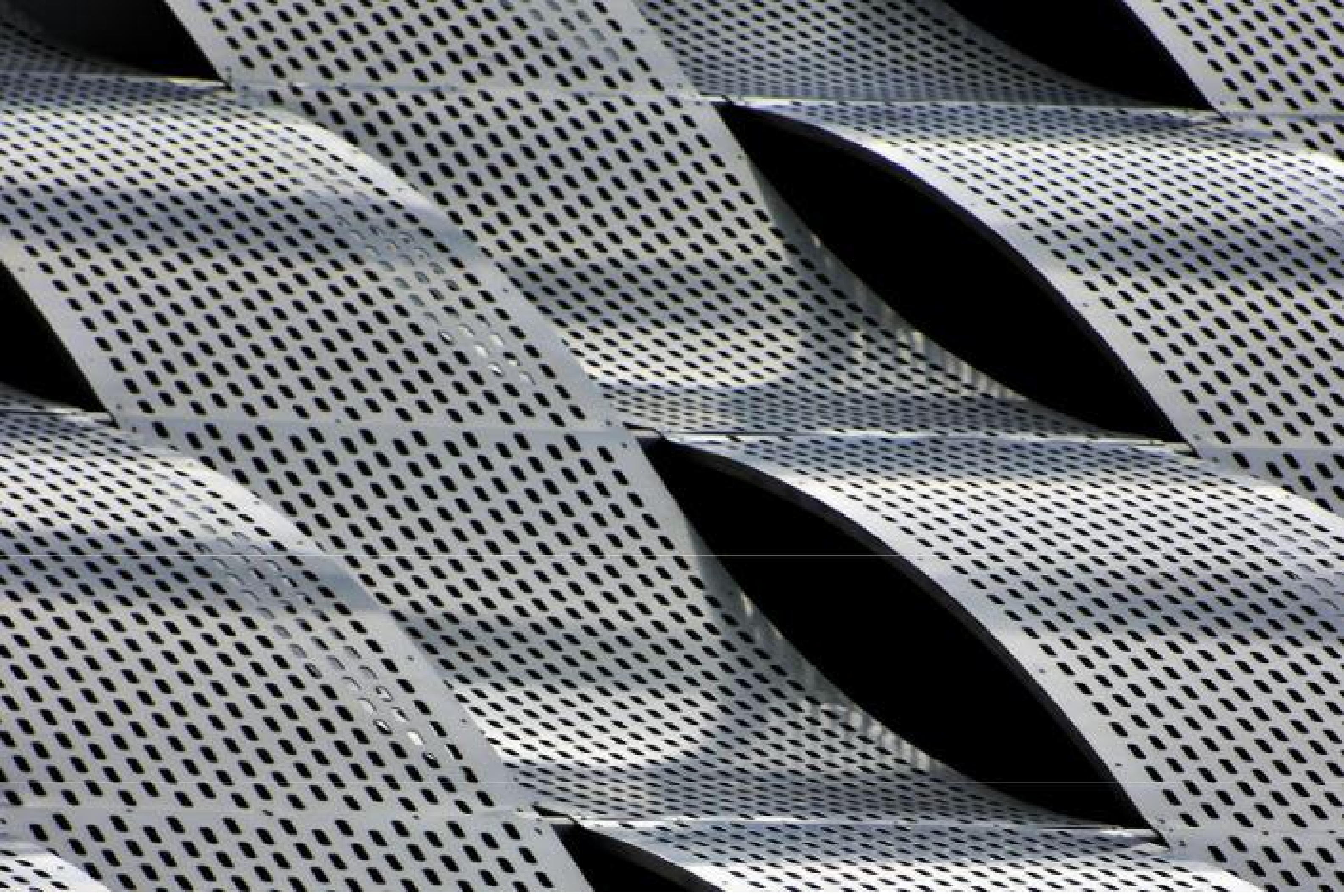

Application Note AN-PAN-1034

Analysis of Bayer aluminate liquors using online thermometric titration

The Bayer Process is the method used to refine alumina from bauxite ore, as smelting aluminum directly from alumina is much more cost- and energy-effective. In this process, «aluminate liquors» are created by digesting the crushed bauxite with CaO and NaOH at high temperatures. Additionally, the CaO causticizes carbonate which forms in the alkaline solution from organic degradation and CO_2 absorption from the atmosphere. Contaminations are removed at various steps in the process, and the liquor is filtered from the alumina crystals before it is recycled back to the digestion step. Before the spent liquor can be reused, a determination of the concentrations of the total hydroxide («caustic»), carbonate, and alumina is required.

This Process Application Note is focused on monitoring total hydroxide, carbonate, and alumina concentrations online in aluminate liquors via thermometric titration with either the 2060 TI Process Analyzer or the 2035 Process Analyzer - Thermometric from Metrohm Process Analytics.

INTRODUCTION

Aluminum is used everywhere: in automobiles, bicycles, soft drink cans, cookware, and is even found in most antiperspirants, yet it does not occur in a natural state. Aluminum is a reactive base metal and is mainly refined from bauxite ore, which contains approximately 60% alumina (Al_2O_3). To smelt aluminum directly from bauxite would be extremely costly due to its high melting point.

The Bayer Process was developed in the late 19th century to extract alumina from bauxite, as purified alumina is much easier to smelt, and this cycle is still used by most alumina refineries today. The bauxite ore must be finely ground to increase surface area, and then mixed with cleaned spent liquor, lime (CaO), and caustic soda (NaOH). This slurry is digested at high temperatures under pressure for several hours (Figure 1).

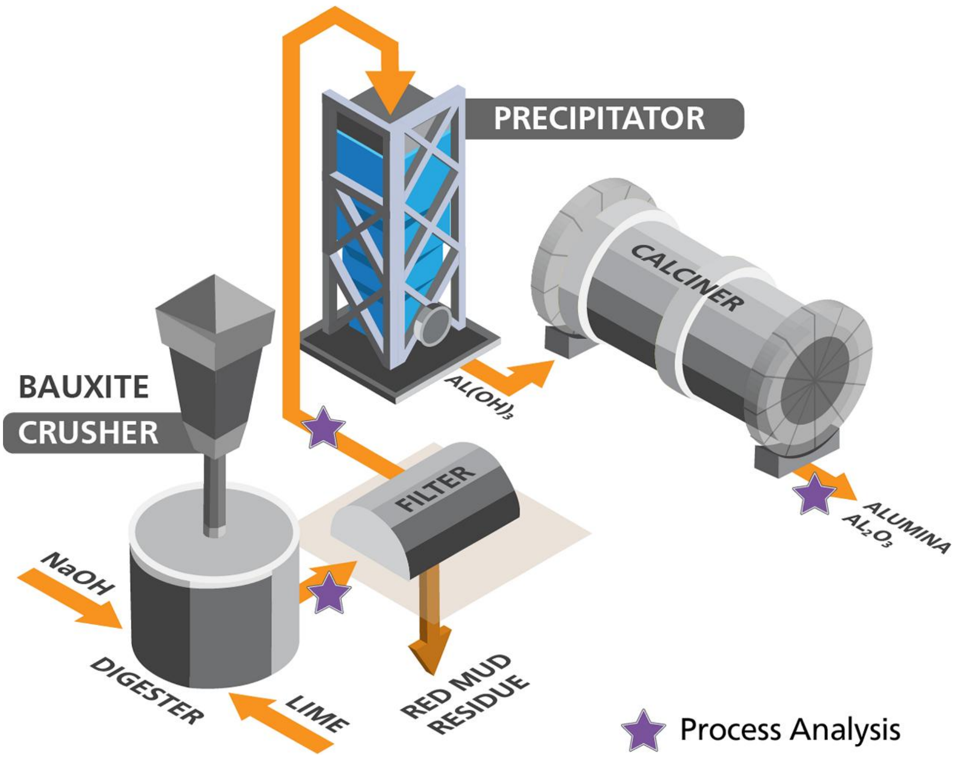

Figure 1. Bayer Process diagram with stars noting areas where online thermometric titration for process analysis can be integrated.

The NaOH selectively dissolves the alumina as sodium aluminate ($NaAlO_2$). The CaO is added to the liquor to causticize carbonate (CO_3^{2-}) which enters the solution through degradation of organics in the bauxite as well as absorption of $CO_{2\ (g)}$ present in the atmosphere. The causticization of CO_3^{2-} yields OH- and precipitates $CaCO_3$, which can then be removed along with the other insoluble impurities and deposits. After cooling the saturated aluminate [$Al(OH)_4^-$] liquor, it is seeded with pure alumina for crystallization, and the digestive liquor is filtered. The resulting precipitate is washed and heated to around 1000 °C to dry, forming a powder which can be further refined into aluminum metal. The liquor is recycled back to the digestion step, after impurity removal and further enrichment in both CaO and NaOH, beginning the cycle once more. There is about a 4:1 ratio between the amount of bauxite needed to eventually produce aluminum, meaning there is a significant amount of byproducts formed.

Analysis of the recirculating aluminate solution is the single most important analytical task in the control of the Bayer Process. Accurate and precise knowledge of the total hydroxide («caustic»), carbonate, and alumina concentrations is required to maintain the highest process productivity from the supersaturated aluminate liquors while maintaining process losses at tolerable levels.

Knowledge of the amount of carbonate is required to optimize the operation of carbonate removal processes, as well as adjusting its level with respect to the required causticity of the liquor.

Metrohm Process Analytics offers fast and reliable online solutions for the analysis of the **total caustic**, **total soda**, and **alumina** in Bayer aluminate liquors using thermometric titration (Figure 2). Thermometric titration is ideally suited for industrial process stream analysis. This method can be used for a wide variety of titration analyses and is well-suited to handle aggressive sample matrices because of the robust thermometric sensor. The sensor requires virtually no maintenance and because endpoints are detected from the second derivative of the titration solution temperature curve, no calibration is required. Moreover, titrations are typically fast, leading to high analytical productivity. Thermometric titration is a problem solver for difficult samples which cannot be titrated potentiometrically.

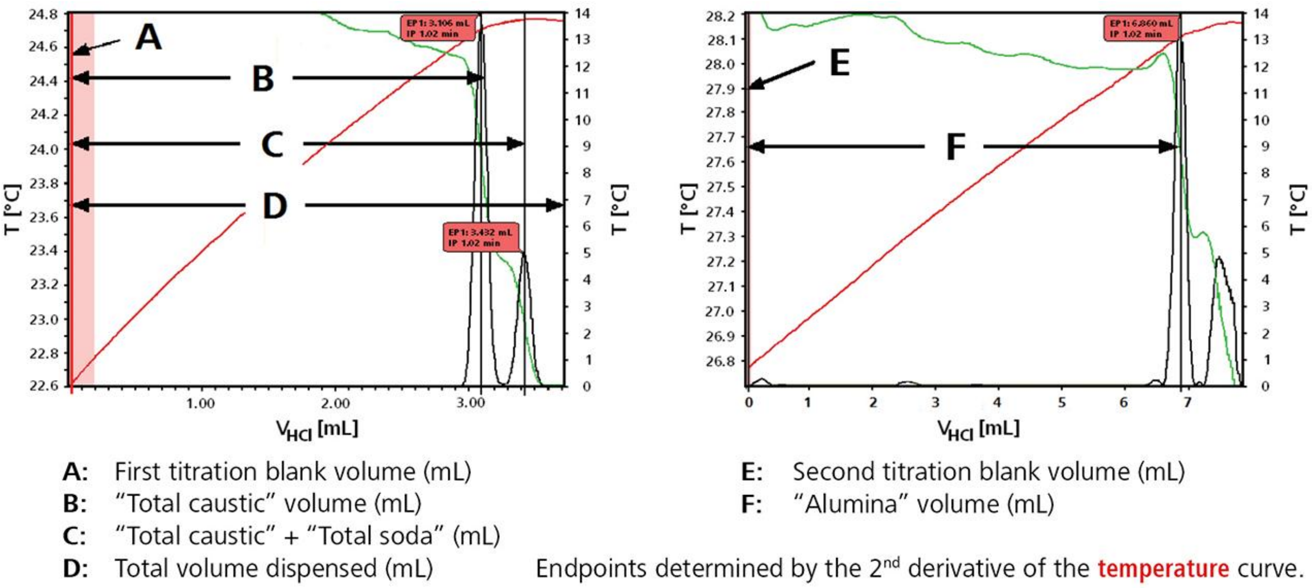

Figure 2. Thermometric titration plots from the determination of total caustic, total soda, and alumina from a sodium aluminate liquor sample.

APPLICATION

The sodium aluminate liquor is diluted with deionized water and complexed with sodium potassium tartrate, releasing one mole of hydroxide for each mole of aluminate present (Reaction 1).

$Al(OH)_4^- + n(C_4H_4O_6)^{2-} \rightarrow Al(OH)_3(C_4H_4O_6)_n^{2-} + OH^-$

Reaction 1.

The total hydroxide content of the liquor (total caustic) and the carbonate (total soda) content are determined by titration with HCl (Reaction 2).

$CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$

Reaction 2.

Potassium fluoride solution is then added to destroy the aluminotartrate complex, forming insoluble potassium sodium aluminum fluoride and releasing three moles of hydroxide (also determined by HCl) for each mole of aluminate (Reaction 3).

$Al(OH)_3(C_4H_4O_6)_n^{2-} + 6\ F^- \rightarrow 3\ OH^- + n\ (C_4H_4O_6)^{2-} + AlF_6^{3-}\downarrow$

Reaction 3.

A second titration is then automatically and immediately performed to determine the aluminate content (as «alumina»). Total caustic is defined as the total hydroxide content of the liquor comprising unassociated hydroxide ions, and one hydroxide ion of the four found in the aluminate $[Al(OH)_4^-]$ anion. Total soda is defined as the sum of the total caustic content plus the carbonate content of the liquor.

Figure 3. 2060 TI Process Analyzer from Metrohm Process Analytics.

Figure 4. 2035 Potentiometric Analyzer - Thermometric.

Table 1. Different parameters measured online with thermometric titration during Bayer Process monitoring.

Parameters	Range
Total caustic	17–150 g/L (as Na_2O)
Total soda	1–155 g/L (as Na_2O)
Alumina	17–170 g/L (as Al_2O_3)

REMARKS

Highly concentrated liquors may need a reduced sample size and modified titrant quantities to effectively complex all aluminate with the tartrate reagent. Very dilute liquors may be titrated directly.

Pure sodium aluminate solutions are also produced for use in water purification, the manufacture of paper and of synthetic zeolites; the method described here is also suitable for these solutions.

CONCLUSION

The 2060 TI Process Analyzer and 2035 Process Analyzer - Thermometric from Metrohm Process Analytics can not only measure the concentration of alumina, but also the total hydroxide and carbonate concentration in aluminate liquors via thermometric titration. This method is the preferred solution since it is suitable for aggressive matrices, does not require sensor maintenance, and is a highly sensitive analysis technique.

RELATED APPLICATION NOTES

AN-PAN-1037 Online measurement of the acid number (AN) in oils with thermometric titration

Brochure: 2060 TI Process Analyzer – Maximum flexibility for the toughest challenges in process analysis

Brochure: 2035 Process Analyzer – Multi-purpose analyzer for the online monitoring of industrial processes and waste waters

BENEFITS FOR THERMOMETRIC TITRATION IN PROCESS

- **Detect process upsets** via automated analysis
- **Increased product throughput**, reproducibility, production rates, dosage of chemicals, and profitability
- **Fully automated diagnostics** – automatic alarms for when samples are out of specification parameters

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