Precipitator Ash Addition to Black Liquor to Reduce Evaporator Scaling – Understanding the Fate of the Ash

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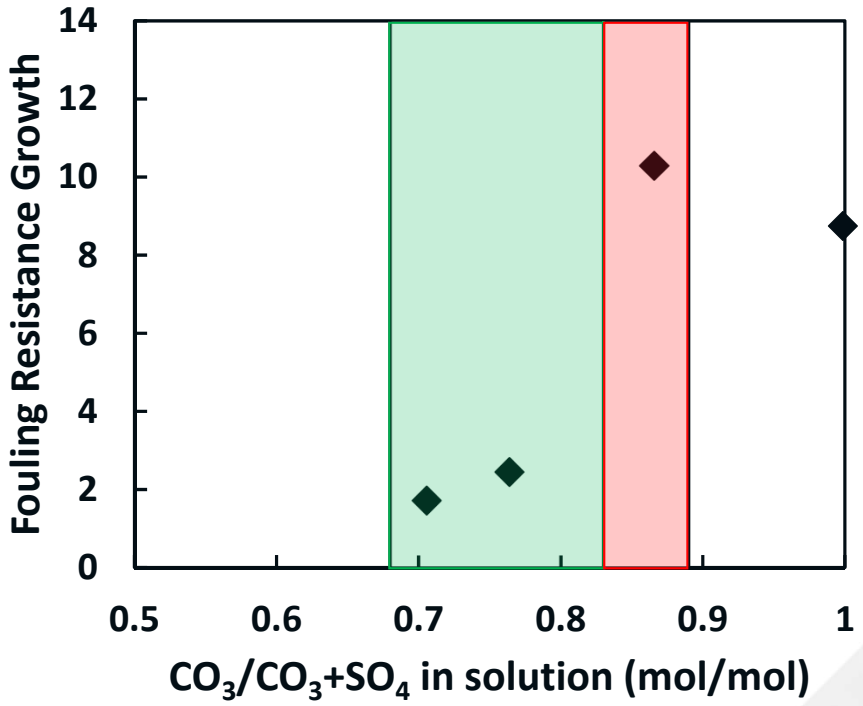
Role of Precipitator (ESP) Ash

- ESP ash forms in recovery boiler and mainly consists of sodium sulfate
- Added below the solubility limit – it can change the CO_3:SO_4 ratio in BL
- Added above the solubility limit – it increases crystal mass in BL
  - Some mills see a benefit, others don't
  - Carbonate-rich salts do not grow on other crystals – anticipating it first dissolves and re-precipitates
- An earlier study indicated the crystals composition of ESP ash might change when added to high solids black liquor, DeMartini & Verrill (2007)

ESP Ash Addition below 50% DS

- To avoid dicarbonate crystallization
  - Dicarbonate is the foulant in modern BL concentrators
  - Introducing sodium sulfate to BL shifts the crystallization from dicarbonate to burkeite

- The Fouling rate by dicarbonate is five times higher than burkeite

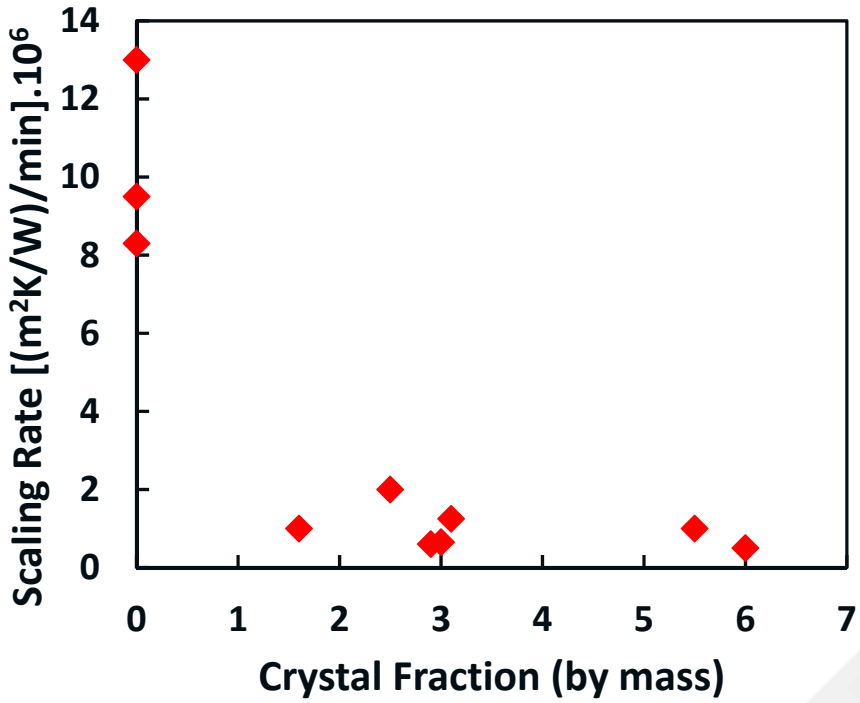


Gourdon (2008)

ESP Ash Addition above 50% DS

- Providing crystal mass to act as seed sites for Na-CO_3-SO_4 salts in the liquor bulk as opposed to equipment surfaces

- A study by Karlsson revealed the scaling rate in BL during primary nucleation (i.e., no bulk crystals present) is tenfold higher compared to continuous crystallization (i.e., certain quantity of bulk crystals present)



Karlsson et. al. (2017)

Objective

- To determine the solubility limit of ESP ash when added **below** 50% DS
- To determine the dissolution time of ESP ash when added **below** 50% DS.
- To determine whether the ESP ash crystals change form when added **above** the 50% DS (i.e. does SO_4 dissolve and CO_3 precipitate)

Experimental - Composition of ESP Ash and Black Liquor

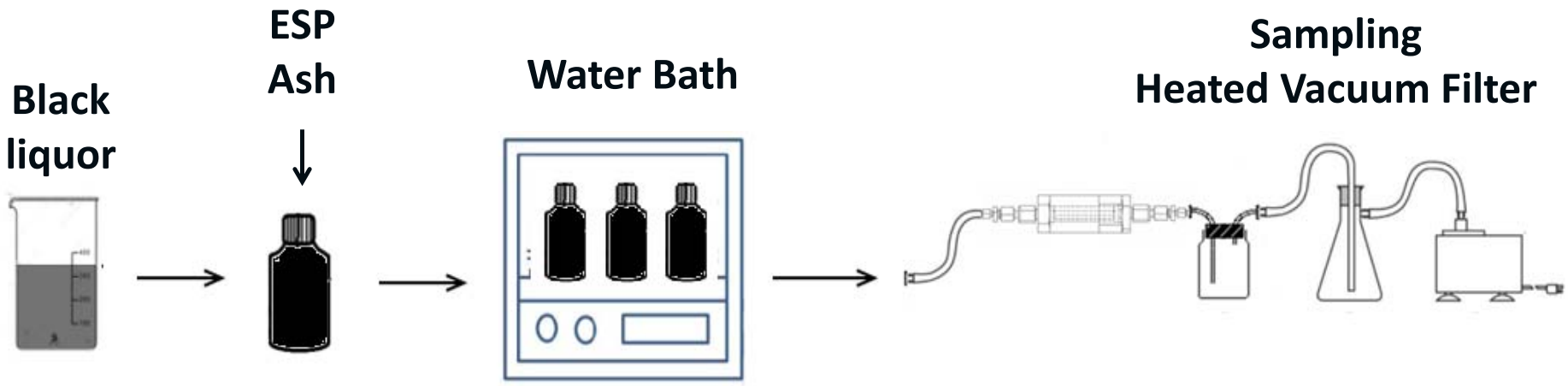
Element	Concentration (wt% d.s.)	
	ESP Ash[a]	Black Liquor
Sodium	28.3	18.1
Potassium	5.86	2.97
Chloride	0.90	0.17
Sulfate	46.1	2.51
Carbonate	12.9	5.31

a: the charge balance of $(Na+K)/(Cl+SO_4+CO_3)$ in ESP ash analysis is 0.97

- Na, K, Cl, and SO_4 analyzed by Ion Chromatography (IC)
- CO_3 measured with a Total Inorganic Carbon Analyzer (TIC)
- Crystallography analysis is done by XRD and SEM

Solubility Of ESP Ash

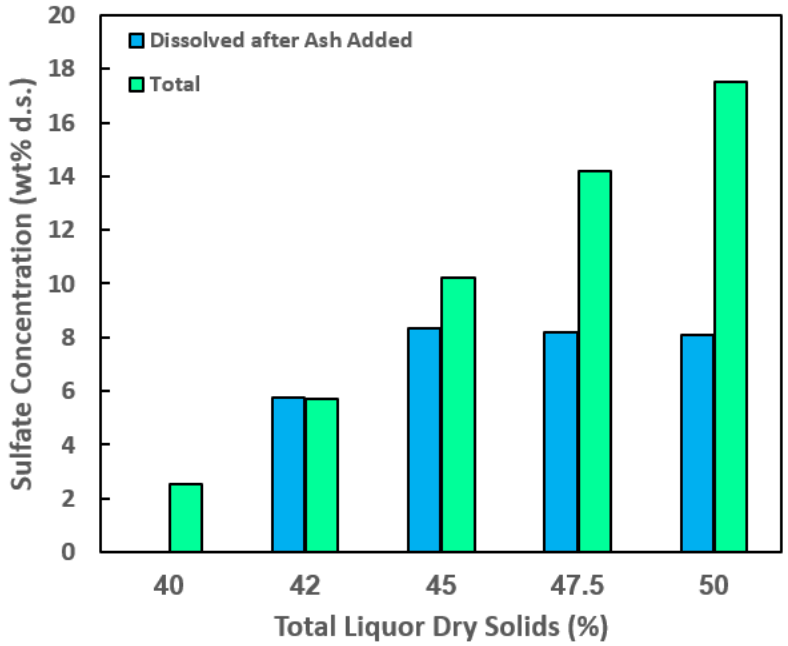
Black liquor solids at the start (%)	40
ESP ash added as total liquor solids (%)	42, 45, 47.5 and 50
Temperature (°C)	95

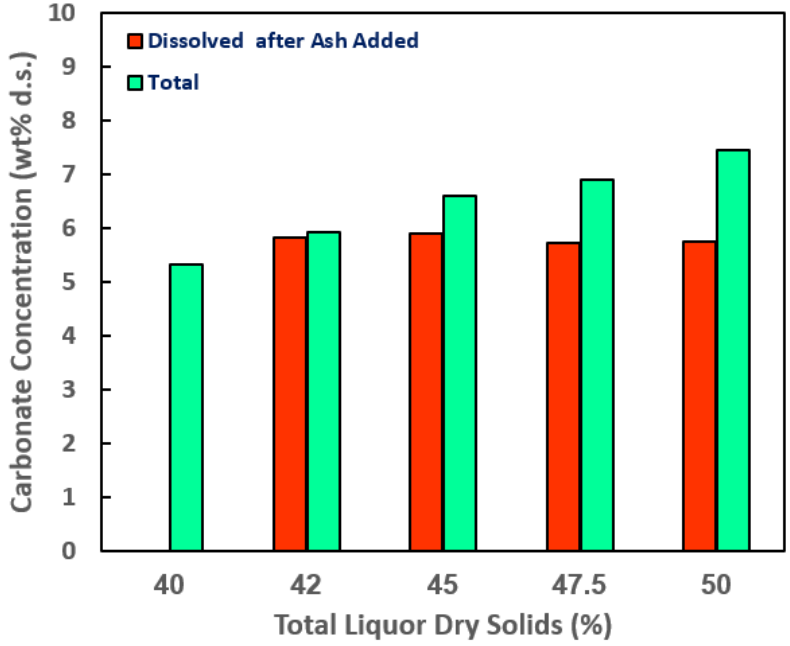


Equilibration time 24 hour

Solubility of ESP Ash at 95 °C

Starting Dry Solids of 40%





Solubility of ESP Ash at 95 °C

Starting Dry Solids of 40%

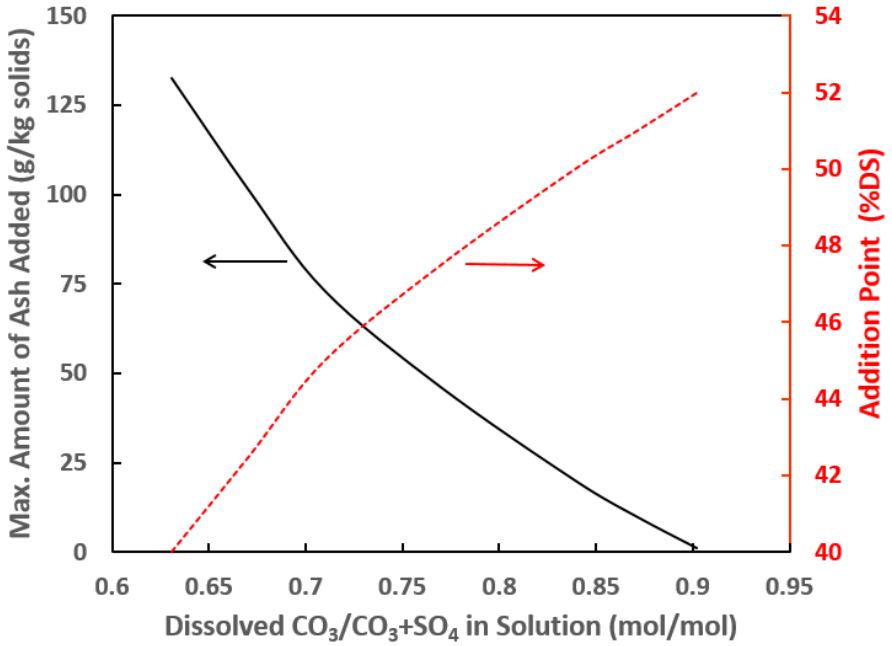
	$CO_3/(CO_3+SO_4)$ mol ratio
Original BL @ 40% d.s.	0.77
BL with Ash Added @ 42% d.s.	0.62
BL with Ash Added @ 45% d.s.	0.53
BL with Ash Added @ 47.5% d.s.	0.53
BL with Ash Added @ 50% d.s.	0.53

Crystallization shifts from a region where carbonate-rich salt is expected to precipitate out to sulfate-rich salt.

Industrial Relevance

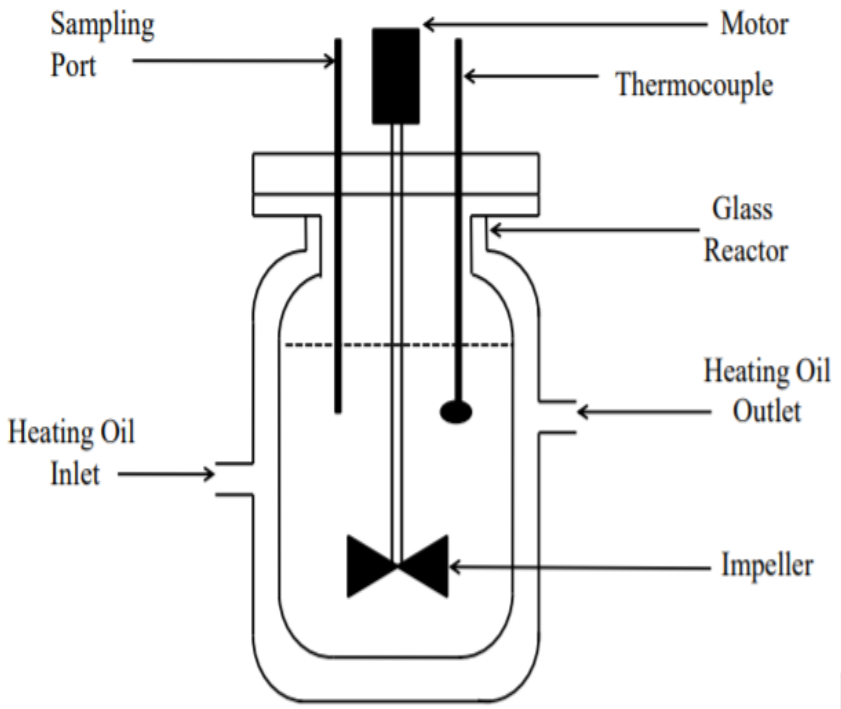
$$SL(\%) = 71.008 - (0.714 \times [Na]_{dis}) - (0.761 \times [CO_3]_{dis}) - (1.448 \times [SO_4]_{dis})$$

$[\mathbf{Na}]_{\mathbf{dis}}$, $[\mathbf{CO_3}]_{\mathbf{dis}}$, **and** $[\mathbf{SO_4}]_{\mathbf{dis}}$ are dissolved conc. of Sodium, Carbonate, and sulfate



Dissolution of ESP Ash at 95 °C

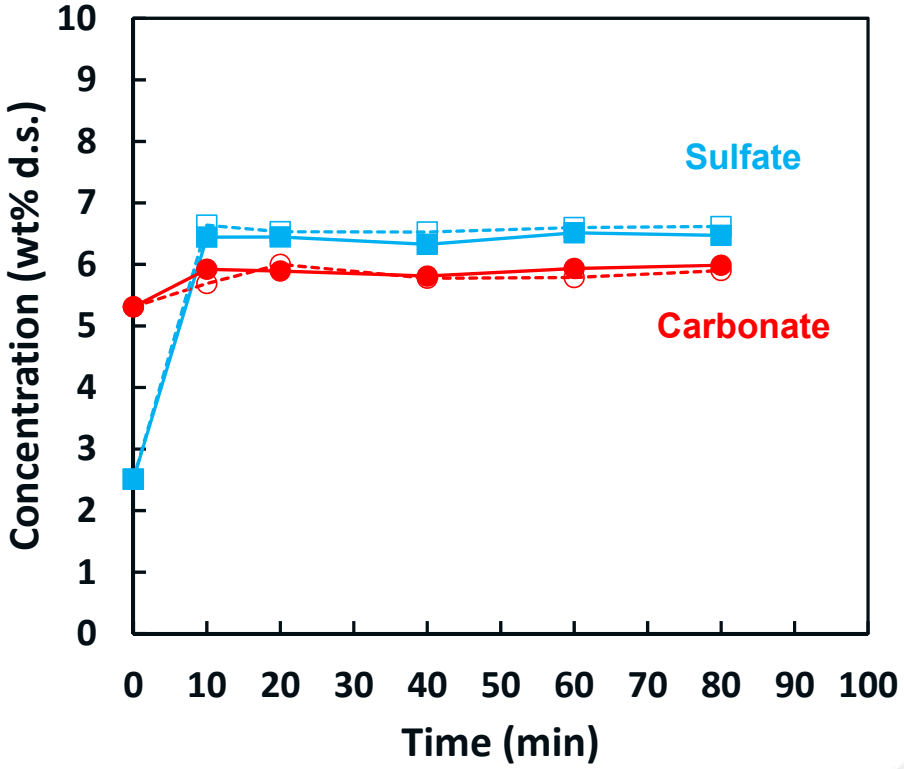
- Black liquor was preheated to 95°C in glass reactor
- Ash was added to the black liquor
- Filtered samples were pulled at regular intervals



Dissolution of ESP Ash

Black liquor solids at the start (%)	40
ESP ash added as total liquor solids (%)	42.5
Temperature (°C)	95

As fast as 10 min are needed to dissolve the ash

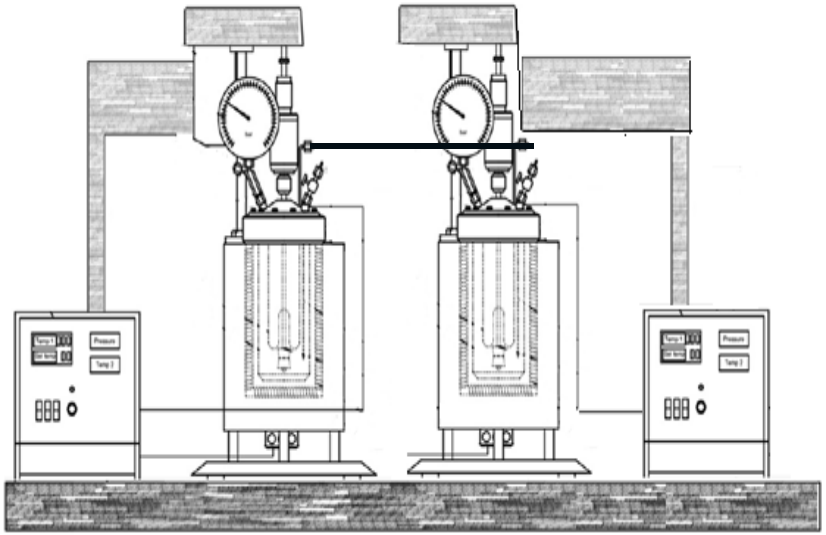


Stability of ESP Ash Crystals in BL

Black liquor solids at the start (%)	52 and 57
ESP ash added (g/kg solids)	22
Temperature (°C)	125

Steps:

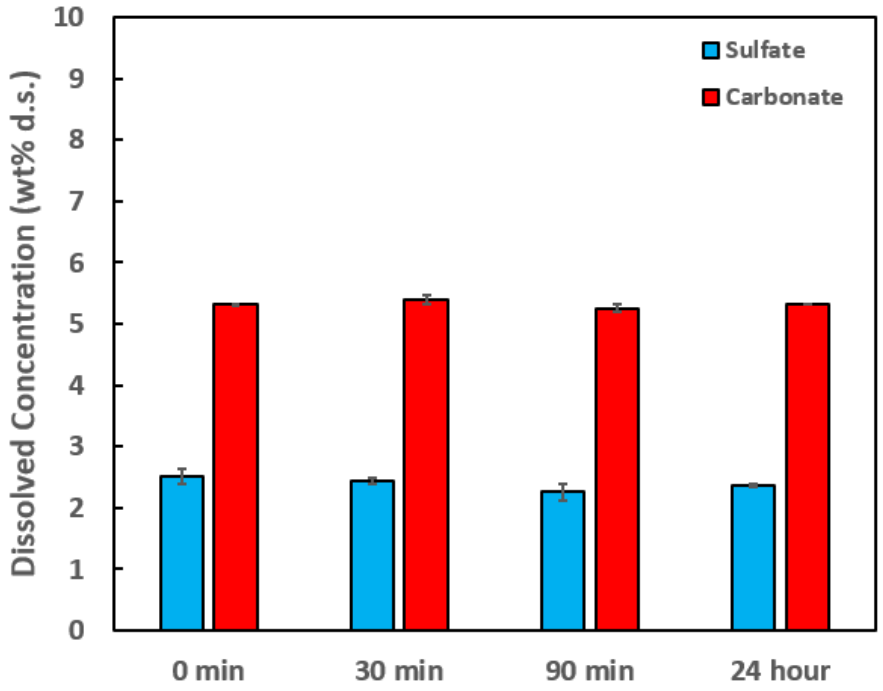
1. Two connected Parr reactors used, one for BL and the other for ESP ash
2. BL is heated and pushed to the other reactor which contains ash and is heated and pressuring to prevent flashing
3. Sampling started at regular intervals



Stability of ESP Ash at 125 °C

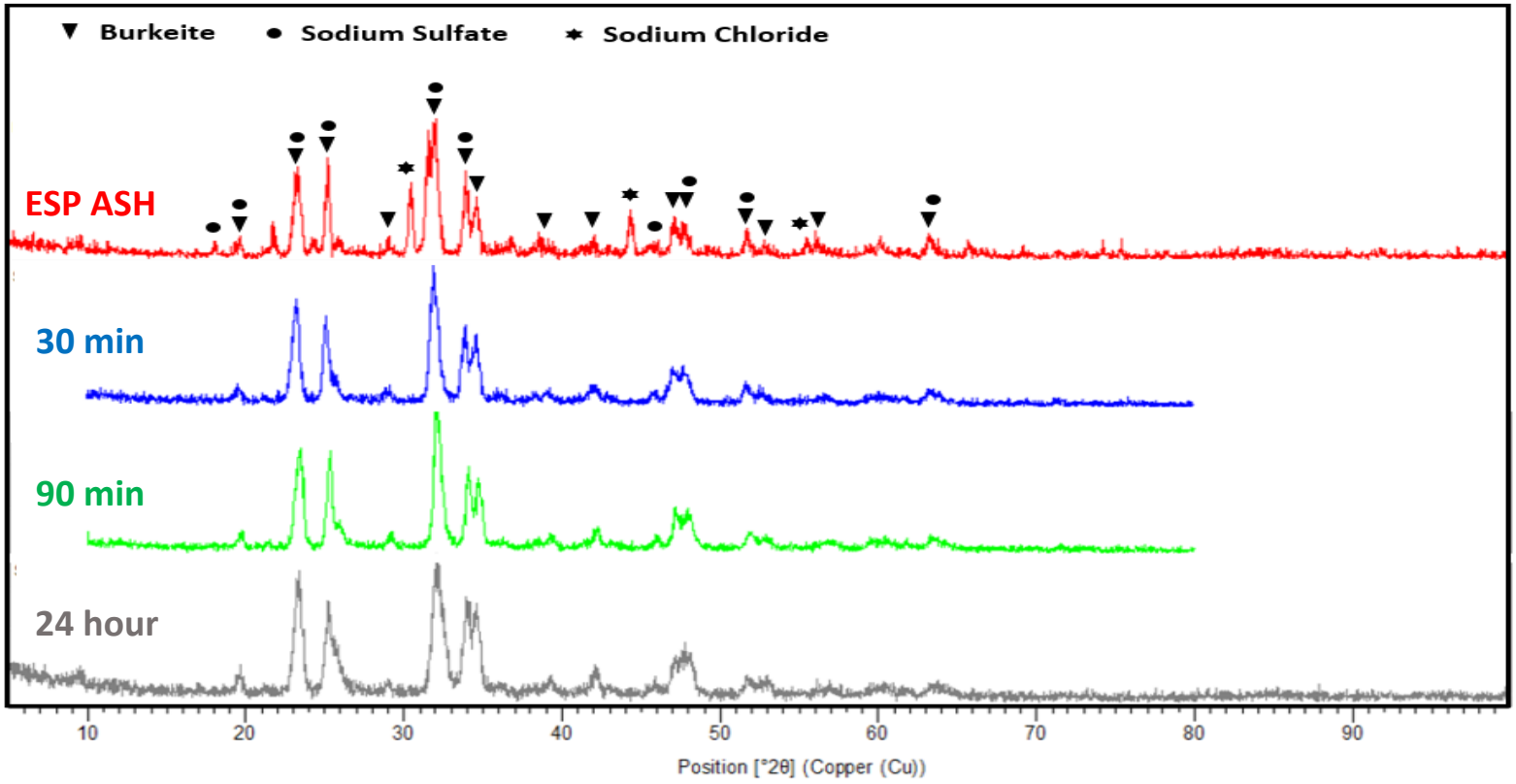
Starting Dry Solids of 52%

No precipitator ash dissolution



Stability of ESP Ash at 125 °C

Starting Dry Solids of 52%



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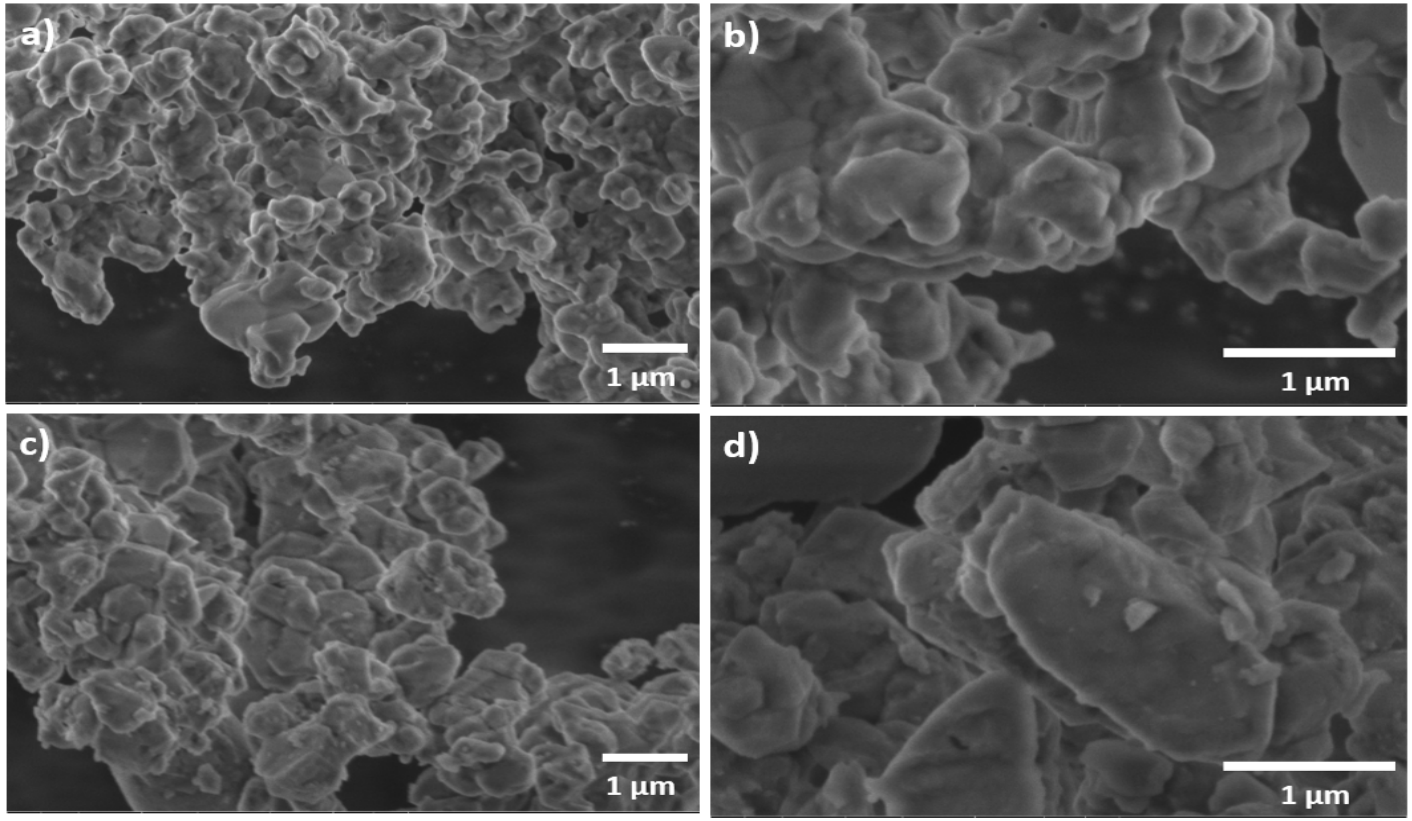
SEM Analysis of Recovered Crystals

ESP Ash

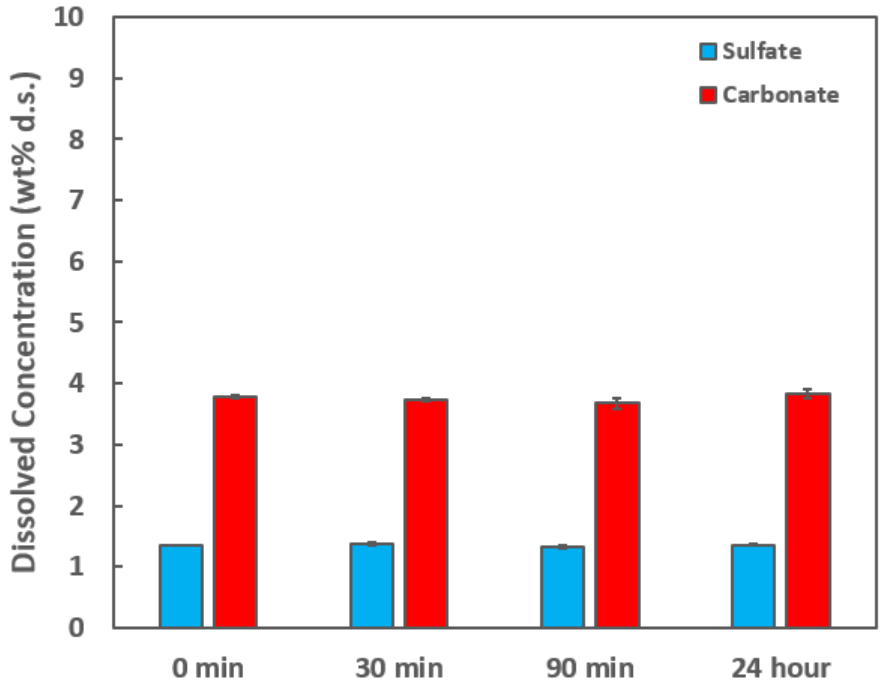
ESP Ash, from 52% BL



Stability of ESP Ash at 125 °C

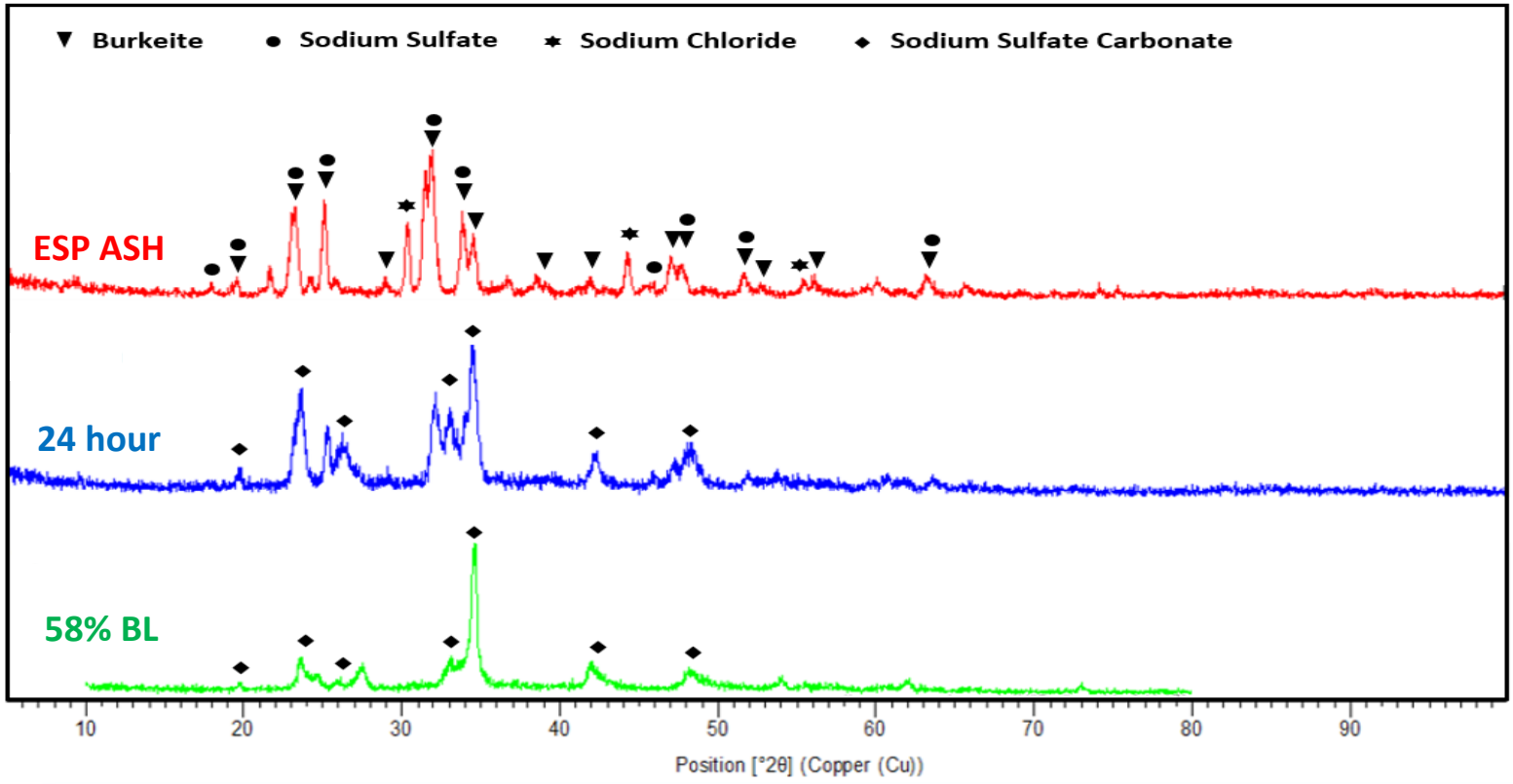
Starting Dry Solids of 57%

No precipitator ash dissolution



Stability of ESP Ash at 125 °C

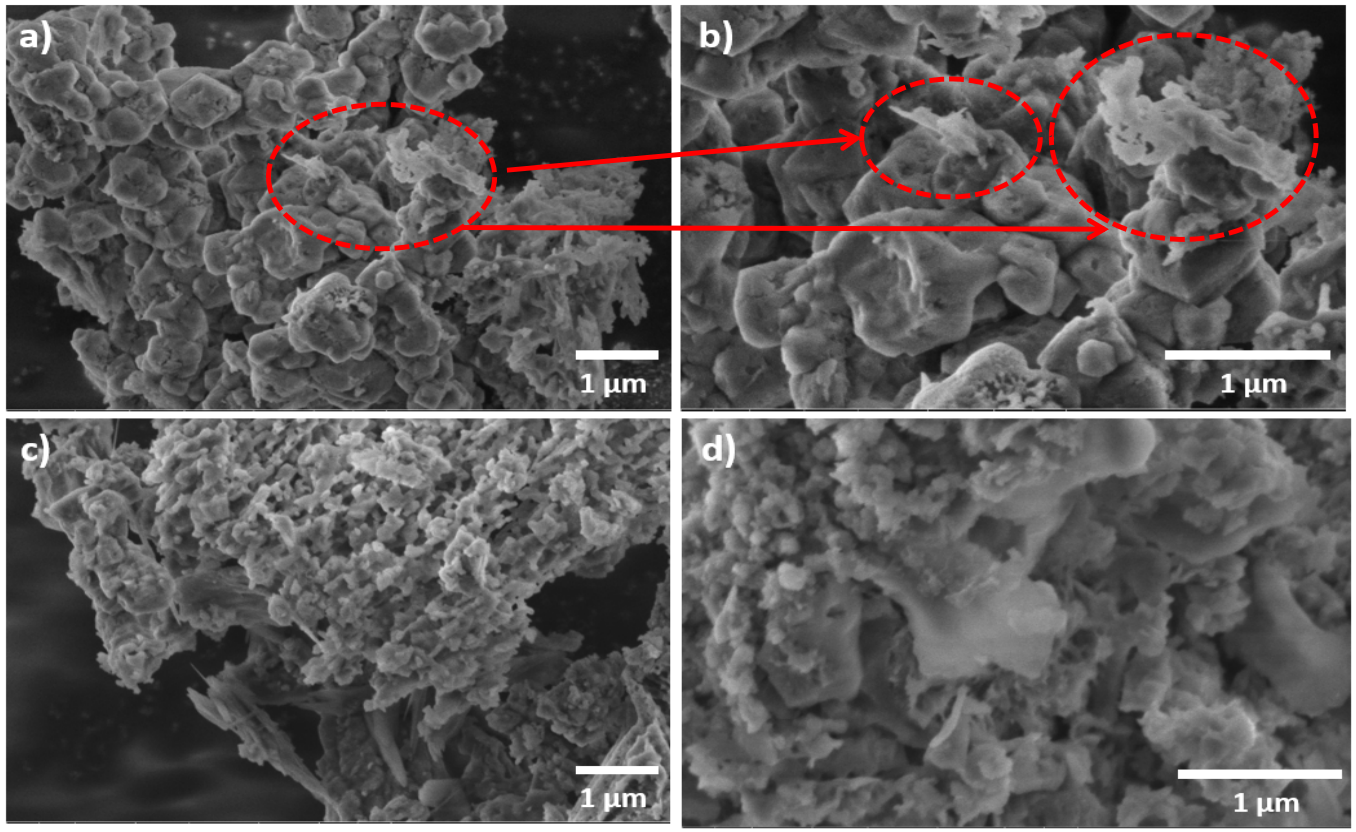
Starting Dry Solids of 57%



SEM Analysis of Recovered Crystals

ESP Ash, from 57% BL

Sodium salt, from 58% BL



Concluding Remarks

- When added below the solubility limit, electrostatic precipitator (ESP) ash dissolution occurs in 10 min or less at the conditions studied.
- The equation developed in the earlier Na-CO_3-SO_4 solubility studies can be used to calculate the maximum amount of ESP ash that can be dissolved for a given initial black liquor dry solids.
- When added above the solubility limit, ESP ash does not undergo dissolution and reprecipitation within 24 h.
- The mechanism by which ESP ash reduces scaling when added above the solubility limit therefore remains speculative.

Thank you!
Questions?

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