



Application Note AN-PAN-1034

Analyse des liqueurs d'aluminate de Bayer par titrage thermométrique en ligne

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 CO₂ 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 $[\text{Al}(\text{OH})_4^-]$ 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.

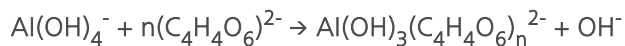
Metrohm Process Analytics offers fast and reliable online solutions for the analysis of the **total caustic**, **total soda**, and **alumina** in Bayer aluminate liquors using thermometric titration (Figure 2). Thermometric titration is ideally suited for industrial process stream analysis. This method 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).



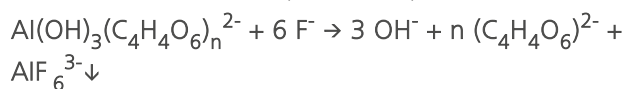
Reaction 1.

The total hydroxide content of the liquor (total caustic) and the carbonate (total soda) content are determined by titration with HCl (Reaction 2). $\text{CO}_3^{2-} + \text{H}^+ \leftrightarrow \text{HCO}_3^-$

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).



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 $[\text{Al(OH)}_4^-]$ 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 ₂ O)
Total soda	1–155 g/L (as Na ₂ O)
Alumina	17–170 g/L (as Al ₂ O 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



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CONFIGURATION



2035 Process Analyzer – Thermométrie

Le 2035 Process Analyzer pour titrage thermométrique réalise des titrages automatisés avec un capteur de température au temps de réponse rapide et d'une grande sensibilité. À la place d'un potentiel électrochimique, le point final est déterminé par enthalpie, p. ex. par variation de la température de la solution en cours de titrage. Le titrage thermométrique est de loin la méthode de titrage la plus robuste qui soit sur le marché. Elle est excellente pour des applications de process online réalisées en 24/7, comme le contrôle de bains d'attaque. Aucun calibrage du capteur n'est nécessaire, ainsi que moins d'étapes de nettoyage. Cette technique autorise une analyse rapide ; des mélanges acides, p. ex., peuvent être analysés en moins de trois minutes.

Le titrage thermométrique peut être utilisé dans une grande variété d'analyses par titrage et est parfaitement adapté à la manipulation de matrices d'échantillons agressives grâce à son capteur thermométrique robuste. Le capteur ne nécessite aucune maintenance, étant donné que l'encrassement et les autres interactions indésirables qu'il subit sont minimales et qu'il ne rencontre aucun problème de membrane ou de diaphragme comme avec les autres méthodes de titrage. Le titrage thermométrique permet de résoudre les problèmes liés aux échantillons difficiles qu'il est impossible de titrer par potentiométrie, c'est aussi la technique préférentielle dans les situations où de l'acide fluorhydrique est présent dans les échantillons.



2060 Process Analyzer

Le 2060 Process Analyzer est un appareil d'analyse par voie humide online adapté à un grand nombre d'applications. Cet appareil d'analyse de processus propose un nouveau concept de modularité reposant sur une plate-forme centrale, dénommée « armoire de base ».

Cette armoire de base se compose de deux parties. La partie supérieure contient un écran tactile et un PC industriel. La partie inférieure contient la partie humide flexible dans laquelle est logé le matériel nécessaire à l'analyse en elle-même. Si la capacité de base de la partie humide n'est pas suffisante pour résoudre un problème d'analyse, vous pouvez ajouter jusqu'à quatre armoires de partie humide supplémentaires à cette armoire de base afin de disposer de suffisamment d'espace pour résoudre les applications les plus difficiles. Les armoires supplémentaires sont configurables de manière à ce que chaque armoire pour partie humide puisse être combinée à une armoire à réactifs avec détection de niveau intégrée (sans contact) afin d'augmenter la disponibilité de l'appareil d'analyse.

Le 2060 Process Analyzer propose différentes techniques de chimie par voie humide : le titrage, le titrage Karl Fischer, la photométrie, la mesure directe et des méthodes d'addition standard.

Pour répondre à toutes les exigences de projet (ou à tous vos besoins), des systèmes de préconditionnement d'échantillons peuvent être fournis afin de garantir une solution analytique robuste. Nous pouvons pour ainsi dire fournir tout système de pré-conditionnement d'échantillon, tels que refroidissement ou chauffage, réduction de la pression, dégazage, filtration et bien plus encore.