SHORT COURSE: MINE WATER TREATMENT TECHNOLOGIES, CASE STUDIES, AND COSTS

CASE STUDY

SULFATE REMOVAL USING ADVANCED ETTRINGITE PROCESS

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ACKNOWLEDGMENTS

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CASE STUDY

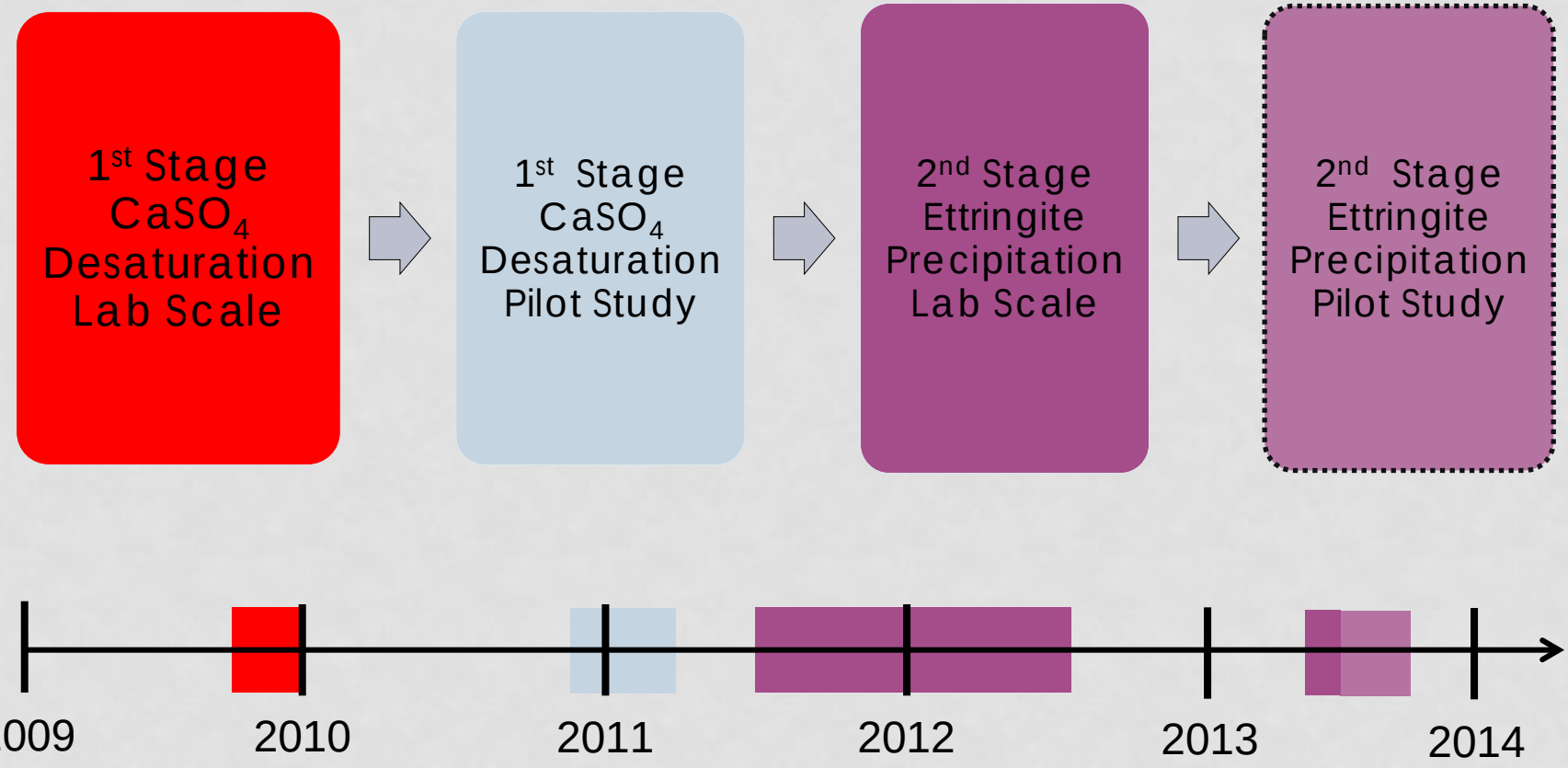
SULFATE REMOVAL USING ADVANCED ETTRINGITE PROCESS

TWO - STAGE SULFATE TREATMENT PILOT STUDY USING ADVANCED ETTRINGITE PROCESS

Overview:

- Reduces sulfate to 100- 200 mg/L by two stage process:
  - 1st Stage: $CaSO_4$ desaturation; SO_4 is reduced to <1500 mg/L
  - 2nd Stage: advanced chemical precipitation; SO4 reduced to < 200 mg/l
- Treated effluent can be reused or discharged to environment.

TIMELINE OF TWO-STAGE PILOT STUDY



1ST STAGE IMPLEMENTATION

- Project site: copper mine in South America
- Tailing pond water contains high sulfate and calcium
- Project requires sulfate to < 250 mg/l; TDS to < 1,000 mg/l

1ST STAGE PILOT STUDY

Tailing Pond Water Characteristics:

Parameter	Value (mg/l unless indicated)		Parameter	Value (mg/l unless indicated)
pH	7.4 s.u.		Na	104
Mg	21		K	124
SO4	1,830		Ca	690
Fe	0.04		Alkalinity	28
Mn	0.17		TDS	3,070
Mo	0.27		Cations	40.02 meq/l
Al	0.05		Anions	44.04 meq/l

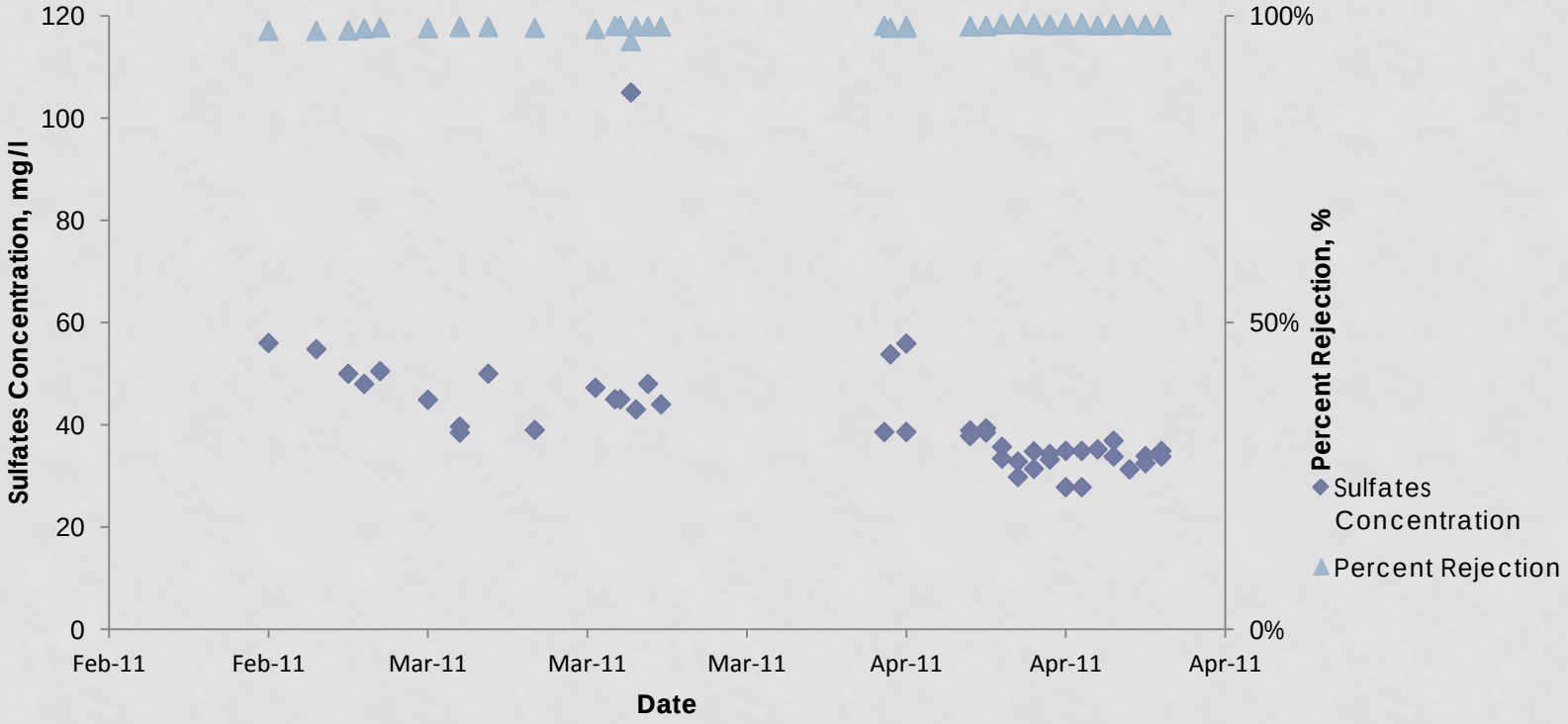
1ST STAGE PILOT STUDY

Pretreatment and membrane:

- Pretreatment includes iron addition, clarification, multi-media filtration and Green Sand filtration
  - Mo was reduced to < 0.05 mg/L
  - Fe < 0.3 mg/L
  - Mn <0.05 mg/L
- SDI = 3
- NF: Dow Filmtec

1ST STAGE PILOT DATA

NF permeate data



1ST STAGE PILOT STUDY

NF Permeate vs Discharge Standards

Parameters	Permeate (mg/l)	Discharge Standard (mg/l)
SO4	35	250
Cl	80	200
Ca	25	60
Al	<0.1	5
Fe	<0.01	5
Mn	<0.01	0.2
As	<0.005	0.1
Cd	<0.005	0.1
Cu	0.01	0.2

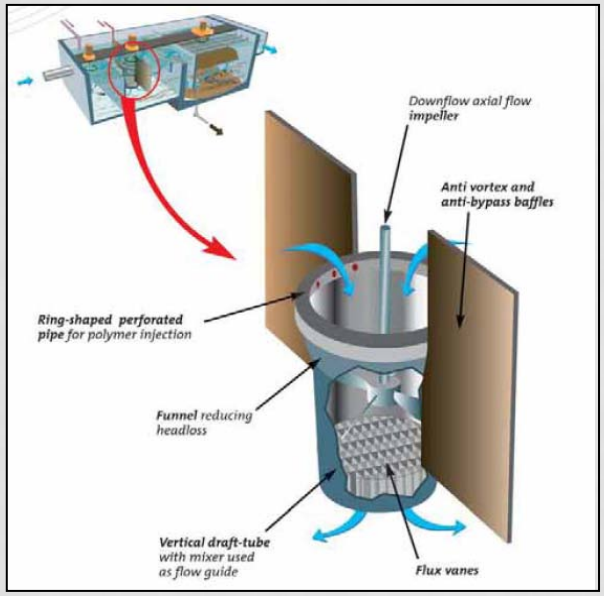
1ST STAGE PILOT STUDY

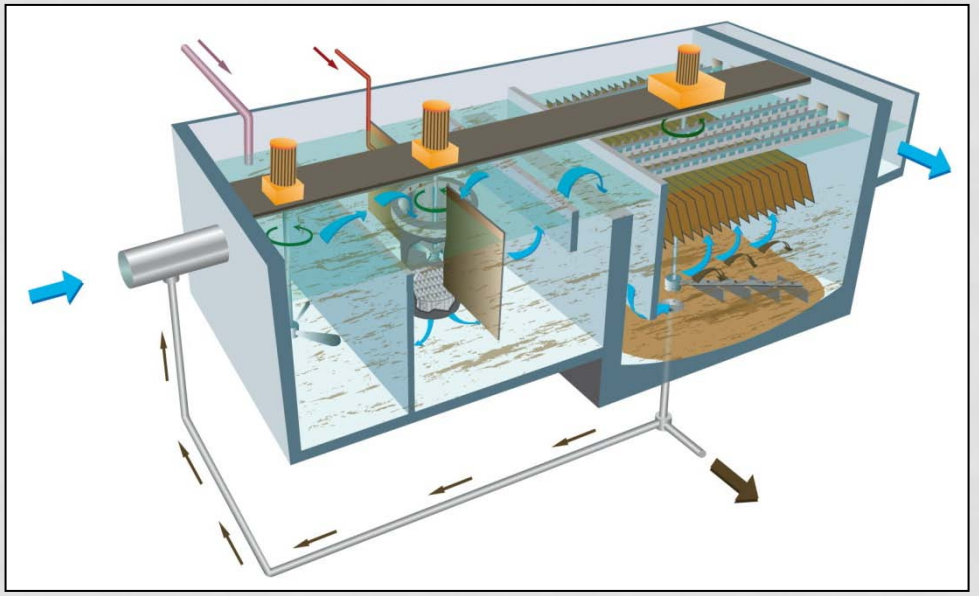
NF Reject Treatment Objectives:

- Precipitate SO_4 as $CaSO_4$
- Use lime or lime/$CaCl_2$ as sources of Ca^{2+}
- Determine the impact of sludge recirculation ratio on $CaSO_4$ nucleation and crystal growth
- Ratio = Mass of solids [$CaSO_4$] in the recycle line/Mass of solids [$CaSO_4$] formed from the fresh wastewater [NF reject]
- Goal was to reduce SO_4 to < 1,500 mg/L as SO_4 (theoretical solubility limit)

1ST STAGE PILOT STUDY

- Calcium sulfate desaturation with sludge recirculation
- NF brine: sulfate - 3200 mg/L
- Desaturation process using Turbomix® Reactor with 30-minute reaction time followed by MULTIFLO™ clarification for solid/liquid separation





1ST STAGE PILOT STUDY

1st stage test results:

- Calcium sulfate precipitation as a function of sludge recirculation ratio:

Sludge Recycle Ratio (Dry mass CaSO4 sludge to influent)	20:1	15:1	10:1	none
pH	9.3	9.3	9.2	9.3
Clarifier overflow SO4, mg/l	1,250	1,100	1,200	2,000

2ND STAGE IMPLEMENTATION

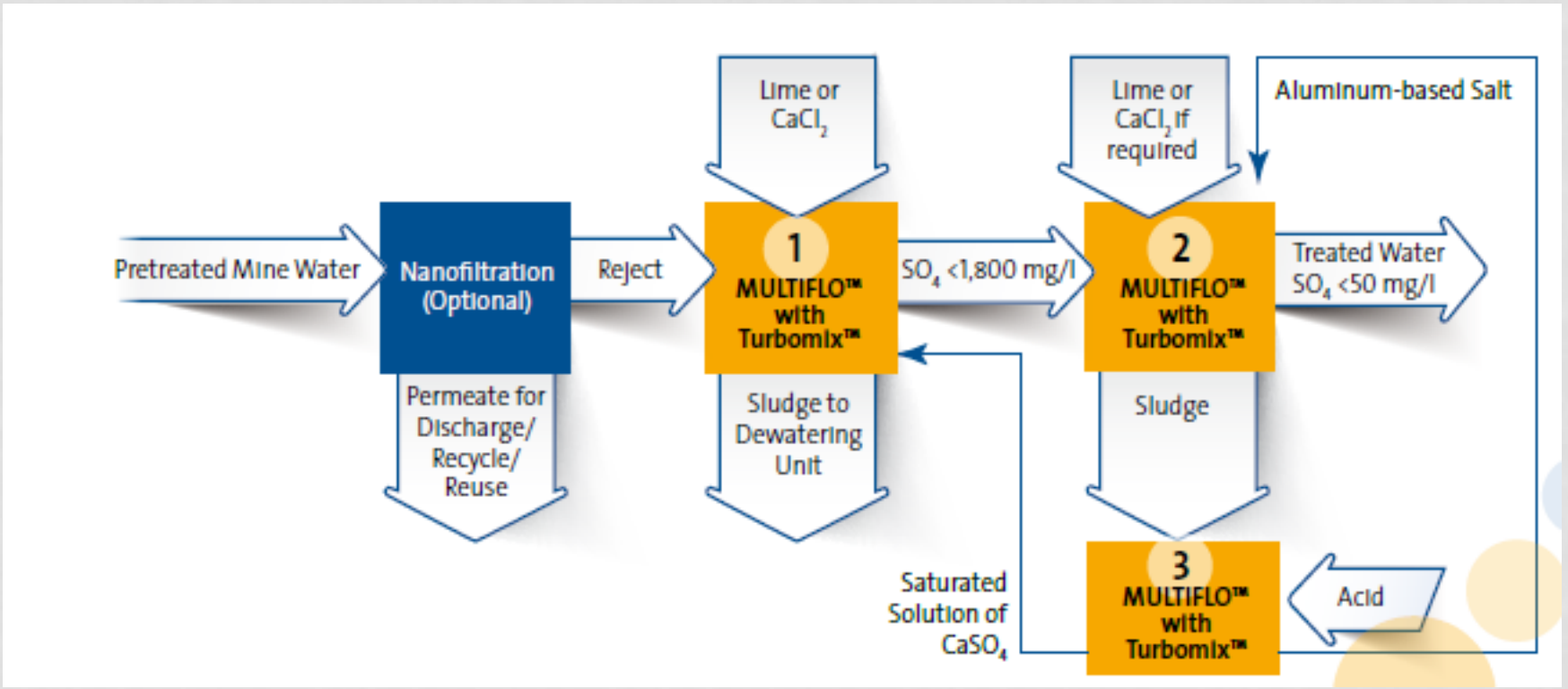
- 2nd Stage Precipitation [Ettringite] Pilot
  - Site: Greene County, PA
  - ARD Water [Effluent from DenSludge™ HDS Process]
  - Study Period: 16 weeks

2ND STAGE OBJECTIVES

- Validate Sulfate Reduction Process: < 200 mg/l SO4
- Validate Gibbsite Regeneration and Recovery
- Use Recovered Gibbsite to Precipitate Ettringite
- Process Optimization
  - pH
  - Time
  - solids ratios
  - chemical dosages
  - settling characteristics

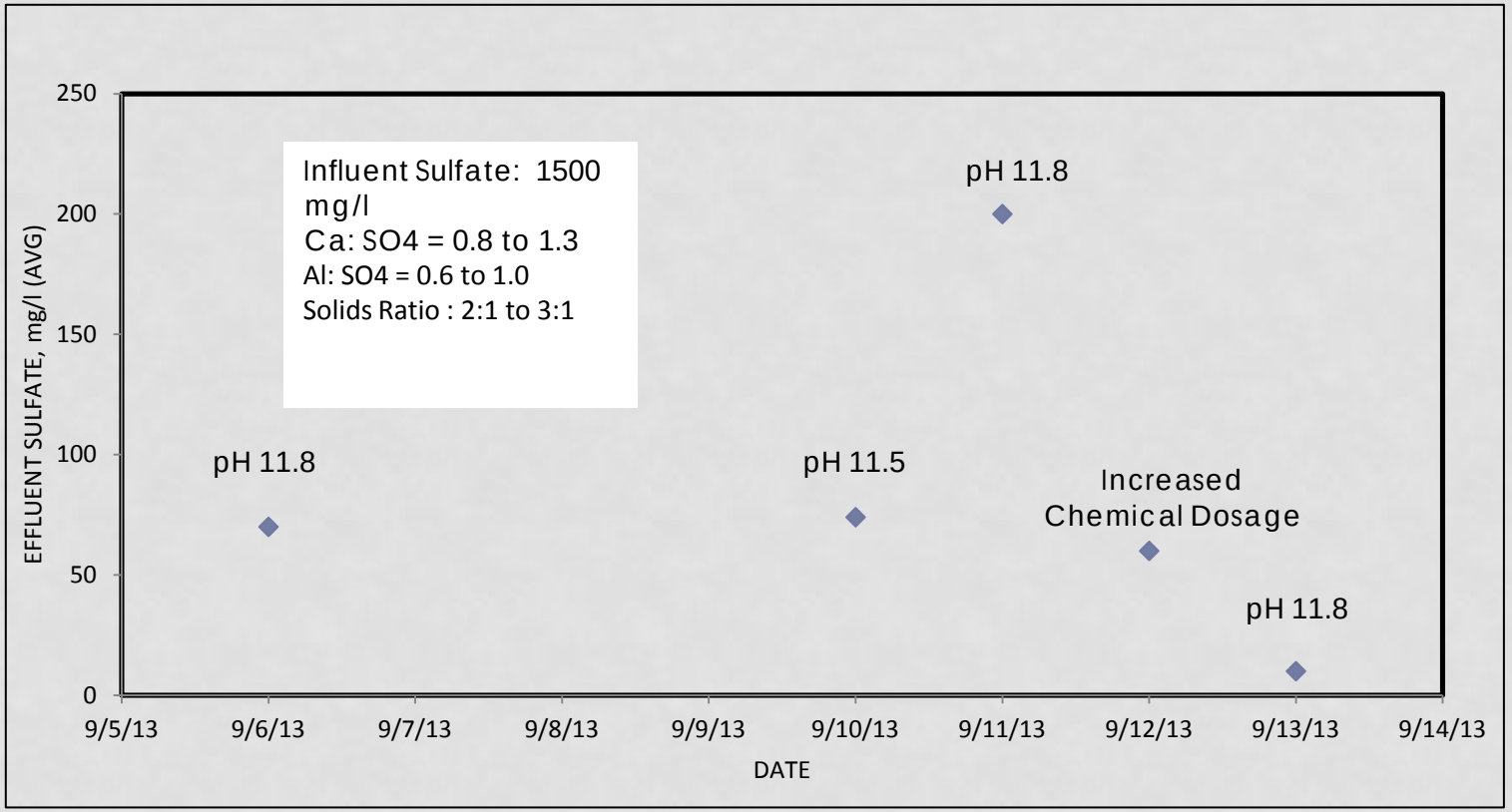
2ND STAGE OVERVIEW

- Generalized flow sheet



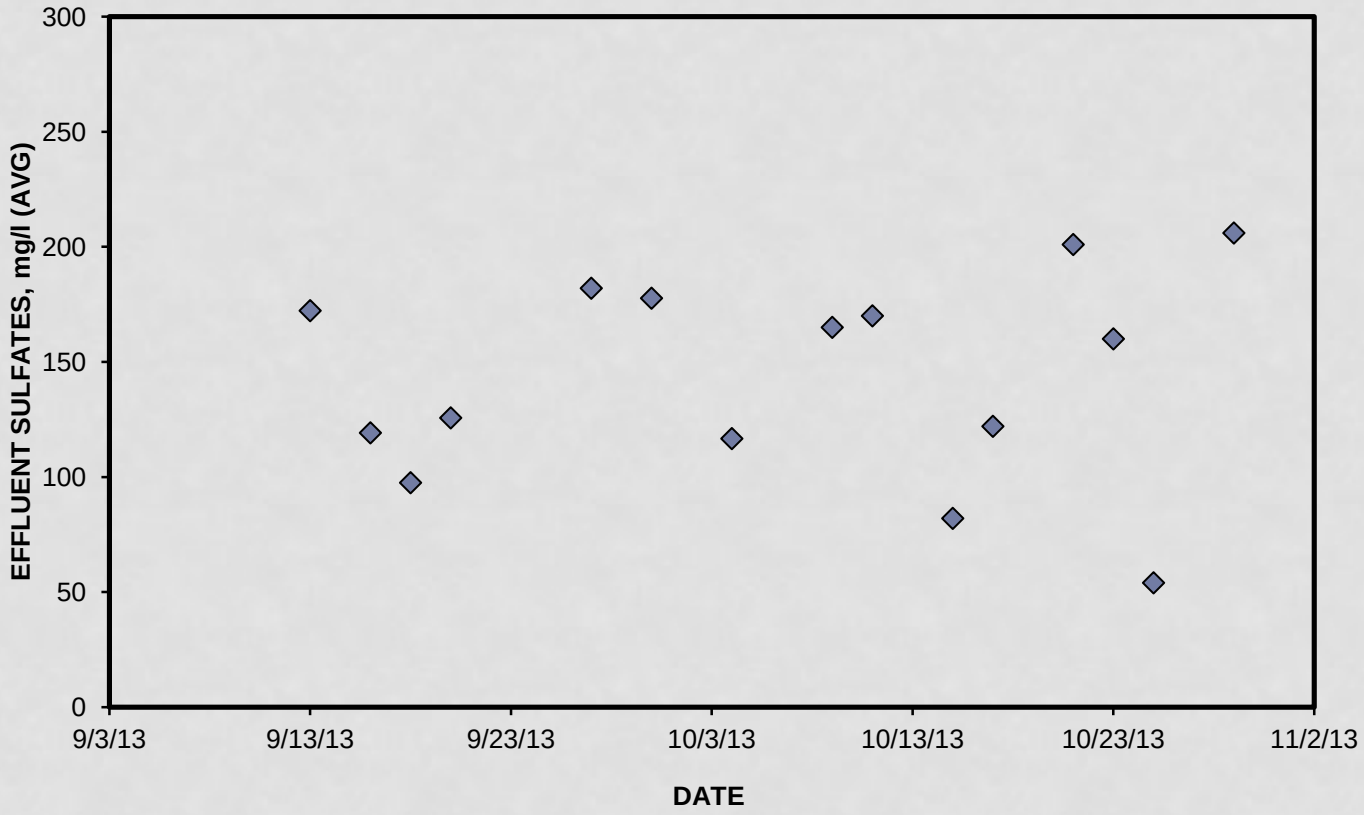
2ND STAGE OPTIMIZATION USING FRESH GIBBSITE

- Effluent sulfate concentration



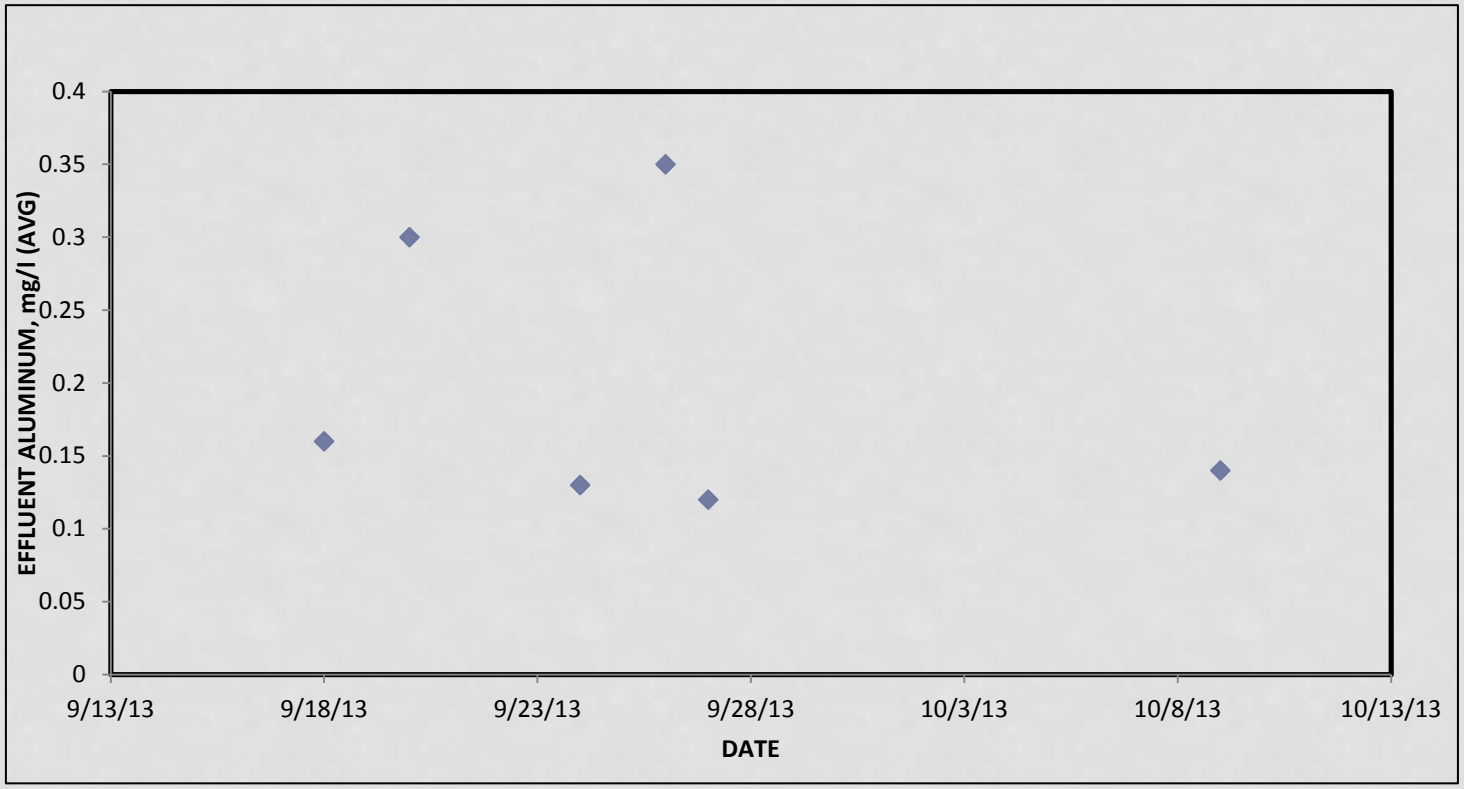
2ND STAGE RESULTS USING REGENERATED GIBBSITE

- Effluent sulfate concentration-regenerated Gibbsite



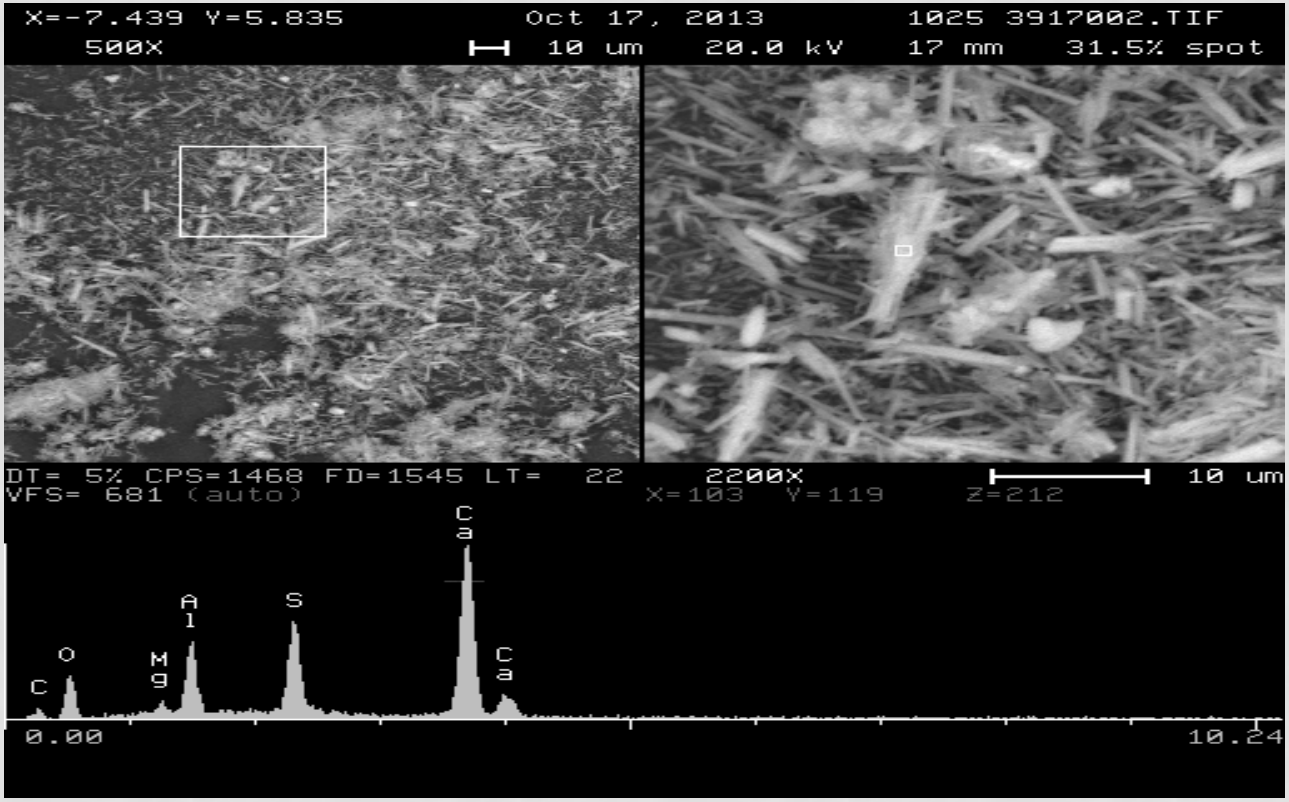
2ND STAGE RESULTS

- Effluent aluminum concentration



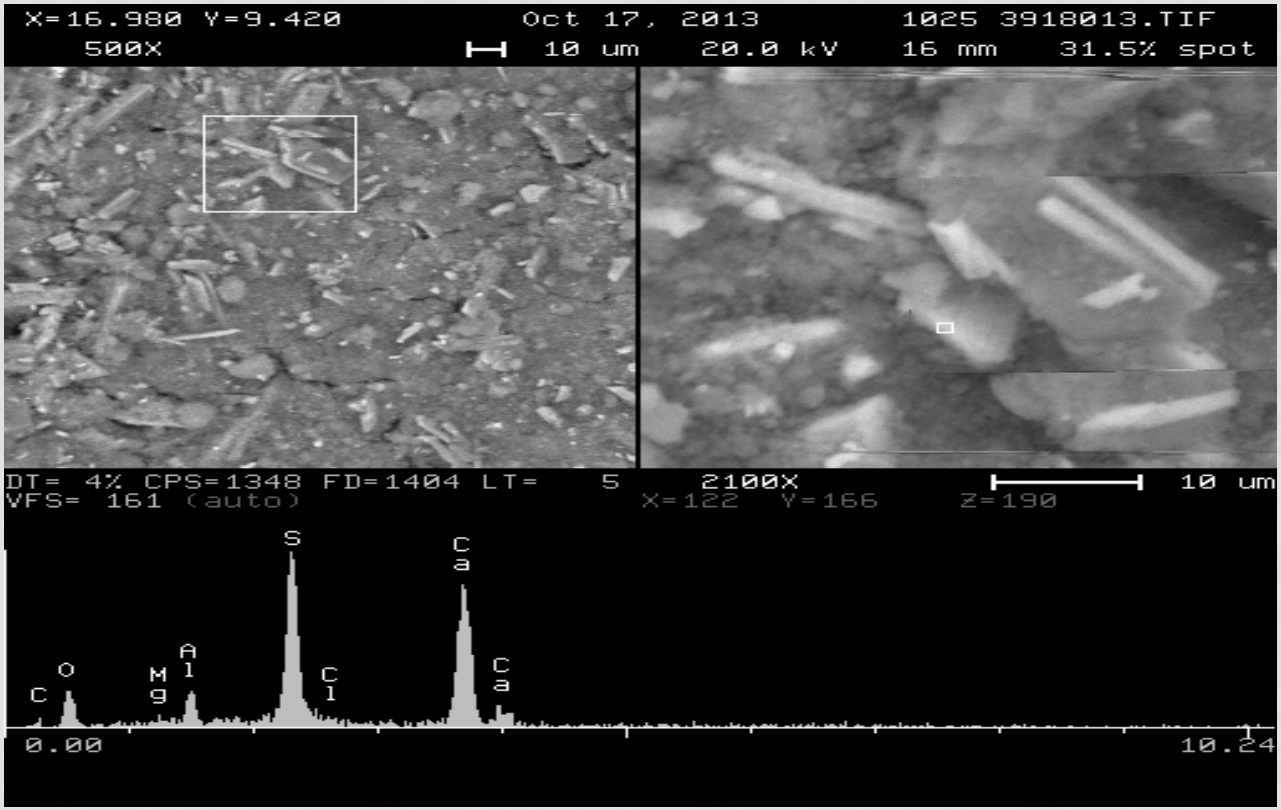
2ND STAGE RESULTS

- Ettringite crystals in effluent



2ND STAGE RESULTS

- Recovered aluminum sludge sample



TWO-STAGE ADVANCED ETTRINGITE PROCESS - OPEX

- Cost comparison for chemicals and power :
  - With Gibbsite recovery and reuse - $1.60 - $1.70 per 1,000 gal
  - Without Gibbsite recovery and reuse - $8.0 - $9.0 per 1,000 gal

CONCLUSIONS

- Initial pre-treatment and NF
  - Capable of reducing sulfate to < 150 mg/L
  - More than 98% sulfate rejection was achieved

CONCLUSIONS

- Sulfate desaturation and Ettringite removal is a combination of chemical precipitation and adsorption processes
- Important Process parameters:
  - pH
  - Reaction Time
  - Ca : SO4 ratio & Al : SO4 ratio
  - Sludge recirculation with an optimized solids ratio
  - Mass of solids in the recycle line per mass of solids generated by the fresh wastewater

CONCLUSIONS

- 1st stage desaturation process:
  - Sulfate from NF reject can be reduced to < 1500 mg/L in presence of a seed material with proper sludge recirculation ratio.
- 2nd stage process:
  - Seed material need be added only once during the crystallization process
  - More than 95% Gibbsite was recovered and reused in the Ettringite process
  - Using 95% recovered Gibbsite and 5% fresh Gibbsite, sulfate reduced to 100 - 200 mg/L