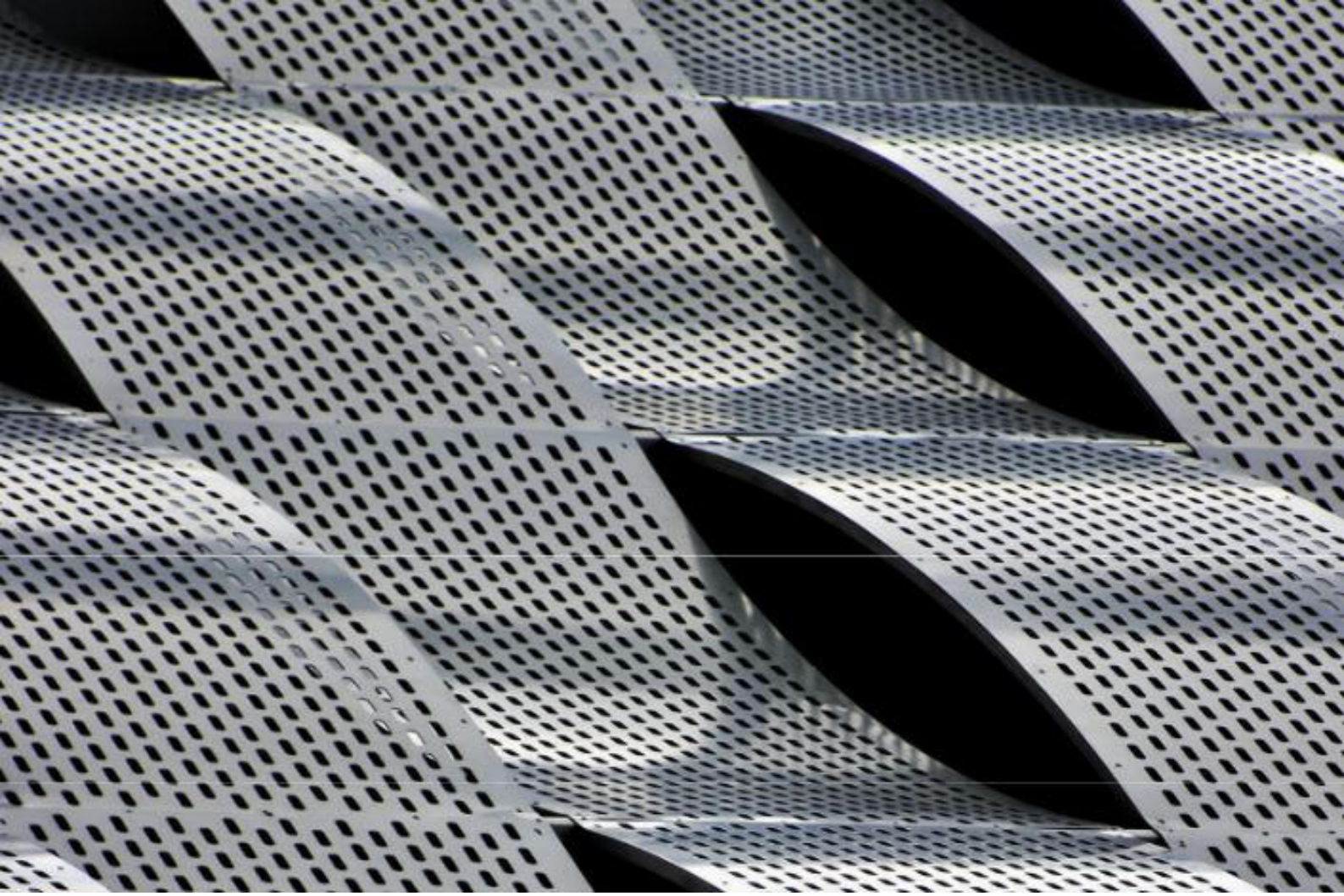

Application Note AN-PAN-1034

通温度滴定分析拜耳法液

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).

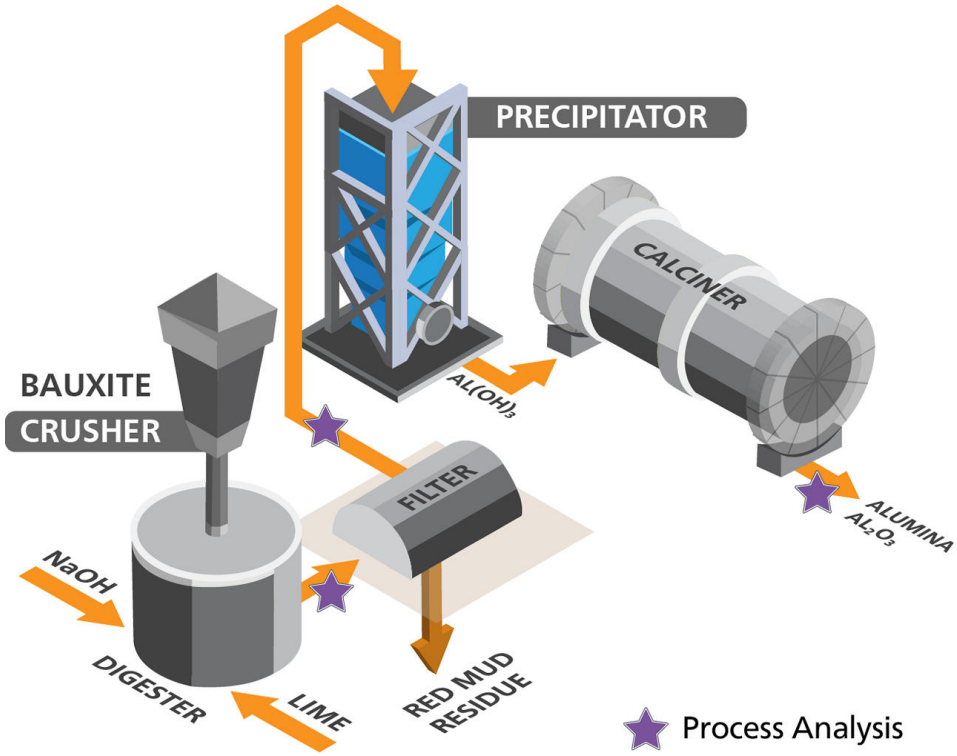

Figure 1. Bayer Process diagram with stars noting areas where online thermometric titration for process analysis can be integrated.

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

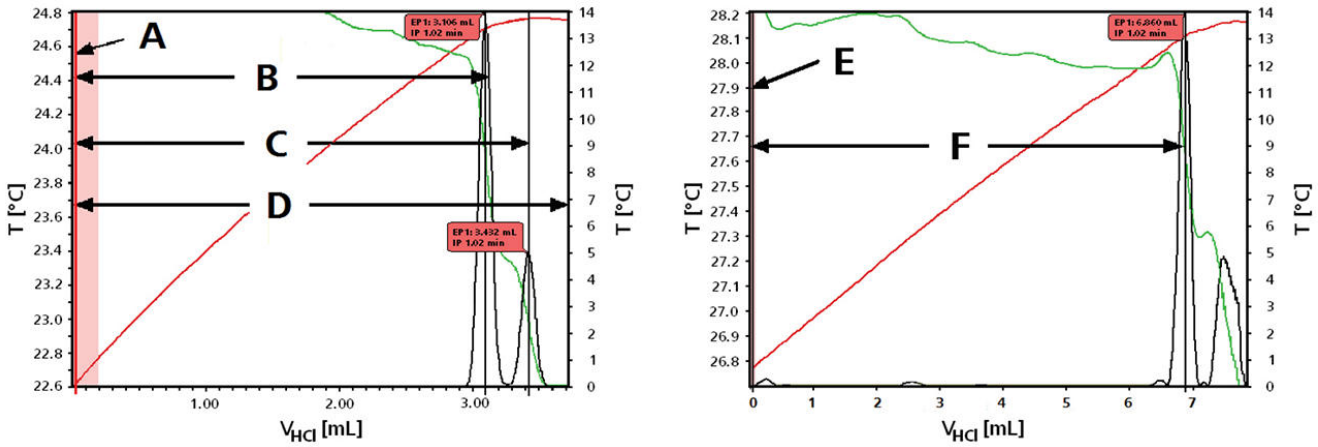

Figure 2. Thermometric titration plots from the determination of total caustic, total soda, and alumina from a sodium aluminate liquor sample.

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).

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

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 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

CONTACT

117702
100085

marketing@metrohm.com.cn

CONFIGURATION

2035 Process Analyzer Thermometric

用于温度滴定的 2035 Process Analyzer 程分析可使用反迅速的高敏性温度感器行自化滴定。取代化学位,通滴定程中的溶液温度化,用来定点。温度滴定是迄今止市上定的滴定方法,可 7 天 24 小在用,例如刻浴的控。无需行感器校准,且清步便。可使用此技行快速分析;例如酸混合物,可在三分之内分析完。

温度滴定可用于各各的滴定分析,因其温度感器固固用,所以非常用于理腐性品基。感器无需,因其少会生垢或不希望的相互反,而且不像其他滴定方法那有薄膜或隔膜。温度滴定是理无法使用位滴定的品的解决方案,于含有 HF 的品来也是一先技。

2060 Process Analyzer

2060 Process Analyzer 是一在湿化学分析,用于无数用。此程分析提供了一个新的模化概念,由一个称«主机»的中心平台成。

主机由部分成。上部包含触摸屏和工算机。下部含有柔性取部,其中放有用于分析的硬件。如果主取部容量不足以分析挑,那主机可以展多四个外的取部机,以保有足的空来具挑性的用。附加机的配置方式使每个取部机可以与具有集成(非接触式)液位的合使用,以增加分析的正常行。

2060 Process Analyzer 提供不同的湿化学技:滴定法、舍滴定法、光度定、直接量和准添加入法。

足所有目要求(或足的所有需求),可提供品理系,以保分析解决方案可靠。我可以提供任何品理系,如冷却或加、和脱气、等。