Evaluation of Alternate Process Chemistries for the Removal of Arsenic and Fluoride from Industrial Wastewater
Background

• Southeastern industrial client discharges process wastewater containing arsenic and fluoride

• On-site lagoons store, manage, and treat wastewater

• Project driver was to reduce operational treatment costs while minimizing capital costs
Project Driver – Reduce Operating Costs

- Current process is labor and chemical intensive
  - Process requires high lime dosage to raise pH over 11.8 before reducing pH with CO$_2$ to 6.0 – 8.5
  - Excess lime causes clogging of piping

- Operators manually monitor lime slurry and outfall

- Site is remote and difficult to deliver bulk lime and CO$_2$
  - Client desired all liquid dosing from totes for simpler operation

- Current operating costs: ~$1,137/MG
Current Treatment Process

• Current treatment process utilizes lime precipitation and CO₂ pH adjustment
  • Arsenic in the arsenite form (at neutral pH and low ORP) is converted to arsenate (at high pH)
  • Fluoride is treated by converting to CaF₂ which is highly insoluble in water
  • The client’s arsenic and fluoride discharge limits are 50 ug/L and 10 mg/L respectively.
  • Avg. As & F removal rates are 93% and 25% respectively
Background
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Methods for As removal

• Chemical Precipitation
• Oxidation
• Adsorption – Activated Alumina
• Ion Exchange
• Reverse Osmosis

Methods for F⁻ Removal

• Chemical precipitation
• Adsorption – Activated Alumina
• Ion Exchange
• Reverse Osmosis

• Based on current infrastructure and long retention time in the clarification pond, Dewberry pursued chemical precipitation treatment of arsenic and fluoride
Treatability Approach - Arsenic

Current Treatment

Proposed Treatment

Raw Wastewater

\[ \text{H}_3\text{AsO}_4 \quad \text{As(V)} \]

\[ \text{H}_2\text{AsO}_4^- \quad \text{As(V)} \]

\[ \text{H}_3\text{AsO}_3 \quad \text{As(III)} \]

\[ \text{H}_2\text{AsO}_3^- \quad \text{As(III)} \]

\[ \text{HAsO}_4^{2-} \quad \text{As(V)} \]

\[ \text{AsO}_4^{3-} \quad \text{As(V)} \]
Treatability Approach - Fluoride

- Current treatment method uses the calcium in lime, $\text{Ca(OH)}_2$, to react to form $\text{CaF}_2$.

- Lime is not very soluble in water: 1.7 g/L

- Dewberry looked at multiple approaches for fluoride removal
  - Improved process mixing
  - Using an alternate calcium salt: calcium chloride
  - Adding an adsorption aid: magnesium hydroxide
  - Using an alternate coagulant: aluminum sulfate
Laboratory Equipment

- pH/ORP probe and meter
- Hach Fluoride TNT test kit
- DR 3900 Spectrophotometer
- Hach Arsenic test kit
- Phipps Bird Gang Stirrer
Arsonic Indicator Test

• Raw water As concentration ~ 50 – 100 ug/L

• Difficult to determine concentration within the 20 – 70 ug/L range

• Arsenic kit was used as a qualitative test
Bench Testing Setup
Bench Testing Reactor Setup

• Order of chemical additions:
  • Oxidant, calcium, magnesium, coagulant

• Mixing
  • 1 min between chemicals
  • 5 min of rapid mixing after chemicals added
  • 15 min of slow mixing
  • 30 min of settling

• Filtering
  • Since client has a large treatment pond, decant was filtered to simulate discharge characteristics
1. Improve existing lime/ferric process
   a) Increase mixing energy & retention time
   b) Optimize lime dose

2. Evaluate alternate process chemistries
   a. Oxidant, calcium chloride, & ferric chloride
   b. Oxidant calcium chloride, aluminum sulfate
   c. Oxidant, Mg(OH)2, CaCl2, alum
   d. Oxidant, alum, ferric
Results - Improved Mixing

**Fluoride Removal**

- **Raw**
  - Fluoride Concentration: 15 mg/L
  - % Removal: 0%

- **Pipe Mix**
  - Fluoride Concentration: 10 mg/L
  - % Removal: 5%

- **Added Mix**
  - Fluoride Concentration: 10 mg/L
  - % Removal: 5%

**Arsenic Removal**

- **Raw**
  - Arsenic Concentration: 60 ug/L
  - % Removal: 0%

- **Pipe Mix**
  - Arsenic Concentration: 40 ug/L
  - % Removal: 0%

- **Added Mix**
  - Arsenic Concentration: 40 ug/L
  - % Removal: 0%

**Conclusions**

- 5% additional fluoride removal with additional mixing.
- 0% additional arsenic removal observed with additional mixing.
Conclusions

- Increasing lime dose showed diminishing returns for As removal
- Additional removal of F required pH of 11
- While increased lime dose increases removal, a lower dose can save on money with minimal impact
Conclusions

• Increasing CaCl₂ dose had no effect on F removal.
  • Even at extreme doses
Conclusions

- Increasing CaCl₂ dose increased F removal until reaching 1,500 mg/L.
- Achieved 28% F removal with no calcium addition.
Conclusions

- Increasing CaCl₂ dose had minimal effect on arsenic removal and no removal of F (not shown)
- Client liked economics of ferric and oxidant condition but wanted ~20% As removal
Results – Other Conclusions

• With additional trial data not shown:
  • Greater than 60% As was removed at ORP levels over 400 mV
  • Mg(OH)\textsubscript{2} did not influence F\textsuperscript{-} removal
  • Calcium did not reduce F\textsuperscript{-} as much as alum

• Client liked economics of oxidant/ferric process needed to achieve a minimum F removal of 20%
Conclusions

- Alum alone demonstrated significant F removals
- F removal was proportional to the amount of alum dosed.
- Alum alone did not remove As
Results – Multiple Parameters

Conclusions

• The presence of ferric chloride facilitated As removal in system
• Oxidant, alum, ferric combination reduced fluoride and arsenic by 20% and 60% respectively.
Conclusions

• Achieved over 25% fluoride removal with ~ 80 mg/L alum
• As removal greatly improved with ferric. F removal improved slightly
• Pre-oxidation not required. Removal rates approximately the same.
## Treatment Costs

<table>
<thead>
<tr>
<th></th>
<th>Current Treatment</th>
<th>Proposed Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Fluoride Removal</td>
<td>32%</td>
<td>30%</td>
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<tr>
<td>% Arsenic Removal</td>
<td>93%</td>
<td>50%</td>
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<tr>
<td>WW Effluent pH</td>
<td>11.8</td>
<td>6.3</td>
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<tr>
<td>Chemical Treatment Cost</td>
<td>$933/MG</td>
<td>$500/MG</td>
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<tr>
<td>Labor Cost</td>
<td>$204/MG</td>
<td>$153/MG</td>
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<tr>
<td>Total Treatment Cost</td>
<td>$1,137/MG</td>
<td>$653/MG</td>
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</table>
Proposed WW Treatment

EXISTING POND 4

EXISTING 1500 GPM PUMP 401

SODIUM HYPOCHLORITE TOTE

CHECK VALVES

ALUM TOTE

FERRIC TOTE

EXISTING PUMP FC1

EXISTING PIPE FLOCCULATOR

RAIN FOR RENT TANK

SAMPLE STORAGE DRUM

TO POND 4A

E)

Pf
Full Scale Trial

• Dewberry performed a full scale trial during the last week of July

• Intent of the trial was to:
  • Determine if the modified process would work with the current mixing setup
  • Collect enough sample for whole and acute toxicity testing

• Trial was cut short due to hurricanes and flooding
# Results – Full Scale Trial

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Trial 5</th>
<th>Trial 6</th>
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</thead>
<tbody>
<tr>
<td>NaOCl, mg/L</td>
<td>17.0</td>
<td>17.0</td>
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<tr>
<td>Alum, mg/L</td>
<td>108</td>
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<td>Ferric, mg/L</td>
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<td>pH</td>
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<td>ORP</td>
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<td>Raw F, mg/L</td>
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<tr>
<td>Raw As, ug/L</td>
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<td>160</td>
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<td>Final F, mg/L</td>
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<tr>
<td>Final As, ug/L</td>
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<td>47</td>
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<tr>
<td>F Removal</td>
<td>20%</td>
<td>30%</td>
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<tr>
<td>As Removal</td>
<td>91%</td>
<td>71%</td>
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</table>
Conclusions

- Oxidant + Ferric effective for As removal at lower pH
- Alum effective for F removal at near neutral pH
- Identified potential for cost savings (~43%) over current lime / CO$_2$ process.
- Improve pH control and dechlorination in pilot system to improve toxicity performance.