New Technology Improves Oxidation of Sulfite

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Billy J. King & Charles M. West

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Wet Process Specialists

Case Study

- Existing lead-acid battery recycler utilizes forced air oxidation for sulfite removal from SO_2 scrubber wastewater
- Increases in production and sulfur content of the feedstock stress the existing air oxidation system performance
- Facility researches root causes of sulfite oxidation issues and evaluates options for resolving problem
- Facility successfully installs new technology for sulfite oxidation

Background

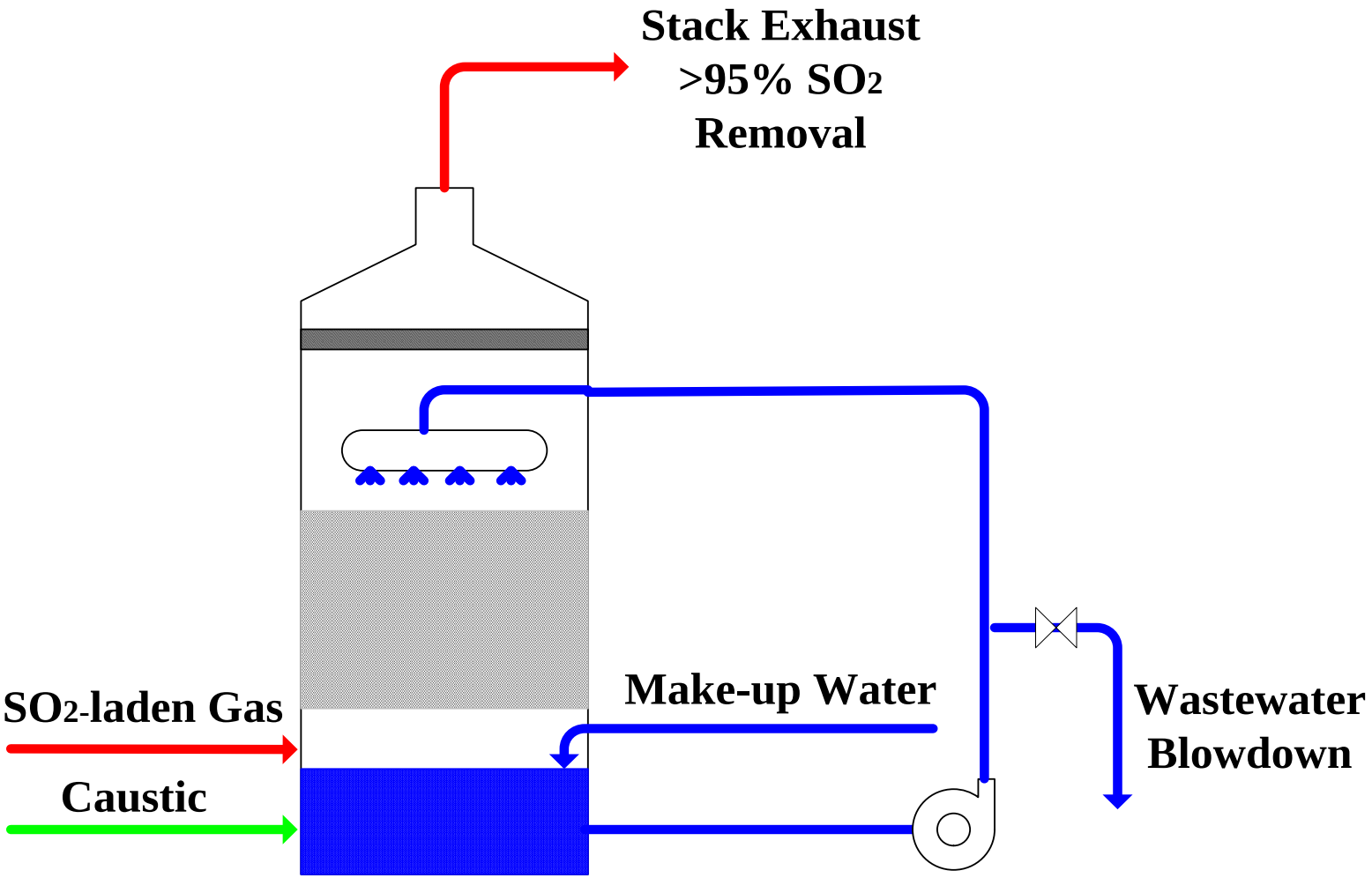
Origins of Sulfite

- Wet caustic scrubbing is a common control technology for removal of SO_2 from lead-acid battery recycling smelter flue gas
- This technology results in the formation of sulfite $(SO_3)^{-2}$ in the scrubber wastewater:

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$H_2SO_3 + 2NaOH \rightarrow Na_2SO_3 + 2H_2O$$

Background

Wet Scrubber Operations



Background

Need for Sulfite Removal

- Sulfite is a powerful oxygen scavenger
- The toxicity of sulfite to aquatic species at relatively low concentrations has been documented
- Sulfite can create oxygen-deficient zones in surface water and interfere with biological treatment processes in municipal sewers when discharged
- Most common method for removal is oxidation to sulfate with forced air:

$$Na_2SO_3 + ½\ O_2 \rightarrow Na_2SO_4$$

Issues

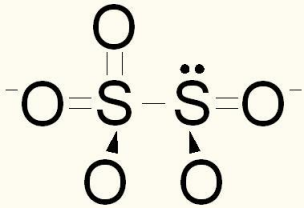
- Facility SO_2 scrubber operating conditions at upper margin of design capacity
- As a result, scrubber blowdown can contain elevated concentrations (near saturation) of sulfite and total dissolved solids (TDS)
  - Concentrations of TDS near saturation, combined with high temperatures, severely limit transfer of oxygen in forced air oxidation systems
  - Elevated levels of TDS can also lead to formation of other oxo-anions of sulfur that are more difficult to oxidize than sulfite

Issues

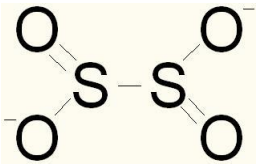
Facility Scrubber Wastewater

Issues

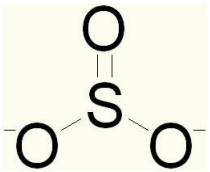
Sulfur Oxo-Anions



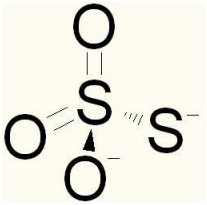
Disulfite



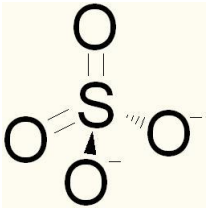
Dithionite



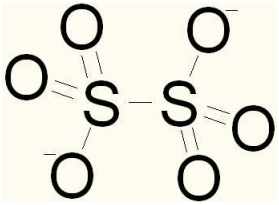
Sulfite



Thiosulfate

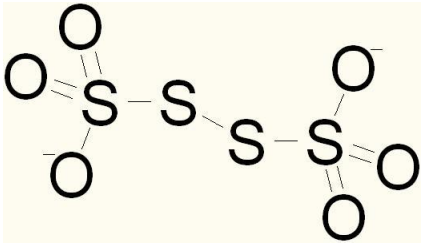


Sulfate



Dithionate

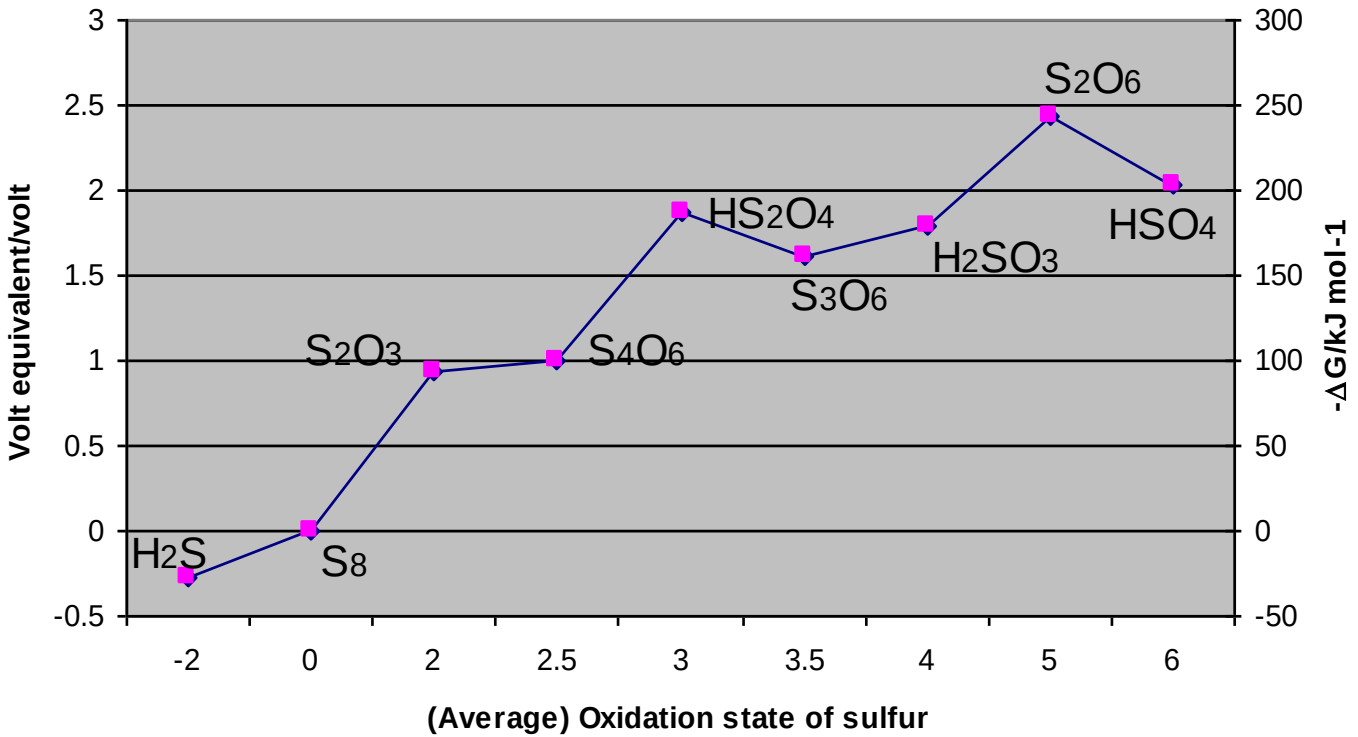
Sulfide



Tetrathionate

Issues

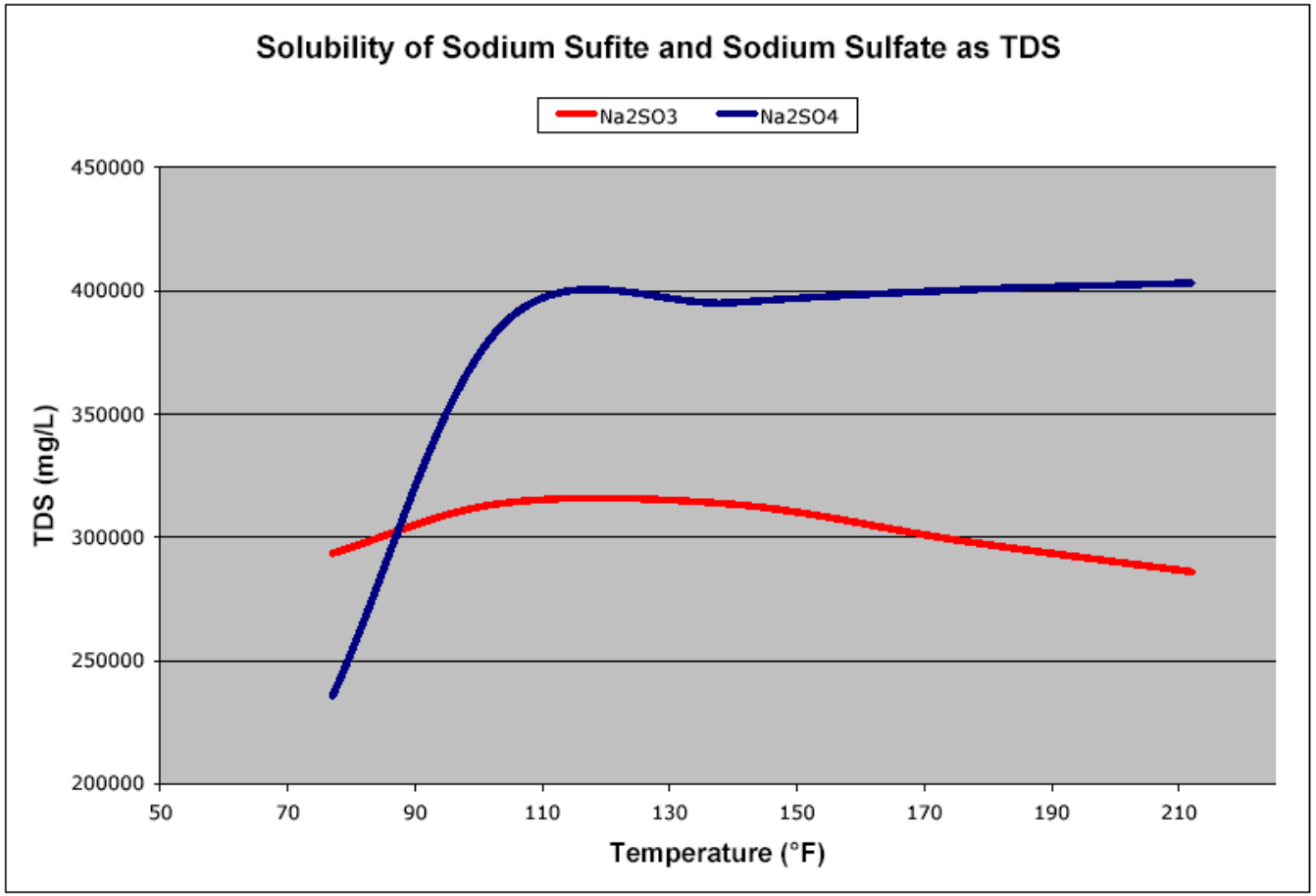
Gibb's Free Energy & Volt Equivalent



Volt equivalent diagram for sulfur-containing species in acid solution.

Issues

Sulfite and Sulfate Solubility



Issues

Existing Forced Air Oxidation Tanks

Options Analysis

- Chemical Oxidation with Hydrogen Peroxide
  - Effectively oxidizes sulfite and other sulfur oxo-anions
  - Low capital costs
  - Extremely high operating (chemical) costs
- Expand Forced Air Oxidation System
  - Predictable but slow oxidation rates
  - Excessive footprint requirements
  - Relatively high operating costs (energy)
- New Technology Utilizing Pure Oxygen and Pressure
  - Dramatically increases transfer of oxygen increasing the rate of treatment
  - Minimal footprint requirements
  - Low capital and operating costs

Options Analysis

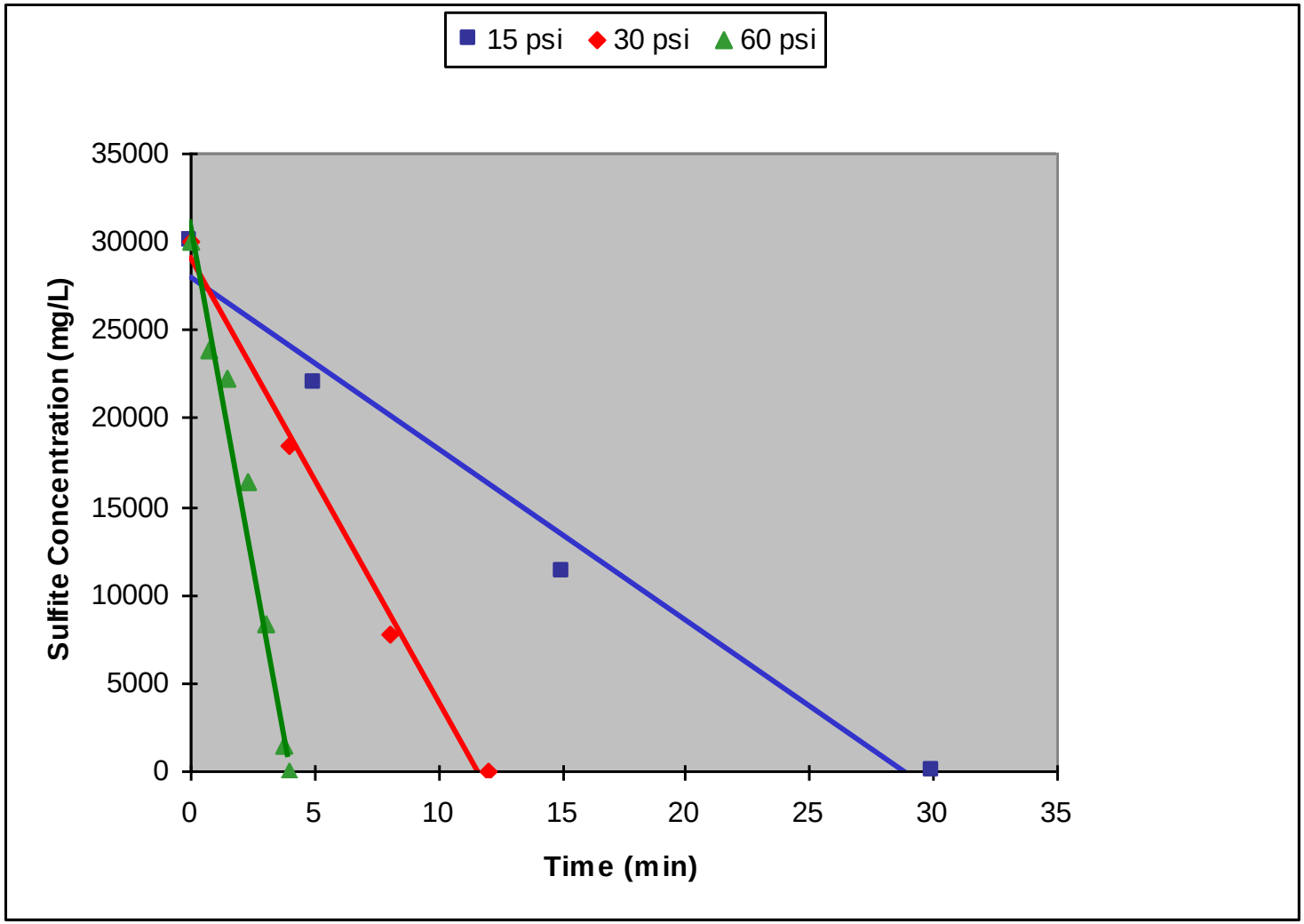
Available Footprint for the New System

Options Analysis

Footprint

- Forced Air Oxidation System
  - Uses a large footprint: $\frac{1\ ft.^2}{lb.SO_3 treated\ per\ hour}$
  - Has a height requirement of 36 ft.
- Pressure Oxidation System
  - Much smaller footprint: $\frac{0.14\ ft.^2}{lb.SO_3 treated\ per\ hour}$
  - Has a height requirement of only 17 ft.

Sulfite Oxidation Reaction Rates vs. Pressure



Options Analysis

Reaction Rate

- Reaction rates will increase as pressure increases
  - Forced Air Oxidation System: Low pressure system, reaction rates near $\frac{40\ mg}{L \cdot min}$
  - Pressure Oxidation System: Higher pressure system, reactions rates can be upwards of $\frac{6000\ mg}{L \cdot min}$

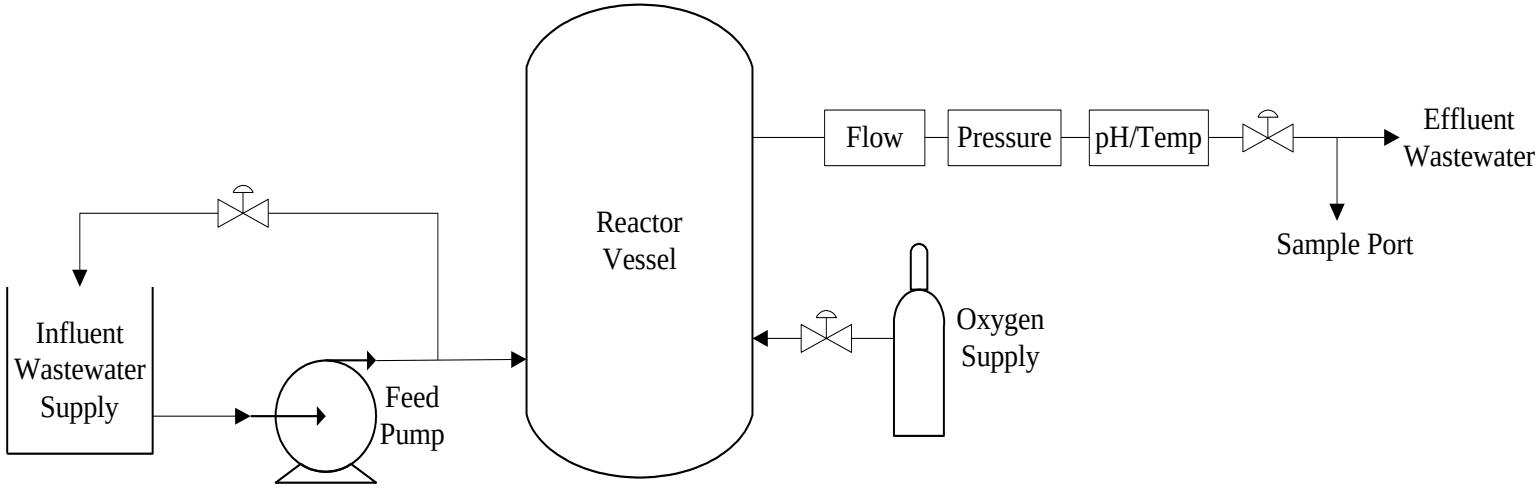
Options Analysis

Technology Cost Comparison

Technology	Normalized Total Cost* [$/ton ($SO_3^{-2}$)]
Chemical Oxidation with H_2O_2	$600
Forced Air Oxidation	$40
Pressure Oxidation	$40

* Based on 10-year capital depreciation

Pressure Oxidation System Schematic



Pressure Oxidation System

Project Successes

- Pressure oxidation system provides complete oxidation of residual sulfite when operated at design conditions
- Average overall sulfite oxidation efficiency at facility increased from 80% to >97%
- Furnace production and utilization increases realized upon installation of pressure oxidation system