

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

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9 **ABSTRACT**

10 Precipitator ash is often added into the black liquor to the concentrators to help reduce sodium salt
11 scaling. In most cases it is added to as-fired black liquor which is then partially recycled back to
12 the concentrator body operating just above the solubility limit. In this scenario, the ash added to
13 liquor above the solubility limit and is intended to increase the crystal mass to provide surface area
14 for sodium salts to precipitate on. Some mills have observed a positive effect while others have
15 not. In some other mills, precipitator ash is added below the solubility limit so that the ash dissolves
16 to increase the dissolved sulfate levels sufficiently that burkeite precipitates first rather than
17 dicarbonate. This is because burkeite scaling is less severe in falling film evaporators than
18 dicarbonate.

19 In this work, we studied the fate of precipitator ash when added above and below the solubility
20 limit. When added to carbonate-rich liquors, equilibrium would indicate that the crystals should
21 dissolve and reprecipitate as carbonate-rich salts or burkeite depending on the liquor chemistry.
22 We added precipitator ash to carbonate-rich black liquors of various solids and found that the
23 precipitator ash crystals were stable over time periods of interest industrially. We also added
24 precipitator ash below the solubility limit. Combined with new solubility limit data we have
25 calculated the maximum solids at which ash can be added to shift to the region where burkeite is
26 precipitated as the first salt.

27
28 **KEYWORDS**

29 Black liquor, ESP ash, Evaporation, Solubility, Dissolution

1 INTRODUCTION

2 Fume is formed due to the volatilization of alkali metal and alkali salts from black liquor droplets
3 burning in the lower boiler furnace and then followed by the condensation of these compounds as
4 the flue gas cools in the upper boiler furnace. Carryover is produced as a result of the combustion
5 of the entrained droplets of black liquor [1]. Carryover and fume form streams of ash that are
6 predominantly collected in hoppers and electrostatic precipitators (ESP) respectively. The amount
7 of ESP ash produced is typically 9-18 g per standard cubic meters of the flue gas exiting the
8 recovery boiler [2]. ESP ash is composed of Na_2SO_4 , Na_2CO_3 , NaCl , K_2SO_4 , K_2CO_3 , KCl , $1.6-$
9 $2.6\text{Na}_2\text{SO}_4\cdot\text{Na}_2\text{CO}_3$ and trace amounts of other salts. The composition of ESP ash depends on the
10 sulfidity, K and Cl content of the black liquor, the lower furnace temperature which is mostly a
11 function of black liquor dry solids content and spray characteristics. Since sodium sulfate accounts
12 for the majority of ESP ash, it is economically and environmentally favorable to recycle it back to
13 the process to minimize chemicals loss. The ESP ash is typically mixed with the as-fired black
14 liquor before injecting to the recovery boiler [3]. It can also be recycled to black liquor below 50%
15 dry solids, so it can dissolve.

16 ESP ash is used to reduce scaling in two different ways. One is to add the ESP ash with black
17 liquor at dry solids where can dissolve. This leads to a shift in the crystallization region from
18 precipitation of dicarbonate/sodium sulfate carbonate to the precipitation of burkeite which leads
19 to a reduced scaling rate. The second approach is to recycle the as-fired black liquor with ESP ash
20 added back to effects operating above the solubility limit to increase the crystal mass in the liquor.
21 The idea is that the ESP ash provides crystal mass, and thus more surface area for sodium salts
22 precipitation in suspension as opposed to precipitation on heat transfer surfaces. A study by
23 Karlsson and co-workers (2017) revealed that the scaling rate in black liquor during primary
24 nucleation (i.e., no bulk crystals present) is tenfold higher compared to continuous crystallization
25 (i.e., certain quantity of bulk crystals present) [4]. In a crystallization study by Shi [5], it has been
26 suggested that sodium double salts do not nucleate on other salts but themselves. Interestingly, a
27 sodium double salt, sodium sulfate carbonate ($\text{Na}_2\text{SO}_4\cdot 1.5\text{Na}_2\text{CO}_3$) was reported by DeMartini
28 and Verrill in 2007. They found this sodium double salt precipitates out in a pilot evaporator
29 experiment in which ESP ash was added to black liquor [6]. This salt has a distinct phase and XRD
30 pattern, but it is very similar crystal size and agglomeration tendency to that of dicarbonate. A
31 hypothesis was that dicarbonate and ESP ash crystals partially dissolve and re-precipitate as
32 sodium sulfate carbonate, where sulfate ions from ESP ash partially substitute the carbonate ions
33 from solution. An objective of this work was to determine if precipitator ash remains as Na_2SO_4
34 and burkeite when added to black liquor above the solubility limit or does it partially dissolve and
35 reprecipitate as a double salt as might be expected based on equilibrium.

36 There are several studies that touch on both anionic and cationic substitution in different systems.
37 One study looked at the incorporation of foreign ions into calcium phosphate crystals during
38 hydrolysis in sodium carbonate solution. It was found that increasing the carbonate concentration
39 in the solution led to a decrease in calcium and phosphate concentration in the solids, suggesting
40 that a coupled substitution of $(\text{Na}+\text{CO}_3)$ for $(\text{Ca}+\text{PO}_4)$ takes place [7]. Another example would be

1 the formation of double salt with a nominal composition of $\text{Na}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$. This salt is
2 obtained because of calcium ion substitution by sodium ion when gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) is stirred
3 in a sodium sulfate containing solution [8]. In addition, ion-ion substitution has been noticed to
4 take a place during CaCO_3 crystallization from CaCl_2 - Na_2CO_3 - Na_2SO_4 - H_2O system. Three
5 different crystalline forms of CaCO_3 (i.e., calcite, vaterite, and aragonite) can precipitate out
6 depending on the initial SO_4 : CO_3 molar ratio in solution. The stability of the distinct crystalline
7 forms is related to the substitution of sulfate for carbonate groups in their crystal structure [9]. The
8 presence of calcium ion in the Na_2SO_4 - Na_2CO_3 - NaOH - H_2O system shows an inhibitory effect on
9 the primary nucleation of burkeite [10]. The proposed governing mechanism for destabilization of
10 primary nucleation is that calcium substitutes for sodium ions in the burkeite crystals [10].

11 As noted above, one objective was to determine if the sulfate in precipitator ash would dissolve
12 over time and the sodium reprecipitate as a carbonate-rich salt. The second objective of this work
13 was to obtain information on the dissolution rate of precipitator ash in black liquor below the
14 solubility limit as well as determine how low the black liquor solids need to be to dissolve
15 sufficient sulfate to shift the species first precipitated to burkeite. For both, studies were carried
16 out at industrial temperatures with a Canadian mill black liquor and ESP ash. For the first objective,
17 experiments were also carried out with an aqueous solution of sodium carbonate as simplified
18 system.

19 **EXPERIMENTAL**

20 **Analytical techniques**

21 The dry solids measurements were performed by oven drying in accordance with TAPPI Standard
22 Test, T650 om-05. For the determination of Na, and SO_4 , Ion Chromatography (Model: Dionex
23 Integion Rfic) was used. For cation determination, the eluent was methanesulfonic acid at a
24 concentration of 6 mM and the column is Dionex IonPac CS17. For anion determination, the eluent
25 was potassium hydroxide at a concentration of 10 mM and the column was Dionex IonPac AS18.
26 Prior to anion measurements, samples were diluted in de-oxygenated water where an oxygen
27 scavenger, Titriplex[®] III, was added to prevent oxidation of sulfite and thiosulfate. A Total
28 Inorganic Carbon (TIC) Analyzer was used for carbonate determination (Model: TOC- V_{CPN}).
29 Scanning Electron Microscopy (SEM), Model: FEI Quanta FEG 250; and X-ray powder
30 diffraction (XRD), Model: Phillips PW3710 diffractometer and X'Pert HighScore analysis
31 software, were used to analyze the crystals.

32 **Na_2CO_3 - Na_2SO_4 - NaOH - H_2O system**

33 A 1L jacketed glass reactor was used to investigate whether sodium sulfate crystals dissolve in a
34 saturated sodium carbonate solution, driving significant sodium carbonate precipitation within 24
35 h. The reactor was heated by circulating silicon oil using an oil bath that is temperature controlled.
36 Agitation was provided by inserting a shaft stirrer from the top of the reactor to maintain
37 homogenous mixing. Sodium carbonate was first dissolved in de-ionized water slightly below the
38 solubility limit, 28% dry solids, then the solution pH was increased by adding 18 g/kg H_2O of

1 sodium hydroxide. The solution was heated to 95 °C in the glass reactor and then an excess amount
 2 of sodium sulfate was added until the total molar ratio of $\text{CO}_3/\text{CO}_3+\text{SO}_4$ was 0.60. This was
 3 allowed it to equilibrate for 24 h. Filtered samples were collected at set time interval (i.e., 0, 1, 4,
 4 24 h) to measure the change in the dissolved concentration of carbonate and sulfate over time. A
 5 vacuum pump was used to pull a sample through a stainless-steel filter with a larger surface area
 6 (12 mm diameter and 60 mm length) and nominal pore size of 2 μm (Norman Filter Co., part
 7 number 4311GG-2XVN). The filter and sampling line were heated to the experiment temperature
 8 using heating tape. The time zero represents the dissolved concentration of sodium carbonate
 9 before the addition of sodium sulfate. The times 1, 4, and 24 h represent the dissolved
 10 concentration of both sodium carbonate and sodium sulfate after the addition of sodium sulfate.

11 Solubility of ESP ash in black liquor below 100 °C

12 Solubility experiments of electrostatic precipitator (ESP) ash were carried out in 250 ml Pyrex
 13 glass bottles heated in a water bath shaker. The black liquor and electrostatic precipitator (ESP)
 14 were provided by a Canadian mill. The concentration of sodium, potassium, chloride, sulfate, and
 15 carbonate have been determined in the as-received samples and ESP ash, Table 1. The
 16 experimental steps were heating black liquor to the desired temperature and then adding the ESP
 17 ash. As shown in Table 2, different additions of electrostatic precipitator (ESP) ash have been
 18 added to a 40% dry solids black liquor and allowed to equilibrate for 24 h. It should be note that
 19 24 h has been found to be sufficient for the system to reach equilibrium. Samples were pulled out
 20 using the heated stainless filter with a vacuum pump at various time interval to establish
 21 equilibrium.

22 **Table 1.** Composition of Black Liquor and ESP Ash. Standard deviation is calculated based on 18 determinations.

Element	Concentration (wt% d.s.)	
	ESP Ash ^a	Black Liquor
Sodium	28.3 (± 0.53)	18.1
Potassium	5.86 (± 0.07)	2.97
Chloride	0.90 (± 0.06)	0.17
Sulfate	46.1 (± 0.75)	2.51
Carbonate	12.9	5.31

23 a: the charge balance of $(\text{Na}+\text{K})/(\text{Cl}+\text{SO}_4+\text{CO}_3)$ in ESP ash analysis is 0.97

24 **Table 2.** Experiment Parameters for ESP Ash Solubility in Black Liquor.

Black liquor solids at the start (%)	40
Liquor solids after ESP ash addition (%)	42, 45, 47.5 and 50
Temperature (°C)	95

25

26 Kinetics and dissolution ESP ash in black liquor below 100 °C

27 The kinetics experiments of electrostatic precipitator ash in black liquor below 100 °C were
 28 carried out in 1 L jacketed glass reactor. A 40% dry solids black liquor was heated to a temperature

1 of 95 °C and then ESP ash was added until the liquor dry solids increased to 42.5%, which is below
2 the solubility limit of sodium sulfate and sodium carbonate. Samples were pulled out using the
3 heated stainless filter after 10, 20, 40, 60, and 80 mins of ESP ash addition.

4 Similarly, the dissolution of ESP ash in black liquor above the solubility limit was investigated at
5 95 °C at two dry solids. In the first experiment above the solubility limit, the black liquor was first
6 concentrated up to 52%, just at the solubility limit, before addition; while in the second experiment,
7 the black liquor was first concentrated up to 59%, which was well above the solubility limit. The
8 black liquor was first heated to 95 °C and then 55 g of precipitator ash was added per kg BL solids
9 or 5.5 wt% d.s.. Samples were pulled out at 4, 8, and 24 h. The sampling steps are the same as
10 describe in the previous sections.

11 **Dissolution of ESP ash in black liquor above 100 °C**

12 The dissolution of ESP ash above the solubility lime and at 125 °C was studied at two initial black
13 liquor dry solids, 52 and 57 wt% d.s.. The experiments were performed by using two connected
14 Parr reactors, one for black liquor and the other for ESP ash, Figure 1. The back liquor was first
15 heated to 125 °C and then pushed to the other reactor which contains the ESP ash, 22 g of
16 precipitator ash was added per kg BL solids, by pressure difference. Both reactors were
17 pressurized above the vapor pressure of water at that temperature to prevent liquor evaporation by
18 flashing while transferring the liquor.

19 Sampling was carried out with the same stainless-steel filter described above. A stainless-steel
20 sampling line connected the filter to the parr reactor and then a second line from the filter went to
21 a stainless-steel vessel that could be pressurized. A Teflon sample bottle with a weighed amount
22 of de-ionized water was put in the stainless-steel vessel so that sampled black liquor would flow
23 to the water and be immediately diluted and cooled. A pressure difference was used to push the
24 black liquor through the filter. Before pulling each sample, the sampling line was attached to the
25 reactor, preheated using heating tab, and then pressurized with air to less than the parr reactor
26 pressure. The reactor sampling valve was then open to allow the liquor to be pushed through the
27 filter by the pressure difference. Filtered liquor and crystal samples were collected for analysis.
28 After sampling, the filter was removed from the sampling line and the crystals were washed while
29 still in the filter by first drawing about 200mL of ethylene glycol through the filter, followed by
30 200mL of ethylene glycol-ethanol mixture (50/50 vol-%), and then 200mL of ethanol. This is
31 based on a method developed by Shi [5]. After washing, the inner part of the filter is disassembled,
32 oven dried for 30 min, then the washed salt crystals are scraped off to be dried over night at 115
33 °C. There were times that washing was not successful because the solvents could not be drawn
34 through the filter.

35

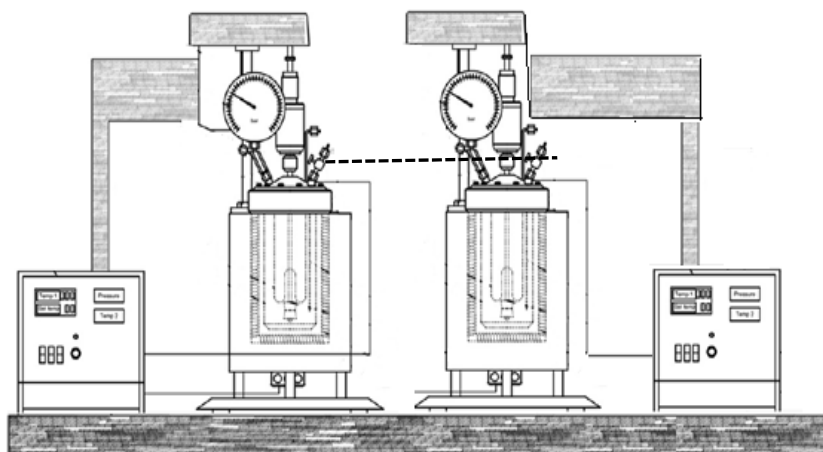


Figure 1. Schematic diagram of two connected Parr reactors.

RESULTS AND DISCUSSION

$\text{Na}_2\text{CO}_3\text{-Na}_2\text{SO}_4\text{-NaOH-H}_2\text{O}$ System

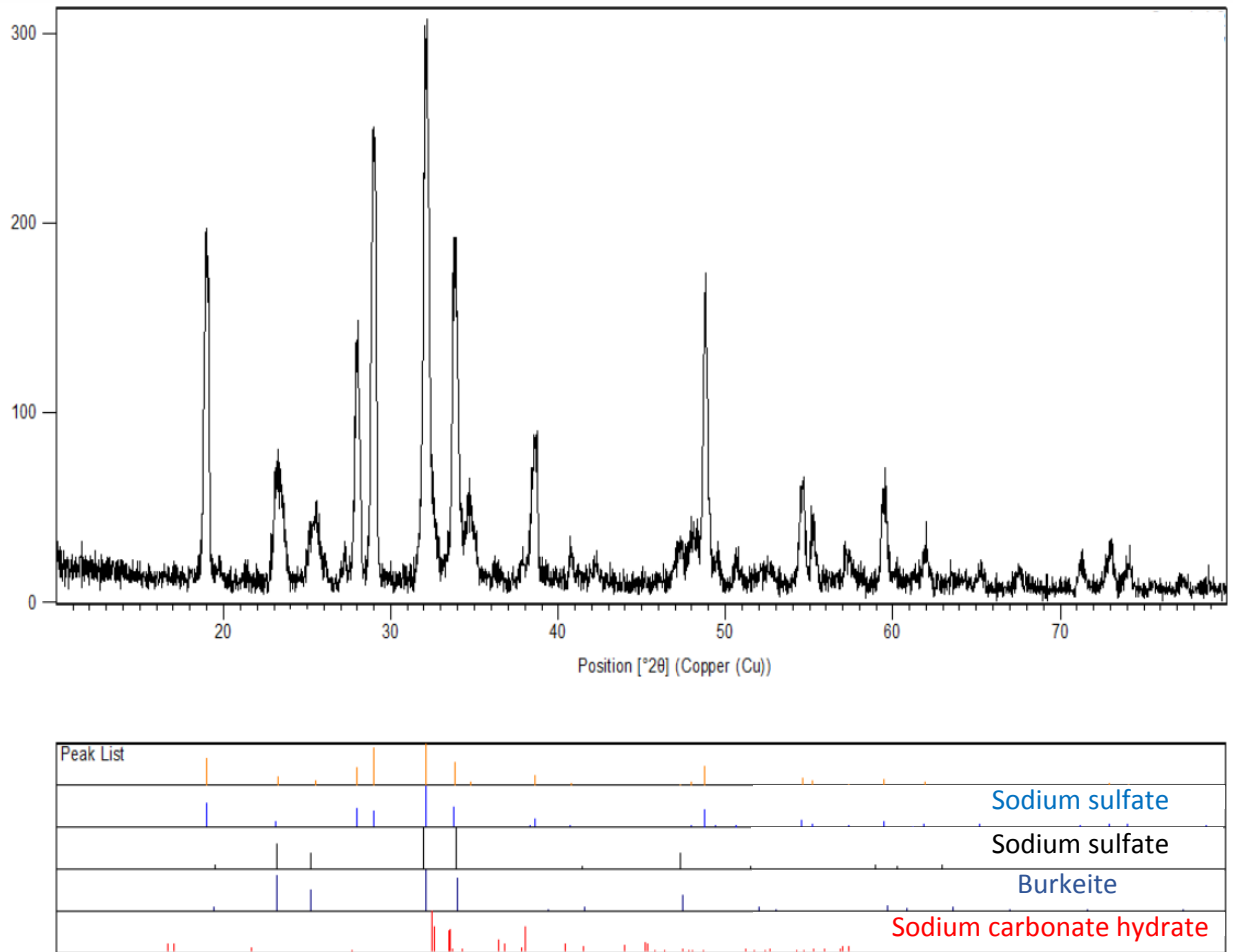
Table 3 shows the results of Na_2SO_4 addition to a concentrated solution of Na_2CO_3 at 95°C . The solution was just below the solubility limit for sodium carbonate. For the first experiment, within the first hour, the dissolved concentration of carbonate remained unchanged and decreased by 7% and 3% after 4 h and 24 h respectively. Similarly, the dissolved concentration of sulfate was 0.040 g/g of filtered solution after 1h of the addition and remained unchanged after 4 h and decreased by 10% after 24 h. In the repeated experiment, the dissolved concentration of carbonate appears to decrease, 15% with 24 h and the dissolved sulfate concentration increased by 14% after 24 h. The Crystals were collected from the bulk solution after 24 h from the second experiment to be analyzed by XRD to investigate whether or not burkeite was formed. The XRD pattern would indicated Na_2SO_4 is present, Figure 2. The major peaks of the solid sample were found at 2θ values $19^\circ, 23^\circ, 25^\circ, 28^\circ, 29^\circ, 32^\circ, 34^\circ, 34.7^\circ, 38.5^\circ, 49^\circ, 54.5^\circ, 55^\circ, 59.5^\circ, 62^\circ, 71.2^\circ, 73^\circ,$ and 74° which are a good match for sodium sulfate. It should be noted that there are two structures of sodium sulfate crystals, orthorhombic and hexagonal. The peaks at the 2θ values 23° and 25° , indicates that burkeite may also be present. There is no clear agreement between the XRD pattern of the crystals and the reference pattern of sodium carbonate hydrate. These results indicate that there may be some burkeite formed by Na_2CO_3 precipitated within 24 h, but the system does not continue moving towards burkeite.

Table 3. Dissolved concentration of carbonate and sulfate in $\text{Na}_2\text{CO}_3\text{-Na}_2\text{SO}_4\text{-NaOH-H}_2\text{O}$ system at temperature of 95°C .

Experiment No.	Concentration (g/g Filtered solution)	Time (h)			
		0	1	4	24
1	CO_3	0.148	0.148	0.138	0.144
	SO_4	0	0.040	0.040	0.036

2	CO ₃	0.156	0.150	0.147	0.133
	SO ₄	0	0.029	0.027	0.033
Average	CO ₃	0.152	0.149	0.142	0.138
	SO ₄	0	0.034	0.033	0.034

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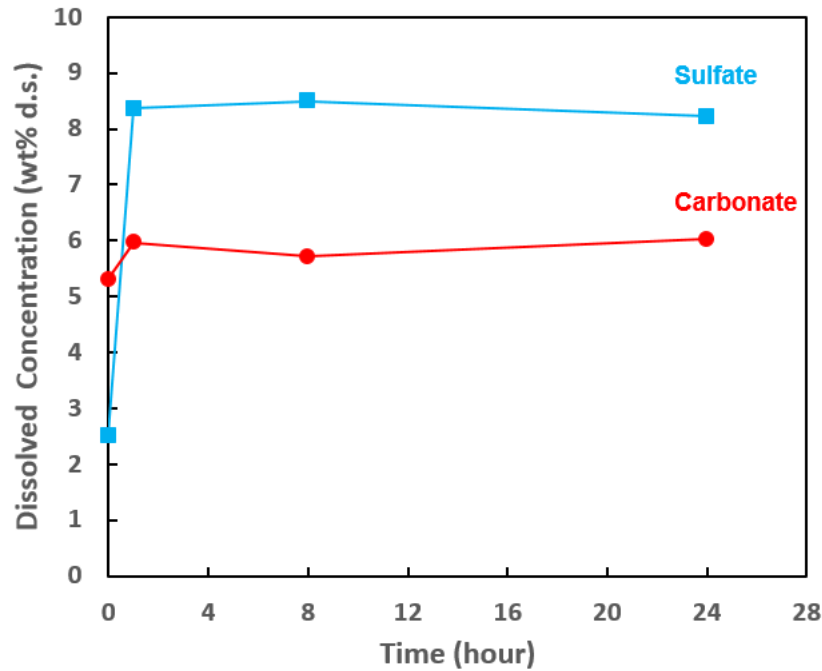
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Figure 2. XRD pattern for crystals isolated from bulk solution of Na₂CO₃-Na₂SO₄-NaOH-H₂O system after 24 h.

5 The solubility of ESP ash in black liquor

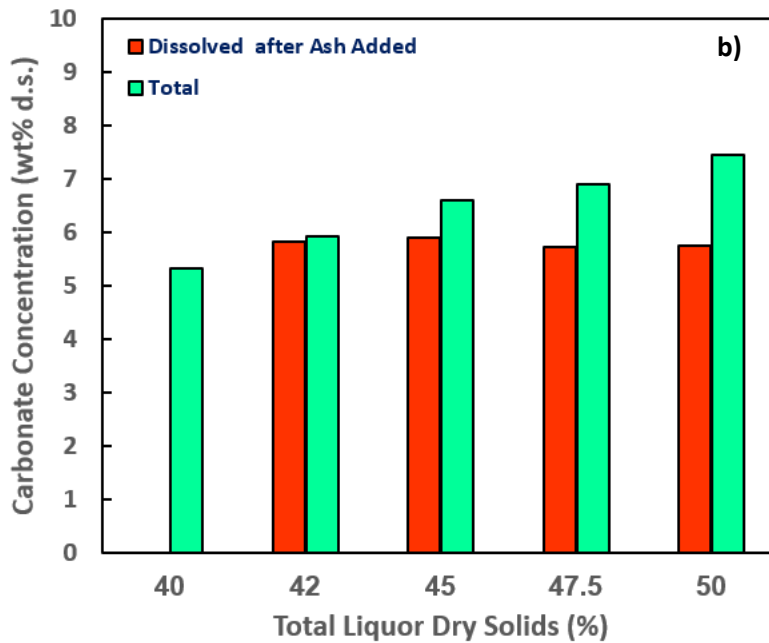
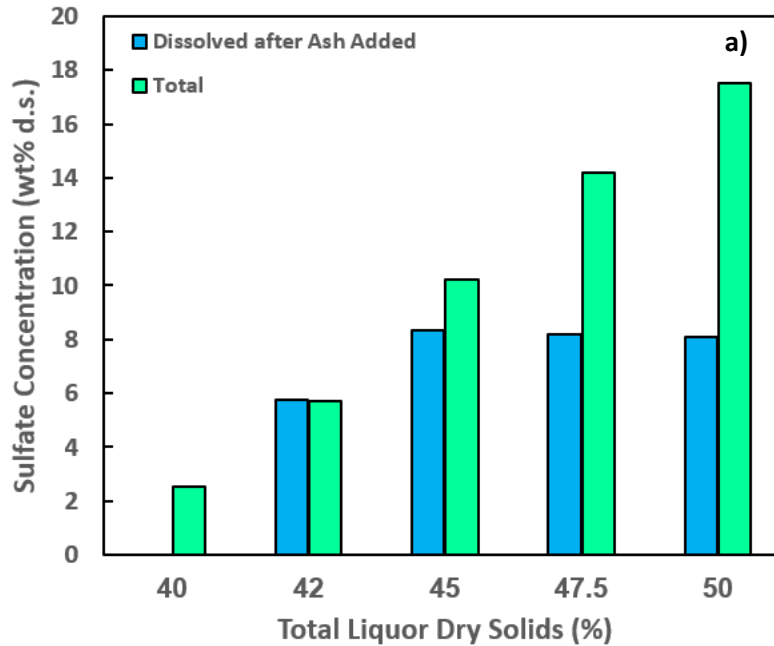
6 The solubility of ESP ash in black liquor was measured in 40% black liquor at a temperature of 95
7 °C. This temperature was chosen as ESP ash added to black liquor below the solubility limit would
8 likely be added at atmospheric pressure and therefore at a temperature reasonably close to 95 °C.
9 The ESP ash was added to black liquor at different doses to increase the total dry solids to 42%,
10 45%, 47.5%, and 50%. The ESP ash additions were 86 g_{ash}/kg_{dry solids}, 227 g_{ash}/kg_{dry solids}, 357
11 g_{ash}/kg_{dry solids}, and 500 g_{ash}/kg_{dry solids} respectively to reach the various total solids. The purpose of
12 these experiments was to determine the solubility limit. First, the equilibration time was
13 determined when ESP ash was added to the black liquor at a dose of 227 g_{ash}/kg_{dry solids} and at a

1 temperature of 95 °C, Figure 3. Equilibrium appears to be attained as soon as the first sample had
 2 been pulled out, which is 1 h after the ash addition. The dissolved concentration of carbonate (8.5
 3 wt% d.s.)_and sulfate (6.0 wt% d.s.) remained the same throughout the sampling period (1-24 h).
 4 This observation was consistent for the other experiments.



5
 6 **Figure 3.** Equilibrium time of ESP Ash in 40% black liquor at temperature of 95 °C. The total liquor dry solids
 7 increased to 45% after ESP ash addition.

8
 9 The ESP ash was found completely soluble when added to 40% black liquor at a dose of 86
 10 $\text{g}_{\text{ash}}/\text{kg}_{\text{dry solids}}$ (i.e., total liquor solids of 42% after ash addition) while it was only partially soluble
 11 when added at a dose of 227 $\text{g}_{\text{ash}}/\text{kg}_{\text{dry solids}}$ and higher (i.e., total liquor dry solids of 45% and
 12 beyond), Figure 4 (a-b). The proportions of how much sulfate and carbonate are dissolved of the
 13 added ESP ash can be calculated based on the concentration difference. For instance, about 98%
 14 of sulfate content in the added ESP ash had been dissolved and 99% for carbonate when the total
 15 liquor dry solids is increased to 42%. When the liquor dry solids increased to 45% after ESP ash
 16 addition, it was found that only a portion of added ESP ash was dissolved. However, the findings
 17 indicate that the solubility limit of ESP ash in the 40% dry solids black liquor was 43% or 131
 18 $\text{g}_{\text{ash}}/\text{kg}_{\text{dry solids}}$. Table 4 shows a significant change in the dissolved carbonate to sulfate molar ratio,
 19 which has been reduced from 0.77 in the original black liquor to 0.53 in the black liquor after an
 20 addition of 227 $\text{g}_{\text{ash}}/\text{kg}_{\text{dry solids}}$, of which 131 $\text{g}_{\text{ash}}/\text{kg}_{\text{dry solids}}$ was dissolved. In this case, the carbonate
 21 to sulfate molar ratio has been shifted from the region in which carbonate-rich salt precipitates first
 22 to that of sulfate-rich salt [11, 12].



1

2

3 **Figure 4.** a) Sulfate and b) Carbonate solubility after ESP ash addition to 40% dry solids black liquor at 95 °C and
 4 after 24 h.

5 **Table 4.** Change of dissolved carbonate to sulfate mole ratio after ESP ash addition to 40% black liquor.

	$\text{CO}_3/(\text{CO}_3+\text{SO}_4)$ 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
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1

2 Extending the results to a mill application may allow us to determine the proper point and addition
3 dose of ESP ash recycling with black liquor. A Canadian kraft pulp mill adds ESP ash to 46% dry
4 solids black liquor typically at a rate of 55 g_{ash}/kg_{dry solids}. The composition of black liquor and ESP
5 ash in this mill is given in Table 1 where the dissolved molar ratio of CO₃/(CO₃+SO₄) in the liquor
6 is 0.77, a region where sodium sulfate carbonate precipitates. To get the ratio where burkeite
7 precipitates out first, the mill would need to add ESP ash to black liquor at a lower dry solids so it
8 can dissolve. The solubility limit can be calculated using Equation 1, which is established from
9 solubility study of Na-CO₃-SO₄ system in black liquor [13]. The maximum amount of ESP ash
10 that can be dissolved in this particular black liquor is 45 g_{ash}/kg_{dry solids} when added to the black
11 liquor at 46% dry solids. This would lower the dissolved molar ratio of CO₃/(CO₃+SO₄) to 0.67
12 where burkeite is expected to precipitate out first. If adding ESP ash at higher rate, for example 50
13 g_{ash}/kg_{dry solids}, not all the added ESP ash will dissolve since the solubility limit is exceeded.

$$SL = 71.008 - (0.714 \times [Na]_{dis}) - (0.761 \times [CO_3]_{dis}) - (1.448 \times [SO_4]_{dis}) \quad /1/$$

14

Where:

15

SL: Solubility Limit (% total black liquor solids)

16

[Na]_{dis}: Dissolved sodium concentration in black liquor (weight % of liquor solids),

17

$$18 < [Na]_{dis} < 22$$

18

[CO₃]_{dis}: Dissolved carbonate concentration in black liquor (weight % of liquor solids)

19

$$5 < [CO_3]_{dis} < 9$$

20

[SO₄]_{dis}: Dissolved sulfate concentration in black liquor (weight % of liquor solids)

21

$$2.5 < [SO_4]_{dis} < 5.5$$

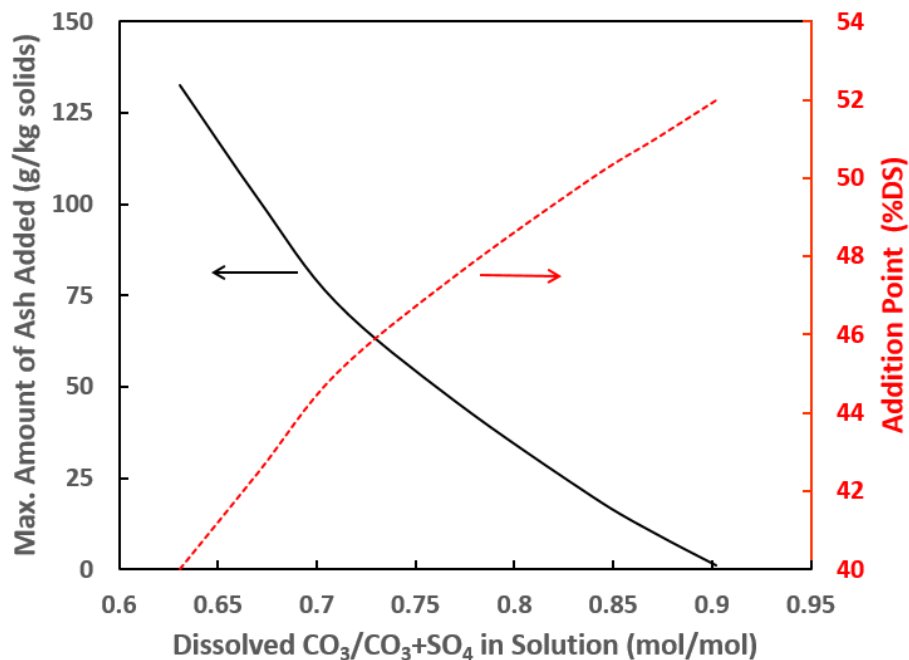
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24 For a given black liquor and ESP ash composition, e.g., Table 5, the amount of ash that can be
25 dissolved at a given solids and the resulting dissolved CO₃/(CO₃+SO₄) can be calculated.
26 Alternatively, the initial and desired CO₃/(CO₃+SO₄) ratio can be used to calculate at which dry
27 solids the ESP ash should be added to achieve the desired ratio. Figure 5 shows the amount of ESP
28 ash that needs to be added to achieve a desired ratio when the starting molar ratio of
29 CO₃/(CO₃+SO₄) in the black liquor is 0.90. The lower the desired molar ratio of CO₃/(CO₃+SO₄)
30 the more ash needs to be added and therefore the lower the dry solids at which it must be added.
31 Based on the calculations, the maximum amount of ESP ash that can be added to 40% dry solids
32 liquor is 133 g_{ash}/kg_{dry solids} where the dissolved molar ratio of CO₃/(CO₃+SO₄) is reduced from
33 0.90 to 0.63. It should be noted that dissolving 133 g_{ash}/kg_{dry solids} of ESP ash in 40% dry solids
34 liquor drops the solubility limit down to 43%. When ESP ash is recycled to 45% dry solids liquor,
35 only 73 g_{ash}/kg_{dry solids} can be dissolved where the CO₃/(CO₃+SO₄) molar ratio is reduced from 0.90
36 to 0.72 and a carbonate-rich salt is still expected to precipitate first [11, 12].

1 **Table 5.** Composition of ESP ash and black liquor used in calculations.

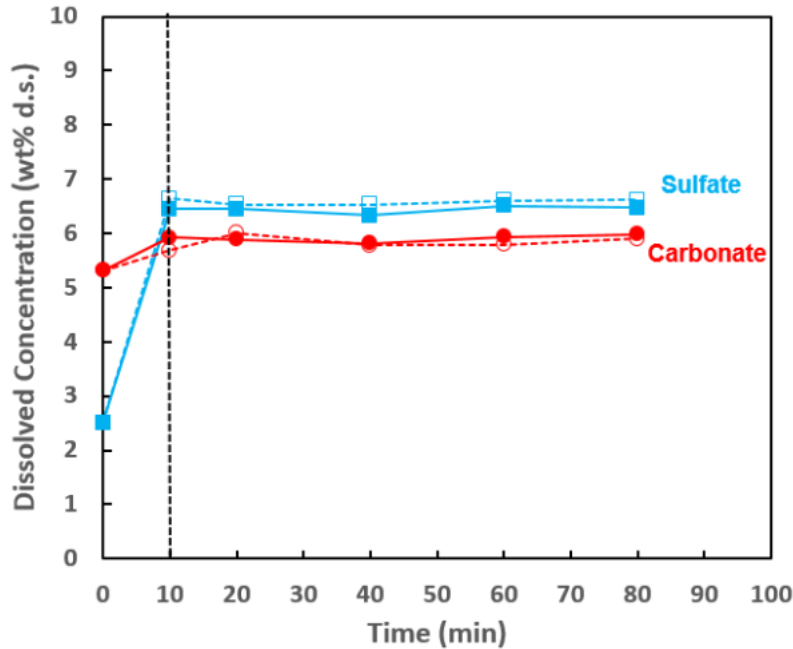
Element	Concentration (wt. % d.s.)	
	ESP Ash	Black Liquor
Sodium	28.3	18.0
Sulfate	46.1	1.00
Carbonate	12.9	6.00
CO ₃ /(CO ₃ +SO ₄)	-	0.90



2
 3 **Figure 5.** Solids at which ESP ash should be added (dashed red line) and mass of ash that can be added (solid black
 4 line) to achieve a dissolved solids CO₃/(CO₃+SO₄) mol-ratio when the initial ratio is 0.9 for the black liquor and
 5 ESP ash analysis given in Table 5.

6 **The Dissolution kinetics of ESP ash in black liquor**

7 Establishing how fast ESP ash dissolves in black liquor, dissolution kinetics was studied for 80
 8 min in 40% black liquor and temperature of 95 °C. The ESP ash was added to black liquor at a
 9 dose of 108 g_{ash}/kg_{dry solids} which is slightly below the solubility limit (i.e. the maximum allowable
 10 dose of ash that can be dissolved at the same condition of 131 g_{ash}/kg_{dry solids}). It should be noted
 11 that while pulling the sample only takes a minute or so, handling the filtered sample after being
 12 pulled out using the heated filter takes about 30-40 min and therefore the experiment has been
 13 repeated a few times at the same conditions to be able to get samples at all times desired. After
 14 introducing ESP ash to the black liquor, the carbonate and sulfate concentrations increased with
 15 time until they reach a plateau within 10 min, Figure 6. The carbonate to sulfate ratio has been
 16 reduced from 0.77 to 0.59 after a complete dissolution of the ESP ash. This indicates that the
 17 crystallization region shifts from carbonate-rich salt to sulfate-rich salt. The experiment has been
 18 repeated twice and the results are in well agreement both for carbonate and sulfate concentrations.

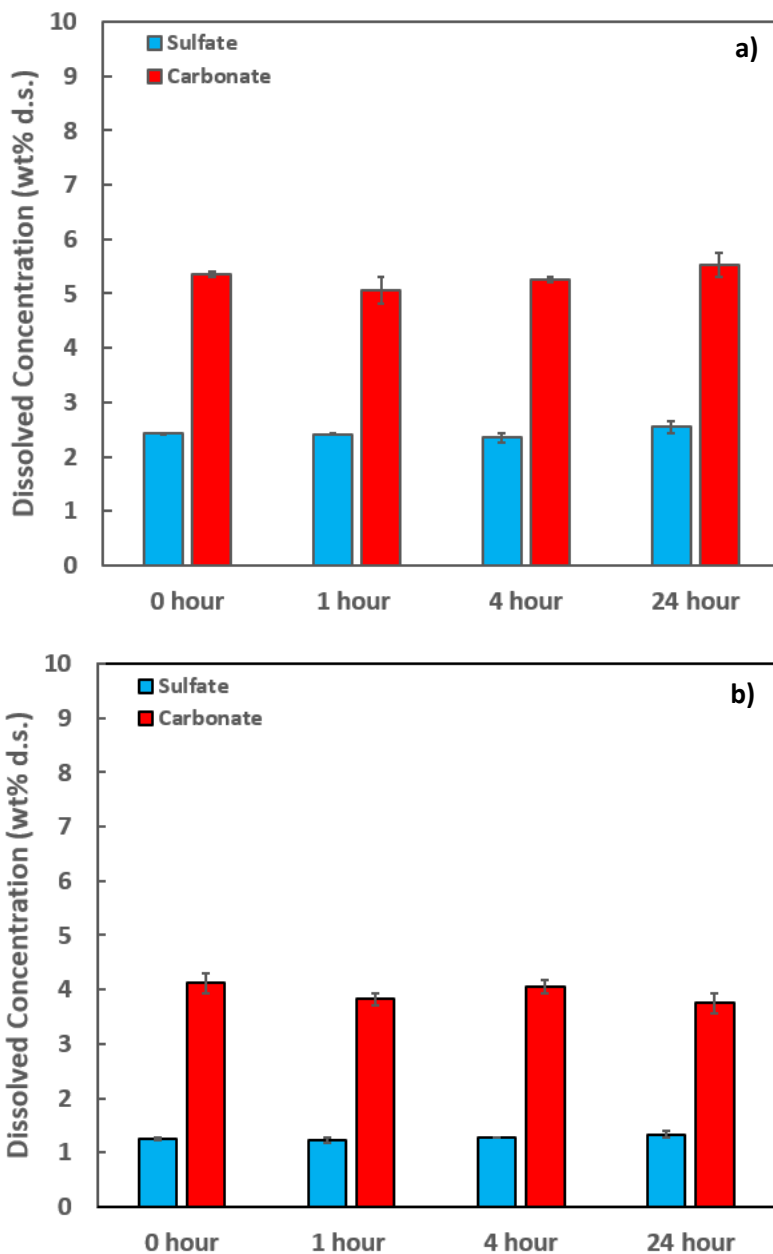


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2 **Figure 6.** The dissolution kinetics of ESP ash in 40% black liquor at temperature of 95 °C. The total liquor dry
 3 solids increased to 42.5% after ash addition.

4 **Ash dissolution in high solids black liquor**

5 In this set of experiments, the stability of ESP ash crystals has been studied when added to black
 6 liquor at dry solids above 50% and at temperature below 100 °C. The purpose of this study is to
 7 determine whether ash crystals dissolves and thus led to change in liquor composition upon the
 8 addition or remain stable. The ESP ash was added at a dose of 55 g_{ash}/kg_{dry solids} to black liquor at
 9 two different initial dry solid contents: 52% which is slightly above the solubility limit and 59%
 10 which well above the solubility limit at 95 °C. As shown in Figure 7 (a-b), no significant change
 11 in the dissolved concentrations of carbonate and sulfate were observed over a time of 24 h at both
 12 52% and 59% dry solids. This indicates that no dissolution of ESP ash took place when added to
 13 high solids black liquor below 100 °C. The dissolved concentration of carbonate and sulfate at
 14 59% was much lower than that of 52%. That is because the solubility limit was reached at liquor
 15 dry solids of 51%. Although the liquor is carbonate-rich, burkeite and sodium carbonate hydrate
 16 are expected to precipitate out since the temperature is below 100 °C. Shi and Rousseau [14]
 17 reported that the carbonate-rich salt, dicarbonate, does not form at temperatures below 109 °C.
 18 The important question here is “was the experiment time long enough for ash crystals to be in
 19 equilibrium with black liquor?”. The possibility of allowing a longer equilibration time may lead to
 20 change in crystals form.



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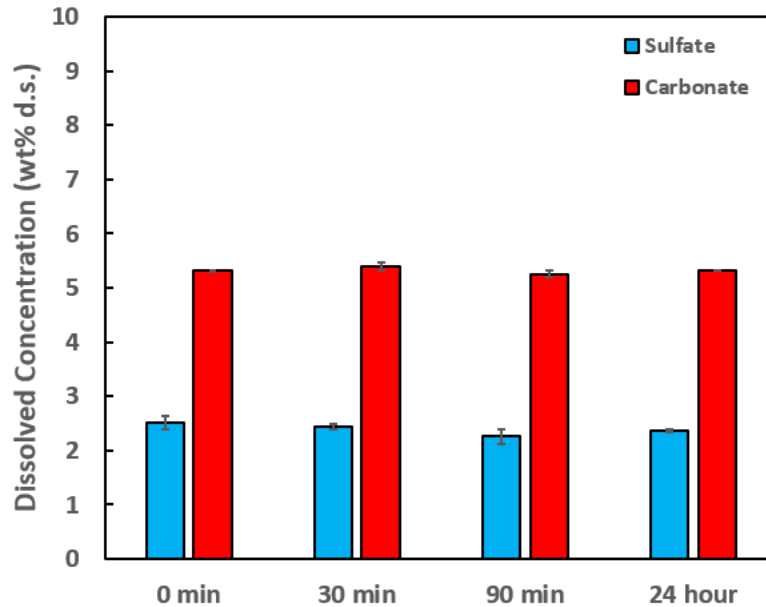
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4 **Figure 7.** Dissolved concentration of carbonate and sulfate after ESP ash addition in black liquor at temperature of
 5 95 °C; a) Dry solids of black liquor is 52% and b) Dry solids of black liquor is 59%.

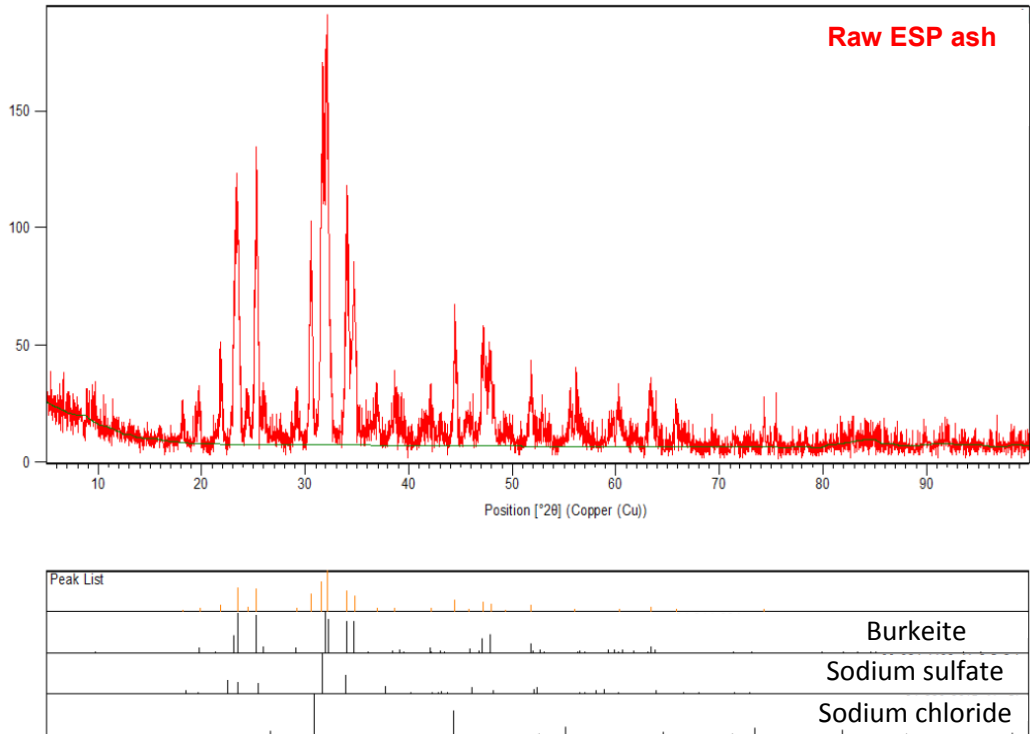
6 Extending the stability study of ESP ash crystals in black liquor at dry solids above the solubility
 7 limit, ESP ash was added to 52% black liquor at dose of 22 g_{ash}/kg_{dry solids} and a temperature of 125
 8 °C. The dissolved concentration of carbonate and sulfate in black liquor remained unchanged up
 9 to 24 h after the addition of ESP ash, Figure 8. These observations indicate that the ESP ash crystals
 10 exhibit no dissolution at the conditions studied which agrees with the findings at 95 °C. It has been
 11 suggested that when ESP ash is added to high solids black liquor evaporators which have
 12 dicarbonate crystals present, it might dissolve and a new salt can precipitate out to bring the

1 solution and crystals back into equilibrium [6]. To further investigate whether or not crystals
2 change form, ESP ash crystals were isolated after 30 min, 90 min and 24 h of equilibration in black
3 liquor. XRD analysis was performed on the recovered crystals to check whether the ESP ash
4 maintains its distinct structure.



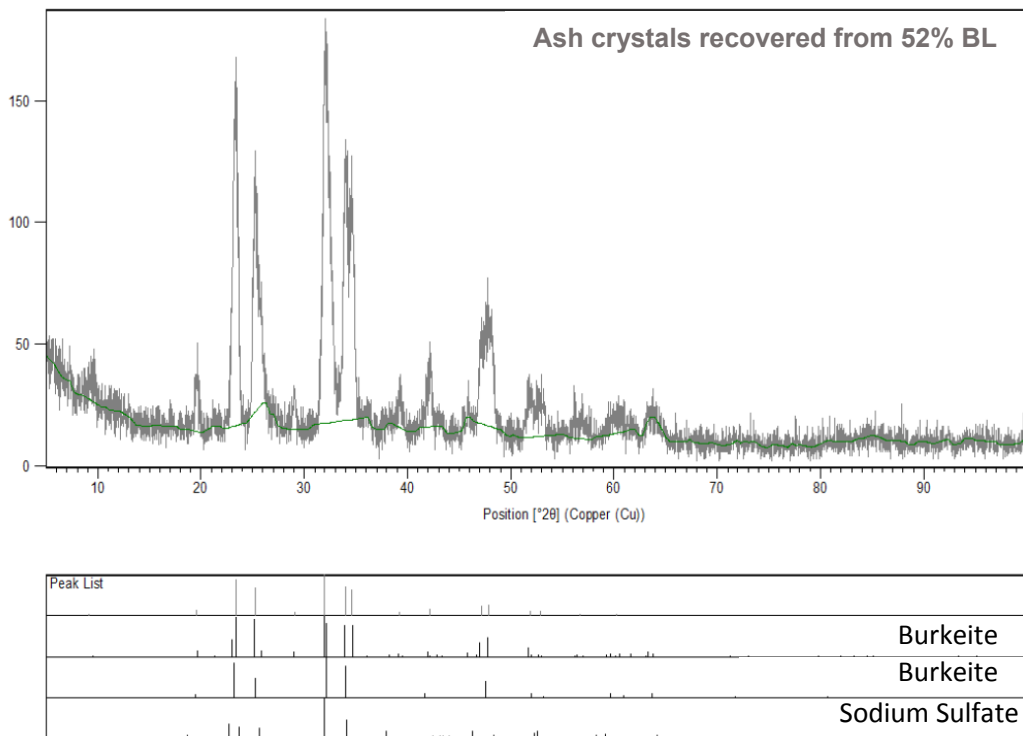
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6 **Figure 8.** Dissolved concentration of carbonate and sulfate after ESP ash addition in black liquor at dry solids of
7 52% and temperature of 125 °C.

8 Because the solubility limit of the black liquor is 51% dry solids, when the ash is added at 52%
9 dry solids, the mass of crystals added as ash is much higher than the mass of crystals in the black
10 liquor. The mass ratio between the precipitated salt in the black liquor at 52% dry solids and the
11 added ESP ash is 0.032. This was done at this solids for that reason, so that the fate of the ESP ash
12 crystals could be more easily followed. It should be noted that the raw ESP ash is referred to the
13 untreated or as-received ESP ash sample obtained from an industrial partner. The XRD pattern
14 shows that the raw ESP ash consists of burkeite, sodium sulfate and sodium chloride, Figure 9.
15 The XRD patterns for ESP ash isolated from black liquor demonstrated all the major peaks of
16 burkeite and sodium sulfate, further indicating that the ESP ash crystals do not change form when
17 added to a black liquor, Figure 10. The peaks at 2θ values 21° , 30.8° , and 44° disappeared in the
18 crystals recovered from 52% black liquor indicating dissolution of sodium chloride. A comparison
19 of XRD patterns of the ESP ash recovered from 52% black liquor at 30 min, 90 min, and 24 h as
20 well as the raw ESP ash is given in Figure 11.



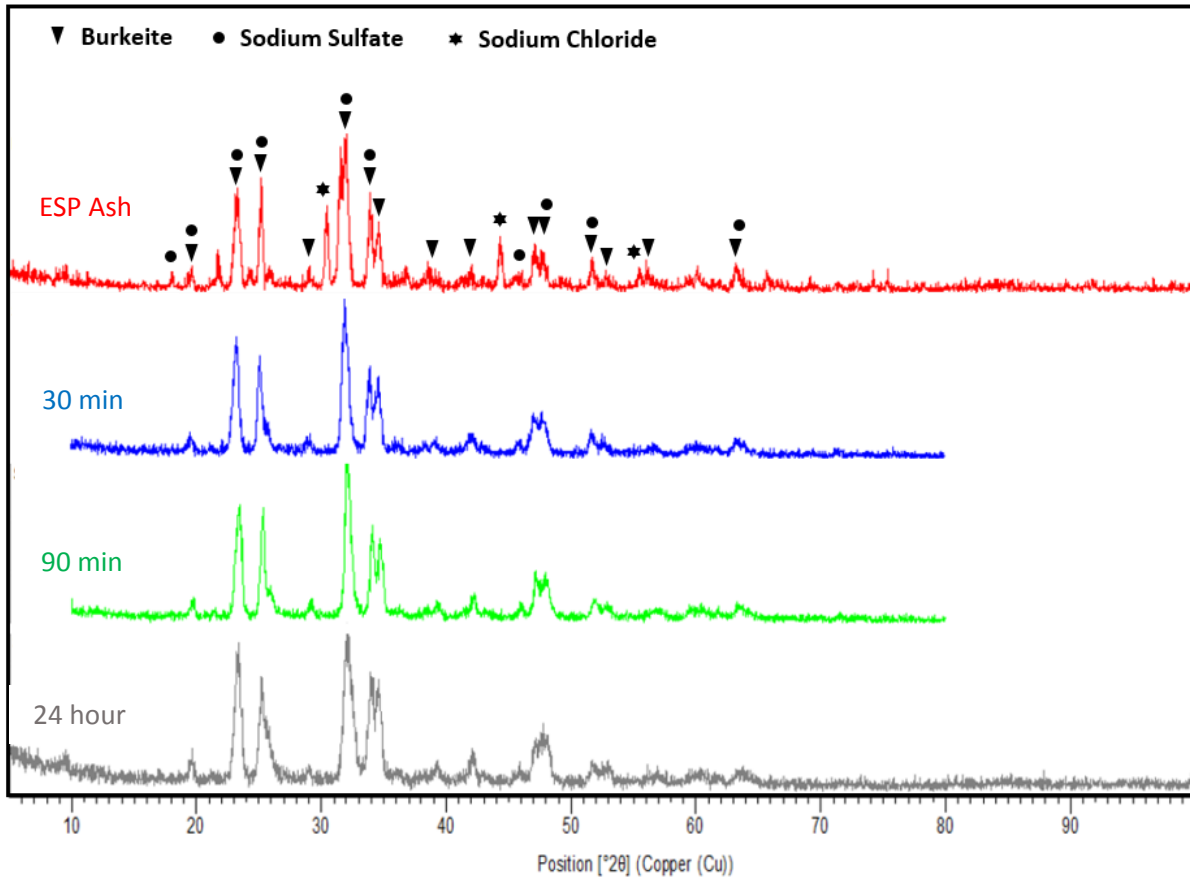
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Figure 9. XRD pattern for ESP ash before addition to black liquor.



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Figure 10. XRD pattern for crystals recovered from 52% black liquor after 24 h of ESP ash addition.



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2 **Figure 11.** XRD patterns for ESP ash, crystals recovered from 52% black liquor after 30min, 90min, and 24 h of
3 ESP ash addition.

4 ESP ash was also added to 57 wt% d.s. black liquor at dose of 22 $\text{g}_{\text{ash}}/\text{kg}_{\text{dry solids}}$ at a temperature of
5 125 °C. It should be noted that, at 57% dry solids, dicarbonate is present in the liquor prior to ash
6 addition. As in earlier experiments when the ash is added above the solubility limit, it was found
7 that the dissolved concentration of carbonate and sulfate in the liquor remains unchanged up to 24
8 h after the addition of ESP ash, Figure 12. In this experiment, a successful isolation of crystals was
9 attained only after 24 h of equilibration.

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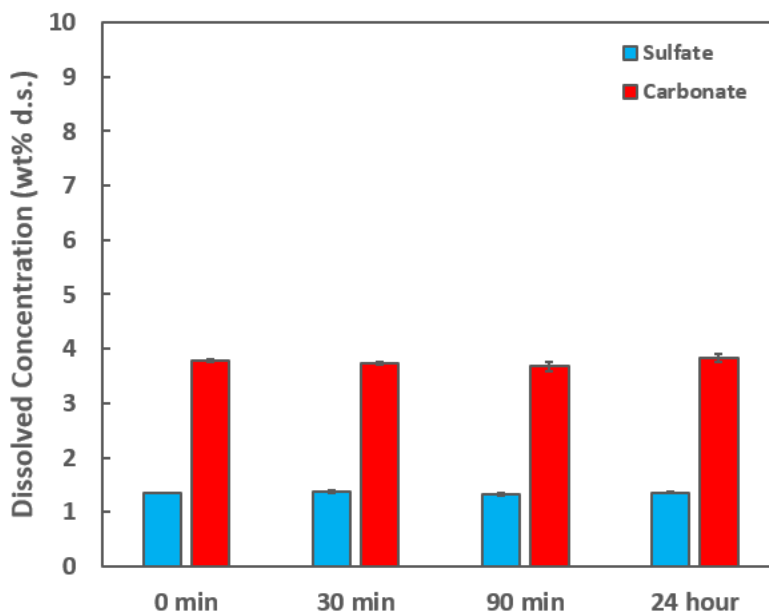


Figure 12. Dissolved concentration of carbonate and sulfate after ESP addition in black liquor at dry solids of 57% and temperature of 125 °C.

XRD analysis have been performed on the crystals recovered from 57% black liquor after ESP ash addition, the sodium double salt crystals precipitated from 58% dry solids liquor before ESP ash addition, and a mixture of the recovered ESP ash and the sodium double salt with 1:1 mass ratio. Comparing the XRD pattern for the crystals isolated from 57% black liquor after ESP ash addition with raw ESP ash, it was found that the peaks corresponding the sodium chloride at 2θ values of 21° , 30.8° , and 44° are no longer seen, Figures 13 and 14. It indicates that the chemical compounds associated with chloride have been leached out in the high solids black liquor. In return, extra peaks have appeared at 2θ values of 27° , 33° , 34.5° , and 42° of which matches the pattern for sodium sulfate carbonate salt. At the conditions studied, the expected salt crystals to precipitate out from the 57% black liquor before ESP ash addition is carbonate-rich, sodium sulfate carbonate and/or dicarbonate, it is reasonable that some of inherently precipitated salt were collected with ESP ash. Based on these observations, one can suggest that ESP ash crystals do not change form when added to black liquor.

Crystals precipitated from black liquor at similar conditions before ESP ash addition has been collected and analyzed by XRD to separate out the effect. The conditions are: black liquor dry solids of 58%, the temperature of 115 °C, and the initial $\text{CO}_3/(\text{CO}_3+\text{SO}_4)$ molar ratio of 0.77. This will provide a better understanding whether or not sodium sulfate carbonate salt is already existing in black liquor prior to introducing ESP ash. Figures 15 and 16, show that the extra peaks at 2θ values of 27° , 33° , 34.5° , and 42° correspond to sodium sulfate carbonate and dicarbonate salt. It is reasonable to suggest that the collected crystals from 57% black liquor after ESP ash addition is a mixture of the sodium double salt already precipitated out and the ESP ash crystals.

1 When mixing the ESP ash and the crystals of sodium double salt that is isolated from 58% black
2 liquor (50/50 mix), it was found that the XRD pattern is very similar to that of crystals recovered
3 from 57% black liquor after ESP ash addition, Figure 17 and 18. It indicates that sodium sulfate
4 carbonate is not a distinct salt phase in this case but rather an artefact of salt mixture. Figure 19
5 shows a comparison of XRD patterns for ESP ash, the crystals recovered from 57% black liquor
6 after ESP ash addition, and the crystals of sodium double salt precipitated from 58% dry solids
7 liquor before ESP ash addition.

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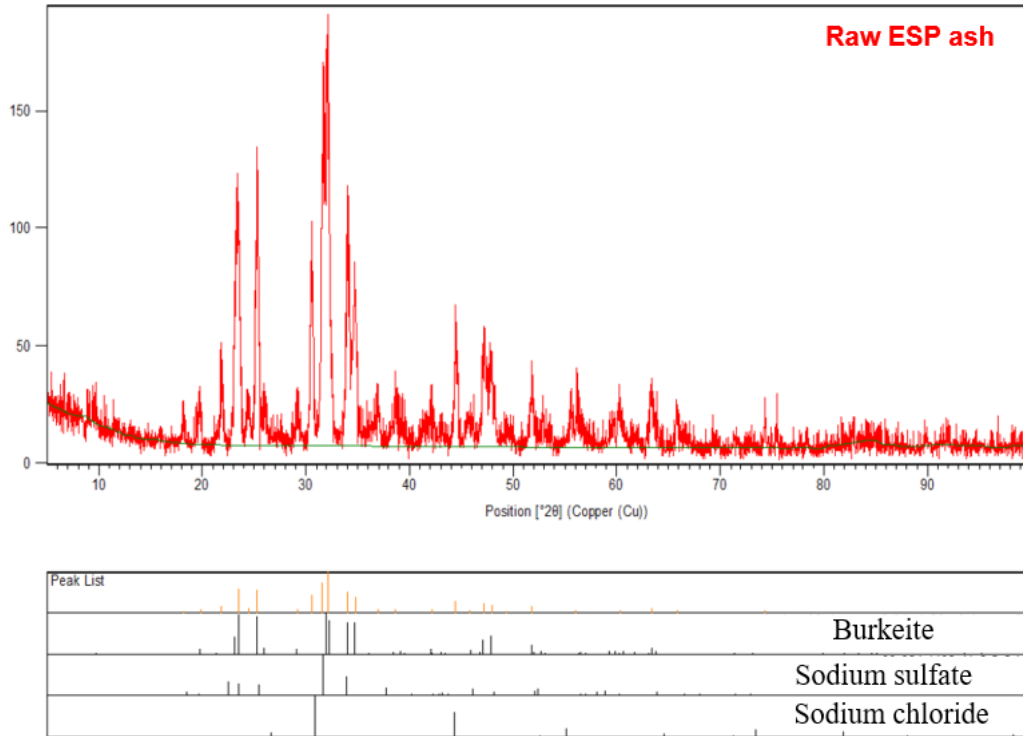
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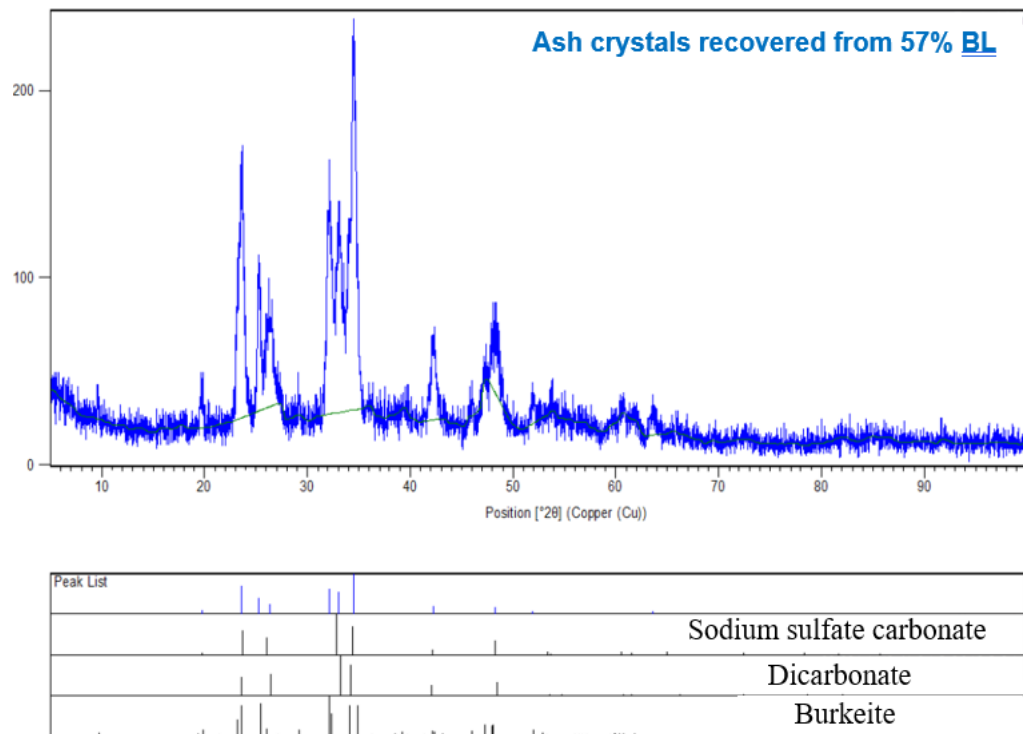
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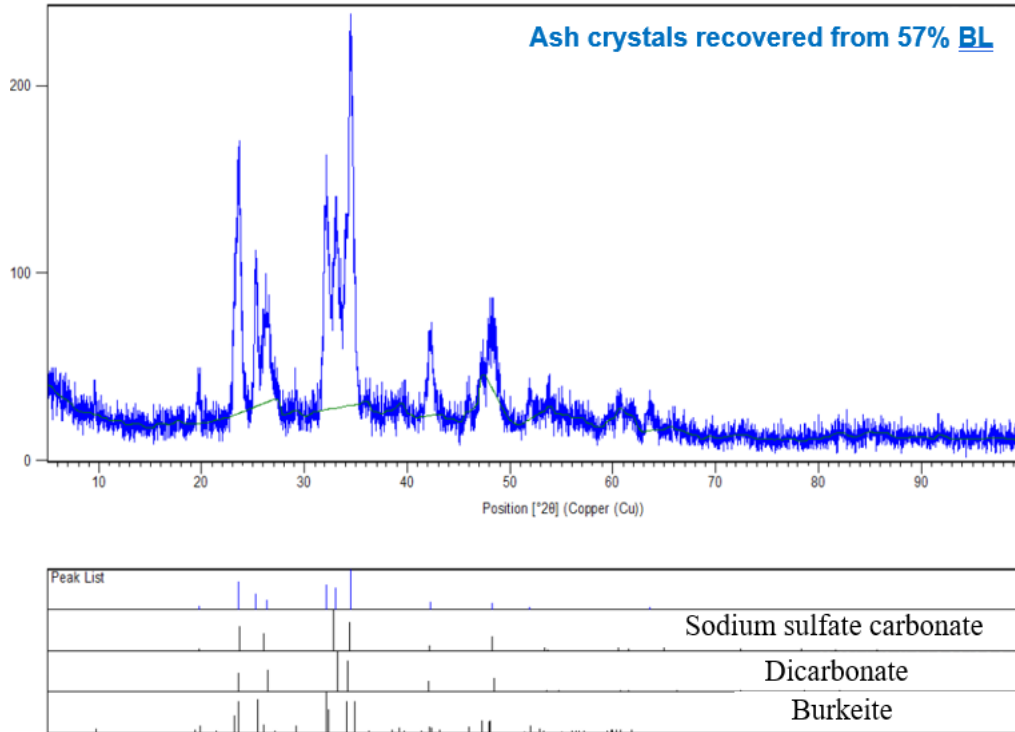
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Figure 13. XRD pattern for ESP ash before addition to black liquor.



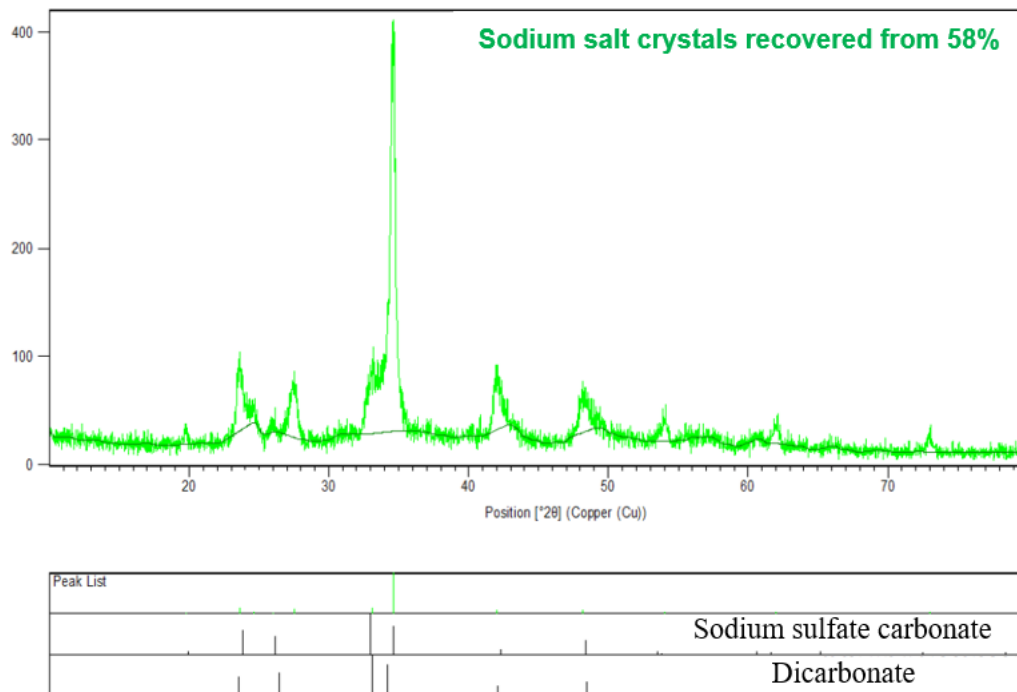
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Figure 14. XRD pattern for crystals recovered from 57% black liquor after 24 h of ESP ash addition.



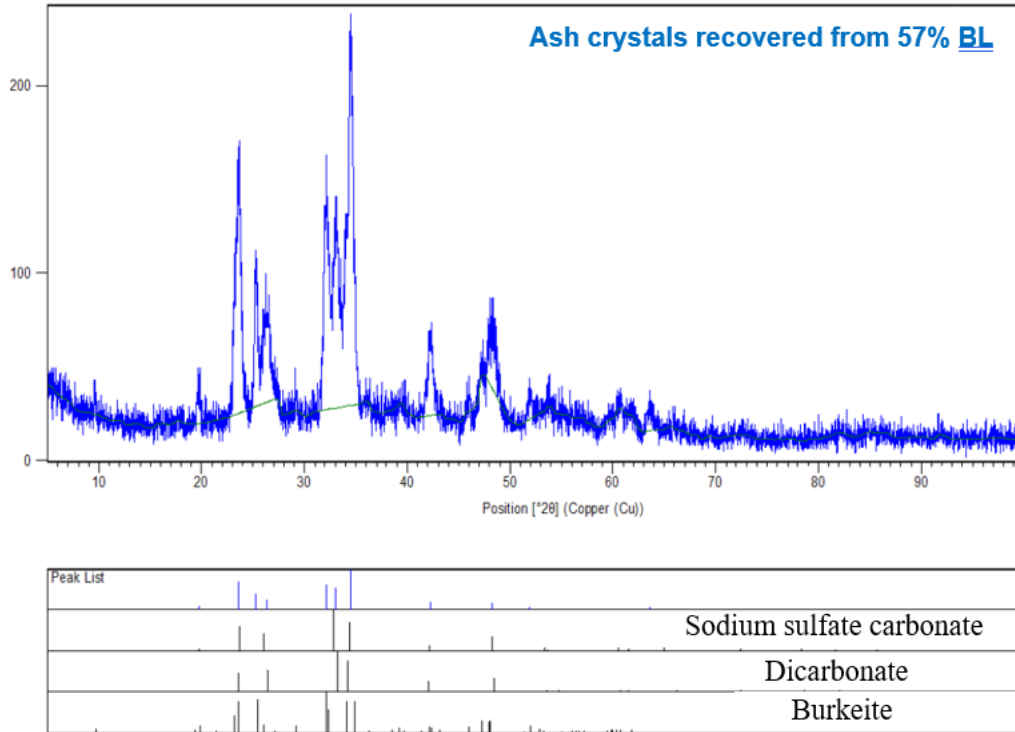
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Figure 15. XRD pattern for crystals recovered from 57% black liquor after 24 h of ESP ash addition.



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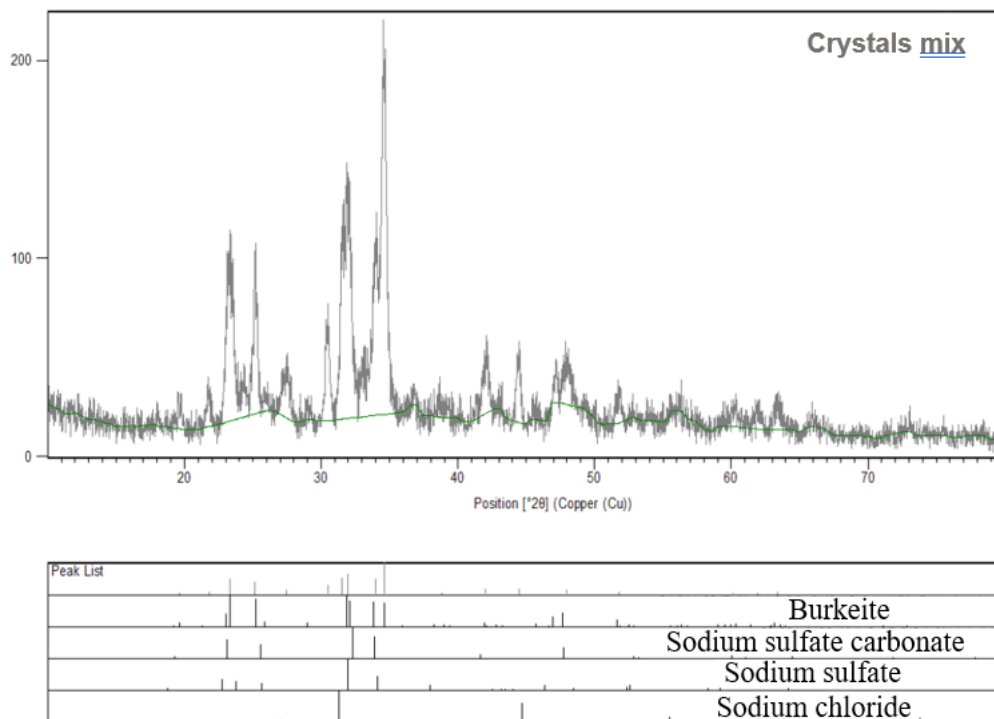
Figure 16. XRD pattern salt crystals recovered from 57% black liquor before ESP ash addition.



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Figure 17. XRD pattern for crystals recovered from 57% black liquor after 24 h of ESP ash addition.

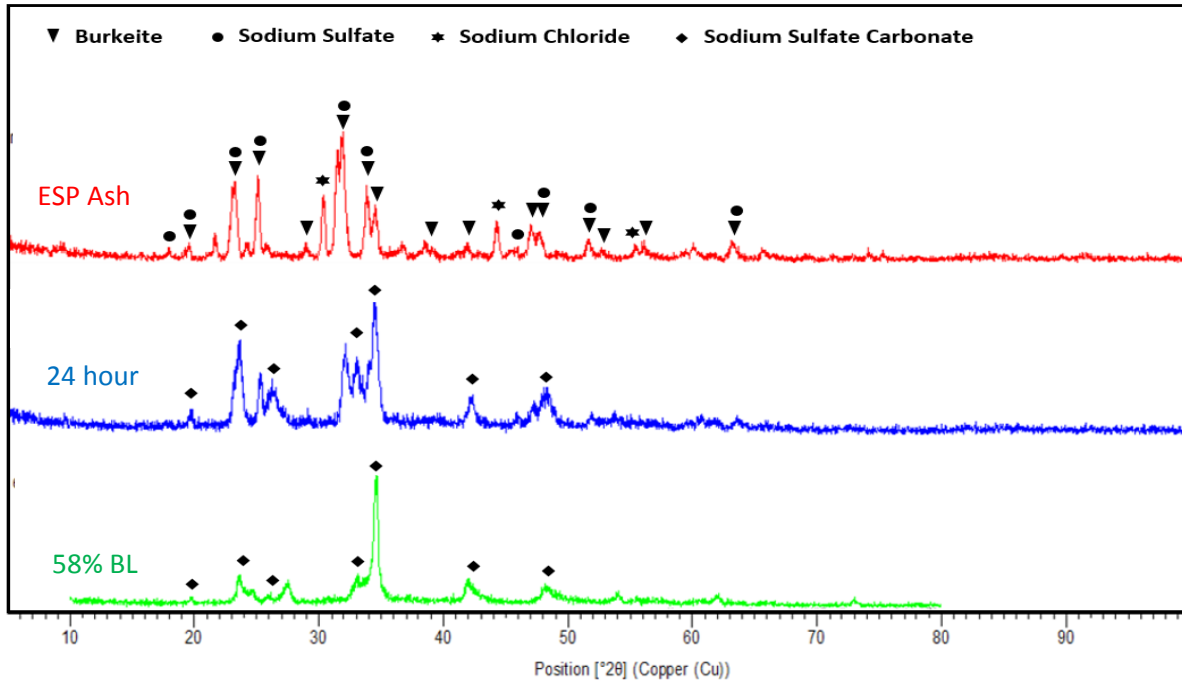


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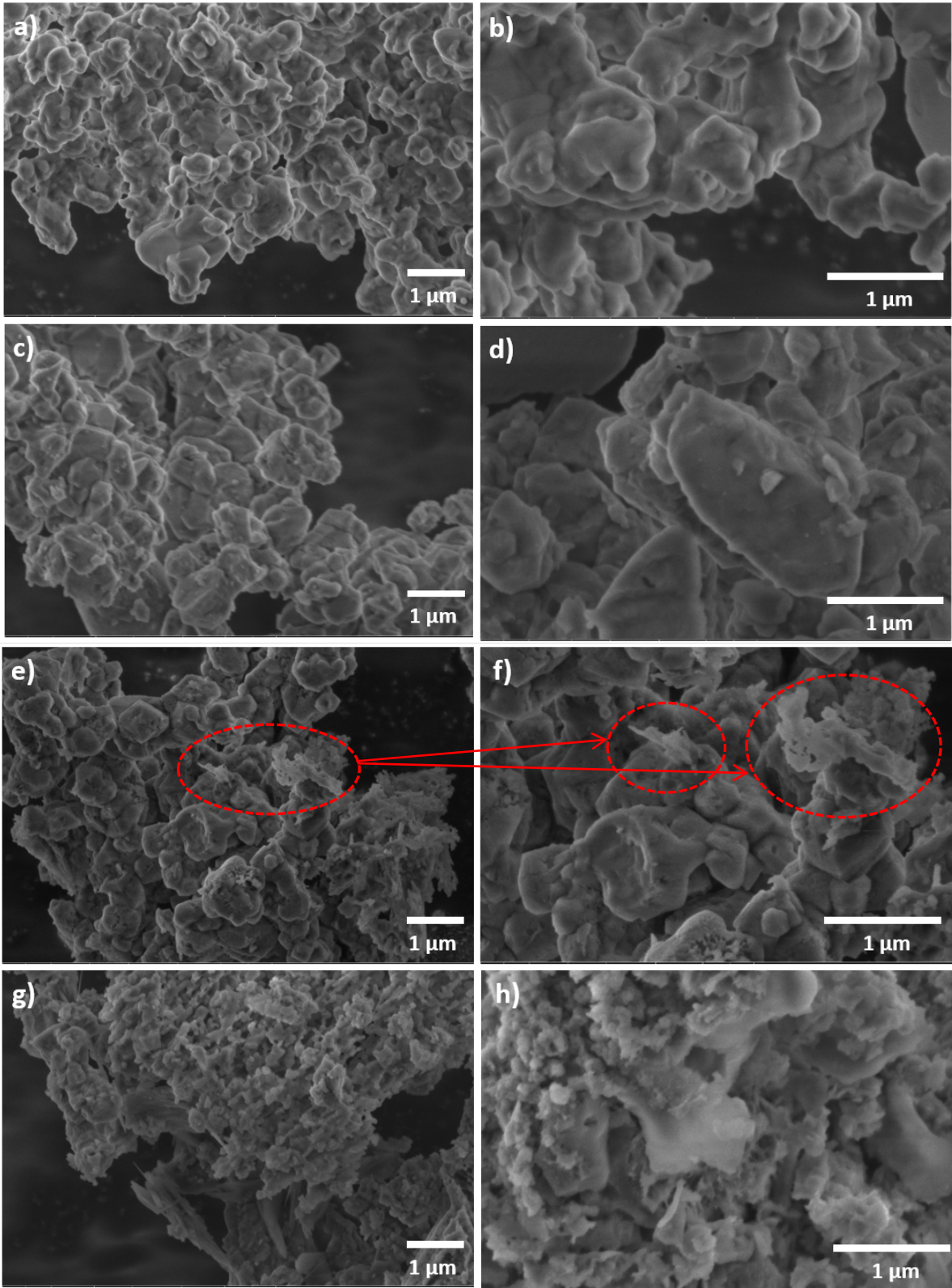
Figure 18. XRD pattern for a mixture of salt crystals recovered from 58% black liquor and the ESP ash.

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 2 **Figure 19.** XRD patterns for ESP ash, crystals recovered from 57% black liquor after 24 h after ESP ash addition,
 3 and crystals recovered from 58% black liquor before ESP ash addition.

4 Upon washing the crystals from the entrained black liquor, SEM analyses have been performed to
 5 determine any signs of change in habit or size. The morphology obtained at various magnifications
 6 for the ESP ash, the crystals recovered from 52% black liquor after 24 h of ESP ash addition, the
 7 crystals recovered from 57% black liquor after 24 h of ESP ash addition, and the crystals of sodium
 8 double salt precipitated from 58% dry solids liquor before ESP ash addition, are depicted in Figure
 9 20. It can be observed that there was no significant distinction in shape and size between ESP ash
 10 crystal before and after the addition to 52% black liquor, (images a-d). However, the crystals
 11 collected from 57% black liquor (images e-f) showed that foreign small crystals were adhered on
 12 the ESP ash agglomerate. The small crystals found with ESP ash were similar to those recovered
 13 from 58% liquor before ESP ash addition (images g-h). While the carbonate-rich salts appear to
 14 adhere to the ESP ash crystals in images g-h, this could be an artifact of the filtering of the black
 15 liquor and washing rather than a clear indication of adhesion of carbonate-rich double salts on
 16 sodium sulfate or burkeite.



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Figure 20. SEM Micrograph: a-b) ESP ash; c-d) Isolated crystals from 52% black liquor after 24 h of ESP ash addition; e-f) Isolated crystals from 57% black liquor after 24 h of ESP ash addition; g-h) Sodium double salt recovered from 58% black liquor before ESP ash addition.

1 **CONCLUSION**

2 When added below the solubility limit, electrostatic precipitator (ESP) ash dissolution occurs in
3 10 min or less at the conditions studied. The experimental set-up, particularly sampling time,
4 limited the time interval of sampling. The equations developed in the earlier Na-CO₃-SO₄
5 solubility studies can be used to calculate the maximum amount of ESP ash that can be dissolved
6 for a given initial black liquor dry solids. Thus mills can determine at what solids the black liquor
7 needs to be added to dissolve sufficient ash to lower the CO₃/(CO₃+SO₄) mole ratio sufficiently to
8 precipitate burkeite out first if that is the strategy.

9 When added above the solubility limit, ESP ash does not undergo dissolution and reprecipitation
10 within 24 h, even though the equilibrium would indicate that given enough time, it would. Thus,
11 industrially it seems likely that the ESP ash crystals remain as sodium sulfate and burkeite in mills.
12 Based on Shi's conclusions, this should not provide a surface area for carbonate-rich double salts
13 to precipitate onto. The mechanism by which ESP ash reduces scaling when added above the
14 solubility limit therefore remains speculative.

15 **DATA AVAILABILITY**

16 All the data discussed in this manuscript are directly presented in table and in graphical form in
17 the paper and therefore they are immediately accessible.

18 **ACKNOWLEDGEMENTS**

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20 Recovery in Pulp and Paper Mills – II & III at the University of Toronto supported by Andritz,
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