Solvay's Solvent Extraction Technology to Remove Organics from Bayer Process

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Abstract

Accumulation of organics in Bayer process liquors has many negative impacts on alumina production, including reduced liquor productivity and precipitation yield, lower quality alumina product and increased energy consumption. Existing organic removal technologies are either too costly or inefficient. A breakthrough organic removal process based on solvent extraction technology, developed by Solvay, has shown great potential to help alumina refineries significantly reduce the total organic carbon (TOC) in their Bayer liquor, and thus improve their production efficiency. This paper presents an overview of the whole organic removal process, footprint, economic and sustainability benefits to alumina refineries, and required equipment setup to run the process.

Keywords: Bayer process, Organic removal, Solvent extraction, Alumina production increase.

1. Introduction

Organic materials are introduced to the Bayer process principally from dissolution and digestion of organic material such as humates in bauxite ore, and addition of organic additives such as flocculants, deformers, scale inhibitors etc. [1]. As the Bayer process is cyclic, any organic matter entering the process stream accumulates with each cycle of the process, with a steady state determined by process input and output streams. The major organic exits are (a) the red mud circuit, (b) with the gibbsite product, and (c) via any organic removal steps in place [2].

Organic accumulation in Bayer liquor has many negative effects on alumina production. Some organic compounds in Bayer liquor, especially the low molecular weight (Mw) organic compounds, can adsorb to the nucleation sites of gibbsite, reducing the crystallization rate, and lowering liquor productivity and precipitation yield [3]. The sodium oxalate in Bayer liquor, if not adequately controlled, can build up to a level of supersaturation before crystallizing in a fine needle-like form. These fine oxalate needles co-crystalize with gibbsite and inhibit its agglomeration, resulting in finer particle size distribution (PSD) of gibbsite particles, decreased filtration rate of gibbsite slurry, increased scale growth rate, excessive foaming in the precipitation stage, and increased occluded soda in alumina after calcination [2-4]. The high molecular weight organics in Bayer liquor, especially humate molecules, bind to gibbsite crystal particles during precipitation, and reduce the brightness of gibbsitesignificantly. Note that the brightness of gibbsite indicates the reflectance of gibbsite across the visible spectrum, and gibbsite with higher brightness has higher reflectance of visible light. Additionally, due to their surfactant-like nature, medium and high molecular weight humic substances are often responsible for liquor foaming [5] and interference with red mud flocculation [6].

Removing organic impurities from the Bayer process can bring several benefits to alumina refineries, such as increased yield and production rate, lower energy consumption and raw material costs, improved product quality (gibbsite brightness, PSD, and occluded soda), and reduced foaming and scaling. Many technologies have been developed and implemented to remove organics from the Bayer process, including liquor burning, seed washing, salting out process, side stream oxalate removal, oxalate cold precipitation process, and humate removal via poly(DADMAC) [1, 7-10]. The comparison of these existing technologies is summarized in Table 1. All of these known technologies require significant costs to operate while having only a modicum of impact on the organics load of the refinery

Table 1. Comparison of existing organic removal technologies for Bayer process.

Name of Technology	Description	Pros	Cons	Organic removal efficiency
Humate removal	Addition of poly(DADMAC) to form complex with humate	Reduce [humate]	Chloride ingress from poly(DADMAC); Only remove humate	low
Oxalate cold precipitation	Use activated carbon to reduce humate content, then precipitate oxalate via cooling	Reduce [oxalate] and [humate]	Low efficiency	low
Side stream oxalate precipitation	Use oxalate seed to induce oxalate crystallization	Reduce [oxalate]	Low capacity; High CAPEX; Only remove oxalate	low
Salting out process	Evaporation of side stream liquor to precipitate organics and carbonate	Remove some organics and carbonate	Energy intensive; High CAPEX and OPEX; High CO_2 emissions	medium
Seed washing	Co-precipitation of oxalate with gibbsite, followed by hot water washing of seed to dissolve oxalate	Reduce [oxalate]	High CAPEX and OPEX; Water ingress; Only remove oxalate	medium
Liquor burning	Evaporation of side stream liquor followed by calcination	Remove 99% TOC in treated stream and recover caustic tied to impurities	High CAPEX/OPEX; High CO_2 emissions: High operation challenges	high

2. Results and Discussion

2.1 Overview of Solvay's Organic Removal Process

Solvay has developed a solvent extraction (SX) based technology to extract organics from Bayer liquor and significantly reduce total organic carbon content (TOC). A schematic flow diagram of this new organic removal process is shown in Figure 1. This technology consists of four units: SX unit, strip liquor recycling unit, regeneration (regn.) liquor recycling unit, and organic destruction unit. The flowsheet allows for essentially only Bayer liquor to enter the process, while clarified Bayer liquor and carbon dioxide exit.

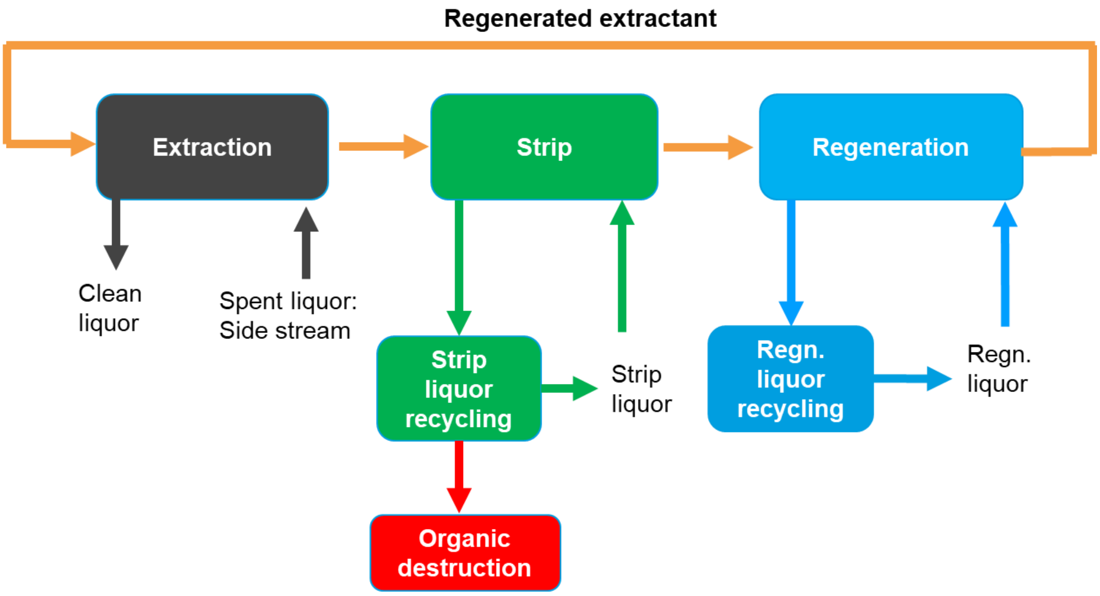

Figure 1. The schematic flow diagram of Solvay's organic removal process.

The SX process utilizes an organic extractant, which is immiscible with aqueous solutions such as Bayer liquor, to extract organic anions from Bayer liquor. The SX unit includes three consecutive steps: extraction, strip and regeneration, operating in unison to recycle the extractant. During the extraction step, organic impurities transfer from Bayer liquor into the extractant phase. Subsequently, during the strip step, those organic impurities are removed from the extractant by an aqueous strip liquor. Finally, a regeneration step, designed to remove the remaining strip liquor impurities, is required to ensure those impurities do not enter the Bayer liquor upon recycling of the extractant to further remove organics from the liquor.

The strip liquor, which contains the extracted Bayer process organic impurities, is purified via a strip liquor recycling unit, allowing for the separation of the organics and recycling of the aqueous strip liquor. The regeneration liquor is also purified, in a separate recycling unit, allowing full recycle of the regen liquor. Lastly, the organics are destroyed in the fourth and final unit of this process.

2.2 Organic Removal via Solvent Extraction (SX)

The concept of the SX process for organic removal is similar to that of traditional copper SX. It utilizes an organic extractant to remove organic impurities from Bayer liquor, and strip and regeneration steps to purify and recycle the organic extractant.

Multi-stage counter-current mixer-settler units are recommended for the SX organic removal process. A schematic diagram of one SX mixer-settler unit is shown in Figure 2.

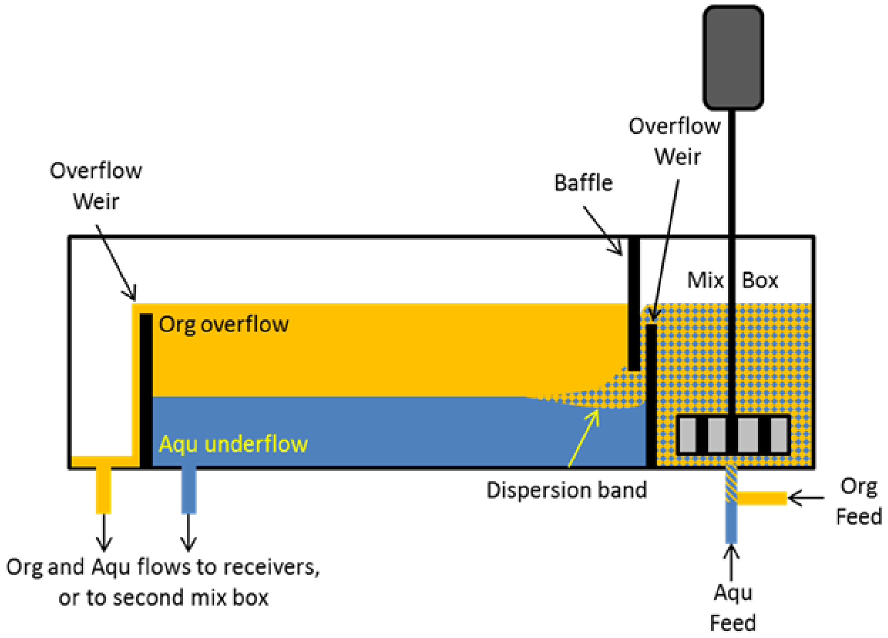

Figure 2. The schematic diagram of one SX mixer-settler unit.

Generally, organic and aqueous feed streams are agitated in a mixed box to form an aqueous or oil continuous emulsion, allowing efficient transfer of a dissolved species from one phase to another, which subsequently overflows to a settler for phase separation. The resulting organic overflow and aqueous underflow in a settler can flow to receivers or to next mix boxes.

The SX efficiency can be tuned by adjusting the number of stages (mixer-settler units) and the O/A ratio (volume ratio of organic and aqueous fees streams) in the process. Increasing the number of stages or the O/A ratio improves SX efficiency. A schematic flow diagram of counter-current two stages extraction process is shown in Figure 3.

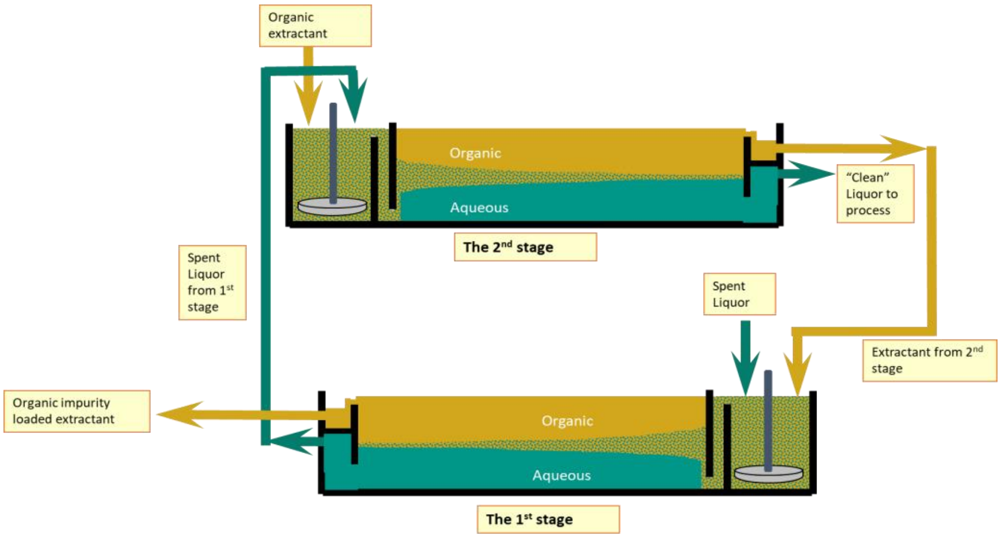

Figure 3. The schematic flow diagram of counter-current two stages SX process for extraction (aqueous feed: spent liquor; organic feed: extractant).

An SX isotherm curve is a plot of the distribution of extracted material between two phases at equilibrium, and is a good indicator of SX efficiency. Isotherm curves are normally generated via simple “shake-out” tests using glass jars and separatory funnels. For example, an extraction isotherm curve for a plant liquor (Figure 4) shows TOC in organic phase as a function of TOC of plant liquor at equilibrium. A McCabe-Thiele diagram (Figure 4) can be plotted on the isotherm curve, which can predict using the plot that to reduce TOC of spent liquor from 11 g/L to 3.6 g/L, two stages of counter-current SX units with 1:1 O/A ratio for feed streams are required.

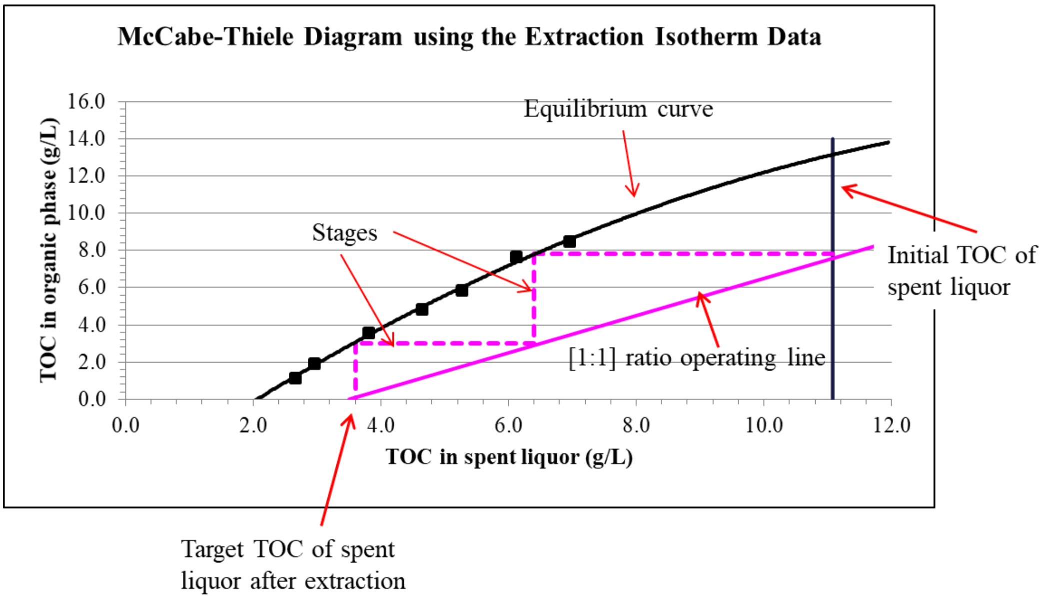

Figure 4. The Schematic McCabe-Thiele diagram using the extraction isotherm data.

Some organic extraction data from shake-out tests with one plant liquor are summarized in Figure 5. As the O/A ratio increased, the % of TOC extracted from the plant liquor increased. The same trend was also observed with specific organic and inorganic impurities in the plant liquor, such as sulfate, oxalate, acetate, and formate. As more organics were extracted from the plant liquor, the color became lighter. Typical strip and regeneration isotherm curves are shown in Figures 6-7, on which McCabe-Thiele diagrams can also be plotted to establish SX configurations.

Extractant:Bayer liquor (O/A ratio)	% TOC removed	% Oxalate removed	% Succinate removed	% Acetate removed	% Formate removed	% Sulfate removed
1:2	36	0	97	41	43	0
1:1	49	0	99	61	66	0
1:0.25	57	14	99	86	89	16

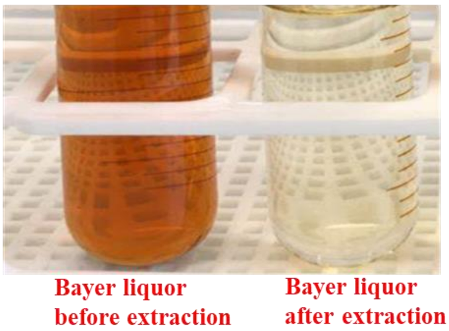

Figure 5. Organic extraction data from the shake-out tests with a plant spent liquor (Note the reduction in color of the plant liquor as organics were removed).

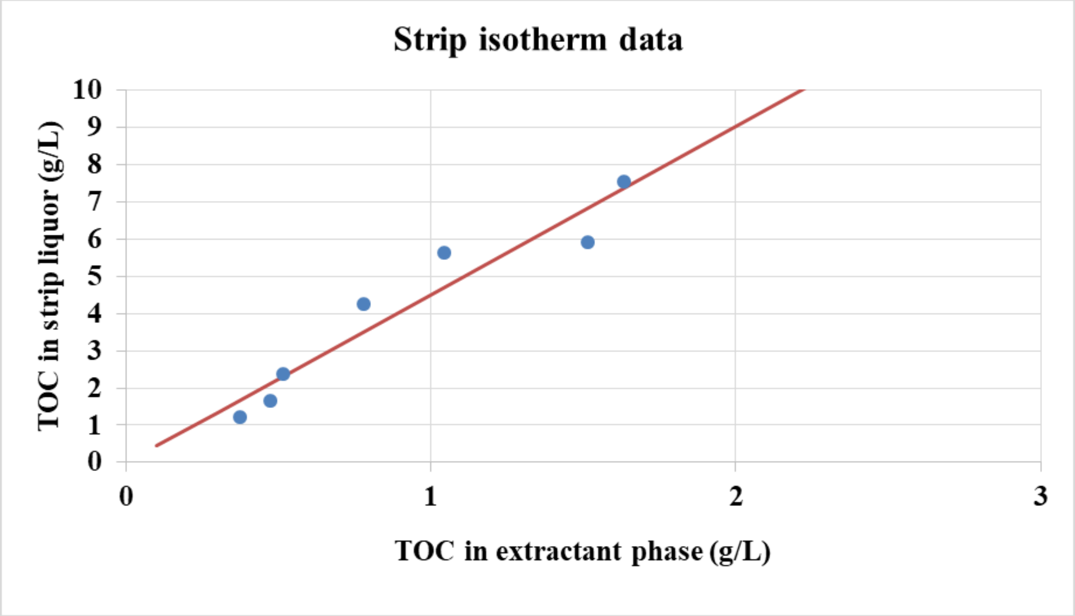

Figure 6. A typical isotherm curve for strip.

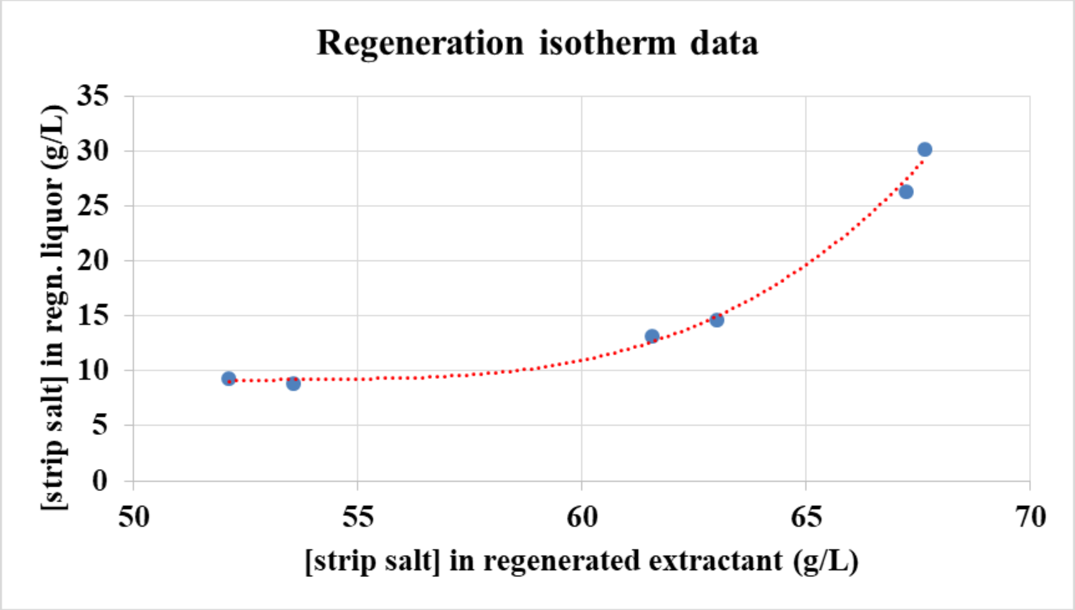

Figure 7. A typical isotherm curve for regeneration.

2.3 Yield, PSD and Precipitation Rate Improvement Associated with TOC Reduction

Significant TOC reduction of Bayer liquor can bring many benefits to gibbsite precipitation, such as yield improvement, precipitation rate increase, and coarsening of precipitated gibbsite solids. To demonstrate that Solvay’s organic removal process can bring these benefits to alumina refinery, lab-based precipitation tests were conducted by following the schematic procedures shown in Figures 8-9.

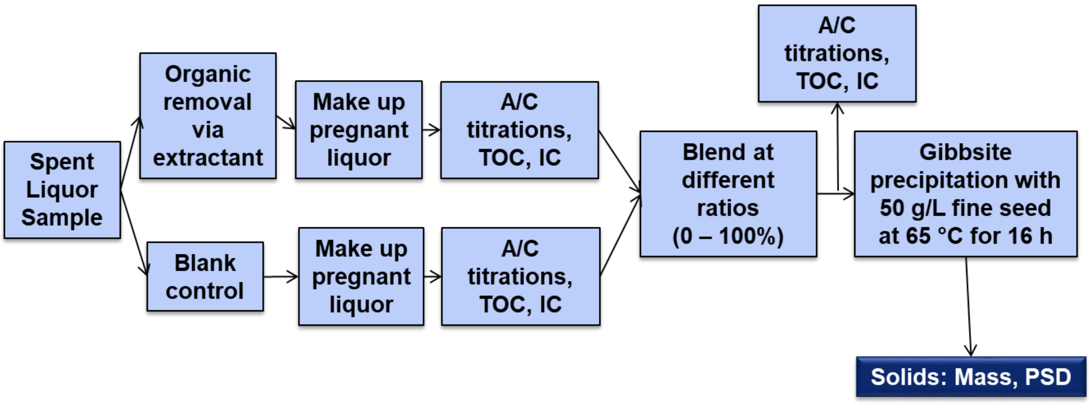

Figure 8. The schematic lab test procedure to measure the yield and PSD of gibbsite as a function of TOC of pregnant liquor (IC = ion chromatography).

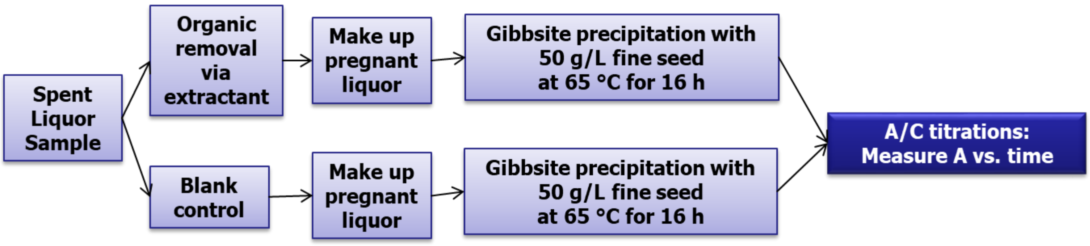

Figure 9. The schematic lab test procedure to measure the gibbsite precipitation rate as a function of TOC of pregnant liquor.

First, a spent liquor was treated with the extractant for TOC reduction. Next, two pregnant liquors, with the same A/C/S values (A: alumina content; C: total caustic; S: total soda) were prepared using either the treated or untreated (blank control) liquors. Then the two pregnant liquors were blended in different ratios to produce a series of pregnant liquors containing varied TOC levels while maintaining the same A/C/S values. Gibbsite precipitation tests were conducted at 65 °C using these liquors, and the yield, precipitation rate and particle size distribution (PSD) of gibbsite solids were measured and compared in Figures 10-12. The data clearly supports that the TOC reduction of Bayer liquor via Solvay's organic removal process significantly improved yield, precipitation rate, and PSD of gibbsite solids.

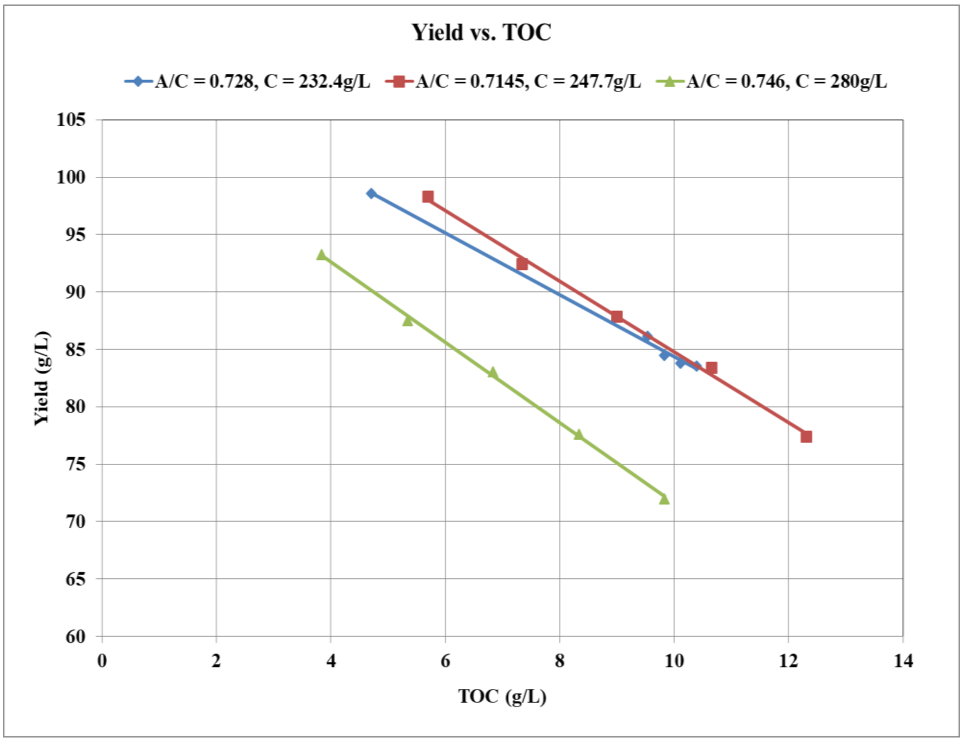

Figure 10. The gibbsite precipitation yield as a function of TOC of pregnant liquor (50 g/L fine seed, 65 °C for 16 h)

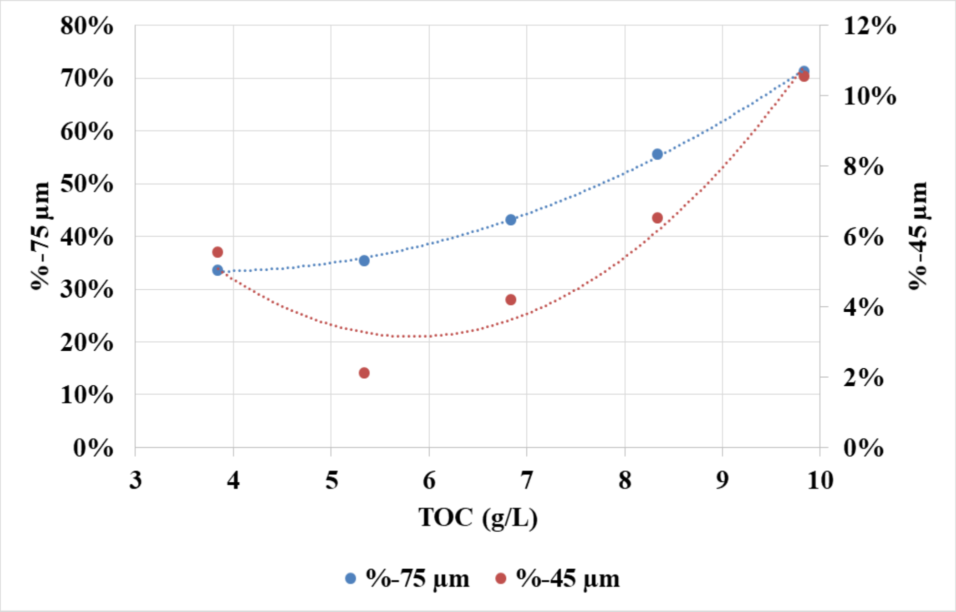

Figure 11. The PSD of precipitated gibbsite solids as a function of TOC of pregnant liquor (A/C = 0.746, C =280 g/L, 50 g/L fine seed, 65 °C for 16 h).

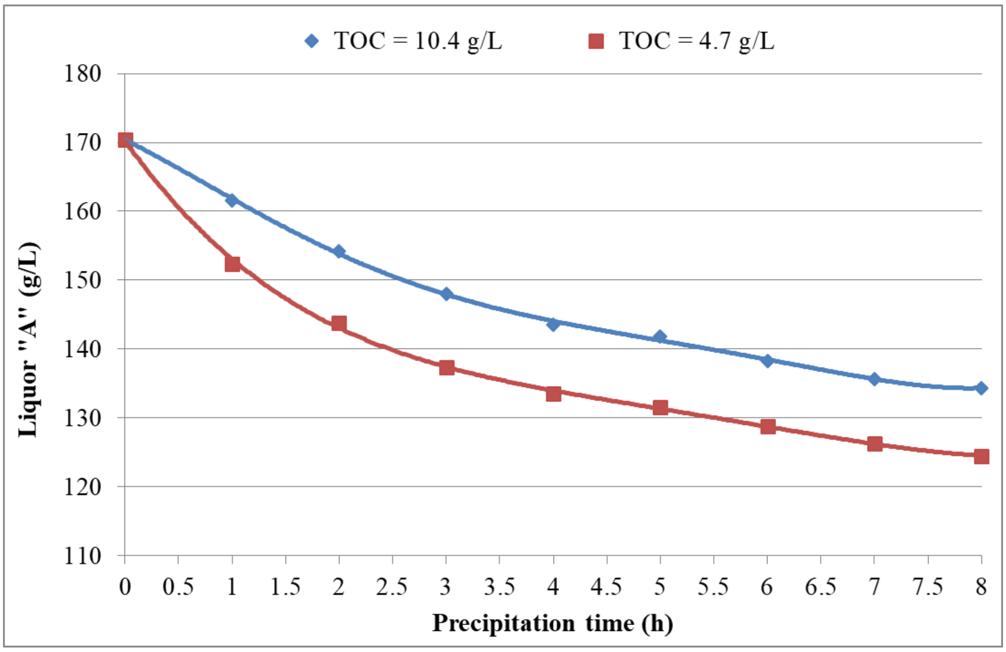

Figure 12. The gibbsite precipitation rate (indicated by Liquor "A", which is the instant alumina content (A) of liquor during precipitation) as a function of TOC of pregnant liquor (A/C = 0.73, C =234 g/L, 50 g/L fine seed, 65 °C for 16 h).

Note that it is not recommended to directly extrapolate the yield/precipitation rate increase values and PSD improvement data from Figures 10-12 to each individual alumina refinery, due to their liquor composition and precipitation condition differences.

2.4 SX Performance through Continuous Operation

A laboratory scale continuous SX circuit (total flow = 40 mL/min), named a "mini-rig", was built to demonstrate its continuous organic extraction performance. This SX mini-rig circuit consisted of two extraction, stripping and regeneration stages (Figures 13-14), and has been operated continuously in a counter-current mode for multiple days.

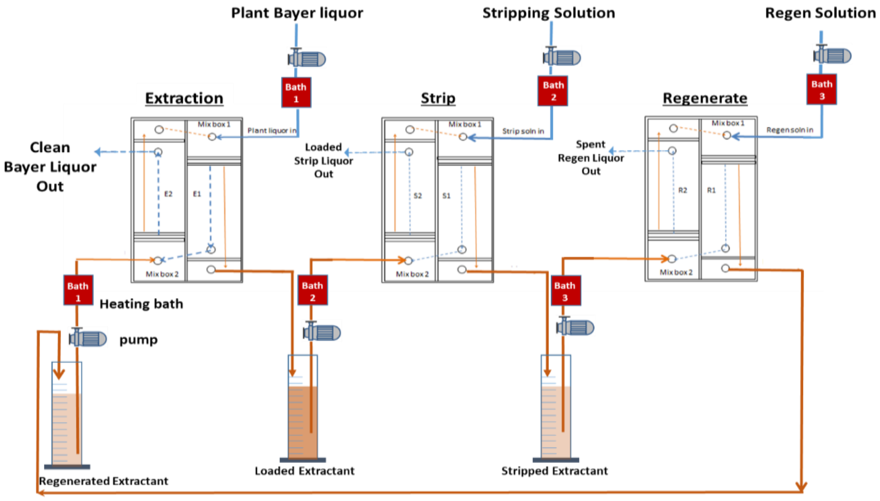

Figure 13. The flow diagram of the laboratory scale SX circuit (total flow 40 mL/min).

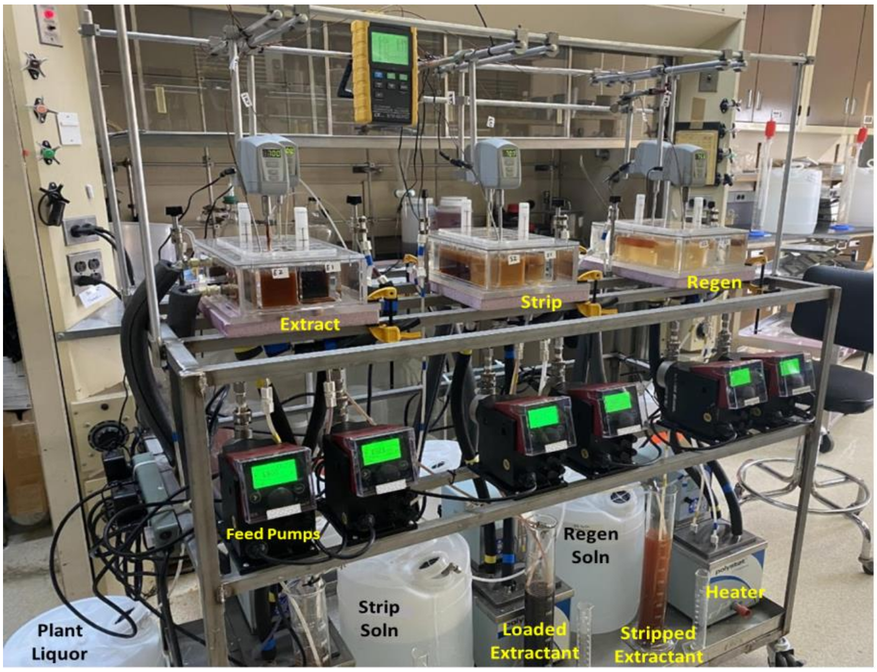

Figure 14. Photograph of the laboratory scale SX circuit in a cart (total flow = 40 mL/min).

During the circuit operation, the extractant was recycled, while plant liquor, strip and regeneration liquors were not. Heating baths were utilized to keep the temperatures of all streams at 60 °C. Results indicated an approximately 50% TOC reduction in treated Bayer liquor with no measurable decrease in extraction efficiency of recycled extractant over one week's operational period. Pilot trials at alumina production sites would be required to evaluate months' performance of the recycled extractant.

During continuous operation of the SX circuit, crud, which is a mixture of particulates and emulsion, may form in the settler at the oil-water interface. To reduce the impact of crud on SX operation, the crud layer at the interface can be removed and transferred to a separation device, such as filtration, or centrifugation to separate crud solids from the extractant and aqueous phases. The purified liquid phases can be circled back to the SX circuit.

2.5 Pilot-scale SX Unit

A pilot-scale (total flow = 200 L/h) prototype of the mixer/settlers for the SX circuit of this process was built by Solvay. A design of a potential SX pilot circuit (total flow = 200 L/h), consisting of 2 extraction stages, 3 strip stages, and 7 regeneration stages, was shown in Figure 15. A 3D layout of this SX pilot circuit is shown in Figure 16, illustrating that the equipment can fit in a shipping container and be easily transported to an alumina refinery for continuous pilot evaluation. To validate the engineering design of the equipment and obtain beneficial operational experiences, a two-stage SX pilot unit was fabricated (Figure 17) and tests have been completed to qualify and optimize its design.

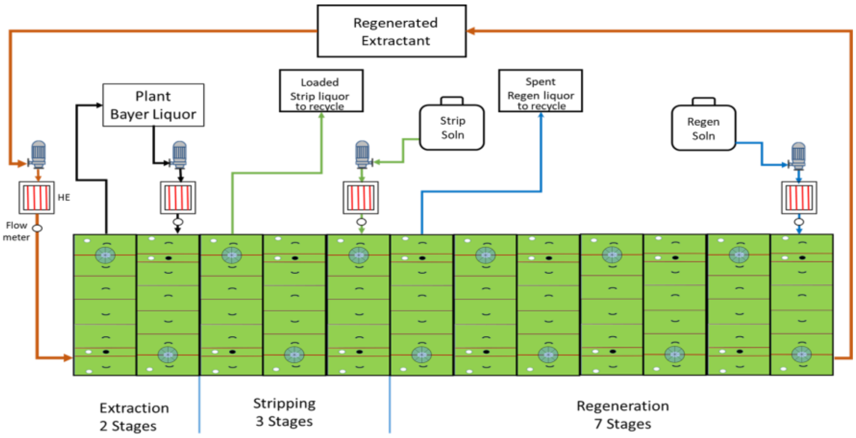

Figure 15. Example of a potential solvent extraction pilot circuit optimized to meet TOC removal targets (total flow = 200 L/h).

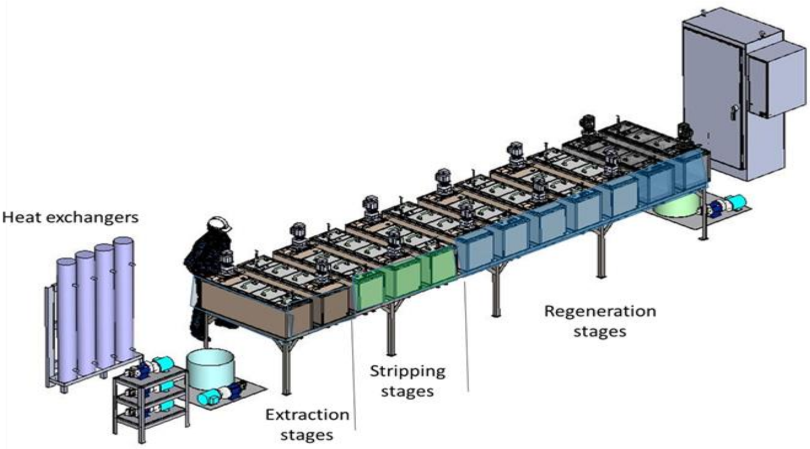

Figure 16. Illustration of a potential pilot scale SX circuit optimized for performance with a given liquor (total flow = 200 L/h).

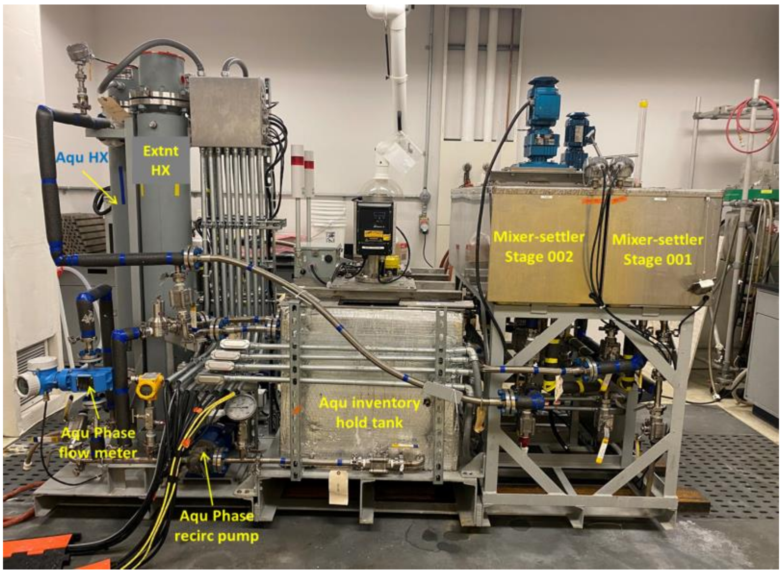

Figure 17. Photograph of the 2-stage SX pilot unit.

2.6 Footprint and Sustainability Impact

Current organic removal technologies available on the market require a significant amount of footprint to install and manpower to operate while providing lower organic removal capacity than Solvay's organic removal process. The required square footage for Solvay's organic removal process can be estimated based on the size and dimension of each operation unit. For example, it was estimated that around 1000-3000 m^2 footprint would be required to build a process treating roughly 1% of plant total spent liquor flow, which is much smaller than building an additional production line for alumina production increase.

Environmental and operational sustainability currently play critical roles in the alumina refining industry. The negative impacts of organics on refinery operations impede the ability of the plants to meet forward-looking sustainability targets, such as greenhouse gas emissions and energy utilization. Due to the relatively small footprint and the efficiency of impurities removal by Solvay's process, this technology can play a unique role in providing significant production benefits in current assets, while simultaneously having a positive impact on plant emissions.

2.7 TOC Prediction Model

To facilitate the economic calculation of Solvay's organic removal process for alumina refineries, a simplified TOC prediction model was developed to predict TOC change of plant liquor over time. As shown in Table 2, the input parameters for the TOC prediction model are total inventory of plant liquor, current TOC of plant liquor, baseline TOC increase rate, flow rate of plant liquor for Solvay's organic removal process, and an equation describing the %TOC removal by Solvay's organic removal process as a function of feed liquor TOC which can be obtained from extraction isotherms. According to the prediction model, an alumina refinery having 160000 m^3 plant liquor inventory, zero baseline TOC increase rate, and a side stream of 25 m^3/h plant liquor treated continuously with Solvay's organic removal process, would take approximately 600 days for TOC of plant liquor to exponentially reduce from 15 g/L to 4 g/L (Figure 18).

The CAPEX/OPEX of Solvay's organic removal process is affected by refineries' target TOC at a new steady state, and the expected operation period to reach the new TOC steady state. Technical exchange and collaboration would be required to customize Solvay's organic removal process for one alumina refinery, to meet their organic removal target and CAPEX/OPEX requirements.

Table 2. The assumptions for building a TOC vs time model with the implementation of Solvay's organic removal process.

Input parameters	Assumption
Total inventory of plant liquor (m^3)	160000
Current TOC of plant liquor (g/L)	15
Baseline TOC increase rate (g/L per year)	0
Flow rate of plant liquor for Solvay's organic removal process (m^3/h)	25
%TOC removal by Solvay's organic removal process as a function of feed liquor TOC	Equation can be obtained via analyzing the extraction isotherm data

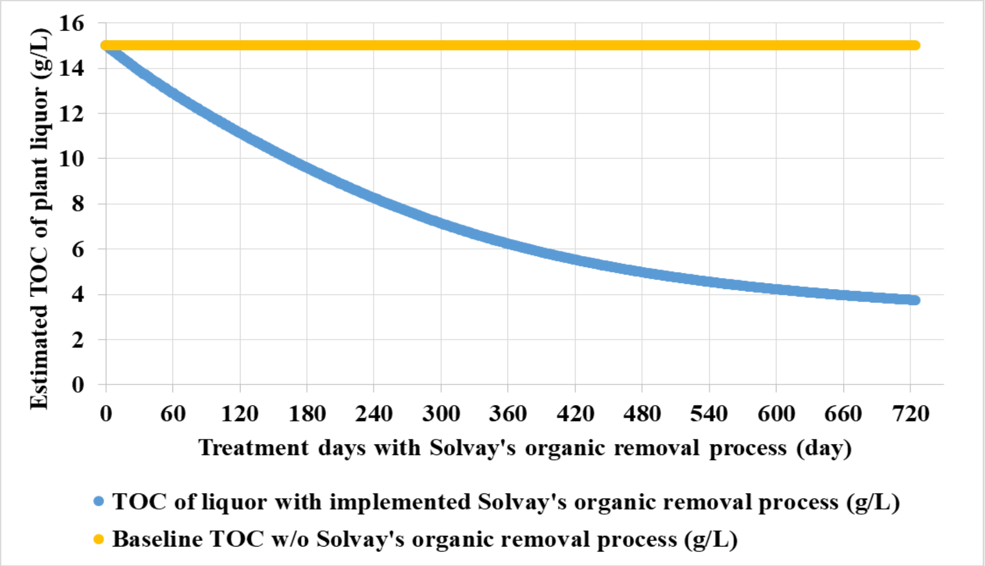

Figure 18. The estimated plant liquor TOC change over time with the implementation of Solvay's organic removal process based on the assumptions in Table 3.

3. Conclusion

In summary, Solvay has developed a breakthrough organic removal process based on solvent extraction composed of four operating units: SX, strip liquor recycling, regeneration liquor recycling and organic destruction. Bench scale and pilot scale tests have been conducted to validate the chemical equilibria, continuous lab-scale operation and engineering specifications, and demonstrate the benefits associated with TOC reduction in plant liquors.

4. References

1. Joseph G. Pulpeiro et al., Sizing and organic control system for the Bayer process, *Light Metals* 1998, 89-95.
2. Andrew R. Hind et al., The surface chemistry of Bayer process solids: a review, *Colloids and Surf. A.* 1999, 359-374.
3. Greg Power et al., Organic compounds in the processing of lateritic bauxites to alumina Part 2: Effects of organics in the Bayer process, *Hydrometallurgy* 2012, 125-149.
4. L. Armstrong et al., Bound soda incorporation during hydrate precipitation – effects of caustic, temperature and organics, *Light Metals* 1996, 37-40.
5. G. Bouzat et al., Physical chemistry models of oxalate and gibbsite solubilities in Bayer solutions. *Light Metals* 1991, 97-102.
6. Gabriella Sipos et al., The role of quaternary amines in the inhibition of sodium oxalate crystal growth in Bayer liquor, *Proc. 14th International Symposium on Industrial Crystallisation* 1999, 1-13.
7. Gervais Soucy et al., Organic control Technologies in Bayer Process, *Light Metals* 2004, 109-114.
8. Steven Rosenberg et al., Process for the removal of oxalate and/or sulphate from Bayer liquors, *US Patent 7244404*, filed Mar. 12, 2004, granted Jul. 17, 2007.
9. B. Gnya and G. Lever, Review of Bayer organics – oxalate control processes, Light Metal 1979, 151-161.
10. Stephen C. Grocott and Ian R. Harrison, Two new oxalate removal processes, *Fourth International Alumina Quality Workship*, Darwin, Australia, 2-7 June, 1996, 423-435.