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http://dx.doi.org/10.1016/j.hydromet.2011.08.002

Königsberger, E., Königsberger, L.C. and Ilievski, D. (2011) *The boehmite 'solubility gap'.* **Hydrometallurgy, 110 (1-4). pp. 33-39.**

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Accepted Manuscript

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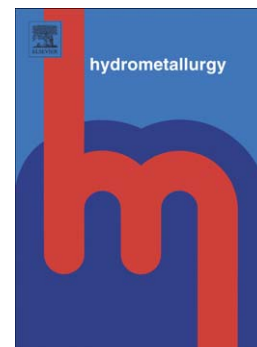
Please cite this article as: Königsberger, Erich, Königsberger, LanChi, Ilievski, Dean, The boehmite 'solubility gap', *Hydrometallurgy* (2011), doi: 10.1016/j.hydromet.2011.08.002

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THE BOEHMITE 'SOLUBILITY GAP'

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Abstract

Boehmite, rather than gibbsite, precipitation has been proposed in the literature as a potential energy-saving modification of the Bayer process for the production of alumina. Previous experimental studies have reported that true equilibrium solubilities were not attained during boehmite precipitation. Instead, a pseudo-equilibrium or an apparent 'steady-state' aluminate concentration of about twice the boehmite solubility was reached. In this work, the dissolution and precipitation reactions in synthetic and plant liquors using seeds of (i) pure boehmite and (ii) various boehmite/gibbsite ratios were investigated at 95 °C. Only boehmite precipitation was observed on pure boehmite seed at relatively low supersaturation (alumina (A)/total caustic (TC) $\lesssim$ 0.56). The aluminate concentrations measured as a function of time decreased continuously and did not exhibit an apparent 'steady state'. Stable equilibrium, as established by boehmite solubility measurements, was approached very slowly and not attained even after ten weeks. At higher supersaturation (A/TC ≈ 0.67), after an initial desupersaturation, 'steady-state' aluminate concentrations of about twice the boehmite solubility were observed. There is convincing evidence that these 'steady states' correspond to metastable solubility equilibria with gibbsite, which is precipitated initially and gradually transforms into the stable phase, boehmite. Gibbsite also nucleated in the case of pure boehmite seeds. 'Steady states' were attained in one up to several days and remained constant for one to ten days. The length of these periods correlated with the gibbsite content of the seeds. After sufficient recrystallisation of gibbsite to boehmite, the aluminate concentrations decreased significantly and eventually approached boehmite solubility, thereby following a much slower precipitation kinetics typical for boehmite. Due to short observation times, previous workers did not detect the end of the 'steady-state' periods and therefore failed to identify the observed 'steady-state' aluminate concentrations as arising from metastable solubility equilibria with gibbsite.

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1   Introduction

The Bayer process is commonly used for the production of alumina, $Al_2O_3(cr)$, from aluminium-containing ores such as bauxite (Hudson, 1987). It involves a leaching step using hot, caustic aluminate solution ('digestion') which, after removal of insoluble residue, is followed by the seeded precipitation of purified gibbsite, $Al(OH)_3(cr)$, at lower temperatures (Eq. 1):

$$Al(OH)_4^-(aq) \rightarrow Al(OH)_3(cr) + OH^-(aq) \qquad (1)$$
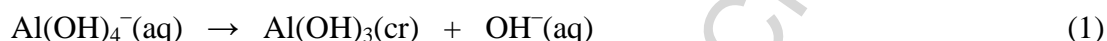
The aluminate-depleted caustic solution is recycled back to the digestion stage and alumina is finally produced from gibbsite ('trihydrate') through the removal of (3 mol H_2O)/(mol Al_2O_3) during calcination at temperatures in excess of 1000 °C.

Boehmite, $AlOOH(cr)$ ('monohydrate'), contains only (1 mol H_2O)/(mol Al_2O_3). Consequently, significant energy savings can be expected at the calcination stage if it is possible to modify the Bayer process and precipitate boehmite instead of gibbsite according to the following reaction (Eq. 2):

$$Al(OH)_4^-(aq) \rightarrow AlOOH(cr) + H_2O(aq) + OH^-(aq) \qquad (2)$$
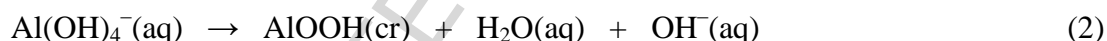
In addition, boehmite precipitation should increase the alumina yield because it has a lower solubility than gibbsite (Schrödle et al., 2010). However, these potential advantages are flawed by slow crystallisation kinetics and small crystallite sizes of boehmite precipitates (Loh et al., 2005). Moreover, based on a thermodynamic simulation of the Bayer process, it was pointed out that the total energy gain from precipitating boehmite rather than gibbsite should be lower than expected from considering calcination alone (Königsberger, 2008). This is because the excess water formed during boehmite precipitation (Eq. 2) needs to be evaporated before the liquor is recycled to the digestion stage.

Another, hitherto unexplained, obstacle to a 'boehmite route' concerns the occurrence of 'steady-state' aluminate concentrations during the precipitation of boehmite from Bayer liquors (Skoufadis et al., 2003; Loh et al., 2005). Skoufadis et al. (2003) studied the precipitation kinetics of boehmite from synthetic liquors. They found 'steady-state' concentrations which were about 1.7 to 1.9 times higher than the value of boehmite solubility under the same experimental conditions. Loh et al. (2005) reported 'steady-state' aluminate concentrations which were ca. 2.3 times higher than boehmite solubilities. These high 'steady-state' concentrations would imply that the advantage of increased alumina yield due to low boehmite solubilities cannot be exploited.

In this study, we investigate dissolution and precipitation reactions of gibbsite and boehmite, as a function of supersaturation, in synthetic and plant liquors at 95 ^{o}C in order to determine the resulting 'steady state' concentrations of aluminate and to characterise the solid phases involved in the reactions. The results, strongly supported by computer simulations, suggest a thermodynamic interpretation of the observed boehmite 'solubility gap'.

2   Experimental

2.1   Apparatus

Dissolution and precipitation reactions were carried out in a special solubility apparatus developed at Murdoch University (Capewell et al., 1999). The essential parts of this apparatus are a slowly rotating carousel, which holds up to 28 syringes containing the heterogeneous mixtures of solids and solutions and a device which permits the sampling of (filtered) saturated solutions at the equilibrium temperature. The complete system is immersed in a water tank designed for precise temperature control. This apparatus allows solubilities of rapidly equilibrating solid-liquid systems to be measured with high accuracy. However, in a preliminary study it turned out that the syringes (50 mL, Terumo, Japan) did not withstand caustic attack at 95 ^{o}C for a very long time. Therefore, they were replaced by Nalgene polypropylene bottles (125 mL) which were attached to the rotating carousel by metal wire. Sampling was performed, as quickly as possible, outside of the thermostatted bath, using syringes equipped with 0.45 µm membrane filters. Since in the present case the kinetics are relatively slow, it is expected that this procedure did not introduce significant errors. To prevent precipitation of solids after filtration, all sampled liquors were stabilised by addition of ca. 5 mg mL^{-1} mannitol.

2.2   Materials and Experimental Conditions

Measurements were performed with boehmite, gibbsite or their mixtures as solid phases at a temperature of 95 ºC. Both synthetic and plant liquors of total caustic (TC) = 140, 165 and 210 g L^{-1} Na$_2$CO$_3$ equivalents were investigated. The 'total caustic' refers to the sum of NaAl(OH)$_4$ and free NaOH concentrations, while 'alumina' (A) is measured in g L^{-1} Al$_2$O$_3$. The ratio of alumina to total cuastic (A/TC) is commonly used by the alumina industry to express the aluminate content of Bayer liquors. Synthetic liquors were prepared at Murdoch University by dissolution of high-purity Al metal in carbonate-free NaOH solutions (Sipos et al., 1998; Sipos et al., 2000). Since the supersaturated liquors were prepared freshly for each series of experiments,

A/TC of the initial solutions varied within ±0.01 units. Well characterised plant liquors and solid phases (boehmite and gibbsite) were supplied by Alcoa.

For each TC, two sets of liquors with different aluminate contents corresponding to under- and supersaturation respectively, were tested. In the case of synthetic liquors, the undersaturated solutions were NaOH solutions made up to the appropriate TC. Undersaturated plant liquors were prepared by seeded precipitation of aluminium trihydroxide at room temperature over several weeks. The resulting solutions were filtered through 0.45 μm membrane filters and analysed before being used.

In this study, the seed loading was 10 g solid per 50 mL of liquor, unless stated otherwise. The following boehmite/gibbsite mass ratios were used: 100:0, 98:2, 95:5, 80:20, 0:100 for precipitation and 100:0, 41:59 (17 g solid per 50 mL of liquor), 0:100 for dissolution.

2.3   Analysis

X-ray diffraction phase analyses of solids as well as the chemical analyses of liquor were performed by Alcoa (TDG, Kwinana).

The presence of gibbsite and boehmite was analysed for using a Philips X'Pert Multi-purpose X-ray diffractometer. The relative amounts of gibbsite and boehmite were estimated from the measured diffraction pattern by a calibration method based on standards prepared by combining known amounts of pure boehmite and gibbsite. Standards comprising 0%, 1%, 2%, 5% gibbsite were used to develop a quantitative analysis program. Boehmite is included in the method, but not calibrated for. The 0% gibbsite standard sample was also examined as a qualitative scan to ensure there was no gibbsite present. The uncertainty in this method has been tested internally at Alcoa, using three different operators and a range of freshly prepared samples of known quantities of gibbsite and boehmite. The variability was found to be +/- 10% at 1 standard deviation. In most of the samples investigated in this study, the amount of the minor phase was too small for quantification.

The aluminate liquor composition analyses were performed using the Connop titration method (Connop, 1996), which is now a standard in the Bayer industry.

3   Computational

The Murdoch Bayer liquor model, incorporated into the BAYER.EXE v5.15 software (Königsberger et al., 2005), was used to calculate the composition of the initial

solutions, as well as the solubilities of boehmite and gibbsite in both synthetic and plant liquors.

4   Results and Discussion

The experimental results obtained in this study are shown in Figs. 1–6. Note that the lower case letters used in the figures identify different experiments, whereas capital B and G stand for boehmite and gibbsite respectively. Aluminate concentrations (A, in g L^{-1} Al_2O_3) were calculated by multiplying the measured A/TC with the corresponding TC values of 140, 165 and 210 g L^{-1} Na_2CO_3 respectively. This approach ensures that runs with slightly different TC are comparable with each other. Experimental uncertainties, particularly dilution errors which affect all concentrations simultaneously, are also smoothed. However, precipitation and dissolution runs had significantly different TC values due to the dissolution of Al metal and hydrate respectively. These differences are clearly visible in Figs. 1 and 4 and discussed in detail below.

4.1   Synthetic Liquors

Results of solubility and precipitation measurements of boehmite in synthetic liquors of TC = 210, 165 and 140 g L^{-1} Na_2CO_3 are shown in Figs. 1, 2 and 3 respectively.

Precipitation experiments with pure boehmite at lower supersaturation (A/TC ≈ 0.56) were run in duplicates (Experiments 210a&b, 165a&b and 140a&b) and showed excellent agreement. The measured aluminate concentrations decreased continuously and did not exhibit an apparent 'steady state'. Boehmite solubility measurements resulted in essentially constant aluminate contents after ca. two weeks, which correspond to a stable equilibrium between liquor and boehmite. Starting from supersaturation, stable equilibrium was approached very slowly and not attained even after ten weeks. Dissolution experiments (NaOH 210a&b, NaOH 165a&b and NaOH 140a&b) resulted in boehmite solubilities that agree very well with BAYER.EXE predictions.

In contrast, the precipitation kinetics from synthetic liquors of TC = 210 g L^{-1} Na_2CO_3 at higher supersaturation (A/TC ≈ 0.67) showed an apparent 'steady-state' aluminate concentration of about twice the boehmite solubility (Fig. 1). In the case of pure boehmite seed (Experiment 210q), the 'steady-state' concentration was reached after two days and remained constant for more than a week. A solid sample taken after 10 days did not contain any gibbsite. For pure gibbsite seed (Experiment 210u), the 'steady state' was attained after one day and the concentration remained constant

for two weeks before decreasing slightly. For seed mixtures (Experiments 210r–t), these times correlated with the boehmite/gibbsite ratio. Since the 'steady-state' aluminate concentrations measured for all samples are very similar to each other, it can be concluded that the 'steady states' correspond to *metastable* equilibria between liquor and *gibbsite*. Given that boehmite is the more stable (less soluble) solid phase under these conditions, thermodynamics requires that gibbsite should recrystallise to boehmite. As a result, the aluminate concentration should decrease, i.e. approach the lower boehmite solubility.

When transformation of gibbsite to boehmite proceeded, it was indeed observed that aluminate concentrations decreased in all cases. Solids harvested from synthetic liquors with boehmite in the seed material contained only traces of gibbsite or no gibbsite at all. On the other hand, XRD phase analysis showed that synthetic liquors seeded with pure gibbsite still contained gibbsite as the "significant" solid phase together with "traces" of boehmite even after 4 months reaction time. It should be noted that the gibbsite-to-boehmite transformation is accompanied by a slight dilution of the liquor, according to the reaction (Eq. 3):

$$Al(OH)_3(s) \quad \rightarrow \quad AlOOH(s) \quad + \quad H_2O(aq) \tag{3}$$
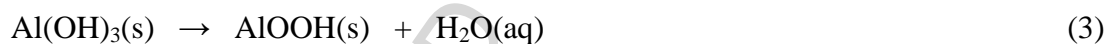
In the present study, progressive dilution of the liquors during the 'steady-state' periods was in fact measured analytically.

Metastable solubility equilibria with gibbsite and corresponding 'steady state' concentrations were also established from undersaturation (Experiments 210v&w). The small 'gap' shown in Fig. 1 between the two aluminate concentration values arising from gibbsite precipitation and solubility measurements is due to different TC values in these two types of measurements. Although the preparation of the solutions in both cases started from the same initial liquor compositions (i.e. NaOH concentrations), the reaction with metallic Al (to prepare a supersaturated $Al(OH)_4^-$ (aq) solution) consumed water so that the resulting synthetic liquor became more concentrated (TC ≈ 223 g L^{-1} Na$_2$CO$_3$, Experiments 210q–u), while during the solubility measurements, the dissolution of gibbsite diluted the liquor (on a molarity basis), leading to a TC of 191 g L^{-1} Na$_2$CO$_3$ (Experiments 210v&w). The resulting concentration differences for all liquor components were taken into account in solubility calculations with BAYER.EXE. Fig. 1 shows that the measured 'steady-state' aluminate concentrations agree very well with the calculated metastable solubility equilibrium with gibbsite.

The present results indicate that gibbsite not only precipitates on seed material containing gibbsite (between 2 and 20 % w/w) but also on pure boehmite seed, evidenced by a 'steady state' corresponding to metastable equilibrium with gibbsite.

This result might be explained by heterogeneous nucleation of gibbsite on boehmite surfaces at these relatively high supersaturations (A/TC $\approx$ 0.67). Precipitation kinetics of gibbsite on pure boehmite seed was slower than in the case of gibbsite-containing seed material (see above). In contrast, only boehmite precipitates on pure boehmite seed at lower supersaturation (A/TC $\approx$ 0.56).

4.2   Plant Liquors

Results of solubility and precipitation measurements of boehmite in plant liquors of TC = 210, 165 and 140 g L^{-1} Na_2CO_3 are shown in Figs. 4, 5 and 6 respectively.

Similar to synthetic liquors, at lower supersaturation (A/TC $\lesssim$ 0.56; experiments 210a–c, 165a&b and 140a–c), a metastable 'steady state' was not found and the stable equilibrium was not attained because of the slow precipitation kinetics. To perform solubility measurements (Experiments 210d, 165d and 140d), undersaturated plant liquors were prepared as described in Section 2.2. BAYER.EXE predictions overestimated boehmite solubilities in plant liquors to some extent.

At higher supersaturation (A/TC $\approx$ 0.67), the results for plant liquors (Fig. 4) are very similar to those obtained with synthetic liquors (Fig. 1). For all boehmite/gibbsite seed compositions, which were the same as for the synthetic liquors, metastable, 'steady-state' aluminate concentration of about twice the boehmite solubility were measured. The small 'gap' found between the 'steady-state' concentrations corresponding to gibbsite solubility and precipitation is due to different TC values, as discussed in Section 4.1. Both of these values agree well with BAYER.EXE predictions.

The main difference between plant and synthetic liquors concerns the onset and the duration of the 'steady-state' periods, both of which depended on the gibbsite content of the seed material. For pure gibbsite seed (Experiment 210m), the 'steady-state' aluminate concentration was attained after one day and lasted for two weeks, while for pure boehmite seed (Experiment 210h), these periods were five days and one day respectively (as compared to two days and more than a week, respectively, for synthetic liquors). The corresponding times for boehmite/gibbsite seed mixtures (Experiments 210j–l) fell in between these extremes. The dependence of the onset and duration of the 'steady-state' periods on the gibbsite content is more pronounced than for synthetic liquors and may indicate some 'mixed' kinetics due to the precipitation of both boehmite and gibbsite. The reason for this may lie in the presence of organic species in the plant liquors, some of which are known to retard gibbsite crystallisation while affecting boehmite precipitation kinetics to a much lesser extent (Baker and Greenaway, 1998; Loh et al., 2005).

The desupersaturation curves at high supersaturation were generally measured for three weeks, which is at least 2.5 times longer than in previous studies. At the end of the 'steady-state' periods, the liquor aluminate content decreased significantly, particularly when the seed contained boehmite. The resulting curves, which were very similar to those observed for boehmite precipitation at low supersaturation, approached boehmite solubilities. This is especially obvious for sample 210e (Fig. 4) which was followed for more than six weeks. It was considered unnecessary to measure the boehmite precipitation kinetics for longer periods of time since the results indicated that the recrystallisation of gibbsite to boehmite was essentially complete. Indeed, gibbsite was neither detected in a solid sample taken after 31 days from the run with a seed mixture of 80% boehmite and 20% gibbsite (Experiment 210e) nor in a solid sample obtained from the run with pure boehmite seed (Experiment 210h) after 10 days. After 4 months reaction time, the solids taken from plant liquors with boehmite in the seed material contained only traces of gibbsite or no gibbsite at all. However, the solids from both the dissolution (Experiment 210p) and precipitation (Experiment 210m) runs with pure gibbsite seed still contained significant amounts of gibbsite together with traces of boehmite.

4.3 Discussion of Previous Studies

As a consequence of the potential energy savings to the Bayer process as outlined above, the precipitation of boehmite from supersaturated sodium aluminate solutions has been studied by a number of workers at temperatures below 100 °C (Skoufadis et al., 2003; Loh et al., 2005; Dash et al., 2007; Dash et al., 2009; Wang et al., 2010). The 'steady-state' aluminate concentrations observed in this work are in accord with reports from the literature (Skoufadis et al., 2003; Loh et al., 2005).

Skoufadis et al. (2003) studied the precipitation kinetics of boehmite from synthetic liquors under conditions similar to the present measurements. These authors reported that 'steady-state' concentrations were ca. 1.7 to 1.9 times higher than boehmite solubilities. In fact, their kinetic data (Skoufadis et al., 2003), measured for only four days, look very similar to the first part of the upper curves in Figs. 1 and 4. It should be noted that these authors (Skoufadis et al., 2003) did not report the presence of gibbsite in their seed material. However, judging from published SEM images (Skoufadis et al., 2003), Loh et al. (2005) suspected that the 'boehmite' seed material used by Skoufadis et al. (2003) might have been contaminated with gibbsite.

Several authors studied the effect of initial supersaturation on the nature of the precipitates. Loh et al. (2005) and Dash et al. (2007, 2009) used boehmite seed material and found that with increasing supersaturation, brought about either through increasing aluminate concentrations or decreasing temperatures, gibbsite precipitation

was increasingly favoured. It should be noted that the latter authors (Dash et al., 2007, 2009) followed the precipitation reactions for only eight hours.

Loh et al. (2005) measured 'steady-state' aluminate concentrations which were ca. 2.3 times higher than boehmite solubilities. These authors found that the product obtained in their precipitation experiments, performed under conditions similar to those in this work (90 °C, A/TC = 0.70, pure boehmite seed with a seed charge of 11.5 g/50 mL), contained 16 % gibbsite after 24 hours. The increase of TC from 100 to 300 g L^{-1} Na$_2$CO$_3$ (at constant supersaturation and temperature) in boehmite-seeded experiments decreased the rate of boehmite precipitation but increased the gibbsite content of the product from 0 to 8 % (as estimated from XRD). Accordingly, SEM images showed gibbsite growth around boehmite particles. The final product after nine days contained 1 % gibbsite (Loh et al., 2005).

While at 150 °C gibbsite transforms to boehmite in caustic solution in ca. four hours (Gong et al., 2003), it appears that at temperatures below 100 °C, reported precipitation times of four (Skoufadis et al., 2003) and nine days (Loh et al., 2005) were too short for a complete recrystallisation of gibbsite to boehmite. Therefore, the end of the metastable 'steady-state' period and the corresponding drop in the aluminate concentration could not be observed (Loh et al., 2005; Skoufadis et al., 2003). Despite the experimentally confirmed occurrence of gibbsite in the boehmite precipitates (Loh et al., 2005; Skoufadis et al., 2003), it was not realised at that time that the measured 'steady-state' aluminate concentrations might have resulted from metastable solubility equilibria with gibbsite.

5   Conclusions

This study provides compelling evidence that the apparent 'steady-state' or pseudo-equilibrium concentrations observed during seeded boehmite precipitation from liquors of high initial supersaturation (A/TC ≈ 0.67) correspond to metastable solubility equilibria with gibbsite. There are indications that the boehmite seed used in some previous studies might have contained gibbsite crystals as an impurity, leading to seeded gibbsite precipitation. However, in our measurements with pure boehmite seed, gibbsite was also formed, probably through heterogeneous nucleation on boehmite. The metastable nature of the equilibria with gibbsite is consistent with its recrystallisation to boehmite, which in this study was found to be essentially complete after up to two weeks when the seed material contained boehmite. In earlier studies (Loh et al., 2005; Skoufadis et al., 2003), observation times were shorter. Thus, although the precipitation kinetics and the 'steady-state' concentrations were very similar to the initial part of our results, the end of the 'steady-state' periods could not be detected. Consequently, the link between the observed 'steady-state' aluminate

concentrations and metastable solubility equilibria with gibbsite was not recognised previously.

In contrast, this study found that only boehmite precipitated on pure boehmite seed at relatively low supersaturation (A/TC $\leq$ 0.56). The aluminate concentrations measured as a function of time decreased continuously and did not show metastable 'steady states'. Stable equilibrium, as confirmed by boehmite solubility measurements, was approached very slowly and not attained even after ten weeks. It can be concluded that high supersaturation and/or the presence of gibbsite seed crystals are required for the establishment of metastable 'steady states'.

Taken collectively, the present results suggest that the 'mystery' of the boehmite 'solubility gap', i.e. the reported occurrence of an apparent 'steady-state' aluminate concentration during the precipitation of 'boehmite' from Bayer liquors has been resolved. We have shown that initial precipitation of gibbsite leads to 'steady-state' aluminate concentration of about twice the boehmite solubility, in accordance with reports from the literature. The experimental 'steady-state' aluminate concentrations agreed well with the results of gibbsite solubility measurements obtained from undersaturation under essentially the same conditions. The reliability of the experimental data was corroborated by the good agreement with results calculated using our Bayer liquor model encapsulated in the BAYER.EXE software (Königsberger et al., 2005). All these results support the conclusion that the apparent 'steady-state' aluminate concentrations during boehmite precipitation correspond to metastable solubility equilibria with gibbsite.

Acknowledgements

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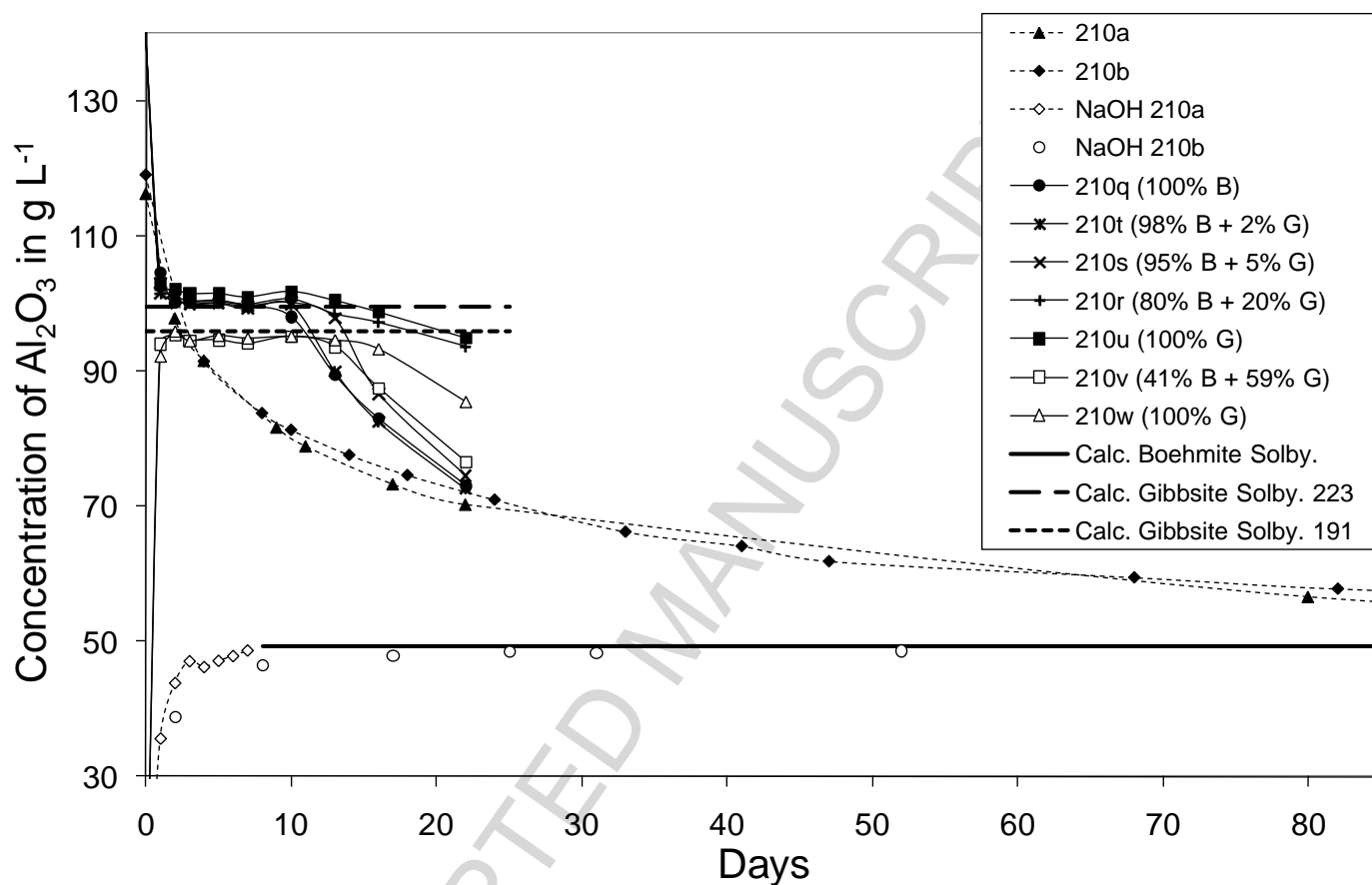
Fig. 1: *Synthetic liquor, TC = 210 g L^{-1} Na$_2$CO$_3$ at 95 °C. Thin dashed lines, low supersaturation (A/TC ≈ 0.56); thin solid lines, high supersaturation (A/TC ≈ 0.67). The lower case letters identify different experiments, whereas capital B and G stand for boehmite and gibbsite respectively.*
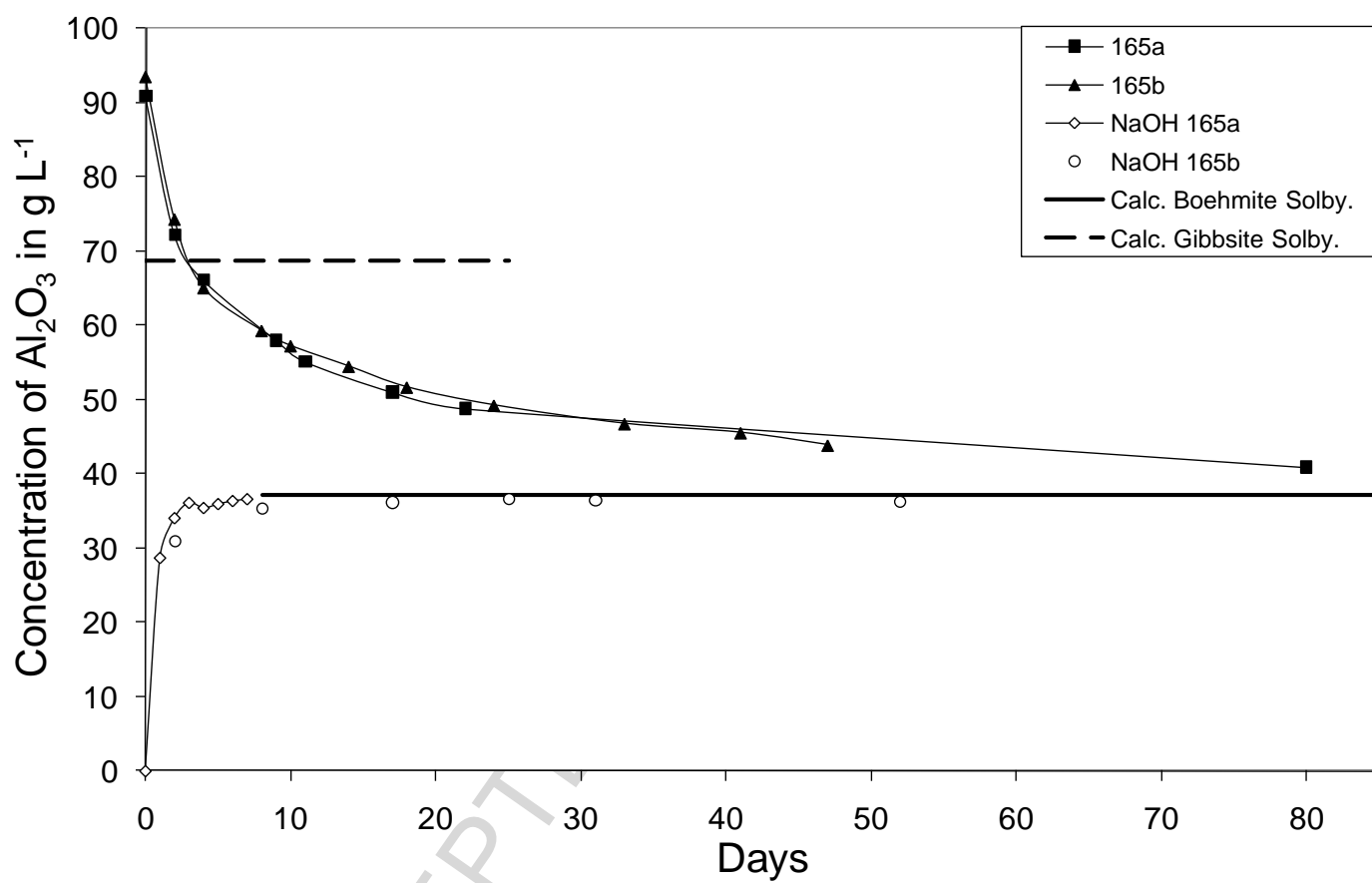
Fig. 2: *Synthetic liquor, TC = 165 g L^{-1} Na$_2$CO$_3$ at 95 °C and low supersaturation (A/TC ≈ 0.56).*
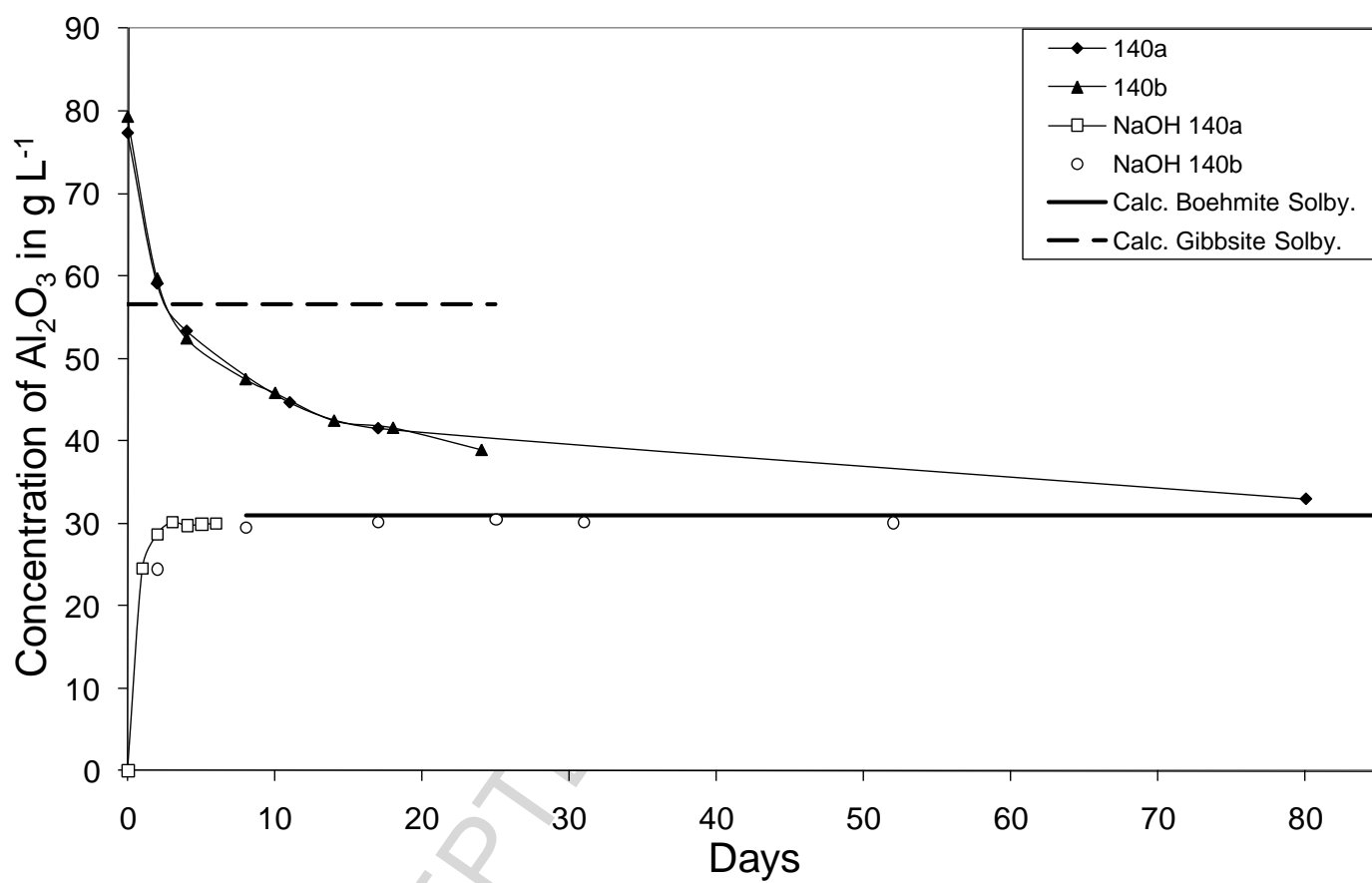
Fig. 3: *Synthetic liquor, TC = 140 g L^{-1} Na$_2$CO$_3$ at 95 °C and low supersaturation (A/TC $\approx$ 0.56).*
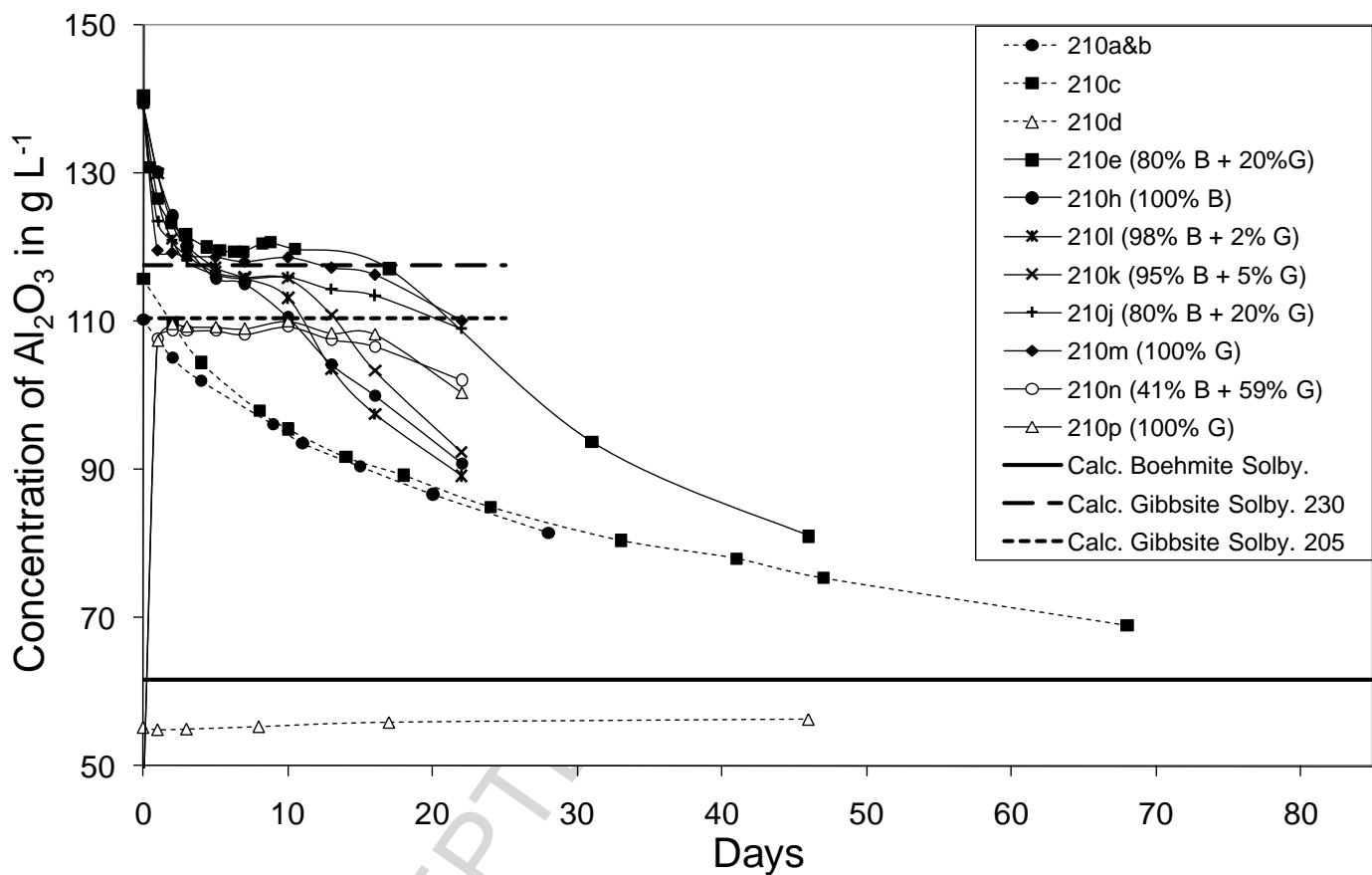
Fig. 4: *Plant liquor, TC = 210 g L^{-1} Na$_2$CO$_3$ at 95 °C. Thin dashed lines, low supersaturation (A/TC ≲ 0.56); thin solid lines, high supersaturation (A/TC ≈ 0.67). The lower case letters identify different experiments (210a&b combines data of 2 experiments), whereas capital B and G stand for boehmite and gibbsite respectively.*
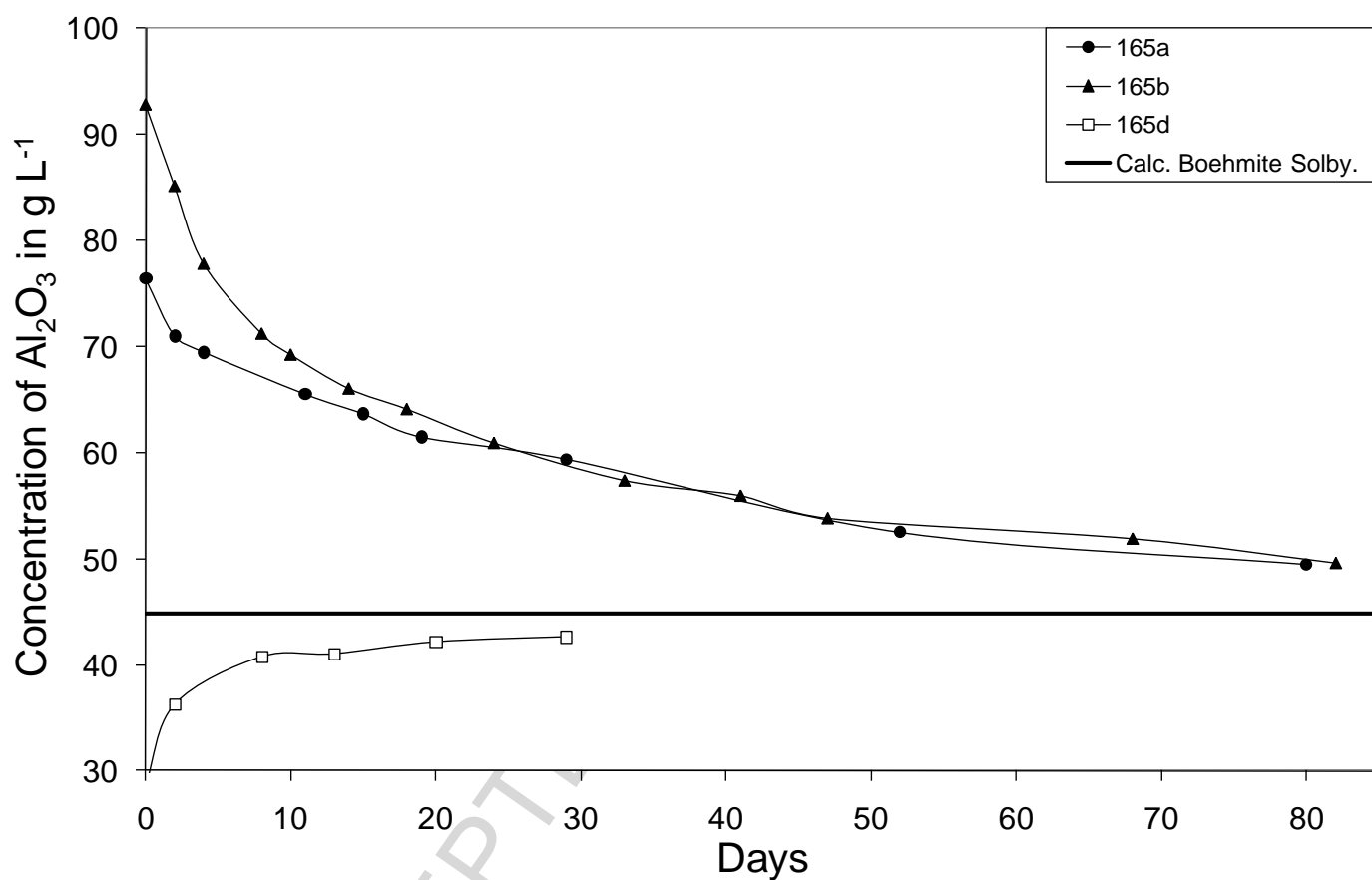
Fig. 5: *Plant liquor, TC = 165 g L^{-1} Na_2CO_3 at 95 °C and low supersaturation (A/TC ≲ 0.56).*
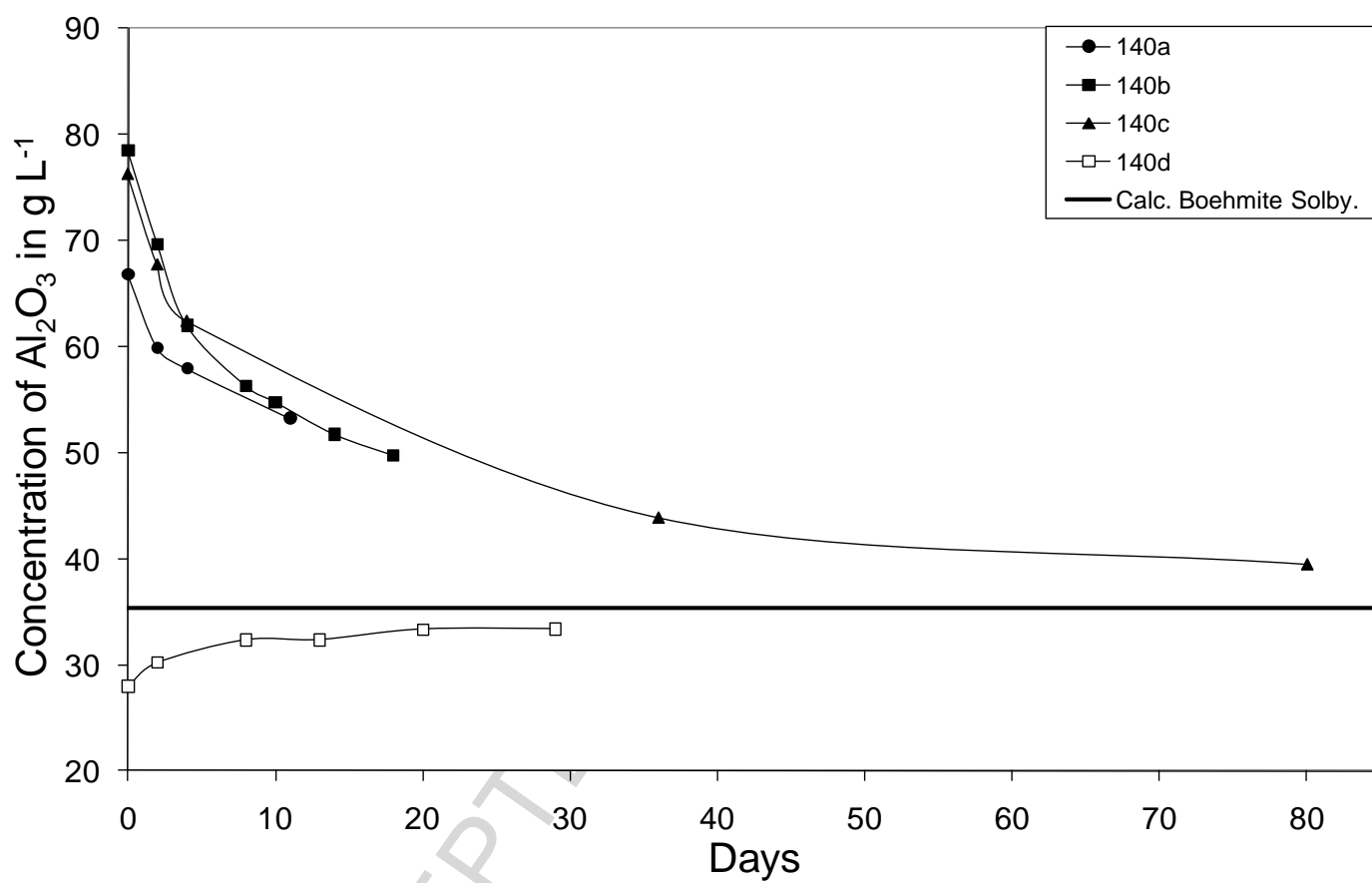
Fig. 6: *Plant liquor, TC = 140 g L^{-1} Na$_2$CO$_3$ at 95 °C and low supersaturation (A/TC ≲ 0.56).*

Highlights

- Boehmite precipitation from synthetic and plant Bayer liquors was studied at 95 °C.
- For high initial supersaturation, steady-state aluminate concentrations were found.
- These were identified as metastable equilibria with gibbsite that lasted 1−10 days.
- Aluminate approached boehmite solubility as gibbsite recrystallised to boehmite.
- For lower initial supersaturation, no metastable steady states were observed.