Biogeochemical Conversion of Calcium Sulfite into Gypsum in Flue Gas Desulfurization Waste

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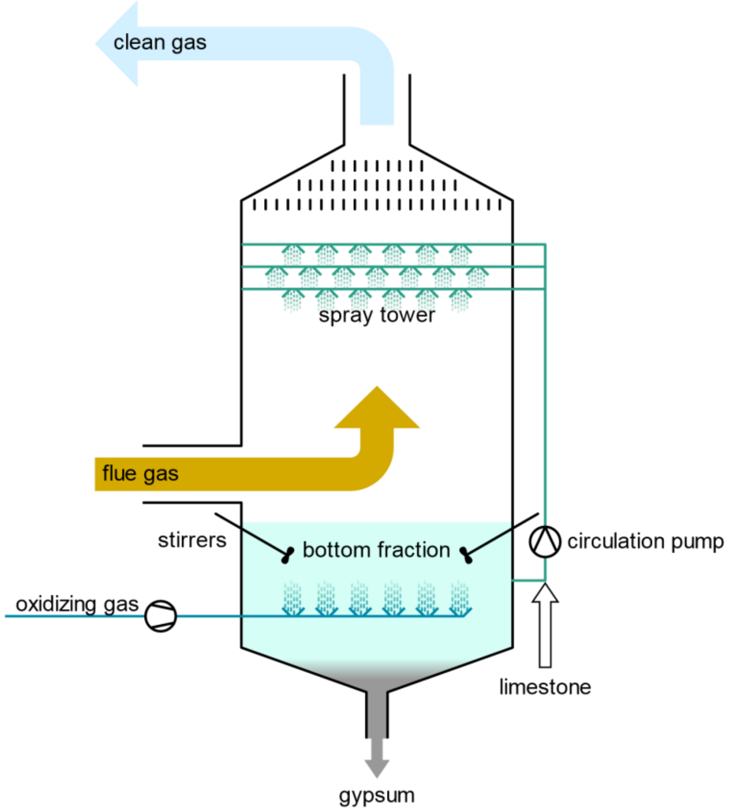
Background

- Coal combustion generates sulfur dioxide (SO_2) in flue gas
- Flue gas desulfurization (FGD) scrubbers most commonly remove SO_2 by reacting flue gas with a lime or limestone slurry
- With excess oxygen, SO_2 forms gypsum ($CaSO_4{\cdot}2H_2O$), under inhibited (oxygen starved) condition hannebachite ($CaSO_3 \cdot 0.5H_2O$) forms



$$SO_2 + CaCO_3 + \tfrac{1}{2}O_2 + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O + CO_2$$

Picture source: https://en.wikipedia.org/wiki/Flue-gas_desulfurization#/media/File:Flue_gas_desulfurization_unit_EN.svg

Problem Statement

- High purity (>80%) FGD gypsum has commercial value comparable to mined gypsum
- Hannebachite is difficult to dewater, has no commercial value
- A coal-fired power plant in SE US produced 3 million tons of low purity gypsum containing 30 to 50% gypsum with the balance being hannebachite (40 to 60%) and limestone (<10%)

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Problem Statement

- The power plant needed to recover for other uses of the 80 acres of FGD waste
- Wanted to avoid landfilling the byproduct
- Sought a means to convert the low purity gypsum into a commercially valuable product

Specification	Wallboard	Agricultural	Cement
$CaSO_4 \cdot 2H_2O$	> 92%	> 85%	> 85%, < 95%
$CaSO_3 \cdot 0.5H_2O$	< 1%		
Moisture	< 15%	< 18%	< 18%
Other	< 7%		

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Our Process Concept

- Evaluated available gypsum enrichment technologies and economics
  - Acidify and allow sulfite to auto-oxidize
  - Chemically oxidize with strong oxidant
  - Effective but expensive with safety concerns
- Identified new alternative to replace dangerous and costly available technologies
- Adapted sulfur oxidizing bacteria to convert sulfite to sulfate

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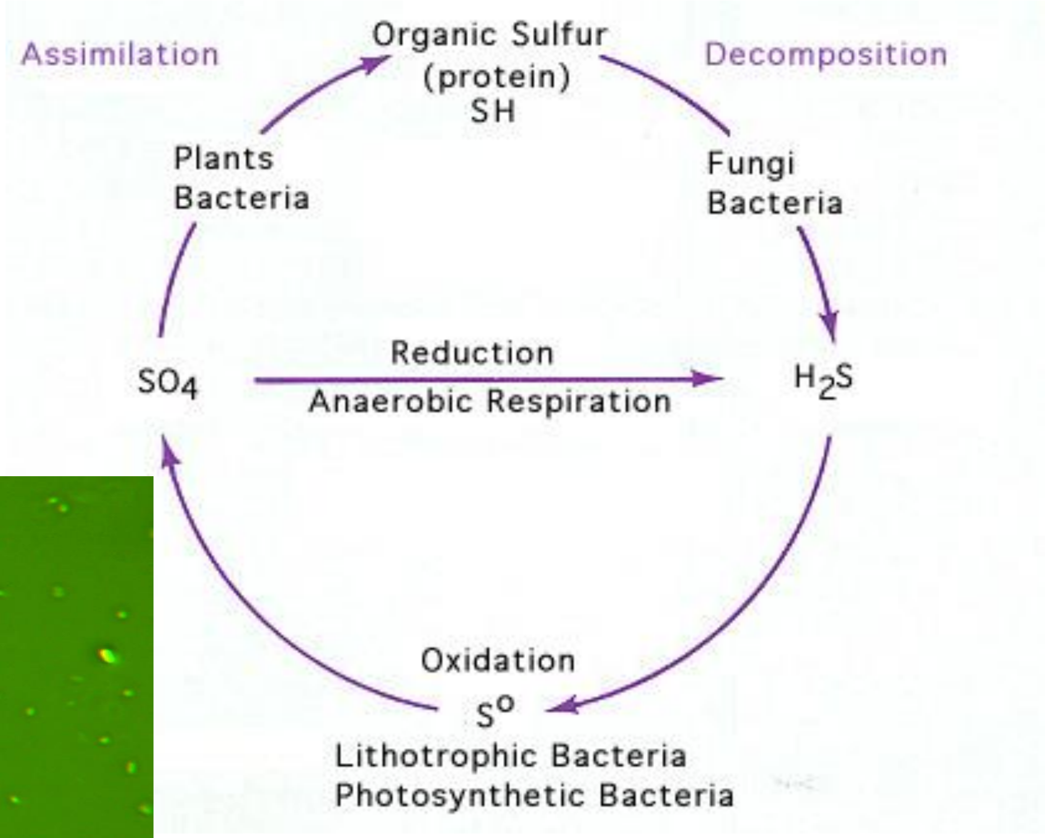
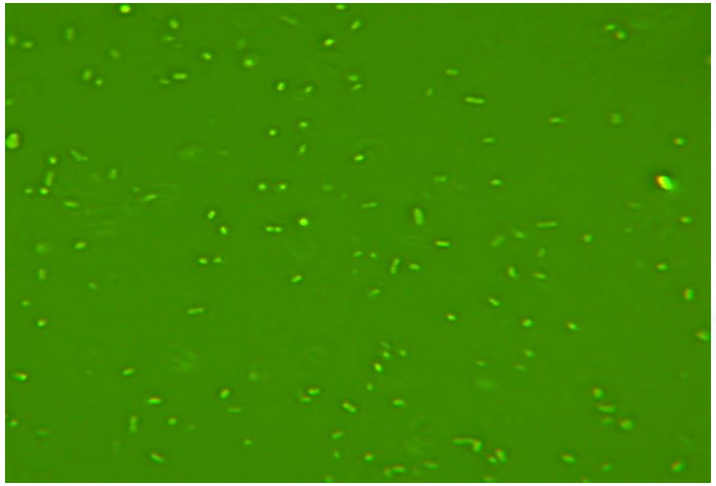
Biogeochemical Approach

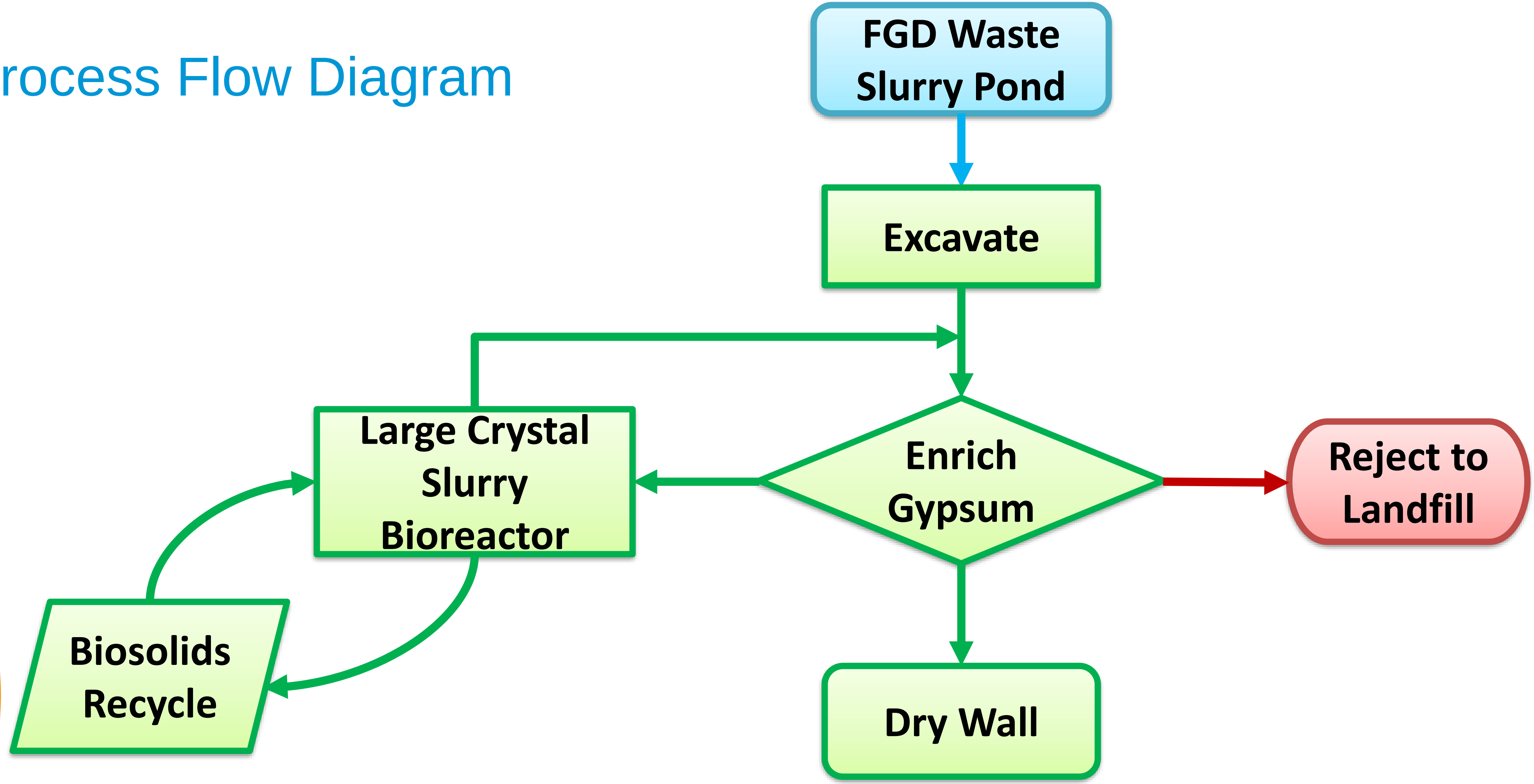
- Natural sulfur cycle
- Sulfur oxidizing bacteria (SOB) are important in the mineralization process
- SOB were isolated from an aged FGD byproduct and cultured





SOB at 1000x magnification

Process Flow Diagram



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Bench Scale Design

Rotated Bottles:
Proof of Concept

Column
Reactors:
shear particles

Cone bottomed tank: gentle mixing

Pulsair: gentle mixing & good aeration

RBC:
Gentle mixing

Diaphragm pump

Peristaltic pump

Stirred tank

CO_2 Scrubber

Pulsair Column

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Optimized Reactor Design

CO_2 free slurry reactor

Stirred slurry reactor

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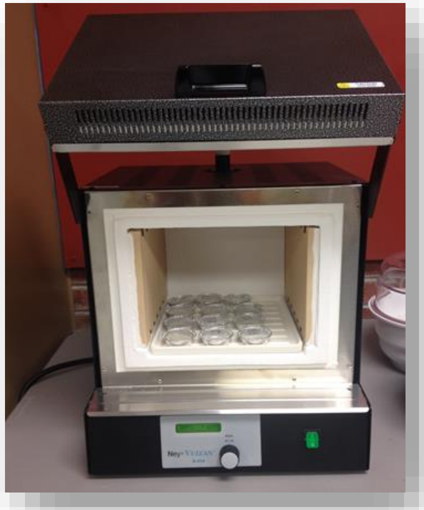
Analytical Methods

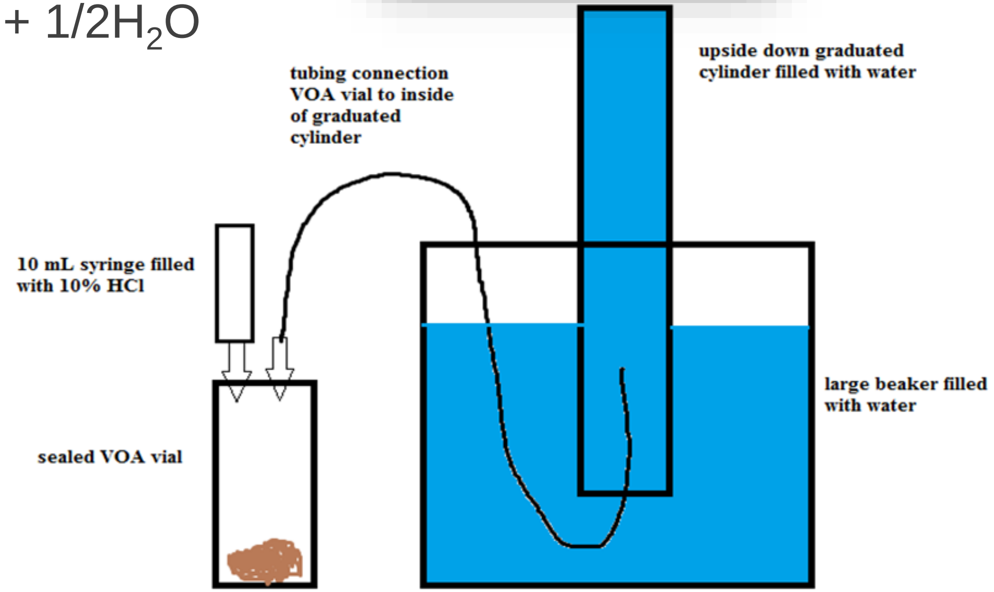
- Stepwise Thermogravimetric Analysis (TGA)
  - Measures sulfite/sulfate conversion
  - Faster and more reliable than wet-chemistry methods

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 + 2H_2O \text{ (160 to 200°C)}$$

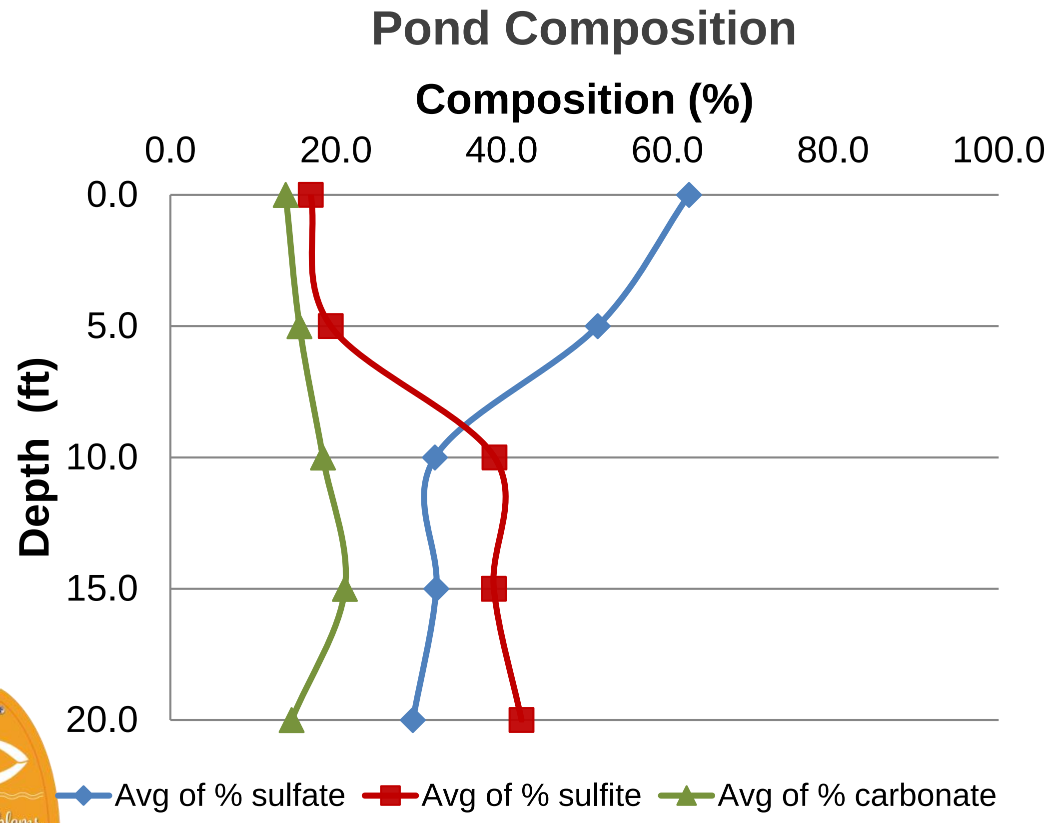
$$(CaSO_3 \cdot CaSO_4) \cdot 1/2H_2O \rightarrow CaSO_3 \cdot CaSO_4 + 1/2H_2O \text{ (400 to 430°C)}$$

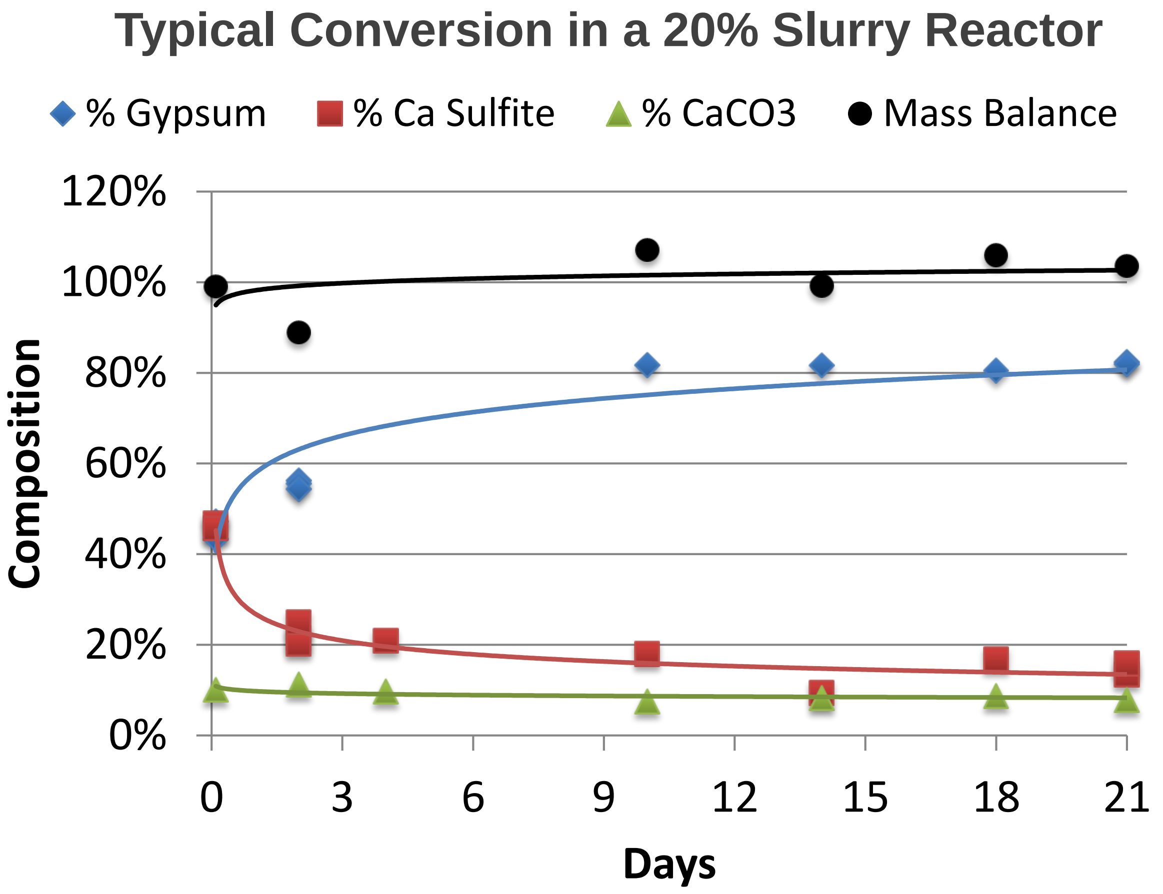
- Off-gas Carbonate Analysis
  - Measures $CaCO_3$ by off-gassing as CO_2





Performance Data





Performance Highlight

	Wallboard Parameters		Treated FGD
	Minimum	**Maximum**	
Gypsum	>92%		96%
Hannebachite		1%	2%
pH	6	8	7
Particle size	20 µm	60 µm	52 µm
Chloride		120 ppm	< 68 ppm
Acid insoluble matter		3.5%	< 1%

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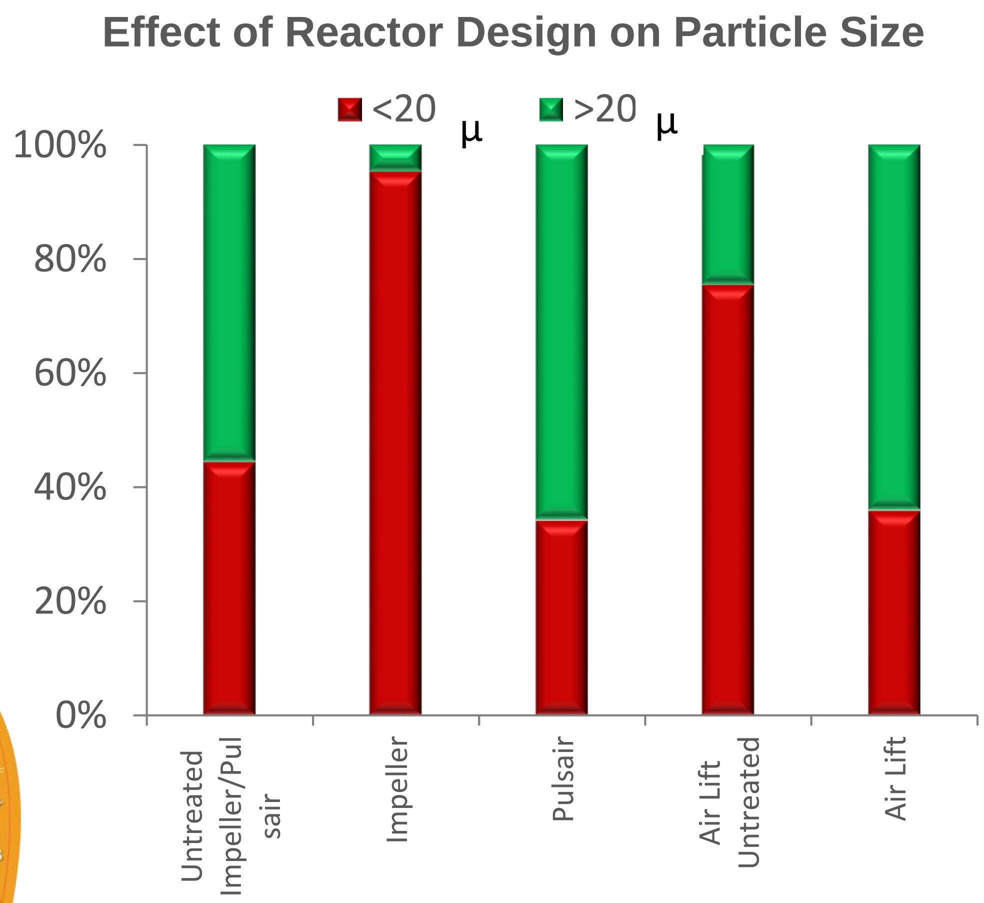
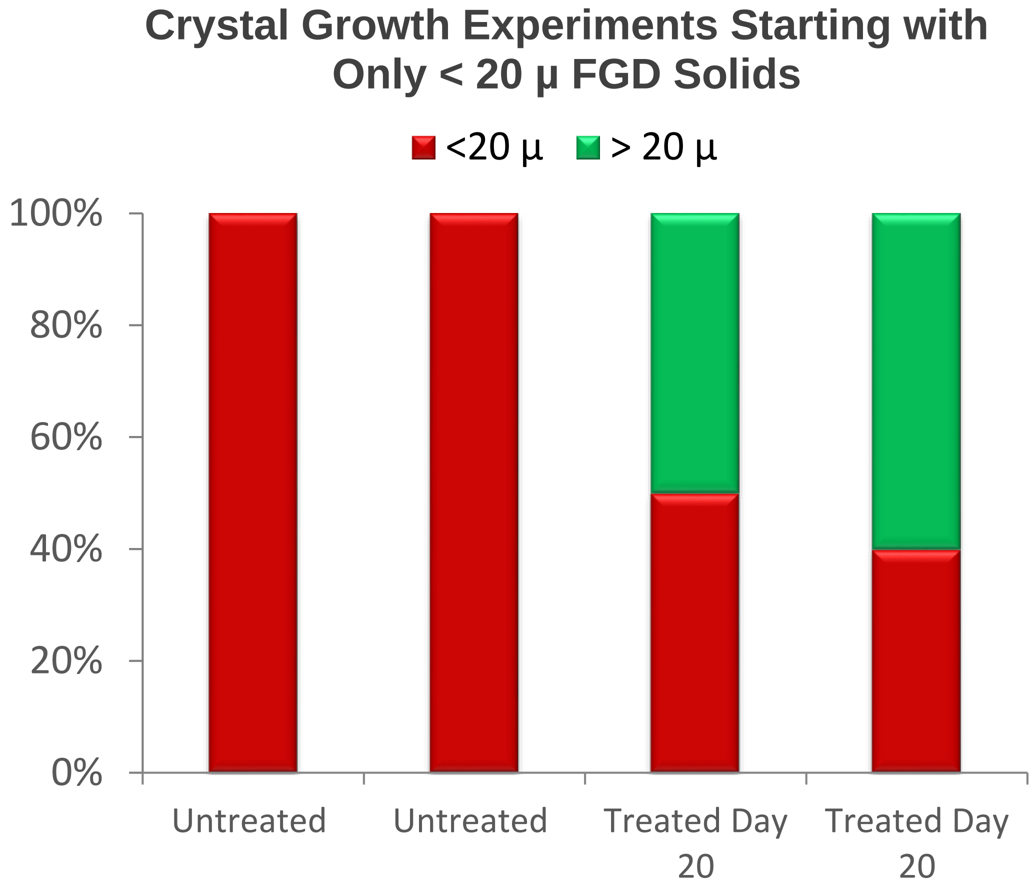
Performance Summary

- SOB biomass directly related to conversion rate
- > 1 x 10^7 cells/mL yields > 1% conversion/day
- Max. conversion rate ~ 5% /day
- Per batch treatment time, ~ 10 days
- Produced commercially desirable gypsum crystals (> 20 microns)
- Required attention to reactor design, mixing methods, and particle classification

Particle Size

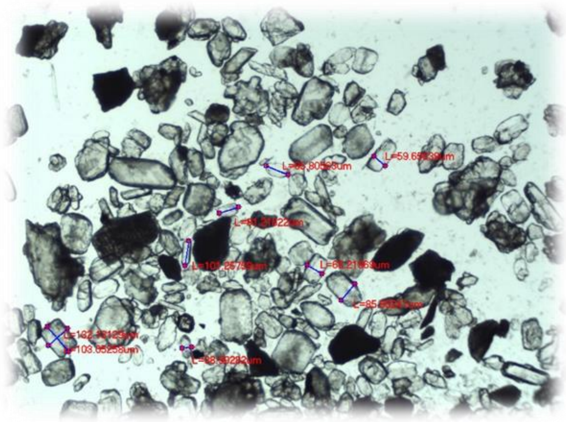




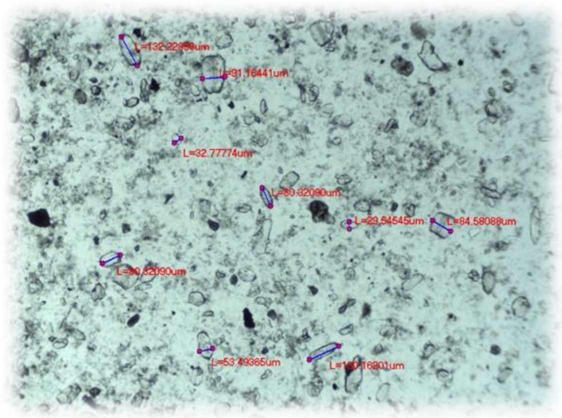
>20 μ crystals = 96% gypsum
<20 μ 54% gypsum, 18% Ca sulfite

Classifier

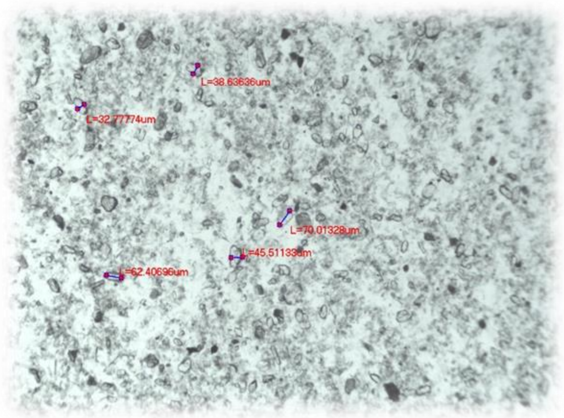
- Recovery of commercially valuable gypsum crystals by size in a classifier
- Particle size gradient was observed



1st compartment
Commercial grade crystals



2nd compartment
Smaller crystals to recycle



3rd compartment
Smaller crystals to recycle

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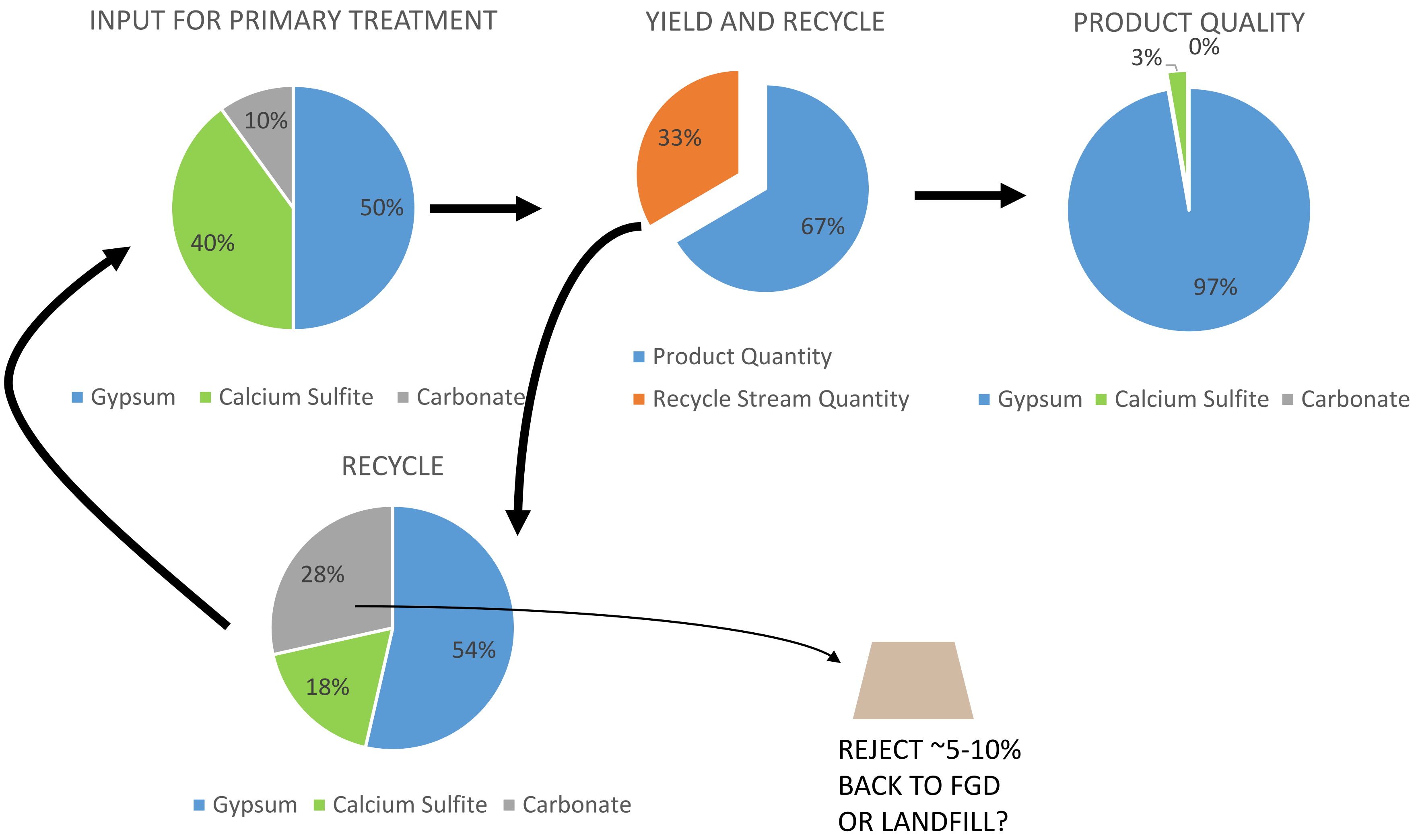
System Performance and Mass Balance



Value Added to the Client

COST ITEM	VALUE
Excavation, T&D	$40/ton avoided
Cost to treat	$10/ton
Product sale price	$20/ton
Value added	**$50/ton**

Conclusions

- Novel application of SOB for the industrial conversion of low-grade FGD byproduct into viable commercial products, namely, gypsum for drywall, cement admixture, and agriculture
- Safe process operates at ambient temperature with no input of hazardous reagents
- Relative simplicity of unit operations allows flexibility in design and use readily available process equipment
- Scale of operation limited by containment, mixing, and aeration equipment

References

- D. Graves, J.J. Smith, L. Chen, A. Kreinberg, B. Wallace and R. White, (2017) Biogeochemical Oxidation of Calcium Sulfite Hemihydrate to Gypsum in Flue Gas Desulfurization Byproduct using Sulfur-oxidizing Bacteria. *Journal of Environmental Management.* (accepted)

- D. Graves, A. Kreinberg, R. White, B. Wallace, B. Adair, L. Chen, S. M. Herr. Biogeochemical Transformations of Flue Gas Desulfurization Waste using Sulfur Oxidizing Bacteria. U.S. Patent. Application No. 15/324,320. Filed Jul 7, 2015.

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