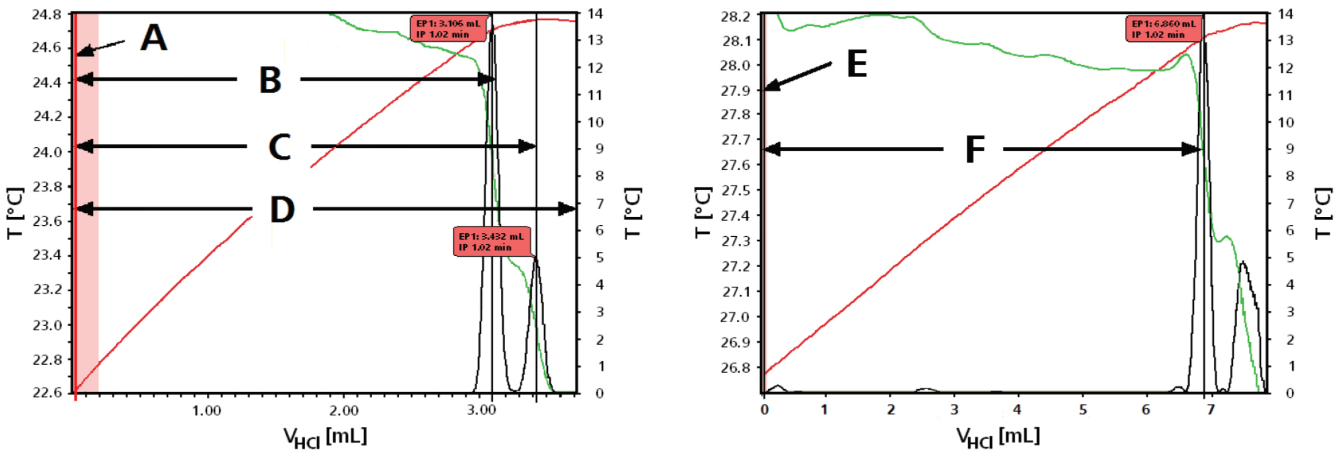
Analysis of Bayer Aluminate Liquors Using Thermometric Titration

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 in order 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. 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 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 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 (60% Al_2O_3) needed to eventually produce aluminum, meaning there is a significant amount of byproducts formed.

Analysis of the recirculating aluminate solutions is the single most important analytical task in the control of the Bayer Process. Accurate and precise knowledge of the total hydroxyl ("caustic"), carbonate, and alumina values is required to maintain the highest process productivity from the supersaturated aluminate liquors while maintaining process losses at tolerable levels. Knowledge of the carbonate level 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.



A: First titration blank volume (mL)
B: "Total caustic" volume (mL)
C: "Total caustic" + "Total soda" (mL)
D: Total volume dispensed (mL)
E: Second titration blank volume (mL)
F: "Alumina" volume (mL)

Endpoints determined by the 2nd derivative of the temperature curve.

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

Metrohm Process Analytics offers a fast, reliable online solution for the analysis of the **total caustic**, **total soda**, and **alumina**

Keywords: Bayer liquid, aluminum oxide, aluminium oxide, alumina, Al_2O_3, 2035, 2045TI

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in Bayer Aluminate Liquors using thermometric titration. Thermometric titrimetry is ideally suited for industrial process control 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 located 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, and is also a preferred technique in situations when HF is present in samples.

Application:

The sodium aluminate liquor is diluted with deionized water and complexed with sodium potassium tartrate, releasing one mole of hydroxyl for each mole of aluminate present (eq. 1). The total hydroxyl content of the liquor (total caustic) and the carbonate (total soda) content are determined by titration with HCl (eq. 2).

Eq. 1: $Al(OH)_4^- + n\,(C_4H_4O_6)^{2-} \longrightarrow Al(OH)_3(C_4H_4O_6)_n^{2-} + OH^-$

Eq. 2: $CO_3^{2-} + H^+ \longleftrightarrow HCO_3^-$

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

Eq. 3: $Al(OH)_3(C_4H_4O_6)_n^{2-} + 6\,F^- \longrightarrow 3\,OH^- + n\,(C_4H_4O_6)^{2-} + AlF_6^{3-}\downarrow$

A second titration is then automatically and immediately performed to determine the aluminate content (as "alumina"). Total caustic is defined as the total hydroxyl content of the liquor comprising unassociated hydroxyl ions, and one hydroxyl of the four 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.

Typical Ranges:

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.

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