)} = 0.111 \text{ meq/mg Al} \)
Product B

CHARACTERISTICS
Hyper+Ion® 4030 is a colorless to amber colored liquid. It is an advanced cationic coagulant and flocculant suitable for industrial and municipal water and wastewater treatment applications.

TYPICAL PROPERTIES
- Formula: Polyaluminum hydroxychloride solution
- C.A.S.: 1327-41-9 (Polyaluminum hydroxychloride)
- pH (neat): 2.1 - 3.1
- Specific Gravity @ 70°F (21°C): 1.16 - 1.19
- Freezing Point (approx.): 25°F (-4°C)
- Density, lbs/gal., U.S.: 9.7 - 9.9
- Aluminum as Al, %: 6.2 - 6.5
- Aluminum as Al₂O₃, %: 11.7 - 12.3
- Basicity, %: 70 - 75
Product B – Example Calculation

\[ \text{Effective acid content} = \frac{300 - 3B}{100(AW)} = \frac{300 - 3(75)}{100(27)} = 0.028 \text{ meq/mg Al} \]

Prehydrolyzed Al product with B = 75%
**Product C**

**Liquid Alum, Acidized 10%**

**PRODUCT DATA SHEET**

**CHARACTERISTICS**
Liquid Alum, Acidized 10% is a colorless to light green colored liquid. It is an advanced cationic coagulant and flocculant suitable for industrial and municipal water and wastewater treatment applications.

**TYPICAL PROPERTIES**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula:</td>
<td>Aqueous solution of aluminum sulfate and sulfuric acid</td>
</tr>
<tr>
<td>C.A.S.</td>
<td>10043-01-3 / 7664-93-9 (Aluminum sulfate / Sulfuric acid)</td>
</tr>
<tr>
<td>pH (neat)</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Specific Gravity @ 70°F (21°C)</td>
<td>1.26 - 1.28</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>Less than 0°F (-18°C)</td>
</tr>
<tr>
<td>Density, lbs/gal., U.S.</td>
<td>10.5 - 10.7</td>
</tr>
<tr>
<td>Aluminum as Al, %</td>
<td>2.8 - 2.9</td>
</tr>
<tr>
<td>Aluminum as Al₂O₃, %</td>
<td>5.2 - 5.4</td>
</tr>
<tr>
<td>Free Acid, % as H₂SO₄</td>
<td>10</td>
</tr>
</tbody>
</table>

**=M**

**=A**
Product C – Example Calculation

Effective acid content = \frac{300}{100(AW)} + \frac{A}{EW(M)} = \frac{300}{100(27)} + \frac{10}{49(2.9)} = 0.181 \text{ meq/mg Al}

Alum with 10\% \text{ H}_2\text{SO}_4
Effective Acid Content - Examples

<table>
<thead>
<tr>
<th>Coagulant Solution</th>
<th>Basicity (B, %)</th>
<th>A, weight % pure acid</th>
<th>M, weight % metal</th>
<th>Calculated Effective Acid Content (meq/mg metal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Sulfate (Alum)</td>
<td>0</td>
<td>0</td>
<td>4.3 (Al)</td>
<td>0.111</td>
</tr>
<tr>
<td>Polyaluminum Chloride (PACl)</td>
<td>80</td>
<td>0</td>
<td>12.3 (Al)</td>
<td>0.022</td>
</tr>
<tr>
<td>Acid Supplemented Alum (Acidized Alum)</td>
<td>0</td>
<td>10 (H₂SO₄)</td>
<td>2.8 (Al)</td>
<td>0.184</td>
</tr>
<tr>
<td>Ferric Sulfate (with 2% excess acid)</td>
<td>0</td>
<td>2 (H₂SO₄)</td>
<td>10 (Fe)</td>
<td>0.058</td>
</tr>
</tbody>
</table>

The effective acid content can also be measured by titration with strong base.
Effective Acid Content

Raw water - pH = 7.3, alkalinity = 38.5 mg/L as CaCO₃ (0.77 meq/L)
Coagulant Product Solutions Used in the Titrations Plotted in the Graph

<table>
<thead>
<tr>
<th>Coagulant Product Solution</th>
<th>Label in Figures</th>
<th>Effective Acid Content (EAC, meq/mg M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid supplemented alum with A =10%</td>
<td>Alum (A=10%)</td>
<td>0.168</td>
</tr>
<tr>
<td>Acid supplemented alum with A = 5%</td>
<td>Alum (A=5%)</td>
<td>0.135</td>
</tr>
<tr>
<td>Conventional Alum (A = 0 and B = 0%)</td>
<td>Alum</td>
<td>0.111</td>
</tr>
<tr>
<td>Polyaluminum chloride with B = 10%</td>
<td>PACI (B=10%)</td>
<td>0.100</td>
</tr>
<tr>
<td>Polyaluminum chloride with B = 50%</td>
<td>PACI (B=50%)</td>
<td>0.056</td>
</tr>
<tr>
<td>Ferric Chloride</td>
<td>Ferric Chloride</td>
<td>0.054</td>
</tr>
<tr>
<td>Ferric Sulfate</td>
<td>Ferric Sulfate</td>
<td>0.054</td>
</tr>
<tr>
<td>Polyaluminum chloride with B = 75%</td>
<td>PACI (B=75%)</td>
<td>0.028</td>
</tr>
</tbody>
</table>
Effective Acid Content

Raw water - pH = 7.3, alkalinity = 38.5 mg/L as CaCO₃ (0.77 meq/L)

meq/L = mg/L x effective acid content
Solubility of the Metal Hydroxide Precipitate

Minimize Residual Aluminum

Establish a Target pH for the Coagulation Process
Aluminum Hydroxide Solubility Diagram

Temperature = 25°C
Ferric Hydroxide Solubility Diagram

Temperature = 25 °C

log[Fe(III)] vs pH diagram showing:
- Fe(OH)$_3$ precipitate
- Fe$^{3+}$
- Fe(OH)$_2^+$
- Fe(OH)$_4^-$
pH of Minimum Al(OH)_3 Solubility

Graph showing the relationship between pH (pHm) and temperature (°C) with pHm defined as pH at minimum soluble Al concentration.
Minimum Soluble Al Concentration

Minimum soluble aluminum concentration Alₘ vs temperature
Alum addition to a solution with an initial alkalinity = 100 mg/L as CaCO$_3$ and initial pH = 8.5
Alum addition to a solution with an initial alkalinity = 10 mg/L as CaCO$_3$ and initial pH = 7.5
Relationship between the initial NOM concentration (TOC) and the HMS dosage
Models for describing HMS dosage – NOM concentration relationship

- Adsorption isotherm approach
  - Steve Dentel, Marc Edwards, Kastl, et al.

- Simple proportionality
  - Van Benschoten and Edzwald, and others

HMS dosage, \( m = R \times \text{TOC}_o \)

\( m = \) hydrolyzing metal salt dosage in mg metal/L  
\( \text{TOC}_o = \) raw water total organic carbon concentration in mg C/L
Magnitude of R (proportionality constant)

The pH on the x-axis is the final value after the acid from the HMS coagulant has reacted with the alkalinity of the solution.
Removal of TOC (when $m = R \times TOC_o$)

$$y = 13.871x - 7.1312$$

$R^2 = 0.5497$

TOC removal % does not depend on the final pH. The SUVA of the raw water NOM is an important indicator.

SUVA = UV light absorbance at $\lambda=254$ nm divided by TOC$_o$. 
Steps to Selecting a HMS Coagulant

- Select a target final pH ($pH_f$) based on minimum precipitate solubility (Al salts).
- Estimate the required coagulant dosage using $R$ at $pH_f$. ($m = R \times \text{TOC}_o$)
- Calculate the final alkalinity at $pH_f$ ($\text{alk}_f$) and the change in the alkalinity ($\text{alk}_o - \text{alk}_f$)
Estimating the change in alkalinity with HMS coagulant addition

- Use the initial pH ($pH_o$), initial alkalinity ($alk_o$), and water temperature to determine the total inorganic carbon concentration of the solution ($C_T$).
Assume $C_T$ remains constant during coagulation (closed-to-atmospheric CO$_2$ assumption) and use the selected value of pH$_f$ with $C_T$ to determine the final alkalinity ($alk_f$) of the solution.

- Spreadsheet programs
- Special nomographs
- Deffeyes diagram
Deffeyes Diagram Method

Inorganic Carbon Concentration, $C_T$ (millimoles/L)

Alkalinity (milliequivalents/L)

$\text{alk}_o = 1.5 \text{ meq/L}$  $\text{pH}_o = 7.7$

$\text{pH}_f =$

$\text{mg/L as CaCO}_3 = 50 \times \text{ meq/L}$

$\text{alk}_f = 0.6 \text{ meq/L}$

$\text{alk}_o = 1.5 \text{ meq/L}$  $\text{pH}_o = 7.7$

$\text{pH}_f =$
Selecting the type of coagulant

Initial alkalinity (meq/L)  Calculated final alkalinity (meq/L)  Dosage of any pH adjustment chemical (e.g., NaOH or H₂SO₄) in meq/L

\[
\frac{alk_o - alk_f}{m} = EAC \text{ of coagulant solution (meq/mgM)} \pm \frac{X}{m}
\]

Calculated dosage of coagulant (mg M/L)

\[m = R \times TOC_o\]
Calculating the dosage of pH adjustment chemical(s)

Dosage (mg/L) = \[ m \left( \frac{\text{alk}_o - \text{alk}_f}{m} - \text{EAC} \right) \left( \frac{\text{mg of additive}}{\text{meq}} \right) \]

Note: When \[ \frac{\text{alk}_o - \text{alk}_f}{m} - \text{EAC} \] < 0 the additive must be a base and the \[ \frac{\text{mg}}{\text{meq}} \] quantity is a negative number.
# pH adjustment chemicals

<table>
<thead>
<tr>
<th>Additive</th>
<th>Additive Dosage</th>
<th>Change in alkalinity (meq/L)</th>
<th>Change in inorganic carbon concentration, C\textsubscript{T} (moles C/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Bicarbonate (NaHCO\textsubscript{3})</td>
<td>1 mg/L</td>
<td>1.19 x 10\textsuperscript{-2}</td>
<td>1.19 x 10\textsuperscript{-5}</td>
</tr>
<tr>
<td>Sodium Carbonate (Na\textsubscript{2}CO\textsubscript{3})</td>
<td>1 mg/L</td>
<td>1.89 x 10\textsuperscript{-2}</td>
<td>9.43 x 10\textsuperscript{-6}</td>
</tr>
<tr>
<td>Hydrated Lime (Ca(OH)\textsubscript{2})</td>
<td>1 mg/L</td>
<td>2.7 x 10\textsuperscript{-2}</td>
<td>0</td>
</tr>
<tr>
<td>Sodium Hydroxide (NaOH)</td>
<td>1 mg/L</td>
<td>2.5 x 10\textsuperscript{-2}</td>
<td>0</td>
</tr>
<tr>
<td>Sulfuric Acid (H\textsubscript{2}SO\textsubscript{4})</td>
<td>1 mg/L</td>
<td>-2.04 x 10\textsuperscript{-2}</td>
<td>0</td>
</tr>
<tr>
<td>Hydrochloric Acid (HCl)</td>
<td>1 mg/L</td>
<td>-2.82 x 10\textsuperscript{-2}</td>
<td>0</td>
</tr>
<tr>
<td>Carbon Dioxide (CO\textsubscript{2})</td>
<td>1 mg/L</td>
<td>0</td>
<td>2.0 x 10\textsuperscript{-5}</td>
</tr>
</tbody>
</table>
Example calculation

- $\text{TOC}_o = 11.5 \text{ mgC/L}$
  - SUVA = 3.5 L/m mg
- Temperature = 25 ºC
- $\text{alk}_o = 1.5 \text{ meq/L (75 mg/L as CaCO}_3\text{)}$
- $\text{pH}_o = 7.5$
Select target (final) pH

- $pH_f = 6.1$

$pH$ - minimum solubility of $\text{Al(OH)}_3$ at $T = 25^\circ\text{C}$
Determine HMS coagulant dosage (m)

- $pH_f = 6.1$
- $R = 0.5 \text{ mg Al/mg C}$
- $m = R \times TOC_0 = 0.5 \times 11.5 \text{ mg C/L} = 5.7 \text{ mg Al/L}$
Determine the final alkalinity (alk$_f$)

- Use pH$_o$ = 7.5 and alk$_o$ = 1.5 meq/L

  \[ C_T = 1.6 \times 10^{-3} \text{ moles C/L} \]

- Use pH$_f$ = 6.1 and C$_T$ = 1.6 $\times$ 10$^{-3}$ moles C/L

  alk$_f$ = 0.6 meq/L
Determine the effective acid content of the coagulant (or coagulant +)

\[
\frac{\text{alk}_o - \text{alk}_f}{m} = \frac{1.5 - 0.6}{5.7} = 0.158 \frac{\text{meq}}{\text{mg Al}} = \text{EAC} \pm \frac{X}{m}
\]

Options:

1) Use alum with EAC = 0.111 meq/mg Al and supplemental strong acid 
\( X/m = 0.158 - 0.111 = 0.047 \) meq/mg Al or \( X = 0.047 \times 5.7 = 0.27 \) meq/L

2) Use acid supplemented alum with A/M = 2.5 % \( \text{H}_2\text{SO}_4/\% \text{ Al} 

Effective acid content (meq/mg metal) = \( \frac{300}{100(AW)} + \frac{A}{EW(M)} \)