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Study of the Behaviour of Gallium during Reagent Carbonization of Aluminate and Zincate Solutions

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Abstract

The behavior of gallium, aluminum, and zinc in the course of reagent carbonization of alkaline solutions is described. It is shown that gallium and zinc may be separated, and separation conditions have been studied. Gallium may be concentrated by co-precipitation with the basic aluminum carbonate to give rich aluminum-free gallate solutions.

Investigation of gallium co-precipitation with aluminum and zinc from alkaline solutions is associated with the development of processes for extracting gallium from the industrial solutions obtained during treatment of bauxites by alkaline methods. To prepare rich zincate-gallate alkaline solutions, gallium with a zinc carrier is electrochemically extracted from an alkaline aluminate solution containing preliminarily added zinc [1]. A method for extracting zinc from such solutions by electrochemical deposition on Ni cathodes has been suggested [2]. One of the industrial procedures for the preparation of gallium is based on stepwise carbonization of aluminate solutions with carbon dioxide [3]. Because of the higher acidity of gallium, the bulk of aluminum (or zinc) can be separated from these solutions by lowering the content of sodium hydroxide. Using $NaHCO_3$ as a carbonizing agent would lead to reduced reaction times and allow more effective control over the reaction that forms carbon dioxide ions required for neutralizing the alkali of the solution.

An aluminate-gallate solution was treated with definite portions of sodium hydrocarbonate for 4 h at ~60 °C. The batching of $NaHCO_3$ was continued out until basic aluminum and gallium carbonates ceased to precipitate. The resulting filtrates and precipitates were analyzed for the content of aluminum (or zinc in subsequent reactions), gallium, NaOH, Na_2CO_3, and $NaHCO_3$. Figure 1 gives the general picture, showing how the contents of the compounds change during carbonization (curves *1, 1′*). Aluminum compounds start to settle concomitantly with the lowering of pH of the solution, while gallium precipitation is observed when the concentration of NaOH is less than 10 g/dm^3. The data obtained confirm that co-precipitation of gallium hydroxide, basic gallium/sodium carbonate (sodium gallocarbonate [4]) and the corresponding aluminum compounds is an isomorphic process. The air-dry gallium concentrate isolated from an industrial solution of (g/dm^3) NaOH 29.9, Na_2CO_3 66.3, Zn 0.4, Al_2O_3 10.42, and Ga 4.0 contained ~5–6 % gallium and ~20 % Al_2O_3; during carbonization with up to 40–48 g/dm^3 of $NaHCO_3$, not more than 10 % of the initial content of gallium is lost with the solution.

To separate aluminum and gallium with the aim of concentrating the latter, a method has been proposed [5] for processing an aluminate solution with calcium oxide whereby aluminum is precipitated in the form of calcium

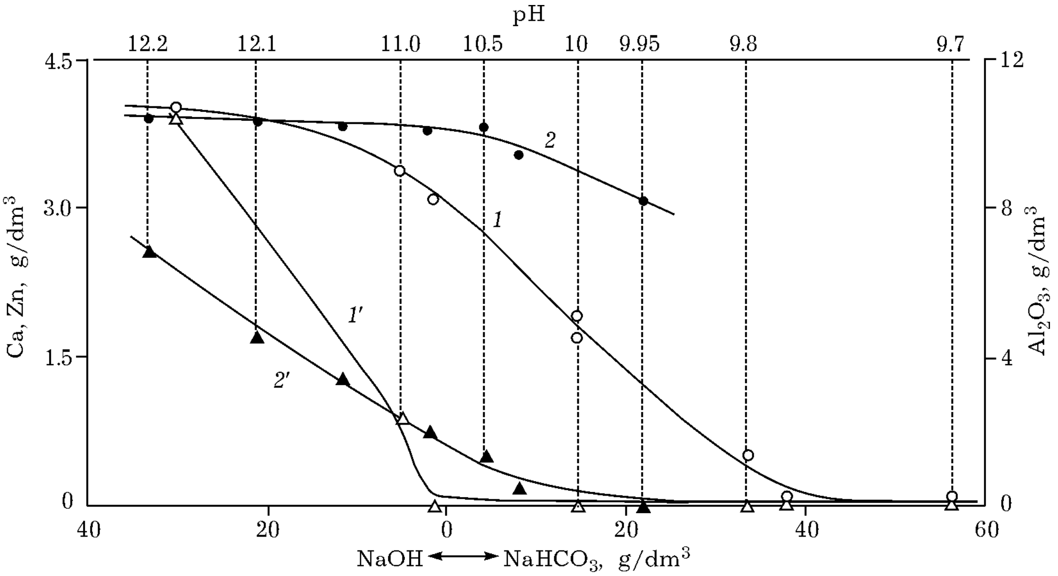

Fig. 1. Contents of the components *versus* solution alkalinity in the course of carbonization: *1, 1′* – Ga and Al_2O_3, respectively, $T = 60$ °C, $\tau = 4$ h, ; at the point of neutralization of NaOH, the content of Na_2CO_3 is 105.97; *2, 2′* – Ga and Zn, respectively, $T = 40$ °C, $\tau = 2$ h, at the point of neutralization of NaOH, the content of Na_2CO_3 is 51.73.

aluminate, while gallium remains in solution. Treatment of the gallium concentrate obtained in the above process with lime milk leads to neutralization of carbonic acid contained in the precipitate and to dissolution of aluminum and gallium oxides. An excess of calcium oxide over the amount necessary for neutralization should lead to precipitation of the aluminum solute in the form of calcium aluminate. The gallium concentrate was dissolved at ~80 °C for 2 h while stirring the pulp (S : L = 1 : 4; molar ratios of CaO/Al_2O_3 were from 1.5 to 3.5). For complete separation of gallium and precipitation of aluminum, calcium oxide is taken in excess (molar ratio): CaO/Al_2O_3 = 3–3.5. The resulting gallate solutions contained (g/dm^3) NaOH ~30, Na_2CO_3 ~3.5, Zn ≤ 0.1, Ga 2–2.5, Al_2O_3 not found.

Gallium extraction (together with the washing solution) into solution amounted to ~97 %. An X-ray diffraction study of the calcium-alumina precipitate showed that the basic compounds are aluminum and calcium carbonate hydrates. An excess of lime milk leads to unjustifiable consumption of the reagent and increased amount of the precipitate, and also to further loss of gallium.

Carbonization of the synthetic zincate-gallate solution (g/dm^3) of NaOH 33.0, Na_2CO_3 7.95, Zn 2.55, Ga 3.90 was carried out with stirring for 2 h at 40–50 °C. The gradual hydrolytic precipitation of zinc oxide (Fig. 1, curve *2′*) started immediately and continued until the $NaHCO_3$ content reached ~13.5 g/dm^3. The increased zinc content in the hydrocarbonate region of the solution may be attributed to the colloid component, while the large amount of the precipitate or the use of coagulants would lead to more complete precipitation. Hydrolysis of gallium compounds (see Fig. 1, curve *2*) started when $NaHCO_3$ was more than 4 g/dm^3 in excess (pH < 10.5). It was reported [4] that during carbonization of an alkaline gallate solution with a Ga_2O_3 concentration of 96 mg/dm^3, gallium did not precipitate even when sodium hydroxide completely transformed into sodium carbonate. The solubility of gallium in a carbonate-hydrocarbonate solution (molar ratio $Na_2O : CO_2 = 1 : 1.8$) is about 42 mg/dm^3 [6] at 20 °C. We have not found any data about carbonization of zincate solutions. The sequence of reactions during carbonization of the zincate-gallate solution with solid $NaHCO_3$ may be as follows. At first, neutralization of the free alkali of the solution takes place; after pH of the solution has been lowered, sodium zincate hydrolytically decomposes, leading to precipitation of zinc hydroxide, which is partially converted into zinc oxide already at 39 °C [7]. Co-precipitation of the basic gallium and sodium carbonate with this residue is markedly less significant. Thus, if nearly all gallium is retained in the yet alkaline solution (NaOH ~0.5 g/dm^3), the zinc content may be lowered to less than 0.5 g/dm^3.

Thus the behavior of gallium during reactive carbonization of alkaline aluminate-gallate and zincate-gallate solutions has been studied. Conditions for separating gallium and aluminum by treatment of the gallium concentrate with lime milk are recommended. It is shown that reactive carbonization is a technique designed for controllable concentration of gallium, leading to a technically more facile process for the preparation of gallate solutions not containing zinc and aluminum.

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