Coagulation 101

David Pernitsky, PhD, PEng

Stantec Consulting Services Inc.

Symptoms of Poor Coagulation

"It's not just about the clarifier…"

- High turbidity from clarifier is only one indication of poor coagulation

"It's really about the filters…"

- Poor coagulation chemistry is often responsible for:
  - High filtered water turbidity
  - Poor filter ripening
  - Low Unit Filter Run Volumes (UFRVs)

Why Do We Coagulate?

Condition raw water particles for clarification/filtration

- Remove turbidity and pathogens

Convert NOM to a solid phase for clarification/filtration

- Remove color
- Remove DBP precursors
- Increase UV transmittance to improve UV disinfection

End Goal: make near-neutral floc particles that filter well

Critical Elements

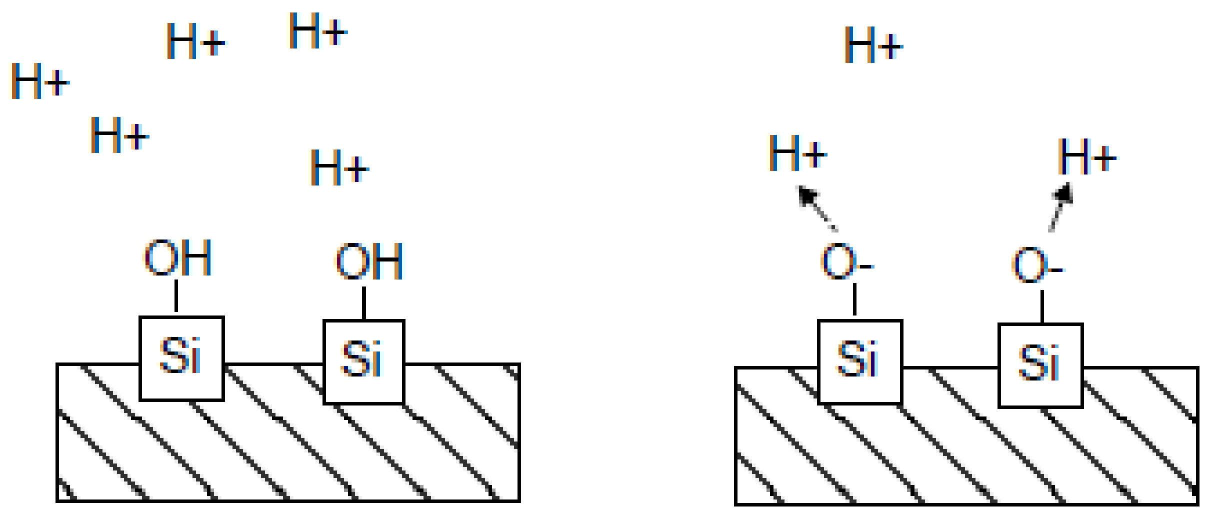
- Chemistry of Contaminants:
  - Particles
  - Dissolved organics
- Chemistry of Coagulants:
  - Metal-salt coagulants (alum, ferric chloride, PACl)
  - Organic polymers
- Solution Parameters (pH, temperature)

Chemistry of Particles

Many types of particles:

- Clays, minerals, algae, organic debris

All have pH dependent surface chemistry



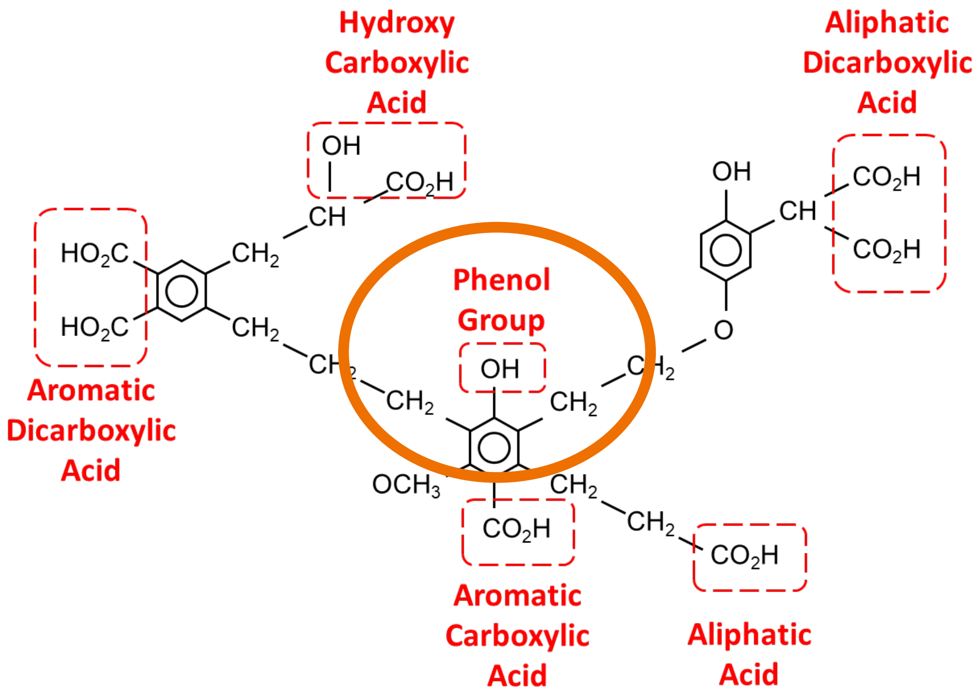
Low pH - high concentration of H+ ions in solution provides driving force to keep H+ ion attached to O- group on particle surface.
Neutral Surface Charge

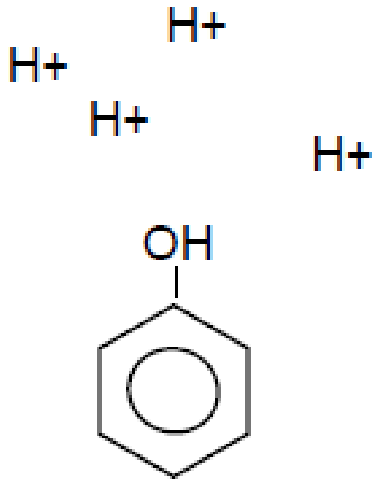
High pH - low concentration of H+ ions in solution provides driving force to release H+ ion attached to O- group on particle surface.
Negative Surface Charge

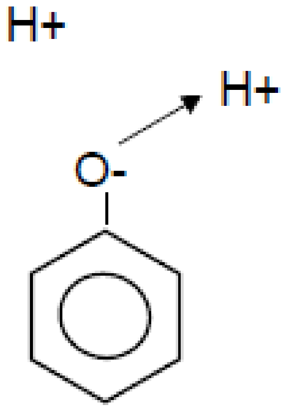
Chemistry of NOM

NOM molecules complicated and unique to each water source

All have pH dependent surface chemistry







Low pH - high concentration of H+ ions in solution provides driving force to keep H+ ion attached to O- group on NOM molecule.
Neutral Charge

High pH - low concentration of H+ ions in solution provides driving force to release H+ ion attached to O- group on NOM molecule.
Negative Charge

Importance of Turbidity versus NOM

Particule Charge

- 10 mg/L TSS (10 NTU)
- 0.5 µeq/mg
- 5 µeq/L

NOM Charge

- 3 mg/L TOC
- 10 to 100 µeq/mg
- 30 to 300 µeq/L

- Turbidity rarely controls coagulant dose
- Dose depends on NOM removal or floc filterability
- Need timely measure of raw water NOM to use for adjusting coagulant dose

Chemistry of Coagulants

Metal-salt coagulants (alum, ferric, PACl):

- Form dissolved & solid (floc) species – pH dependent
- Charge of dissolved species and floc surface is pH dependent
- More positive (+ve) at low pH
- Generate $Al(OH)_3$ or $Fe(OH)_3$ sludge

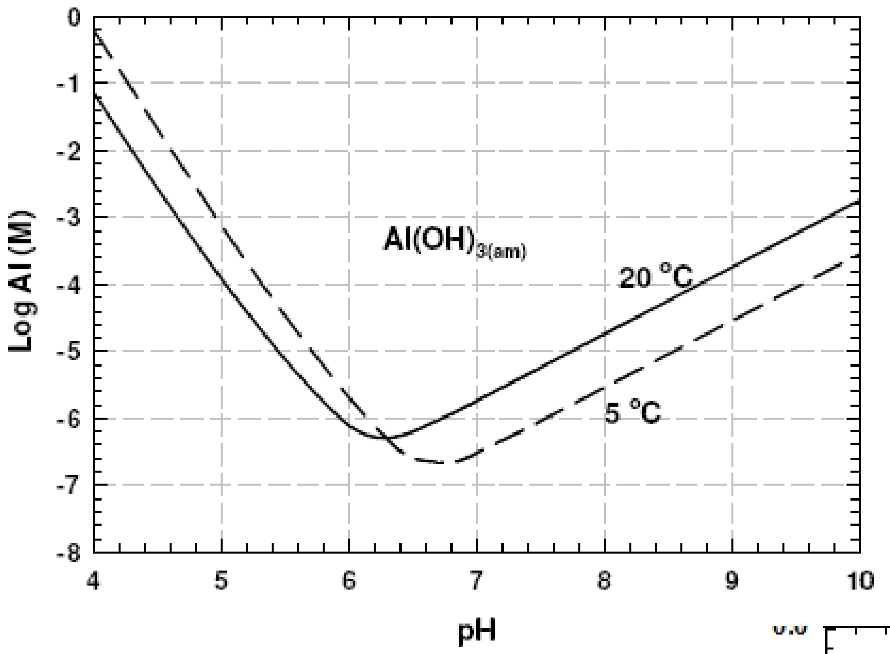
Organic Polymers:

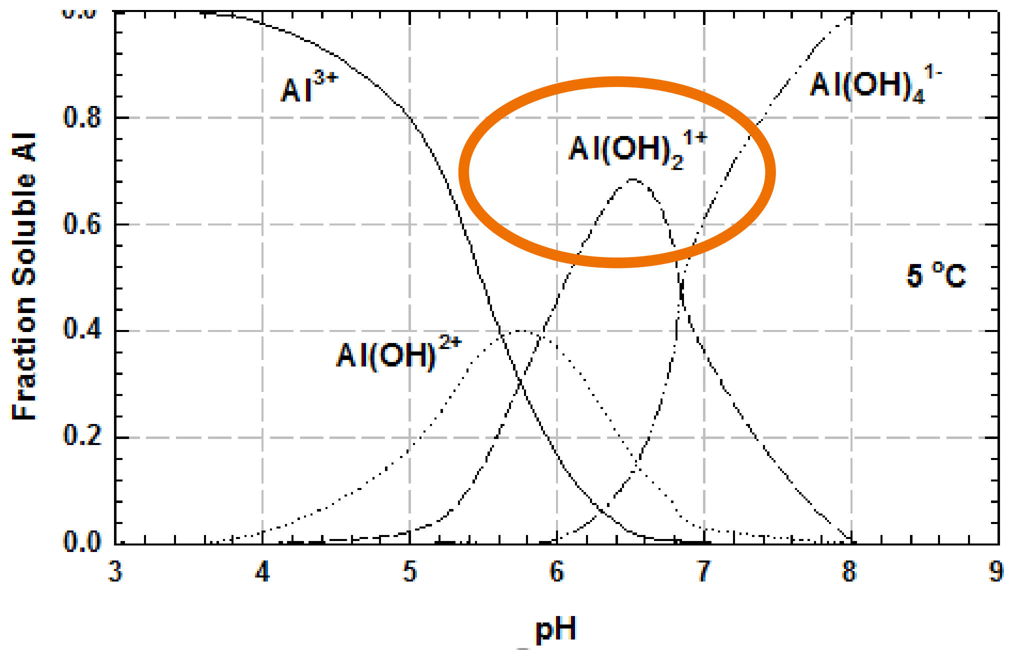
- Operate via charged functional groups
- Charge is largely unaffected by pH
- Less sludge generation

Alum Chemistry

Solubility and speciation are pH-dependent

- Dissolved Species represent only a small part of total aluminum; most is floc
- Strong positive charges of dissolved species only at very low pH





PACl Chemistry

Titration of OH^- into $AlCl_3$ forms an Al_{13}^{7+} polymer

Characterized by "Basicity" or degree of neutralization

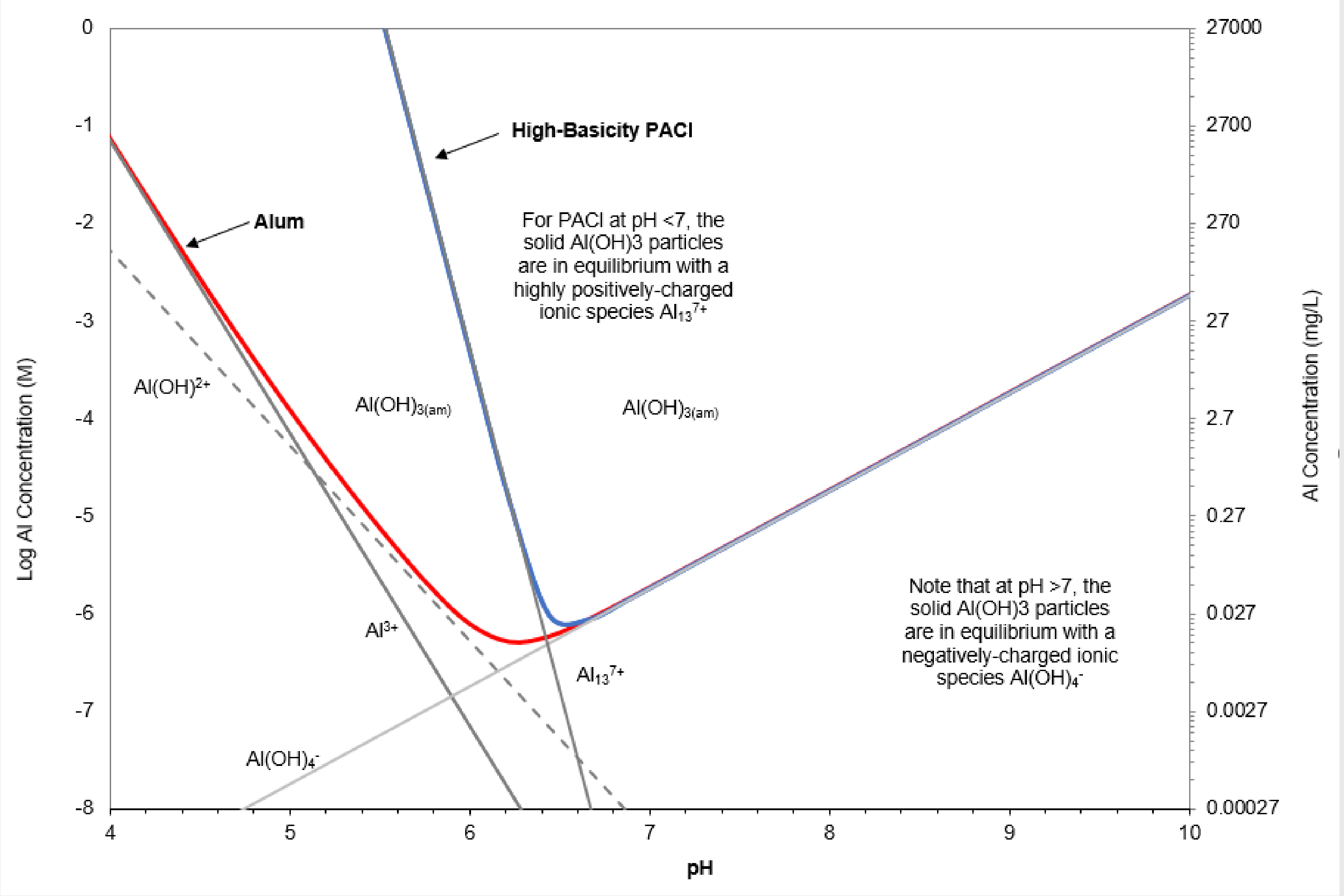
- Fully neutralized: $Al^{3+} + 3OH^- \leftrightarrow Al(OH)_3$
- Basicity = $[OH^-]/3[Al_T]$ x 100%
- **Higher the basicity, higher the Al_{13} content**
- 20% (low), 50% (med), 75% (high), 85% (ACH)
- **Higher the basicity**, lower the alkalinity consumption

Can contain additives: sulfate, silicate, organic polymers

Match: basicity / raw water alkalinity / coagulation pH

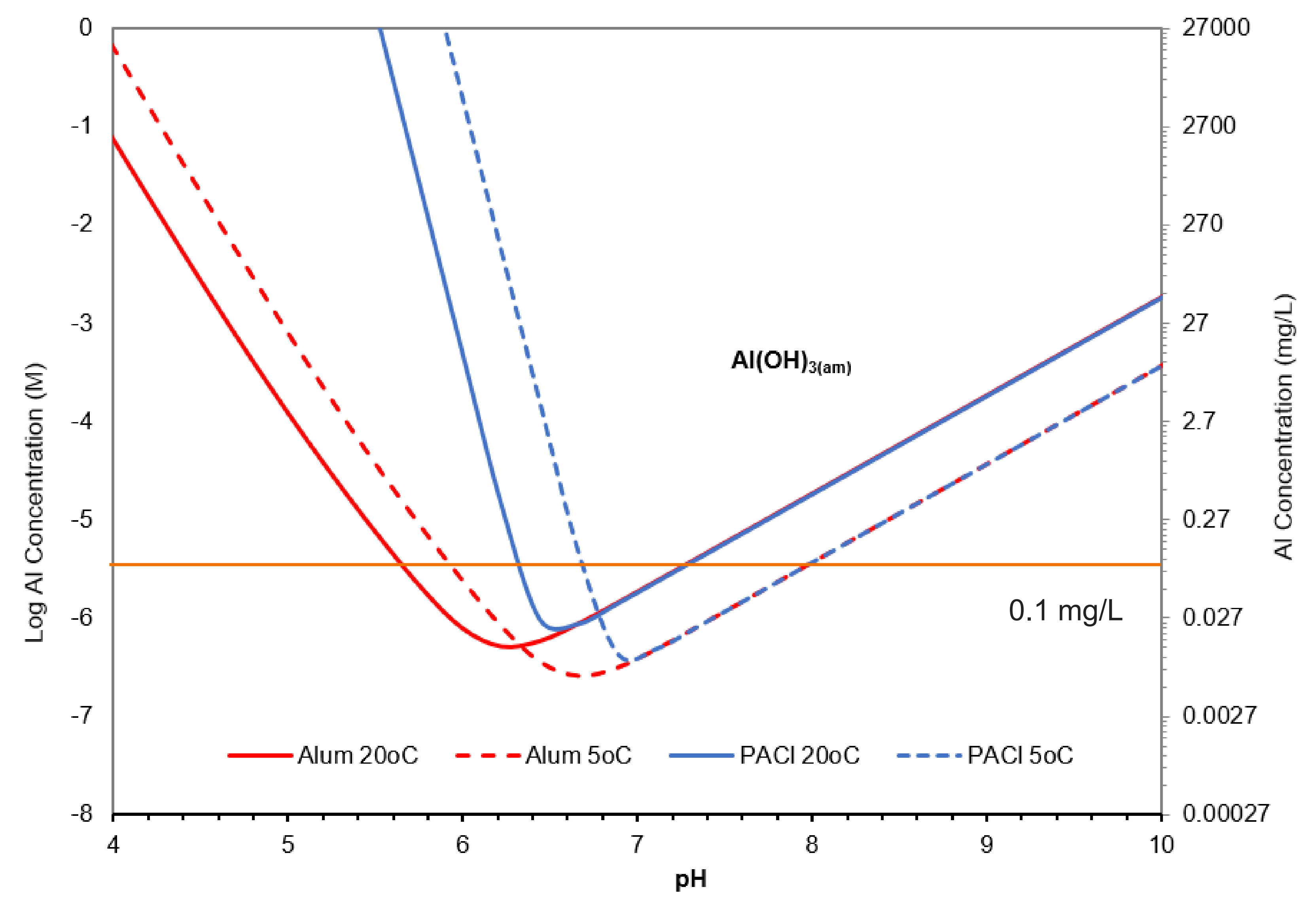
Alum and PACl

- Al_{13}^{7+} polymer defines solubility for PACls
- Very little floc formation for high basicity PACls below pH 6.5
- Alum and high basicity PACl shown: medium and low basicity PACls are between these two extremes



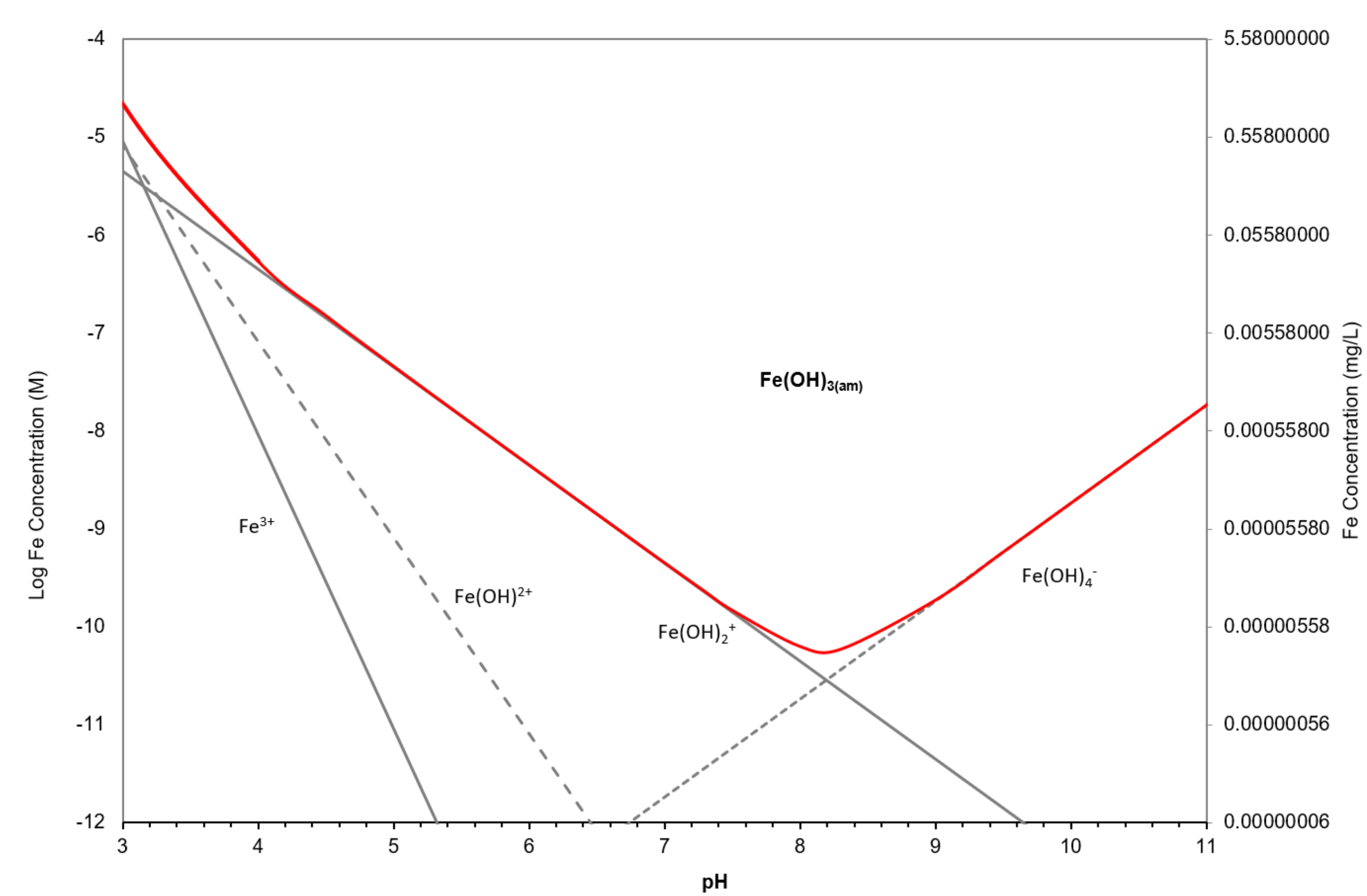
Residual Al

- pH of minimum solubility changes with temperature
- Harder to meet residual Al targets in summer
- Need pH to be in low 7's



Ferric Coagulants

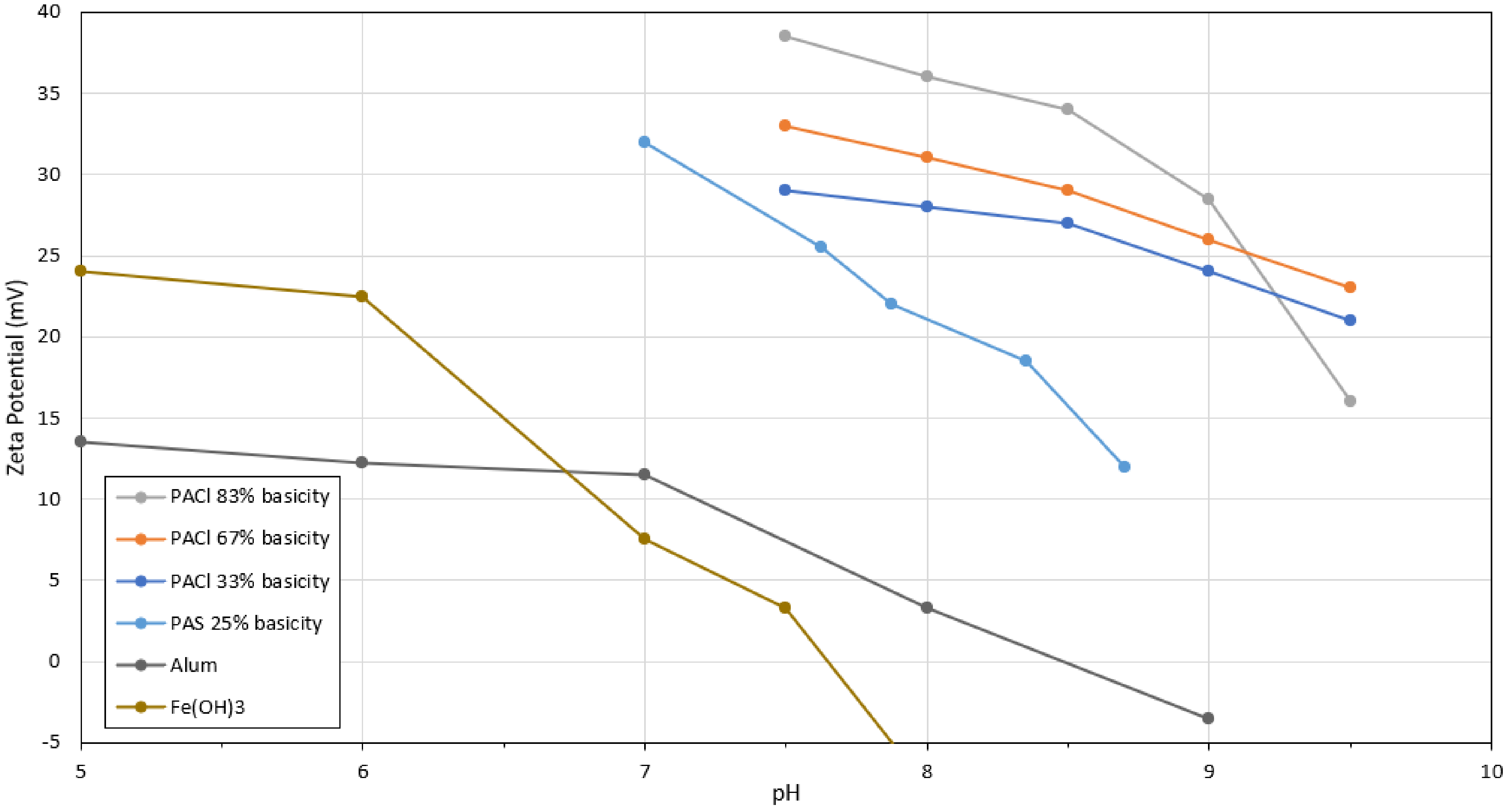
- $Fe(OH)_3$ solubility is very low over a wide pH range
- Dissolved-phase coagulant species are more positive at lower pH
- *Note*: Ferric sulphate has slightly less positive charge than an equivalent amount of ferric chloride due to effect of SO_4^{2-}



(Adapted from: Stumm and Morgan 1996)

Floc Charge

- Alum and Ferric have reduced floc charge at higher pH
- PACls maintain higher floc charge at higher pH



Data for PACls and PAS from Solomentseva et al. 1999, Data for Alum from Duan et al. 2014, Data for $Fe(OH)_3$ from Guan et al. 2008

NOM Removal

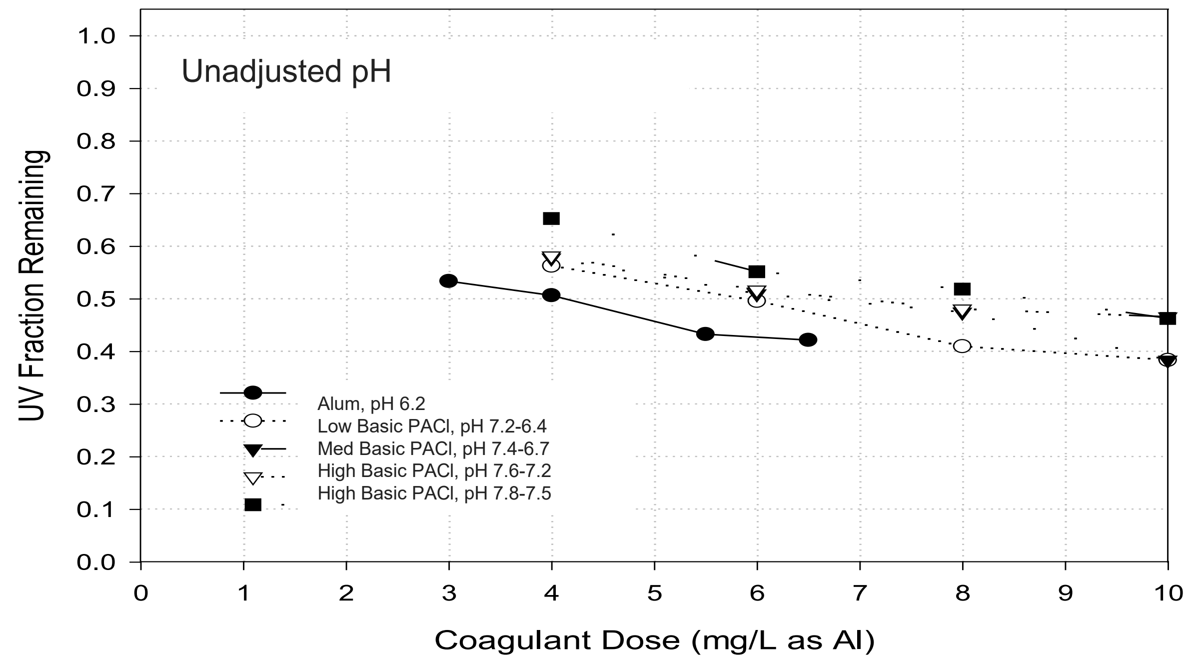
Lower basicity PACls depress pH more and can remove more NOM

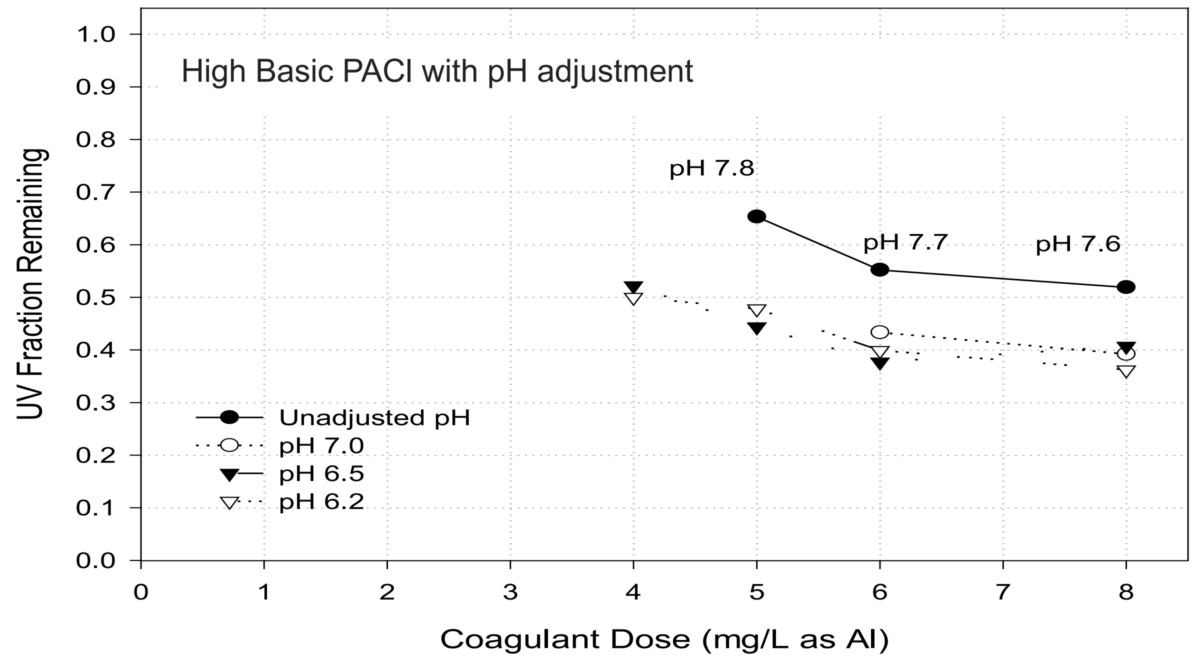
NOM removal with PACls can be enhanced by reducing pH

- pH 7 adequate
- 50% UV removal with alum at pH 6.2
- 50% UV removal with High Basic PACl at pH 7

Even though PACls have highly positively-charged floc at high pH, NOM removal still requires relatively low pH

- Still need to test





Summary of Chemistry

pH	Low	High
NOM Charge	Less Negative (easier to remove)	More Negative (harder to remove)
Particle Charge	Less Negative (easier to neutralize)	More Negative (harder to neutralize)
Coagulant Charge	More Positive (more powerful)	Less Positive (less powerful)

Keys to Coagulation Control

How much NOM?

- Must satisfy charge demand of NOM

What is pH after coagulation?

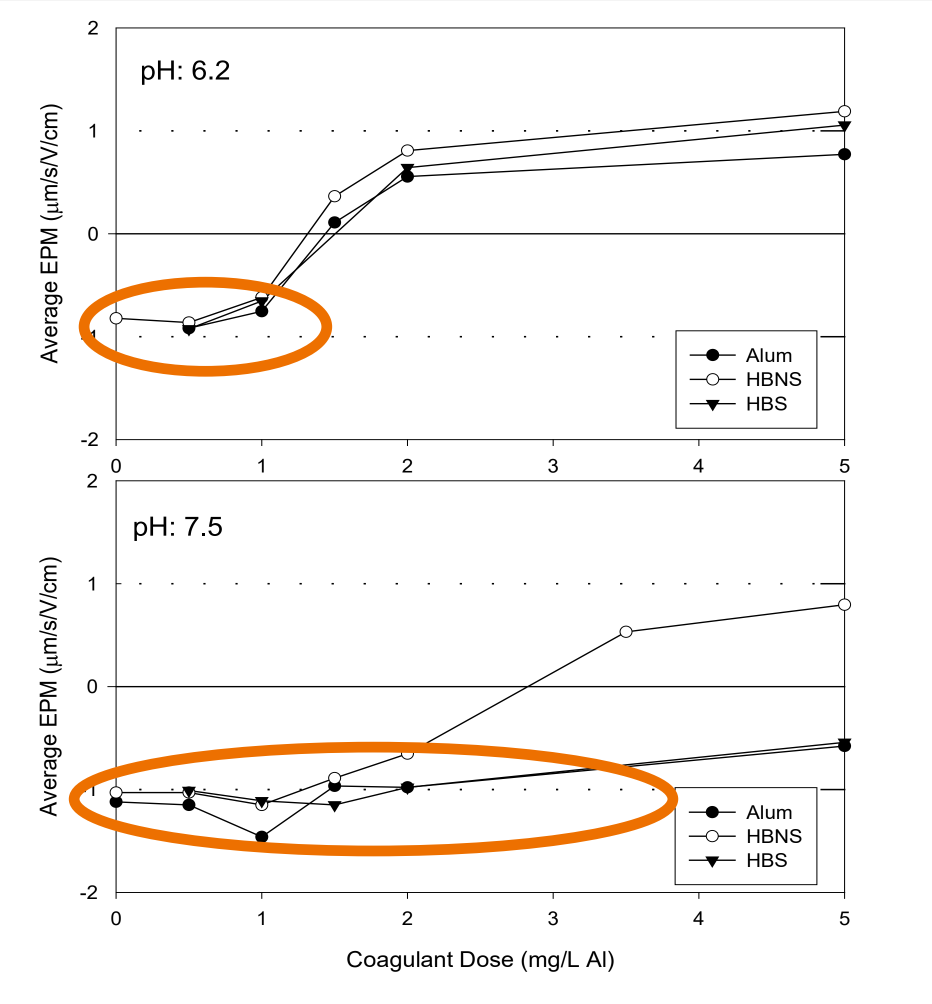
- Controls residual Al/Fe concentrations
- Determines efficiency of NOM removal
- **Determines floc surface charge**
    - Affects clarification/filtration performance

pH-Related Coagulant Demand

- Graphs show floc charge after coagulant addition for same water
- Must satisfy charge demand of NOM before particle charge changes
- At high pH, coagulant demand much higher
- Coagulant selection critical at high pH

Coagulants used:

- Alum
- High-basicity no-sulfate PACl (HBNS)
- High-basicity PACl with sulfate (HBS)



(Source: Pernitsky and Edzwald 2006)

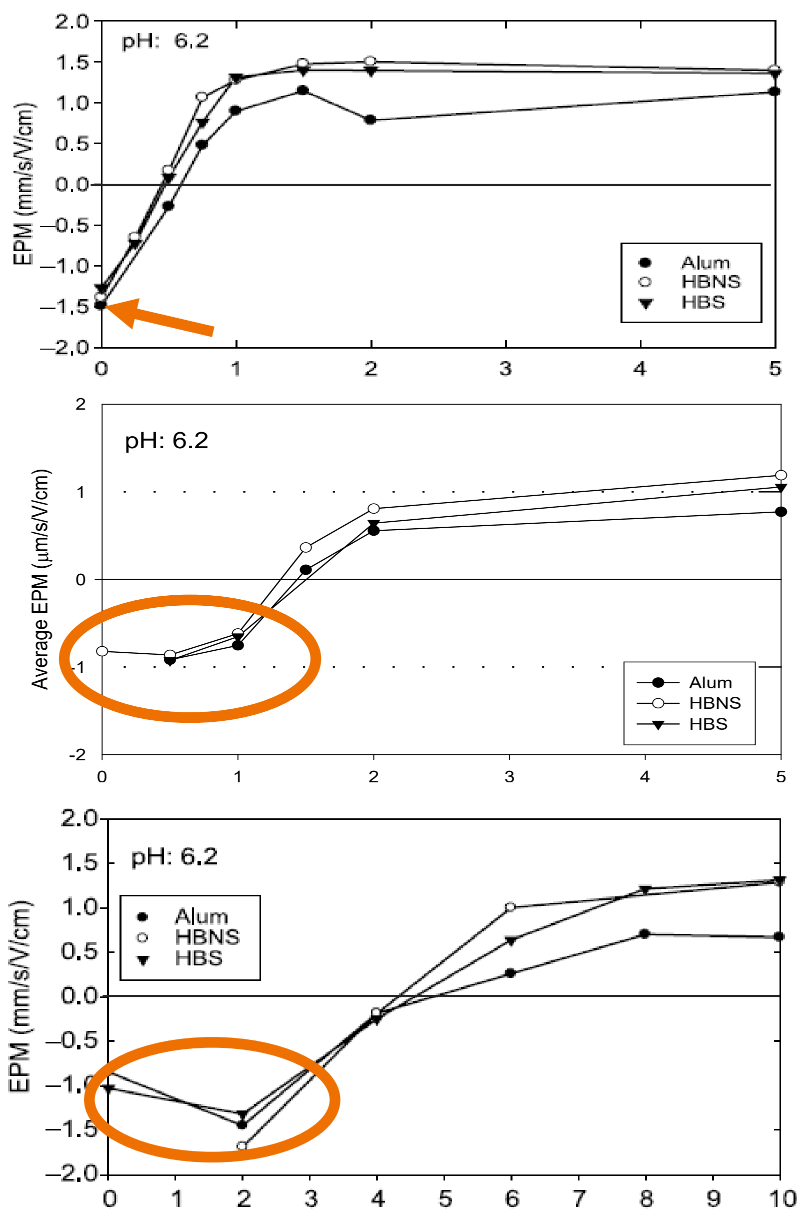
NOM Related Coagulant Demand

Water	Turbidity (NTU)	TOC (mg/L)	SUVA	Dose to neutralize (mg/L as Al)
1	16	2.5	2.2	0.8
2	0.8	2.8	3.0	1.5
3	0.7	6.1	4.5	4.2

Coagulants used:

- Alum
- High-basicity no-sulfate PACl (HBNS)
- High-basicity PACl with sulfate (HBS)

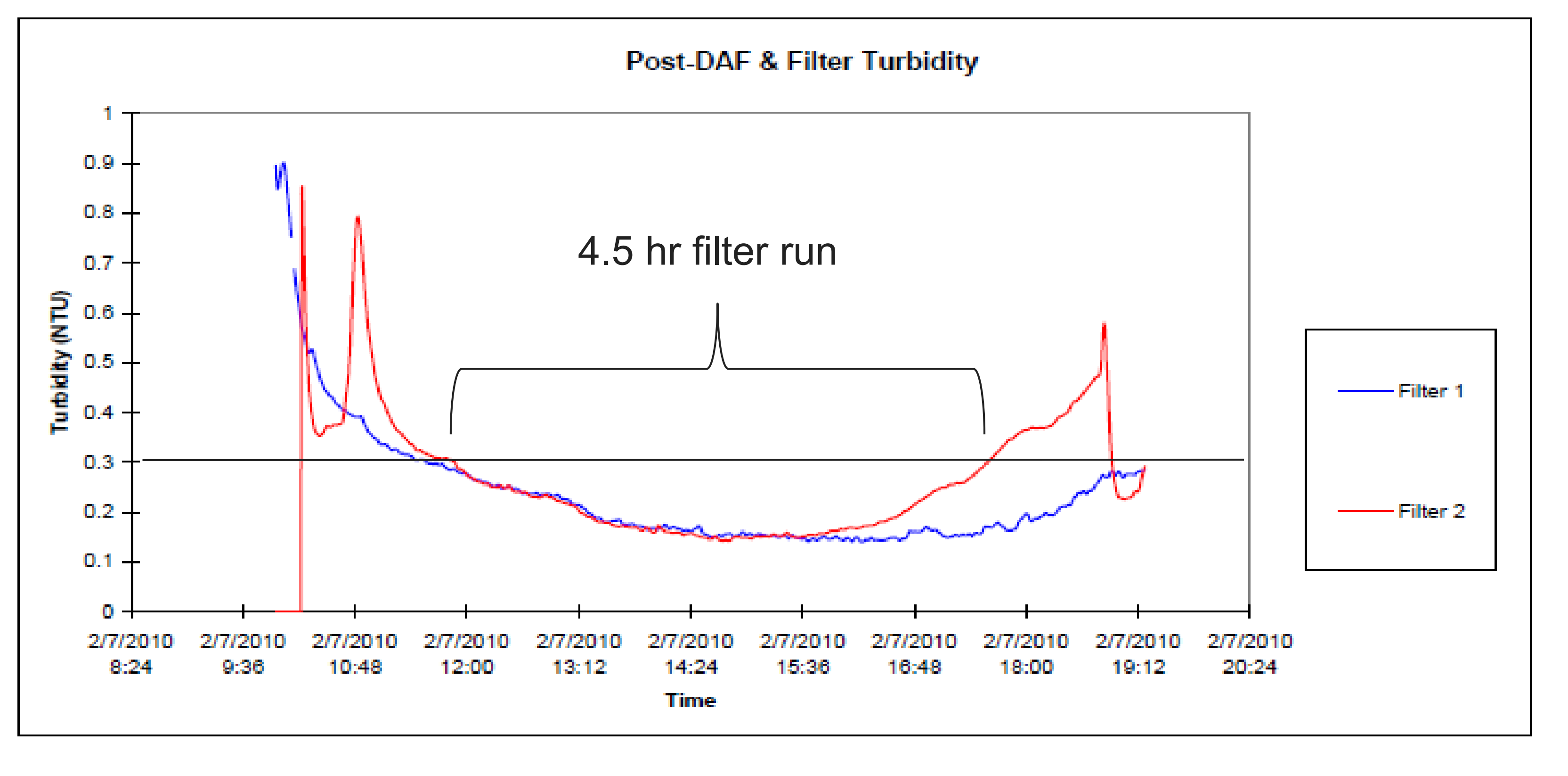
Source: Pernitsky and Edzwald 2006



Poor Coagulation Causes Poor Filter Performance

Low UFRVs, long ripening times, early breakthrough

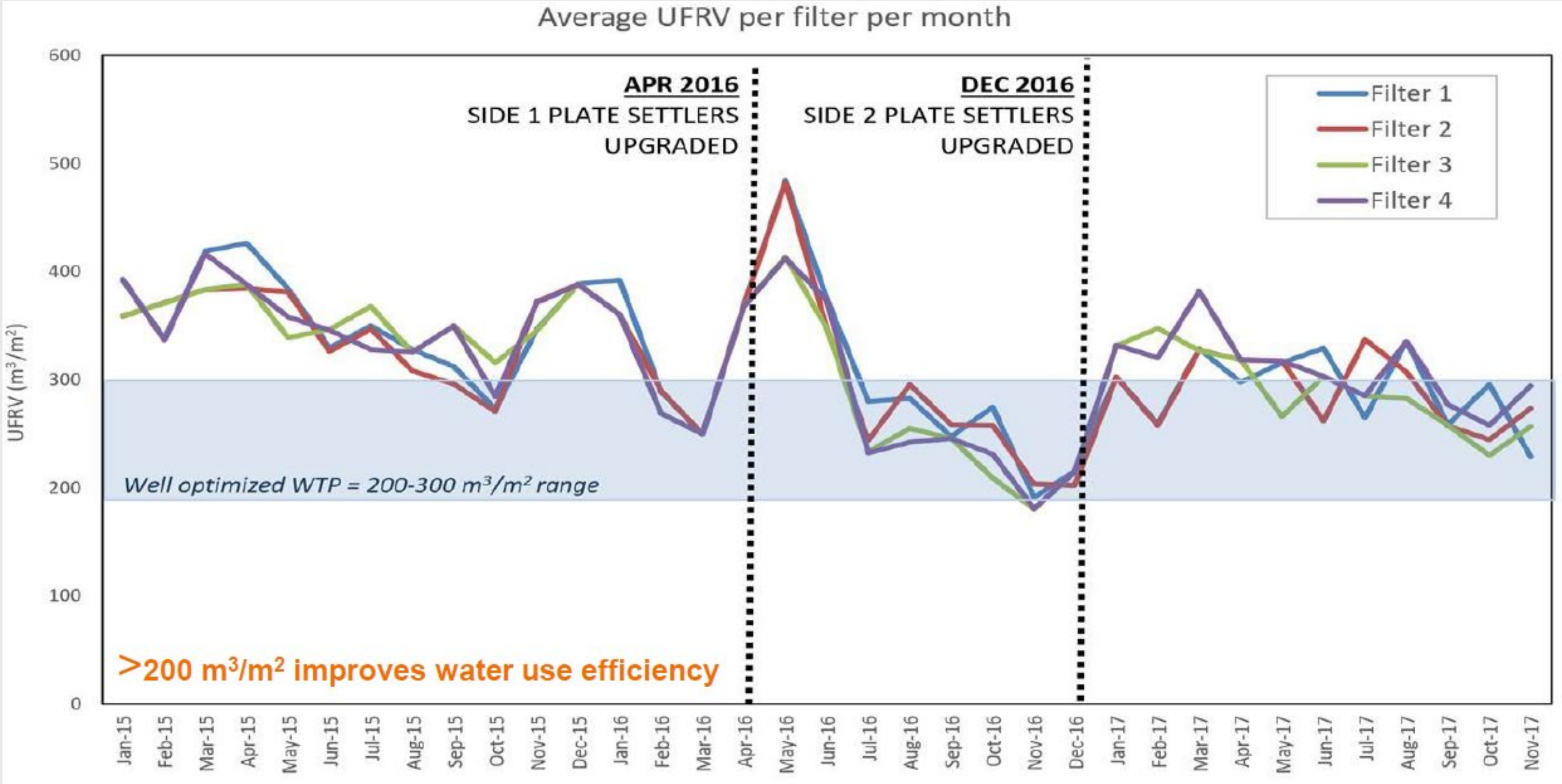
Conventional jar tests give little indication of filterability of floc



Filter UFRV

Water produced (between ripening and end of run) per unit area

Allows comparison of filters independent of loading rate and size

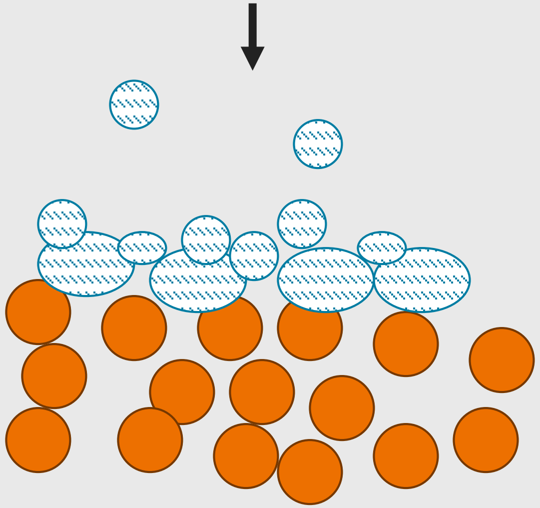


Filtration Mechanisms

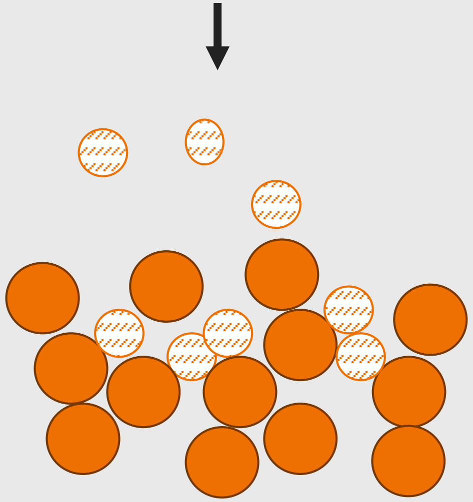
Particles smaller than void spaces need to be "near-neutral" in charge to adhere to surface of media grains

If weakly attached, small particles can be removed by hydraulic shear as bed gets full and interstitial velocity increases

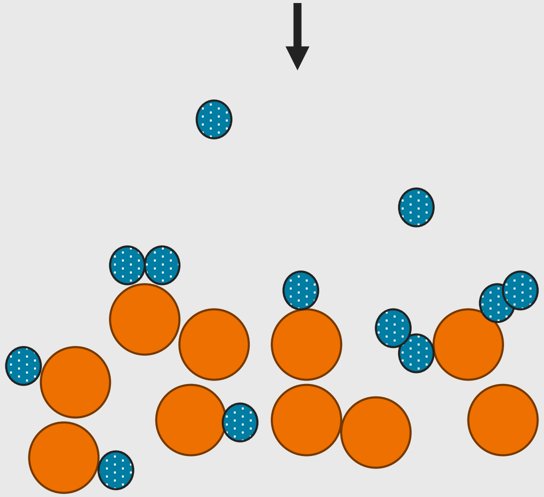
Surface Straining (Physical)



Interstitial Straining (Physical)



Attachment (Phys/Chem)



Floc Charge & WTP Performance

"Near-Neutral" floc leads to good filter performance

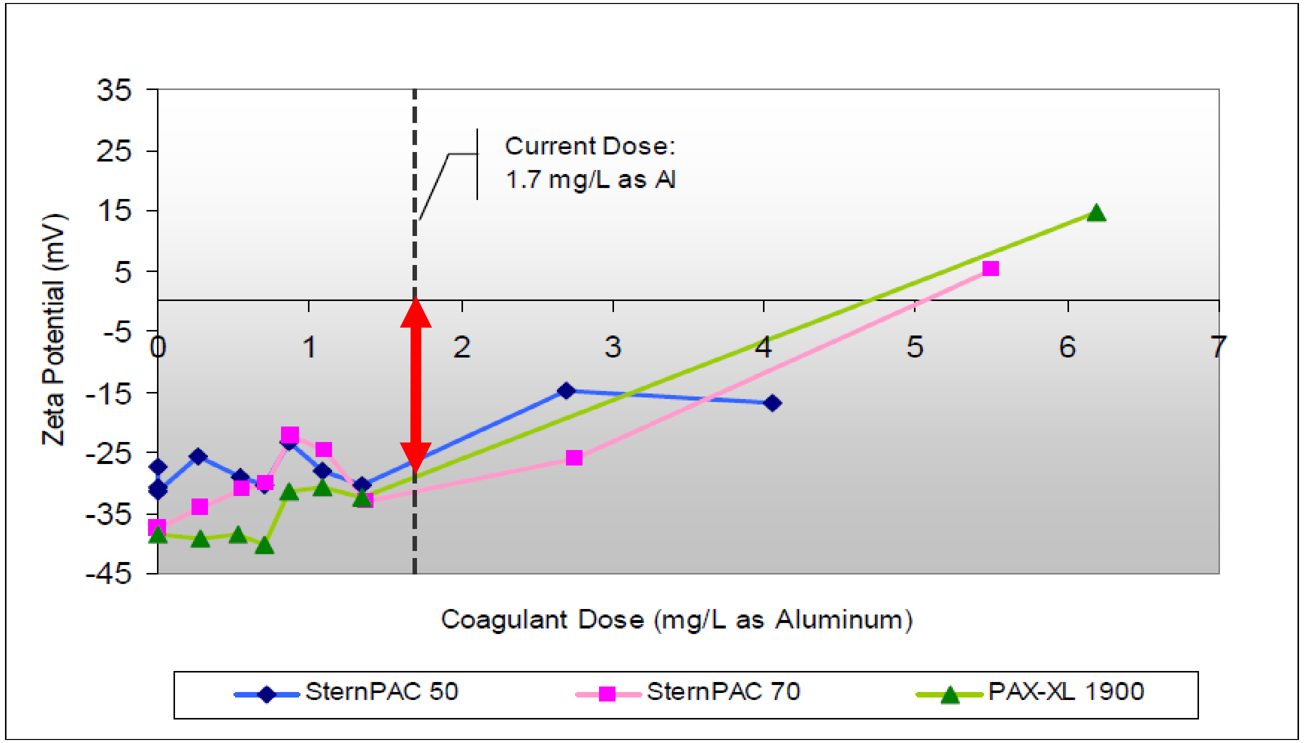
- Can measure with zeta potential or streaming current

Table 2.1 – Zeta Potential Ranges for Effective WTP Operations

Utility	Type of WTP	Zeta Potential Target (mV)	Reference
Calgary, AB	Conventional (Actiflo)	-5 to +5	Kundert, 2014
Epcor (Edmonton, AB)	Conventional with seasonal Direct Filtration	-5 or greater	James et al., 2015
Tittesworth, UK	Conventional	-10 to +3	Sharp et al., 2015
Various Great Lakes, ON	Conventional	-7 or greater	Waller et al., 2012
Muskoka, ON	Direct Filtration	-5 or greater	Pernitsky et al, 2010
Halifax, UK	Conventional	-10 to +5	Sharp et al., 2005
Fort Collins, Colorado	Conventional	-5 to +5	Morfesis et al., 2009
Adelaide, Aus	Conventional	-10 to -5	Holmes et al., 2015
Waterford, NY	Conventional	Zero, +/- 5	Riddick, 1961
ASTM	Generic Standard	-5 to +5	ASTM, 1987
Laboratory	Algae Settling and DAF	-10 to +2	Henderson et al., 2008

Case Study: Polymer for Direct Filtration

- Direct filtration plant
- To get 0.3 NTU, high coagulant dose and high headloss/short run
- Drop coagulant dose and get early breakthrough/short run
- Bench-scale zeta potential analysis
- Can't get neutral floc particles with reasonable PACl doses
- Need to evaluate cationic polymers

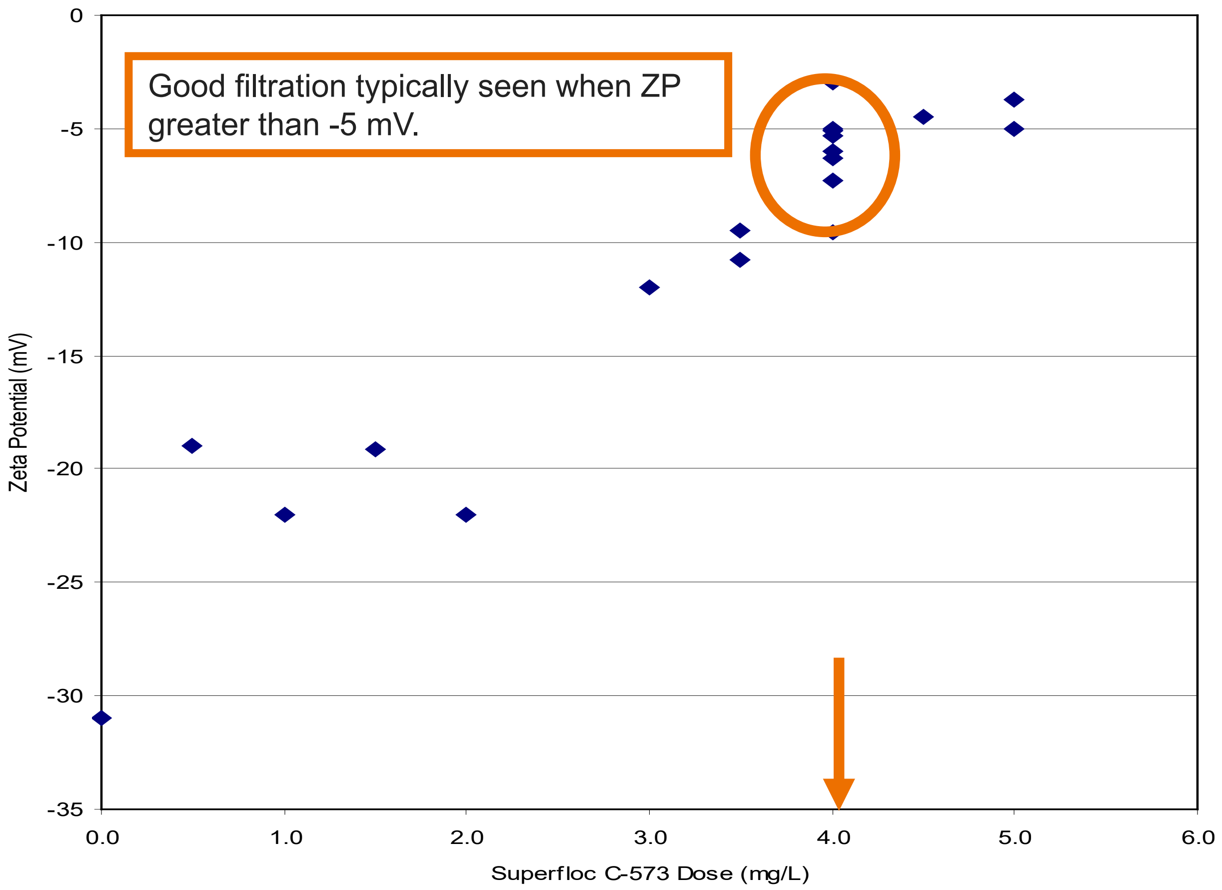


Source: Pernitsky et al. 2010

Evaluate Polymers for Charge Neutralization

Kept baseline PACl dose (1.7 mg/l Al) and added polymer

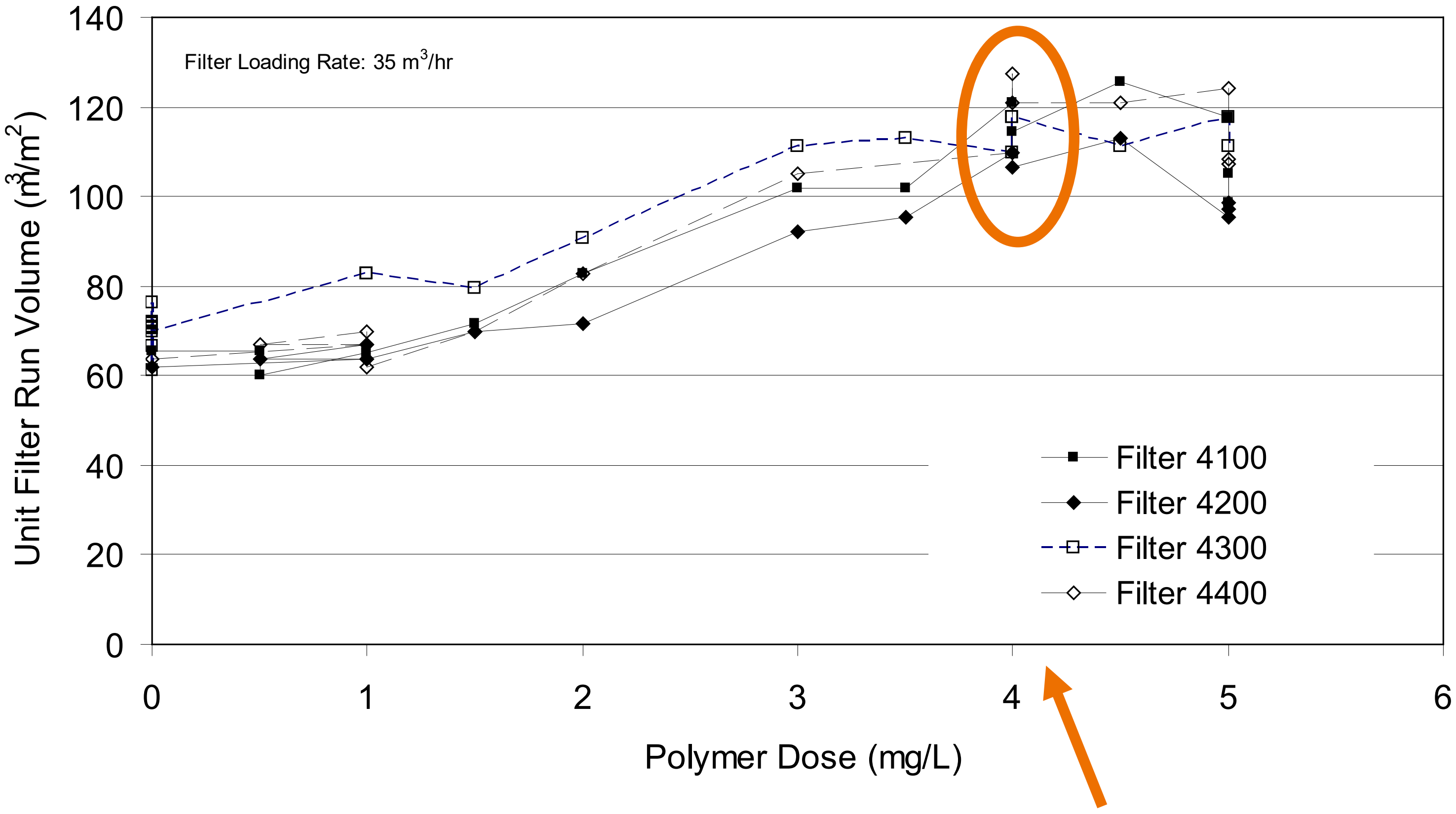
4 mg/L polymer needed to get to target zeta potential of –5mV



Full-Scale Polymer Trials

Kept baseline PACl dose (1.7 mg/l Al) and added polymer

4 mg/L and target zeta potential of –5 mV gave highest UFRVs

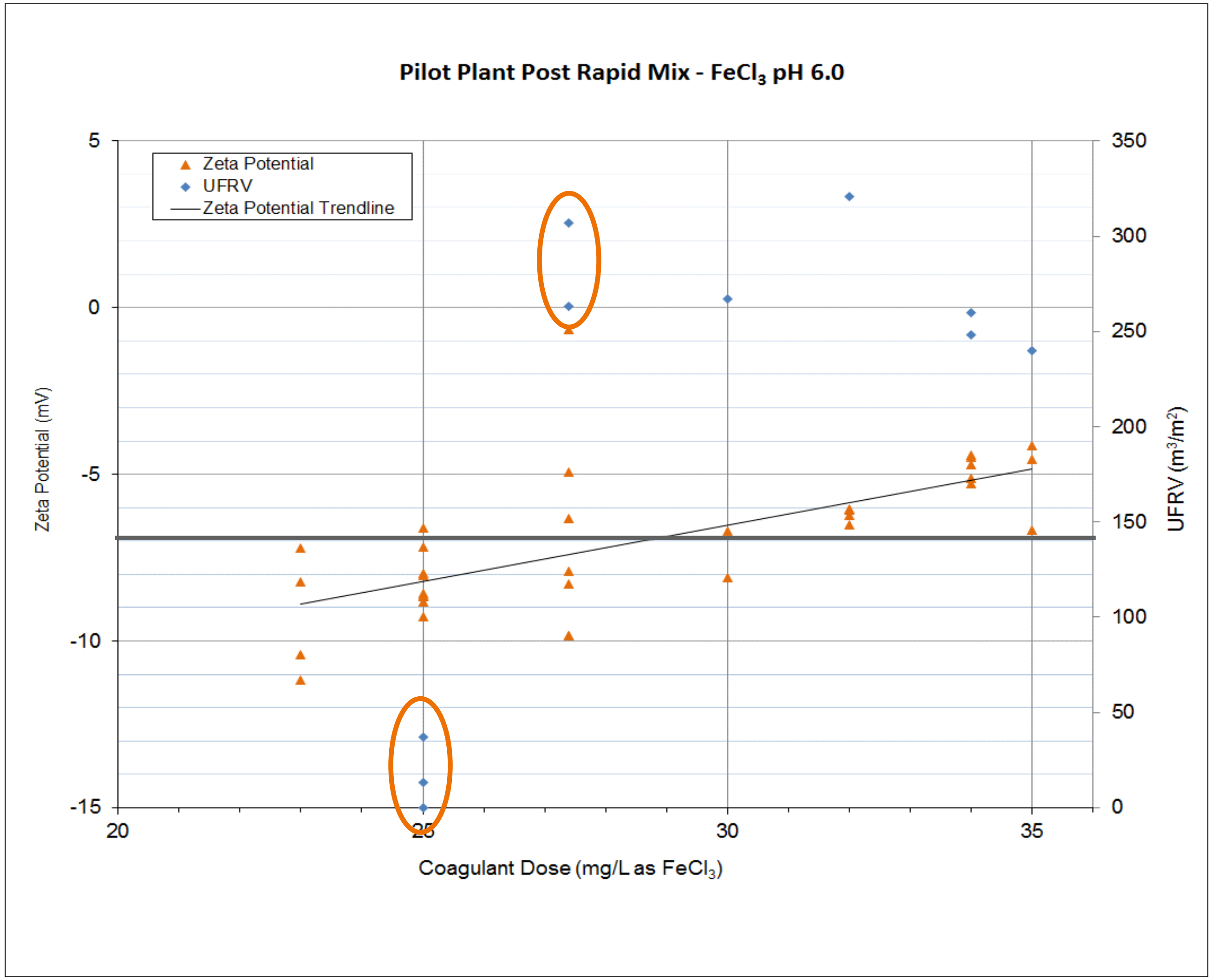


Evaluating Pilot Filter Performance

Need good data analysis to pick up on subtle changes in filter performance.

Zeta potential measurements are best measure for controlling coagulation

Unit Filter Run Volumes (UFRVs) should be primary KPI for evaluating effects of WTP variables (everything from coag dose to floc mixer speed)



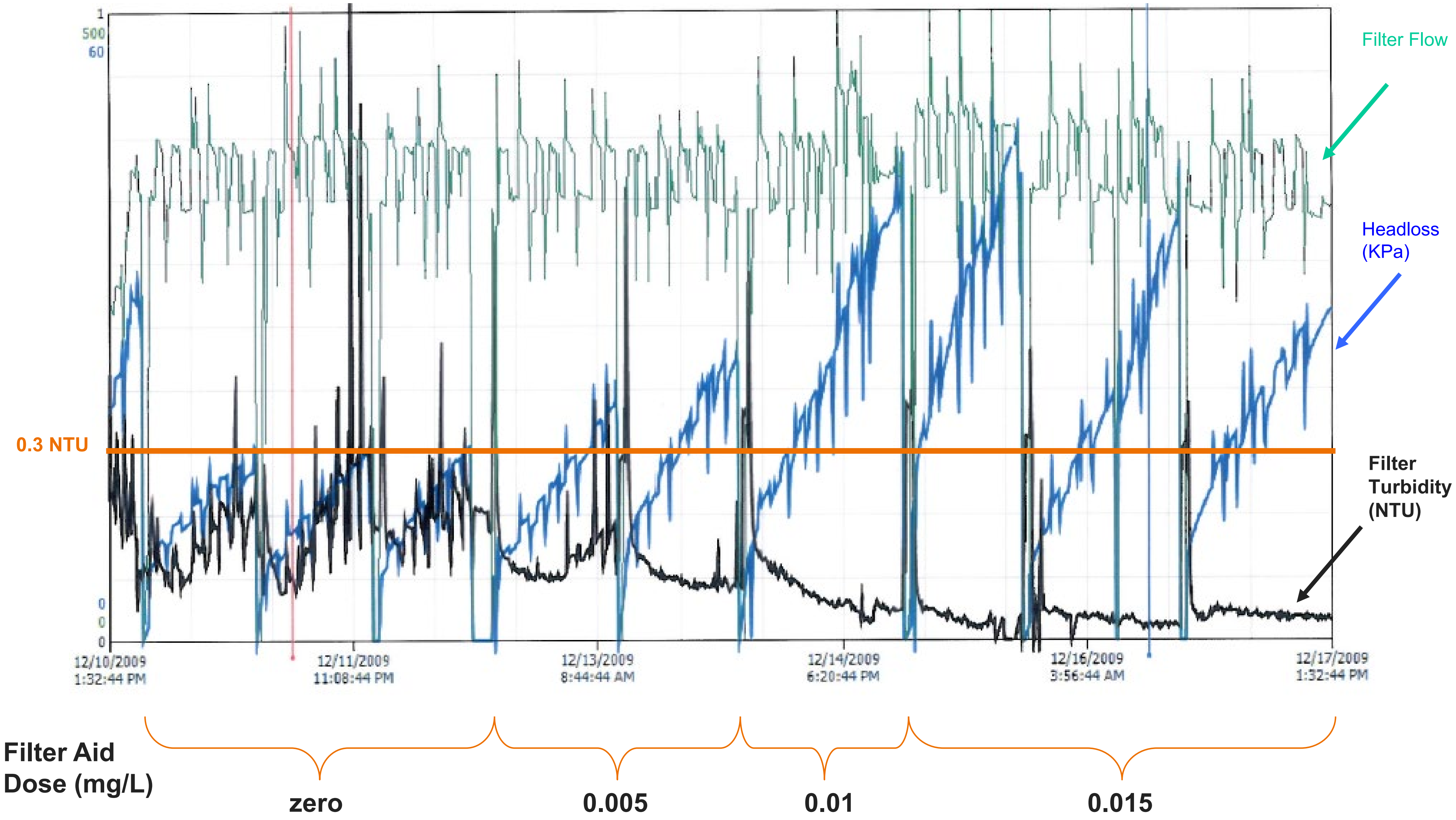
Filter/Floc Aids

Not a charge neutralization application

Certain floc particles are neutrally charged, but too small or fragile to be retained in filters

High molecular weight polymers used at low doses to enlarge and strengthen floc

Balance particle retention and headloss


Filter Flow
Headloss
(KPa)
0.3 NTU
Filter
Turbidity
(NTU)
1
500
60
0
0
0
12/10/2009
1:32:44 PM
12/11/2009
11:08:44 PM
12/13/2009
8:44:44 AM
12/14/2009
6:20:44 PM
12/16/2009
3:56:44 AM
12/17/2009
1:32:44 PM
Filter Aid
Dose (mg/L)
zero
0.005
0.01
0.015

Coagulation Chemistry Summary

NOM controls coagulant dose

Alum best at pH 6.0 to 7.0

PACls best at pH 6.5 to 7.5 (pH ↑ as basicity ↑)

Ferric coagulants best at pH 5.5 to 6.5

Acid or base may be needed to maintain these pH ranges

Key Performance Indicators

- Measure Zeta Potential or Streaming Current
- Measure UFRVs not just settled turbidity

References

- American Society of Testing and Materials (ASTM). 1987. Annual Book of ASTM Standards. v11.01. Philadelphia: ASTM.
- Duan, J., Wang, J., Guo, T., Gregory, J. 2014. Zeta potentials and sizes of aluminum salt precipitates – Effect of anions and organics and implications for coagulation mechanisms. Journal of Water Process Engineering, 4(2014) 224-232.
- Henderson, R.K., Parson, S. A. and Jefferson, B. 2008. Successful removal of algae through the control of zeta potential. Separation Science and technology, 43:1653-1666.
- Holmes, M., P. Reeve, C. Pestana, C. Chow, G Newcombe, and J. West. 2015. “Zeta Potential Measurement for Water Treatment Coagulation Control”. SA Water.
- James, W., Craik, S., Heidary-Monfared, S., Solonynko, G., and Pors, M. 2015. “Using Zeta Potential to Optimize Seasonal Direct Filtration”. Western Canada Water Conference, Sept. 15-18, 2015, Winnipeg MB.
- Kundert, K. 2014. “Alberta Flood 2013 – City of Calgary Water Treatment System Resiliency”. 16th Canadian National Drinking Water Conference, Oct. 26-29, 2014, Gatineau QC.
- Morfesis, A., A.M. Jacobson, R. Frollini, M. Helgeson, J. Billica, and K.R. Gertig. 2009. “Role of zeta (ζ) potential in the optimization of water treatment facility operations.” Industrial and Engineering Chemistry Research. 48(5): 2305-2308.
- Pernitsky, D.J., R. Cantwell, E. Murphy, N. Paradis, J. Boutilier, and G. Bache. 2010. First Aid for Direct Filtration – Using Zeta Potential to Improve Operation. Presented at the 2010 AWWA Water Quality and Technology Conference, November 15, 2010, Savannah, GA.
- Pernitsky, D.J. and J.K. Edzwald. 2006. Selection of alum and polyaluminum coagulants: principles and applications. Journal of Water Supply: Research and Technology—AQUA. 55(2): 121–141.
- Pernitsky, D.J. and J.K. Edzwald. 2003. Solubility of polyaluminum coagulants. Journal of Water Supply: Research and Technology—AQUA. 52(6): 395–406.
- Riddick, T.M. 1964. Role of zeta potential in coagulation involving hydrous oxides. Tappi. 47(1): 171A.
- Sharp, E.L., Rigby, R., Hall, A., Moore, K., Jefferson, B. “Using online zeta potential measurements for coagulation control: A first for the UK Water Industry”. IWA Specialist Conference on Natural Organic Matter in Water, Malmo, Sweden, 7-10 Sept. 2015.
- Sharp, E.L., J. Banks, J.A. Billica, K.R. Gertig, R. Henderson, S.A. Parsons, D. Wilson, and B. Jefferson. 2005. “Application of zeta potential measurements for coagulation control: pilot-plant experiences from UK and US waters with elevated organics.” Water Supply. 5(5): 49–56.
- Solomentseva, I.M., Barany, S., and Gregory, J. 2004.Surface properties and aggregation of basic aluminum sulphate hydrolysis products 1. Electrokinetic potential and hydration of BAS hydrolysis product particles. Colloids and Surfaces A: Physiochem. Eng. Aspects 230(2001) 117-129.
- Solomentseva, I.M., Gerasimenko, N.G., and Barany, S. 1999. Surface properties and aggregation of basic aluminum chloride hydrolysis products. Colloids and Surfaces A: Physiochem. Eng. Aspects 151(1999) 113-126.
- Stumm W., and Morgan, J.J. 1996. Aquatic Chemistry, 3rd Edition. John Wiley and Sons Inc.
- Waller M., R. Cantwell, Q. Muylwyk, Pernitsky, D.J. 2012. Rethinking Coagulation Practices on the Great Lakes Using Zeta Potential. Presented at the 2012 AWWA Water Quality and Technology Conference, November 4-8, 2012, Toronto, ON, Canada.

Thank You

David Pernitsky, PhD, PEng

david.pernitsky@stantec.com

Scan to learn more about Stantec