Using Laboratory Charge Measurement for Quickly Determining Optimum Coagulant Dose

Presented By: John Clark
Topics

- Fundamentals of Coagulation
- Review of Charge Measurement Technologies
- Lab Charge Analyzer Testing procedure
FUNDAMENTALS OF COAGULATION
The removal of natural organic material (NOM) and colloidal particles occurs via four primary mechanisms:

Cationic, Dissolved Coagulant Species (e.g. Al(OH)$_{2+}$):
- Charge neutralization/destabilization (Colloids)
- Complexation/precipitation (NOM)

Solid Phase Coagulant Species (i.e. Al(OH)$_{3}$):
- Enmeshment (Colloids)
- Adsorption (NOM)

For most surface waters, coagulant dosage is determined by NOM concentrations.
Charge Neutralization & Flocculation

- **Alum**

- **Soluble Cation Species**
  - e.g. Al(OH)$^{2+}$

- **Colloidal Hydroxide**
  - Precipitate Al(OH)$_3$(s)

- **Amorphous Hydroxide**
  - Precipitate Al(OH)$_3$(am)

**Neutralization / Complexation**

**Microfloc Formation**

**Enmeshment / Flocculation**

**Stable**
The Aluminum cation (Al\(^{3+}\)) combines with hydroxide anions (OH\(^{-}\)) to form these hydrolysis products:

\[ \text{Al}^{3+} + \text{OH}^- = \text{Al(OH)}^{2+} \]

\[ \text{Al(OH)}^{2+} + \text{OH}^- = \text{Al(OH)}_{2}^{1+} \]

\[ \text{Al(OH)}_{2}^{1+} + \text{OH}^- = \text{Al(OH)}_{3} \quad \text{Insoluble Phase} \]

\[ \text{Al(OH)}_{3} + \text{OH}^- = \text{Al(OH)}_{4}^{1-} \]
Alum Hydrolysis Products vs. pH

Mole Fraction

Al(OH)$_3$(am)

Al(OH)$_2^+$

Al(OH)$_4^-$

Al$^{3+}$

Al(OH)$_2^+$

Al(OH)$_3$(am)
Ferric Hydrolysis Products vs. pH

![Graph showing the mole fraction of various ferric hydrolysis products as a function of pH.](image-url)
Pre-Hydrolyzed Coagulants

- Aluminum Chlorohydrate (ACH), PolyAluminum Chloride (PACl)

- Contain highly charged polymeric species ($\text{Al}_{13}^{7+}$), capable of charge neutralization at higher pH’s.

- Charge neutralization performance is related to basicity.

- ACH has the highest basicity (>80%), PACl’s come in a range of lower basicity.
Low Molecular Weight Organic Coagulants

- Polydadmac, Polyamine, EPI/DMA

- Highly charged polymeric species capable of charge neutralization at higher pH's.

- Available in a blend with inorganic coagulants
CHARGE MEASUREMENT
Double Layer Model

- Distance From Surface
- Potential
- Zeta Potential
- Surface Potential
- Negative Colloid
- Negative Ion
- Positive Ion

Stern, Diffuse, Solution
Charge Measurement Technologies

- **Micro-Electrophoresis**
  - Applied electric field causes movement of colloids, measured as electrophoretic mobility (UE).
  - Velocity at which the colloid moves is proportional to the colloids Zeta Potential.

- **Streaming Current**
  - Mechanical movement of colloids produces electrical current referred to as Streaming Current.
  - The generated current is proportional to average Zeta Potential of colloids coating the sensor surfaces.
Micro-Electrophoresis

Water Sample

Negative Electrode

Positive Electrode

Microscope / Laser Doppler
Micro-Electrophoresis

Electrophoretic Mobility (UE) = \( \frac{V_p}{E_x} \)

\( V_p = \) Particle Velocity (μm/s)
\( E_x = \) Applied Electric Field (volt/cm)
Streaming Current

- Water Sample
- Reciprocating Piston (4 - 5 Hz)
- Annulus (0.005” Clearance)
- Ring Electrodes (Probe)
Streaming Current

Stern Layer

Diffuse Layer

$nA$
Streaming Current

Alternating Current
UNDERSTANDING STREAMING CURRENT RESPONSES
Streaming Current

Alum

pH: 6.0

SCV: -560
Streaming Current

SCV: -50
Alum
pH: 6.3
SCV: 650
Streaming Current

SCV: -50

Lime

pH: 6.8

SCV: 650
Alum Hydrolysis Products vs. pH

Mole Fraction

2 3 4 5 6 7 8 9 10

Al(OH)₃(am)
Al(OH)₂⁺
Al(OH)₂⁺
Al(OH)₄⁻

Al³⁺

Al(OH)₄⁻

Al(OH)₂⁺

Al(OH)₃(amide)
Understanding Online SC Response

SCV: -200

Alum & Lime

SCV: 0

Raw pH: 6.8 / Alkalinity: 30

SCV: -50

pH: 6.0

SCV: -100

SCV: -150

Lime

SCV: -220

pH: 8.0

MIXING

FLOC BASIN

SEDIMENTATION

FILTRATION

FINISHED
Understanding Online SC Response

SCV: -220

Alum

SCV: -180

pH: 7.8

Raw pH: 8.0 / Alkalinity: 150

MIXING

FLOC BASIN

SEDIMENTATION

FILTRATION

FINISHED
Potential Issues With Online Charge Measurements

- pH and Alkalinity not always in ideal range, and sometimes unstable.

- Not always possible to install close enough to point of coagulant addition.

- Changes in plant flow can impact lag time.

- Fouling causes signal drift. High manganese levels can cause significant measurement error.

- Mechanics / sensor wear over time and cause loss of signal strength.
How Lab SC Charge Analysis Is Different From Online SCM
How Lab SC Charge Analysis Is Different From Online SCM

- Sample chemistry (namely pH) can be adjusted to produce accurate measurement results.

- Sensor first exposed to untreated sample, allowing anionic colloids to coat piston.

- Coagulant is then titrated into the raw water sample, real-time charge neutralization of colloids is measured.

- Sensor fouling and wear easily managed.
How Lab SC Charge Analysis Is Different From Online SCM

- By controlling chemistry and measuring charge neutralization in real-time, an optimum* dosage of coagulant can be determined in ~5 mins.
  *optimum in terms of NTU & TOC reduction, not lowest cost.

- Provides simple method of accurate dosage determination of pH adjustment chemicals.

- Excellent tool for profiling coagulants and performance testing incoming product.
LAB CHARGE ANALYZER
TEST PROCEDURE
Important Test Considerations

- Test must be done at optimum pH. This may require addition of acid or base.

- Additives fed to the process before or directly after coagulant addition are fed to jar first with exception of lime/caustic.

- Titration with coagulant needs to be done in a timely fashion (< 5 minutes ideally). Use fresh solution if using diluted coagulant.
Place sample under sensor, and lower sensor until water level is at the openings.

Allow reading to stabilize.

If necessary, add acid to reduce sample pH.
Charge Titration Procedure

- Begin titrating sample with coagulant. Initial dose should be at least 50% of expected dose.
- Inject coagulant near the stir bar to ensure rapid, efficient mixing of coagulant.
- Continue incremental injections until a neutral charge is reached.
Keep Watch on pH

- Raise pH back to “Target pH” (e.g. 6.3 for Alum) if it drops more than 0.3 units below.

- Do not raise pH too high as this will result in needing to feed a higher dosage of coagulant.

- Continue with chemical additions until charge equals 0 and pH is at target.
Streaming Current vs Time

![Graph showing streaming current vs time with data points and a trend line. The graph includes axes labeled 'Coagulant (ppm)' and 'Charge (SCV)' with corresponding scales. The graph is titled 'Manual Titration.' ]
Actual 30 Day Coagulant Dose Comparison at a Municipal Water Plant
Questions?
Automatic Titration
ALTERNATE PROCEDURE
Alternate Procedure

- Grab sample from flash mix.
- Titrate sample to neutral using coagulant* or DADMAC (organic polymer) solution.
  
  *Addition of acid may be required first on higher pH samples.
- Record how much chemical was needed to reach zero.
- Correlation can be developed to determine optimum “charge demand” at flash mix.
Verification Procedure
Verification Procedure

- Clean probe, piston, and sample beaker and then rinse well with DI water.
- Add 10 ml of PVSK solution (anionic, 0.001 N) to beaker filled with DI water.
- Titrate sample to neutral using DADMAC solution (cationic, 0.001 N).
- Should require 9 to 11 ml of DADMAC to neutralize sample.