

## **Feasibility Study to Remove Impurities from CBA's Liquor as an Alternative to Increase Precipitation Yield**

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### **Abstract**

CBA's alumina refinery aims to increase its precipitation yield to reduce its specific consumptions, mainly live steam, thus reducing its CO<sub>2</sub> emissions. Precipitation yield is directly related to the impurities level present in Bayer liquor. CBA has developed a feasibility study to evaluate different technologies to remove organic and inorganic impurities from liquor as an alternative to increase precipitation yield. This paper details the studies and tradeoff analyses of different technologies available to promote the removal of impurities present in CBA's liquor. Laboratory tests were carried out with the selected technologies to evaluate the impurities removal efficiency and yield gains.

**Keywords:** Bayer liquor, Impurities removal, Precipitation yield.

### **1. Project Description and Opportunities**

One of the projected challenges up to 2050 for alumina industries operating with the Bayer process is to reduce energy consumption [3,5]. Improving energy recovery, reduce scaling in heat exchanger and increase precipitation yield are some enablers to achieve this goal.

The precipitation yield in the Bayer process is directly related to the precipitation kinetics, ionic solutes thermodynamics, process conditions variations, design of equipment and impurities level in the liquor. One of the ways to directly improve the precipitation yield is through the removal of impurities in the liquor resulting in a purer liquor. With a purer liquor, there is a reduction in the encrustation rate on heat exchangers and reduction of energy consumption, also contributing to reduce CO<sub>2</sub> emission.

CBA runs its refinery with 3 different sources of bauxite (Barro Alto, Miraí and Poços), which has a relative high input of impurities to the liquor. These impurities can be classified basically in three categories: sodium oxalate, sodium carbonate and organics in general.

The refinery's energy consumption is of 10 units and the precipitation yield is of 100 units. The level impurities control is through soda purge in the bauxite residue.

### **2. The Potential Solutions**

Innumerable methods of control and removal of impurities from Bayer liquor are known, totalizing more than 60 patents of this subject [2]. Each one of these methods has its operating characteristics, efficiency, and specific controls. An important factor to be considered is, in addition to removing these impurities, is to carry out the correct destruction treatment and/or storage of impurities removed from liquor due, for example, sodium oxalate is toxic, and its destruction or disposal must follow strict safety and environmental controls. A potential benefit of sodium oxalate destruction or disposal is the possible recuperation of sodium hydroxide that was lost in the process during sodium oxalate's generation [6].

An evaluation study of the technologies of liquor's impurities removal was performed according to the Table 1. It was considered the most used or with the most potential for application, generated benefits, and challenges to be overcome.

**Table 1. Evaluation of the main technologies of impurities removal.**

<b>Technology</b>	<b>Principles</b>	<b>Pros</b>	<b>Cons</b>
Dawsonite Process	CO <sub>2</sub> bubbling in the aluminate, that reacts to generate the compound as Dawsonite (NaAlCO <sub>3</sub> (OH) <sub>2</sub> ). Filtered and sent to calcinate.	Efficient process on impurities removal	Loss of caustic and alumina. CO <sub>2</sub> emission on calcination.
Wet oxidation	CO <sub>2</sub> injection in digestion tubes to oxidate TOC under 270 °C temperature.	Relatively low capex	Decomposition of organics generates CO <sub>2</sub> , CH <sub>4</sub> and H <sub>2</sub> . Operational risk (explosion). Generation of Na <sub>2</sub> CO <sub>3</sub> in the digesters (yield impact).
Liquor Burning	Mix of spent liquor with bauxite. Solid undergoes grinding and calcination. TOC is degraded and the sodium generates carbonate, which is leached with spent liquor. Liquor returns to the process and the residue is sent to the mud circuit.	Effective process on organic carbon's removal.	High investment cost. Complex operation. Odor generation. CO <sub>2</sub> emission.
Plasma treatment	Liquor is subjected to plasma (4 000 °C), the organics are degraded and the solution returns to the process	Does not generate carbonate nor scaling, reduces foam and changes liquor's color (improves hydrate's whiteness)	Technology in lab-scale. Generation of gases (CO <sub>2</sub> ). High investment.
Liquor's ozonation	Bubble the liquor with air + 3 % ozone to generate sodium oxalate, which is removed by centrifuge for adequate destination. The liquor returns to the process.	Reduces foam generation and clarifies the liquor.	Carbonate generation, which can reduce the yield. Generation of toxic waste (challenge for adequate destination + costs). Operational difficulty.
Coagulant additives (precipitation)	Polymer addition to generate a complex with humates, which precipitates and can be incorporated in the waste or are removed by filtration.	Low investment. Does not generate carbonate.	Relatively low efficiency. Limited to organic impurities.

Oxalate columns /	Use of columns to adsorb organics compounds, mainly humates present in the liquor.	Low investment, does not generate carbonate neither emits CO <sub>2</sub> .	Limited to volume and solids reposition. Low efficiency of impurities removal. High opex.
Salting Out Evaporation	Liquor's concentration to the limit of impurities' solubility, precipitates and removes by filtration or centrifuge. The solids can be treated chemically.	High efficiency in removing inorganic impurities. Does not emit CO <sub>2</sub> . Can contribute to the plant's volume control. Potential reduction of caustic consumption. Possibility of treating the solids to recuperate caustic soda.	High investment. Challenge in oxalate separation. Vapor consumption.

### 3. Criteria for Evaluating the Solution

The criteria for selecting the technology to be evaluated in more details were defined, in lab-scale, to determine the most appropriate selections for CBA.

Criteria:

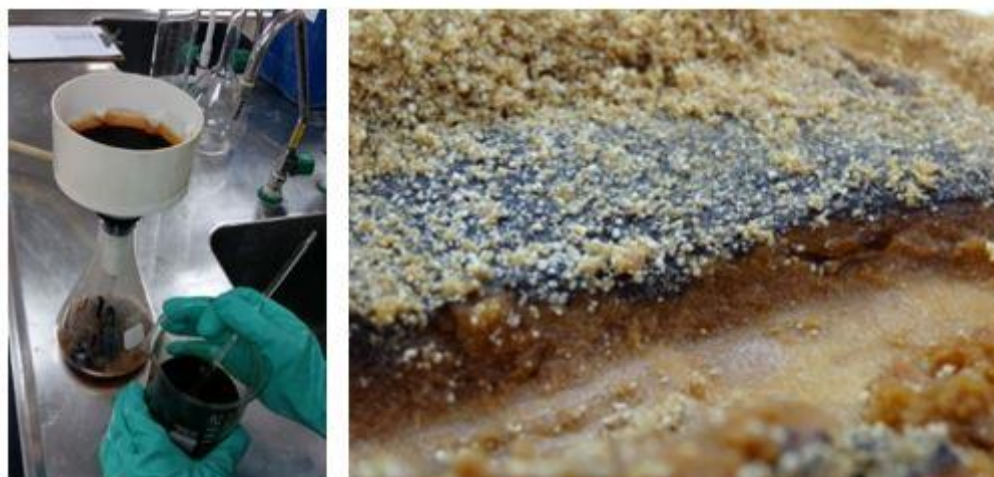
- Efficiency in removing carbonate and sodium oxalate;
- Reduction or elimination of GHG emissions;
- Reduction or elimination of waste generated in the process (impurities);
- Possibility to recuperate soda;
- CapEx / OpEx;
- Operation

In view of the pre-established criteria as the most relevant for CBA, the following technologies were chosen: filtration with diatomaceous, use of coagulant additives and salting out evaporation to be evaluated in lab-scale.

## 4. Experimental Data

### 4.1 Filtration with Diatomaceous

20 g of Diatomite (Radiolite 700 – Buntech) was added to 1 L of Bayer liquor under the temperature of 80 °C. It was agitated for 30 min, then a simple filtration was performed, using a 45 µm paper. The liquor before and after the filtration was collected, as shown in Figure 1, for absorbance analysis, caustic content, aluminium, TOC and oxalate analyses. The same procedure was performed using Perlite (Clarigel 200 – Buntech).



**Figure 1. Filtration test with detail of the organic compound removed in the filtration process.**

A test simulating the precipitation stage was performed to measure the yield with the liquor with the least impurities level. The results are shown in the Table 2.

**Table 2. Liquor results after filtration with diatomaceous.**

Sample	ABS (691 nm)	Efficiency (%)	TC	Na <sub>2</sub> CO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Oxalate	TOC	Yield
Branco	1.982	-	100.0	100.0	100.0	100.0	100.0	100.0
Perlite	0.739	62.7	95.7	99.1	97.4	99.0	96.6	102.2
Diatomita	0.733	63.0	96.0	99.2	98.2	99.3	92.4	105.2
<b>Increase (%)</b>								<b>5.2</b>

A reduction in the absorbance value of the liquor after filtration was observed, but no significant reduction in the results of TOC and oxalate were observed. This indicates that possibly the removal of humates in the liquor occurred. It was also observed that there was a reduction in the aluminium content contained in the solution, which is not desirable.

The increase in the yield of the precipitation stage was 5.2 % in relation to the liquor without treatment.

#### **4.2 Precipitation by Coagulant Additives**

Blow-off sample was collected and 100, 300, 500 and 1000 ppm of additive Cyquest 365 - Cytec® was added. In sequence, a sedimentation process was performed for 30 min, in a graduated cylinder, and the liquor sample was collected for analysis.

A test simulating the precipitation stage was performed to measure the yield with the liquor without treatment with the least level of Impurities. The results are shown in the Table 3.

**Table 3. Liquor results after filtration step.**

Sample	ABS (691 nm)	TC	Na <sub>2</sub> CO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Oxalate	TOC	Yield
Ref.	1.075	100.0	100.0	100.0	100.0	100.0	100.0
100 ppm	0.894	100.5	97.0	99.9	98.9	96.5	101.3
300 ppm	0.807	100.5	98.0	99.9	98.5	94.7	103.0
500 ppm	0.732	99.9	94.4	99.8	98.5	92.4	103.5
1000 ppm	0.676	100.0	99.3	99.9	98.3	90.6	107.3
<b>Reduction (%)</b>	<b>37.1</b>	<b>0.0</b>	<b>0.7</b>	<b>0.1</b>	<b>1.7</b>	<b>9.4</b>	

A reduction in absorbance values and TOC of liquor after decantation was observed, but a significant reduction in the other results was not observed, which is an adequate condition for the aluminium.

An increase in the precipitation yield was observed, 7.3 % in relation to the liquor without additive.

#### 4.3 Precipitation by Coagulant Additives + Filtration with Diatomaceous

Doses of 100, 300, 500 and 1000 ppm of additive Cyquest 365 - Cytec® were added in the liquor and then a filtration was performed according to the procedure in Section 4.1. The results are shown in the Table 4.

**Table 4. Liquor results after filtration – mix of techniques.**

Sample	ABS (691 nm)	TC	Na <sub>2</sub> CO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Oxalate	TOC	Yield
Ref.	0.920	100.0	100.0	100.0	100.0	100.0	100.0
100 ppm	0.614	91.6	97.6	92.2	92.9	93.7	101.7
300 ppm	0.540	92.2	96.5	93.4	95.3	93.0	103.6
500 ppm	0.509	93.0	95.4	93.6	93.6	93.7	104.6
1000 ppm	0.442	90.5	93.2	91.2	90.4	90.9	105.8
<b>Reduction (%)</b>	<b>52.0</b>	<b>9.4</b>	<b>6.8</b>	<b>8.8</b>	<b>9.6</b>	<b>9.1</b>	

It was observed that there was a reduction in the value of absorbance, carbonate, aluminium, oxalate and TOC of the liquor after filtration with addition of additive. A reduction in aluminium content is not desirable, because it impacts the precipitation yield. The precipitation yield increase was 5.8 % in relation to the liquor without treatment.

There was a change in the liquor's colour after the process. It was also observed that there was a retention of organic compounds in diatomaceous after the filtration process as showed in Figure 2.

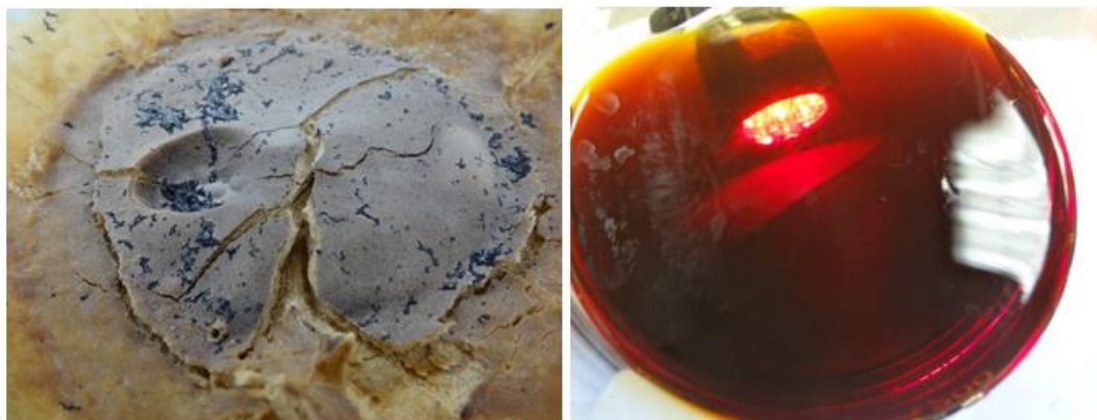


Figure 2. Diatomaceous and liquor with additive (1000 ppm) after filtration.

#### 4.4 Salting out Evaporation

6000 mL of liquor was submitted to evaporation, at the controlled temperature of 95 °C, and after each 30 min samples were collected for analysis. Upon reaching the final volume of approximately 2000 mL, a filtration was performed to separate the solid as shown in Figure 3. With the liquid, a precipitation test was performed to evaluate the yield. The results are shown at the Table 5 and the solubility curve is represented in Figure 4.



Figure 3. Removed impurities and liquor after the evaporation process.

Table 5. Liquor results during the evaporation process.

Sample	TC	Na <sub>2</sub> CO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Oxalate	TOC	Yield
Ref.	100.0	100.0	100.0	100.0	100.0	100.0
#1	104.0	105.2	102.6	104.8	101.1	
#2	110.6	106.6	110.2	110.9	104.8	
#3	117.5	113.9	116.8	114.3	105.3	
#4	123.7	115.8	123.1	119.0	117.1	
#5	125.9	122.4	124.7	122.9	118.7	
#6	130.7	124.9	129.2	128.2	121.9	
#7	135.3	129.7	137.2	121.7	126.7	
#8	138.5	130.4	138.3	101.5	118.2	
#9	139.5	132.8	139.1	117.9	117.6	

Sample	TC	Na <sub>2</sub> CO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Oxalate	TOC	Yield
#10	141.6	132.0	140.5	129.1	118.7	
#11	140.1	130.1	140.9	202.1	136.9	
#12	143.2	128.0	143.7	260.8	186.6	
#13	142.4	125.2	142.2	234.3	194.7	
#14	145.8	122.0	144.8	205.7	188.8	112.3

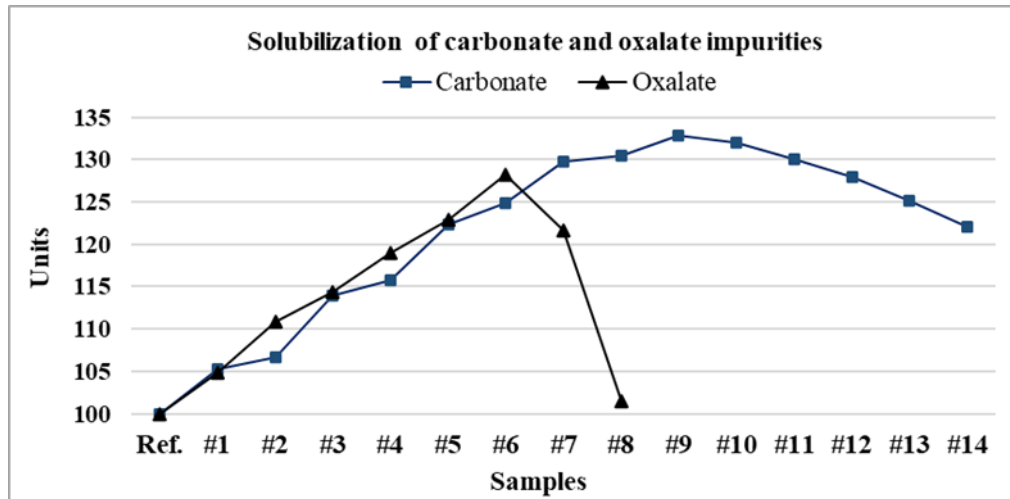


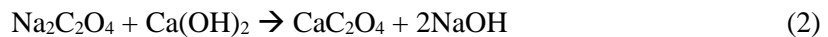
Figure 4. Solubilization graph of carbonate and oxalate impurities.

Carbonate precipitation was observed when the caustic content reached 132.8 units and for the oxalate was 128.2 units.

The liquor was recomposed and adjusted to the process conditions and a precipitation test was performed. The precipitation yield's increase was 12.3 % in relation to the liquor without treatment.

With the solids removed from the solution a causticization test was performed, which is a known process and part of CBA's refinery. The efficiency of this process determines the causticity of the main liquor, and by consequence, the precipitation yield [4].

The causticization consists of a reaction of carbonate and sodium oxalate with calcium hydroxide, with sodium hydroxide, carbonate and calcium oxalate being the products, according to the Equations 1 and 2 respectively and as shown in Figure 6.





**Figure 6. Causticization tests.**

The thermodynamics and kinetics of this reaction has been extensively studied [1]. Factor like stoichiometry, temperature, and residence time directly affects the efficiency of the reaction. The conditions to have a good conversion efficiency of up to 90 % are: stoichiometry 1:1; temperature 95 °C; residence time: 120 min [1]. The efficiency of this reaction can reach up to 80 % [6]. It was in these conditions that the tests were performed. The results are shown in the Table 6.

**Table 6. Results of causticization process.**

<b>Time</b>	<b>Na<sub>2</sub>CO<sub>3</sub></b>	<b>Carbonate Conversion (%)</b>	<b>Oxalate</b>	<b>Oxalate Conversion (%)</b>
0	<b>100.0</b>	<b>0</b>	<b>100.0</b>	<b>0</b>
60	67.3	59	78.9	35
120	58.5	71	68.6	42
180	51.9	80	61.5	53
240	45.1	88	73.7	65
300	59.1	91	45.1	78
360	36.5	98	37.6	92

The causticization reaction of carbonate showed a conversion efficiency of up to 98 % with a residence time of 360 min, and for the oxalate was up to 92 %.

## **5. Feasibility Study to Define the Technology**

Based on the increase of precipitation yield, the potential gains for each technological route were calculated. An investment estimate was constructed based on the references of similar projects. The results are shown in the Table 7.

**Table 7. Indicators for feasibility study comparison.**

<b>Technology</b>	<b>Yield</b>	<b>Yield increase (%)</b>	<b>Yearly gain (units)</b>	<b>Capex (units)</b>
Current situation	100	-	0.0	0.0
Filtration diatomaceous	100	5.2	0.74	10
Precipitation by additive coagulants	100	7.3	1.04	5
Precipitation by additive coagulants+ filtration diatomaceous	100	5.8	0.84	15
Salting out evaporation	100	12.3	4.17	40

For the Salting Out Evaporation Technology, through balances and simulations, it was identified that there is a potential steam consumption reduction of 1.5 units, which represents a reduction of up to 17.4 % in the energy consumption of CBA’s refinery.

According to the established criteria and the results obtained in the evaluation, a scale of contribution, relevance and impact of the technology for CBA to select the best alternative as shown in Table 8, with 1 – low, 5 – middle, 10 – high. The scores were defined by project team and stakeholders in specific meeting using voting criteria.

**Table 8. Premises and criteria to define the best technology.**

<b>Criteria</b>	<b>Filtration with diatomaceous</b>	<b>Precipitation by additive coagulants</b>	<b>Precipitation by additive coagulants+ filtration diatomaceous</b>	<b>Salting out evaporation</b>	<b>Ref.</b>
Efficiency of carbonate and sodium oxalate removal.	1	5	5	10	10
Does not increase / generate new emissions (GHG / Odour).	5	5	10	1	1
Reduction or elimination of waste generation.	1	5	10	1	1
Caustic soda recovery possibility.	1	1	1	10	10
Capex / Opex.	5	1	5	10	1
Operation difficulty	5	1	10	1	1
Contribution to the plant’s volume control.	1	1	1	10	10
Precipitation yield increase	1	5	1	10	10
<b>Score</b>	<b>1</b>	<b>2</b>	<b>0</b>	<b>7</b>	<b>8</b>

## 6. Conclusion

This study evaluated the pros and the cons of the main technologies applied to the removal of liquor's impurities according to its characteristics. In established criteria, there was a classification of 3 that were evaluated in lab-scale.

All the technologies evaluated showed a level of impurities removal in the liquor and by consequence an increase in precipitation's yield. The results showed an increase of up to 12.3 % in precipitation yield for the technology Salting Out Evaporation.

It was possible to carry out the treatment of the waste generated in SOE's process through causticization process, and the efficiency results were 98 % for the carbonate and 92 % for the oxalate. Soda recovery is significant, and it was not considered in this study as gain.

Using increase precipitation yield obtained in the test, it was calculated the reduction of liquor flow in alumina refinery and vapor equivalent saved to heat this flow. The reduction in the refinery's energy consumption can reach 17.4 %.

Through the viability study, the technology that shows the best benefit for CBA is Salting Out Evaporation.

## 7. References

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