



Review

The structure of Al(III) in strongly alkaline aluminate solutions – A review

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ARTICLE INFO

Article history:

Received 8 May 2008

Received in revised form 6 November 2008

Accepted 26 January 2009

Available online 10 February 2009

Keywords:

Bayer process

Aluminate solutions

Concentrated solutions

Electrolytes

Solution speciation

Alumina

Gibbsite

Hydrometallurgy

Al(OH)₄⁻

Raman/IR spectroscopy

²⁷Al NMR

UV/Vis spectra

²⁰⁵Tl NMR

Potentiometry

Viscosity

Dielectric relaxation spectroscopy

EXAFS/XANES spectroscopy

Solution X-ray diffraction

Ga(OH)₄⁻Fe(OH)₄⁻⁷¹Ga NMR

Mössbauer spectroscopy

Ion pairs

Dimerization

ABSTRACT

Research papers dealing with the identity and abundance as well as the structure of aluminium-bearing species present in pure and homogeneous, strongly alkaline aluminate solutions (often called synthetic Bayer liquors) published in the open literature since the 1970's have been reviewed. On the basis of critical evaluation of the data, four solution species (all aquated), *i.e.*, Na⁺, OH⁻, Al(OH)₄⁻ and a dimeric complex (most probably (OH)₃Al–O–Al(OH)₂²⁻) along with their ion pairs, are sufficient to account qualitatively and, where appropriate, quantitatively for all the experimental observations collected for concentrated alkaline aluminate solutions at temperatures up to 100 °C. An extended network of these entities held together by electrostatic forces and hydrogen bonds seems also to be likely. The presence of other species, like the dehydrated monomers (AlO₂⁻ or AlO(OH)₂⁻) or higher complexes (Al(OH)₅²⁻ and Al(OH)₆³⁻) in significant concentrations can be excluded. Aluminate species formed *via* release of hydroxide from Al(OH)₄⁻ and subsequent oligomerization are also conclusively eliminated. Hexameric aluminate complexes, believed to be the docking species during gibbsite crystallization were also found to be experimentally undetectable. If such species exist at all, they can only be present in very small quantities and are therefore “invisible” for the currently available experimental techniques. The question, whether the T_d → O_h transformation of aluminium involves a (minor) solution species or it takes place on the surface of the gibbsite during crystallization, appears to remain unresolved.

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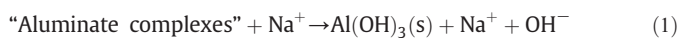
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1. Introduction and overview

1.1. The importance of the chemical speciation of Bayer liquors and the uncertainties associated with it

The principal way of mass-producing pure alumina ($\text{Al}_2\text{O}_3(\text{s})$) from bauxite has been invented by Karl Bayer in 1888. The first alumina plant using the Bayer process was opened in 1893, and since then alumina production became a multi-billion dollar industry [1–4]. During the Bayer process, first, the aluminium-bearing minerals in bauxite are selectively extracted from the insoluble components (mostly iron-oxides and silica) by dissolving them in extremely alkaline ($\text{pH} > 14$), concentrated aqueous solution of sodium hydroxide ($[\text{NaOH}]_T \leq 7 \text{ M}$)¹, at elevated temperatures (140 °C–270 °C) and pressures (up to 35 atm). Crystalline gibbsite ($\text{Al}(\text{OH})_3(\text{s})$) is then precipitated from the digestion liquor in a process reverse of the extraction, according to



where “aluminate complexes” represents the various aluminium-bearing hydroxo-complexes (anionic or neutral) present in the liquor. Gibbsite is then calcined to form alumina ($\text{Al}_2\text{O}_3(\text{s})$) for the smelting of aluminium.

Because of its industrial importance, the composition and abundance of these aluminate complexes present in Bayer liquors (*i.e.*, the chemical speciation) as well as their structure is among the most intensely investigated questions in the chemistry of aluminium over the last 120 years. The estimated number of scientific publications dealing with this particular question is well over a thousand. Despite the tremendous scientific effort and resources deployed, well-established knowledge of the speciation in Bayer-liquors is limited. A wide variety of experimental techniques has been used, but the conclusions are most often contradictory. This might be associated either with the dubious methodology employed or with the well-known practical difficulties (*e.g.*, dealing with extremely high concentrations and alkalinity) of studying these solutions (or in some cases with both). Furthermore, due to the lack of a suitable

model of chemical interactions occurring in Bayer liquors, reliable interpretation of the experimental data is often impossible. In the realm of the extremely concentrated aqueous solutions, the experimental parameters influencing the interactions in solution cannot be varied independently, therefore the individual contribution of each parameter is not known, which makes understanding of the results at least complicated.

The Bayer process can be considered an industrial scale recrystallization of gibbsite in presence of various organic (*e.g.*, oxalate, succinate, acetate, *etc.*) and inorganic (*e.g.*, carbonate, chloride, sulphate, *etc.*) impurities. “Real” liquors also contain particulate matters, *e.g.*, crystals, seeds, and other macroscopic inhomogeneities. Relatively little work has been done on the chemical speciation of these multicomponent and inhomogeneous “real” liquors. The majority of published works are concerned with the (seemingly!) less complicated “synthetic” Bayer liquors, which are homogeneous, and consist only of three components: H_2O , NaOH and dissolved $\text{Al}(\text{III})$.

The current review deals with these “synthetic” Bayer liquors in the context of chemical speciation and structure of aluminium in them. Beside the critical assessment of the available experimental observations published in the open literature, we will attempt to construct a robust speciation model of precipitate free Bayer liquors.² To the best of our knowledge, the last critical review in this field with extensive number of citations appeared in 1970 [5], therefore the relevant literature back to the early 70’s will be elaborated here. Where appropriate, the discussion will be extended to alkaline aluminate solutions containing cations other than Na^+ (*i.e.*, K^+ , Cs^+ , Li^+ and $(\text{CH}_3)_4\text{N}^+$). The majority of the data available are related to ambient conditions, but certain critical measurements have been carried out at $T > 25 \text{ °C}$, which will also be included. Finally, the behaviour of $\text{Al}(\text{III})$ in alkaline conditions will be briefly compared with that of structurally related trivalent cations, such as $\text{Ga}(\text{III})$ and $\text{Fe}(\text{III})$.

¹ The square brackets denote concentration and the subscript T signifies total or analytical values.

² The data presented in this review will include (beside a selection of works in this field) the already published findings of a collaborative research project (AMIRA P380 “Fundamentals of Alumina Precipitation”) jointly sponsored by the largest alumina producing companies in Australia. The author of this review participated in one of the three modules of the project, “Chemical speciation of synthetic Bayer liquors”.

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