Minimizing Solvent Oxidation with NO_2 Pre-Scrubbing

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Trimeric Corporation

- Background on Trimeric
  - Providing technical services to industry
  - Process engineering, chemical engineering, R&D
  - ***Specialized****….* in process/chemical engineering
  - ***Diversified****….* across multiple industries
- Trimeric's Resources
  - Regular Staff
  - Senior Associates
- Selected Clients
  - Oil & Gas Production, Oil Refining, Silicon Processing, R&D/Govt, Other (Petrochemicals, Food, etc.)

Acknowledgement

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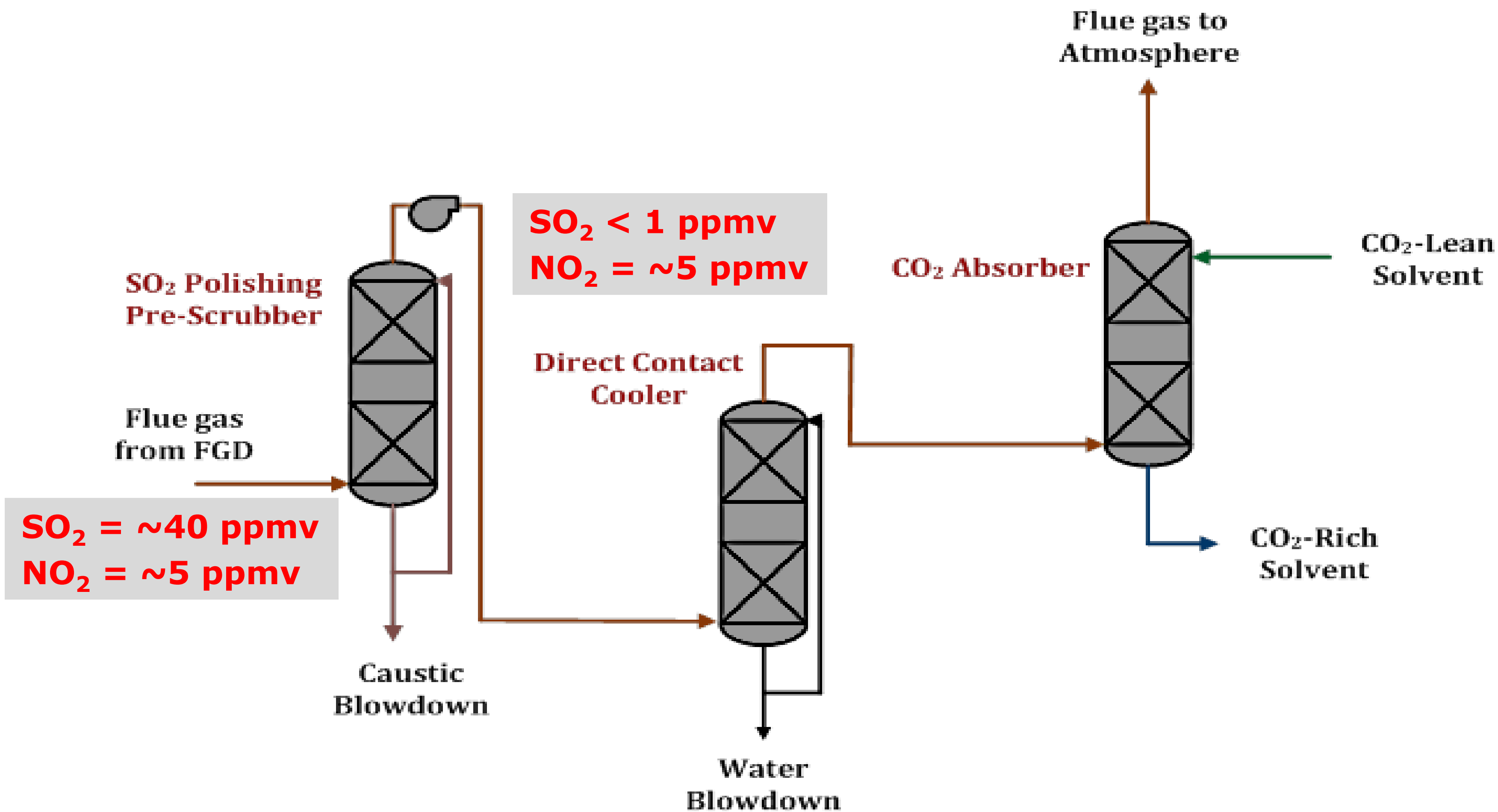
Overview

- Background and Objectives
- Solvent Oxidation
- NO_2 Pre-Scrubbing
- Laboratory Testing
- Techno-Economic Engineering Evaluation
- Summary

Background and Objectives

- DOE SBIR FY16 Phase I Release 2: Carbon Capture System Improvements
  - Aerosols, Reclamation, Oxidation
- Amine-based solvents = Ready for Deployment
- Flue gas contaminants oxidize amines (↑ costs)
- **R&D needed to reduce costs/risks of amine-based capture**

CO_2 Capture Pre-Treatment



Solvent Oxidation Risk

- Pre-scrubbing *does not* address NO_2 (1 – 10 ppmv)

  $R_2NH + NO_2 \rightarrow HNO_2 + R_2N\cdot$

  $R_2N\cdot + R_2N\cdot \rightarrow$ Oxidation products

  $R_2N\cdot + NO\cdot \rightarrow$ R_2NNO (nitrosamine)

- Nitrosamines = potential environmental/health risk
- 1 mole of NO_2 may oxidize 2 – 4 mols amine[1] = $
- **Opportunity: Integrate NO_2 removal into SO_2 pre-treatment**

1: Fine, 2015

NO_2 Pre-Scrubbing Concept

- NO_2 absorbs in sulfite solutions[2](SO_2 polisher)
  - Issue: Sulfite is rapidly consumed by oxidation
  - Solution: Introduce oxidation inhibitors to reduce sulfite oxidation rate
- No new unit operations required
- Commercially available additives:
  - Thiosulfate (Oxidation Inhibitor)
  - Tertiary Amines (Scavenger)

2: Shen, 1997

Technology Status

- UT: Initial proof of concept at bench scale[1]
- UT/Trimeric: Path to commercialization:
  - Extended laboratory testing with multiple additives
  - Techno-economic engineering evaluation
  - Pilot test experimental design
  - Pilot-Scale field testing at NCCC
- Future collaboration with industrial partners

1: Fine, 2015

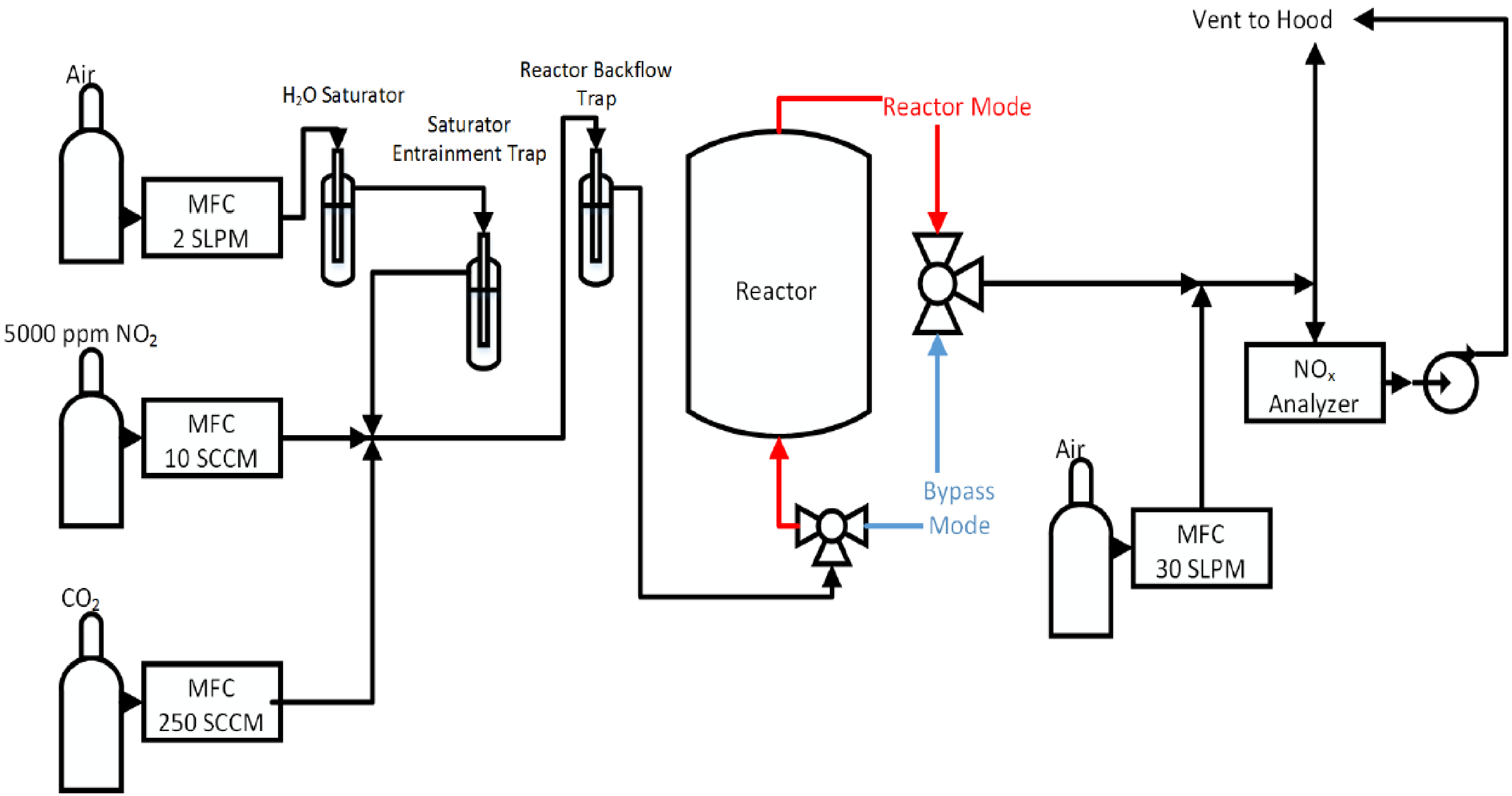
Laboratory Testing: Methods

- High Gas Flow Apparatus (UT): Batch gas-sparged reactor (see next slide)

- Measure as a function of time:
  - NO_2 absorbed
  - Sulfite concentration in liquid
  - Sulfite oxidation inhibitor concentration in liquid

- Goal: Quantify normalized ratio of sulfite oxidation per mole of NO_2 absorbed as a function of process conditions

Laboratory Testing: Apparatus



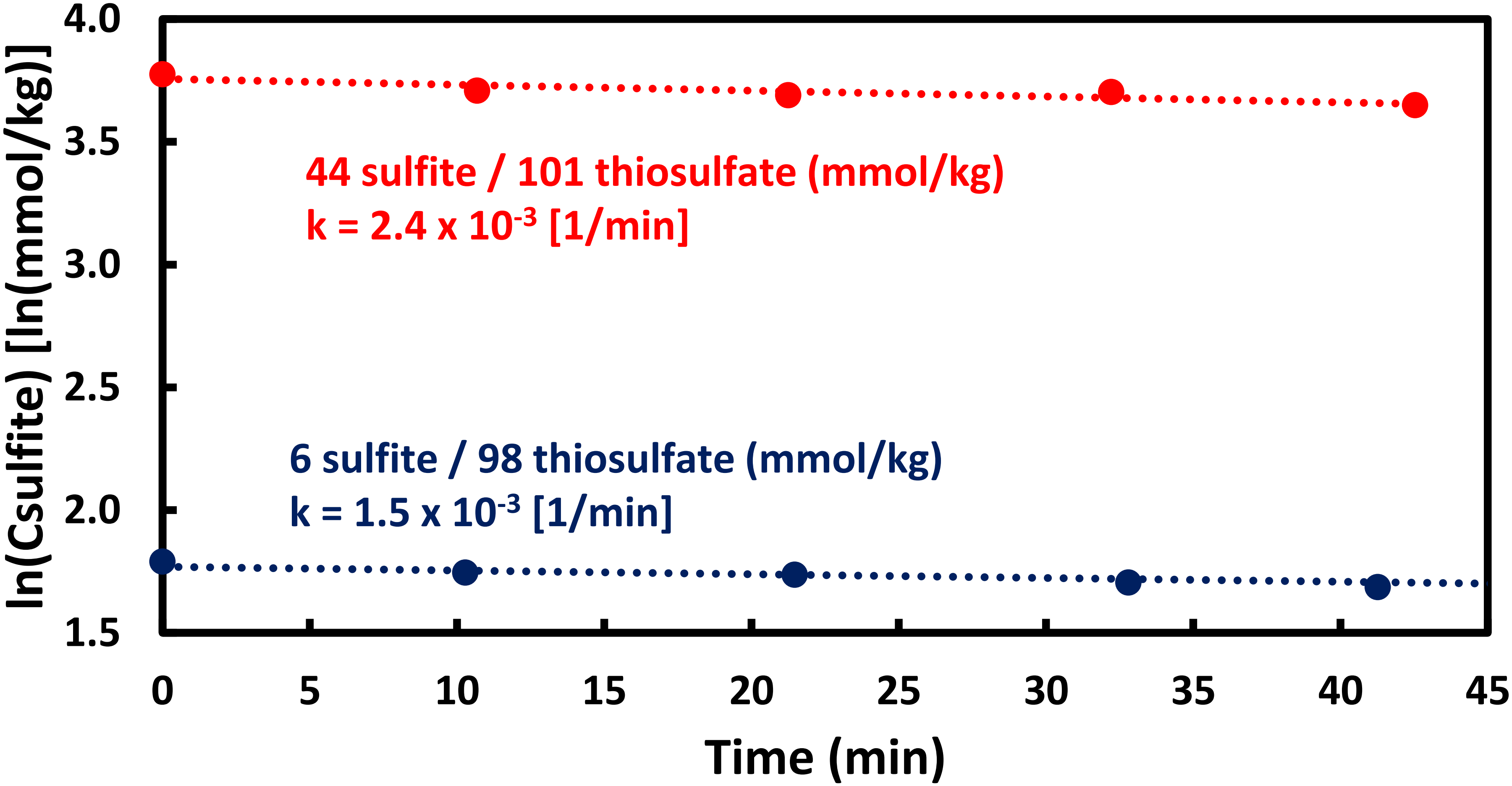
Laboratory Testing: Test Parameters

Parameter	Units	Value
NO_2 Concentration	ppmv	1-5
Temperature	°C	25-55
Sulfite Concentration	mmol/kg	4-50
Thiosulfate Concentration	mmol/kg	0-200
Tertiary Amine Concentration	mmol/kg	5-200
Metals Concentration	mmol/kg	0.1-0.5
EDTA Concentration	mmol/kg	0.02-1

1: Metals may be present in flue gas and catalyze oxidation

2: EDTA (Ethylenediaminetetraacetic acid) chelates metals to inhibit oxidation

Laboratory Testing: Example Results



Laboratory Testing: Summary of Key Results

- Validated theoretical inhibition effect of thiosulfate
- Demonstrated the effectiveness of EDTA:
  - Small amounts of EDTA important to chelate trace background metals
  - EDTA effect separate from oxidation inhibitor
- Identified new inhibitor (proprietary)
  - Oxidation rates ~10x lower than comparable thiosulfate
- Demonstrated low-cost pathway to introduce inhibitor into scrubbing solution (proprietary)

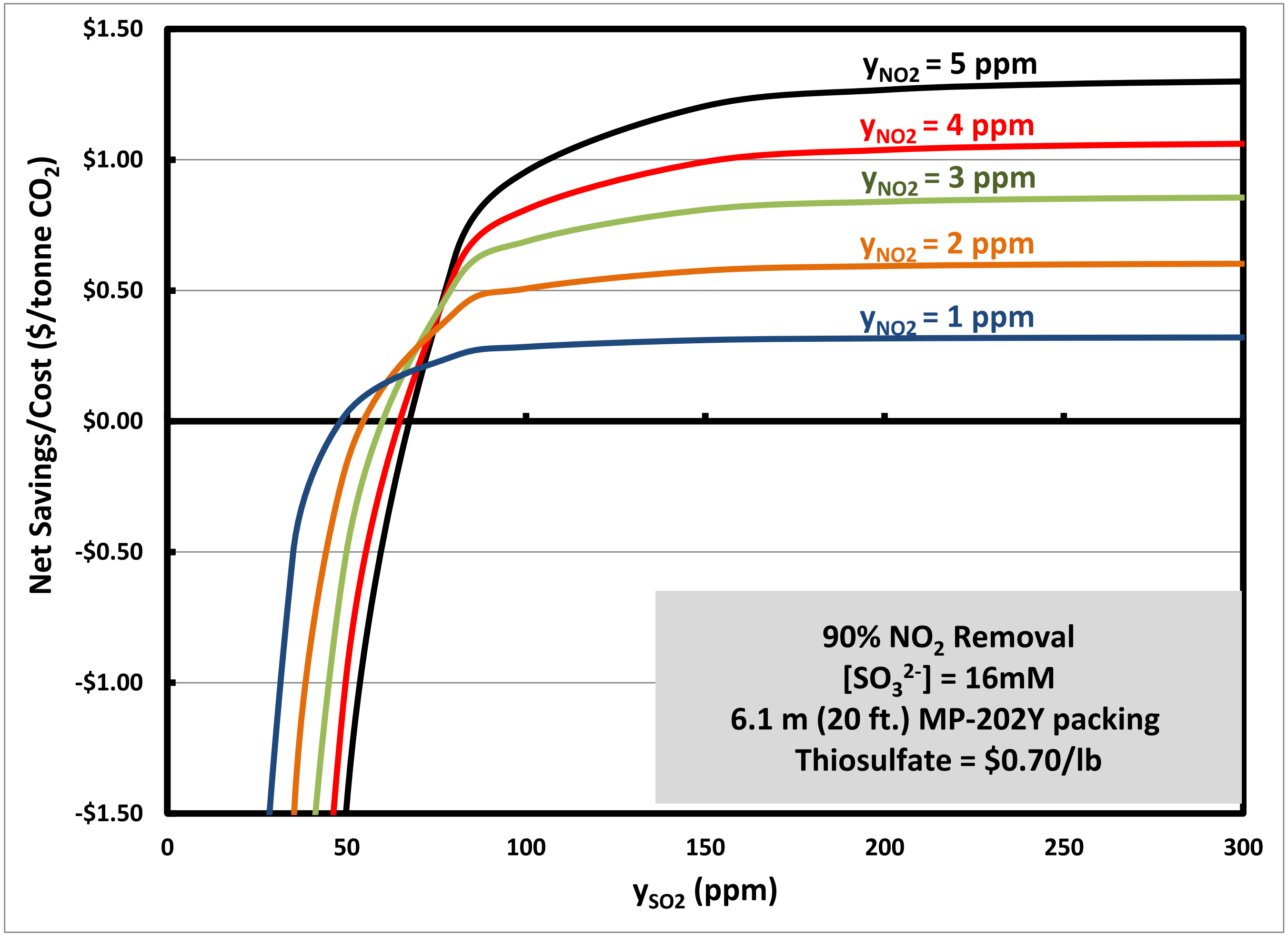
Techno-Economic Engineering Analysis

- Developed empirical model for sulfite oxidation, NO_2 absorption[1]
- Performed steady-state modeling of SO_2 polisher:
  - Estimate inhibitor make-up rates
  - Estimate NO_2 removal percentage
  - Estimate steady-state sulfite concentration in solution
- Used internal solvent degradation model[2] to:
  - Estimate reduction in solvent losses and solvent makeup (operating costs)
  - Estimate reduction of solvent reclaiming system (capital costs)
- **Estimate cost/savings of NO_2 pre-scrubbing as function of operating conditions**

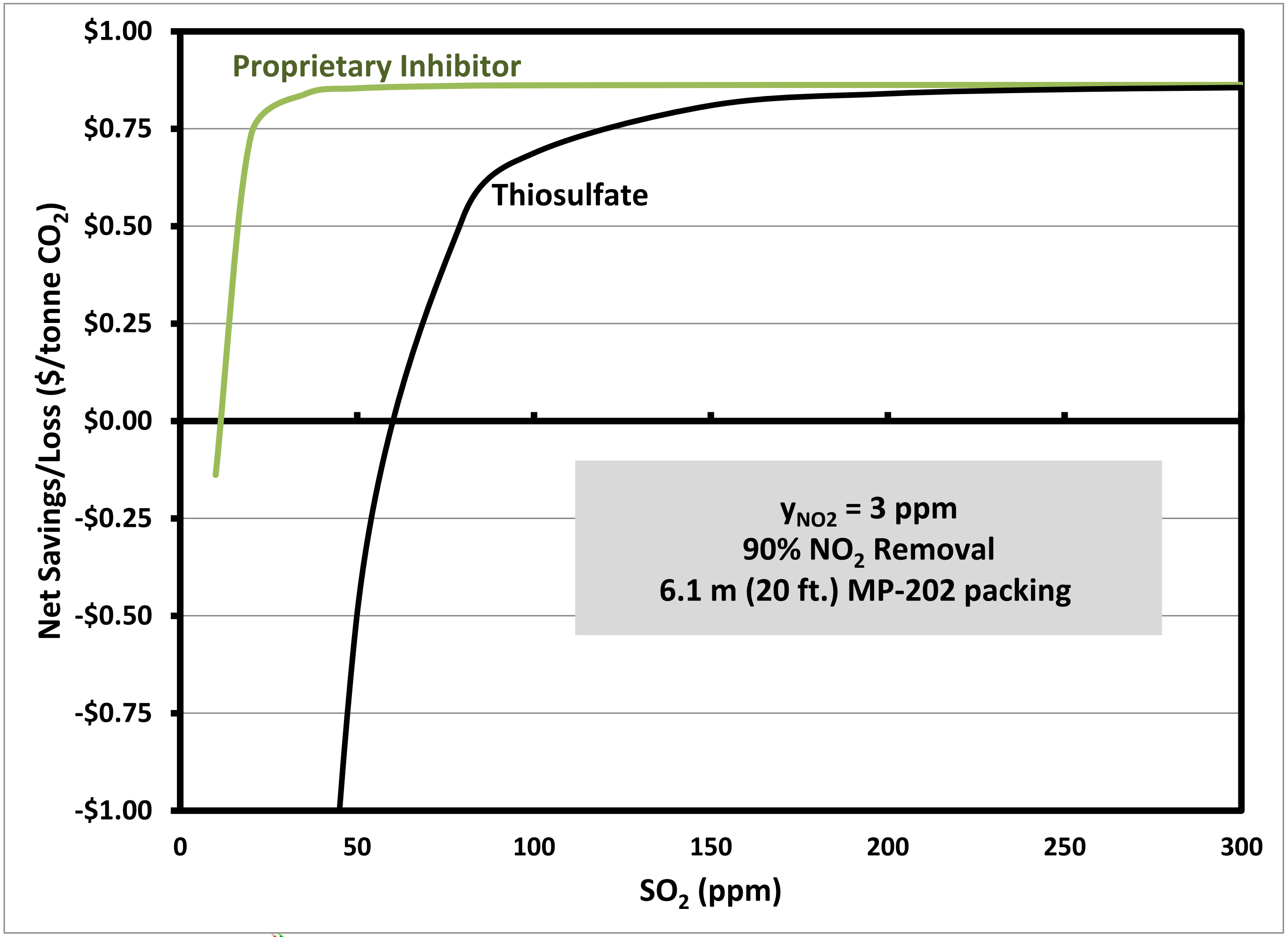
1: Absorption rate data from Fine, 2015

2: Developed by Trimeric and UT

Techno-Economic Analysis: Results for Base Case System



Techno-Economic Analysis: Benefits of Improved Additive



Techno-Economic Analysis: Results

- Savings > $1 /tonne of CO_2 are possible
  - Up to $5MM in annual savings for full-scale plant
- Alternatives to thiosulfate expand envelope of acceptable operating conditions
  - Low cost inhibitor sources
  - Proprietary inhibitor (stronger inhibitor = reduced make-up)
- Combination of additives allow cost-savings across entire range of conditions (NO_2 = 1–5 ppm, SO_2 = 10–300 ppm)

Summary

- Absorption of NO_2 with sulfite + oxidation inhibitors validated at bench and field scale
- Multiple routes to low-cost chemical additives identified at bench-scale
  - Novel inhibitors identified
- No new unit operations required
- Potential net savings > $1/tonne CO_2 captured

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- National Carbon Capture Center
  - Justin Anthony, John Carroll

- Contact Information: andrew.sexton@trimeric.com

Results of Pilot Testing

- Joe Selinger, University of Texas

Pilot Testing: Test Plan

- Vary NO_2 feed concentration
  - Installed NO_2 injection system to raise inlet NO_2 up to 5 ppmv
- Vary additive combinations and concentrations
  - Semi-batch operation = additive concentrations vary with time (reaction, dilution)
- Analyze liquid samples
  - Quantify oxidation rates

Pilot Testing: Preliminary Results

- Demonstrated effectiveness of thiosulfate
  - Sulfite concentrations ↑ time when thiosulfate is present
- Achieved NO_2 removal from 80% to 99%
- Validated liquid sampling methods, NO_2 injection and measurement, and batch operation and control of pre-scrubbing system
- Testing on-going at NCCC

Pilot Testing: NO_2 Removal