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# $LiAl_2(OH)_6OH.2H_2O$ solubility product and dihydrogen radiolytic production rate under γ-irradiation

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ABSTRACT

The solubility product of hydrated lithium aluminate $LiAl_2(OH)_6OH.2H_2O$ was measured at 25 °C, giving $\log(Ks) = -5.6 \pm 0.2$ for reaction $[LiAl_2(OH)_6]OH.2H_2O + OH^- = Li^+ + 2Al(OH)_4^- + 2H_2O$. Such value was approximately 20% higher than the only previously reported data, and improved markedly the thermodynamic simulation of aqueous systems comprising $Li^+$, $Al(OH)_4^-$ and $OH^-$ species. Moreover, the $LiAl_2(OH)_6OH.2H_2O$ apparent radiolytic hydrogen production yield was measured to be close to $0.08 \pm 0.02$ $10^{-7}$ mol $J^{-1}$. These new data relative to $LiAl_2(OH)_6OH.2H_2O$ mineral will be of great interest to (i) describe the acceleration of Calcium Sulfoaluminate Cement (CSA) hydration by lithium ions containing aqueous waste and (ii) to assess the radiolytic production rate of dihydrogen by CSA cement-based nuclear waste forms submitted to gamma irradiation.



## 1. Introduction

Calcium Sulfoaluminate (CSA) cements are of great interest to stabilize and solidify several hazardous wastes [1–6]. For example, they have a good potential for the conditioning of borate- [7] and lithium-containing [8] low- or intermediate-level radioactive (ILW) waste streams produced by the nuclear industry [9–11]. The retarding effect of borate anions on the hydration of CSA cement is reduced as compared with Portland cement and can be counteracted by the introduction of lithium ions that independently accelerate CSA cement hydration [12]. The underlying mechanism is still not fully elucidated and many hypotheses have been postulated to explain the acceleration by $Li^+$ ions [8].

When a CSA cement is mixed with a lithium-containing solution, Cau-dit-Coumes et al. [8,12] reported that the solution present in the pores is over-saturated from the beginning of hydration with respect to hydrated lithium aluminate $[LiAl_2(OH)_6]^+OH^-.2H_2O$, when using the sole solubility product value reported by Matsuo et al. [13]. As a consequence, it has been proposed that $LiAl_2(OH)_6OH.2H_2O$ precipitation during the course of hydration would play a role in the accelerating effect. However, despite the depletion of lithium ions from the pore solution, neither $LiAl_2(OH)_6OH.2H_2O$ nor any other lithium-containing crystalline phase has ever been identified by X-ray diffraction analysis with $Li^+$ concentrations lower than 50 mmoL/L in the mixing solution. It has thus been suggested that $LiAl_2(OH)_6OH.2H_2O$ precipitates in too small amounts to be detected or that a Li-containing hydroxide aluminum phase precipitates. The relevance of these hypotheses relies on the accuracy of the $LiAl_2(OH)_6OH.2H_2O$ solubility product value used for saturation index calculations, or on the existence of a Li-containing aluminum hydroxide compound different from the $LiAl_2(OH)_6OH.2H_2O$ mineral.

In the well described $LiAl_2(OH)_6OH.2H_2O$ Layered Double Hydroxide (LDH) compound [14–17], lithium ions are located in the vacant octahedral sites within the gibbsite-like $Al(OH)_3$ layers and contribute to the positive charge of the hydroxide layers. The layer charge is compensated by the incorporation of anions in the interlayer space, accompanied with water molecules, resulting in a general formula of $[LiAl_2(OH)_6]^+OH^-.xH_2O$. In fact, many interlayer hydroxide anions substitutions have been reported in literature [18–23]. Due to this structural versatility, these materials have been extensively used for many applications such as lithium extractor, catalysts, catalyst precursors for high surface area γ-$LiAlO_2$ elaboration, stabilizers in polymer composites, drug delivery materials or adsorbents for wastewater treatment [24,25]. Intercalation mechanisms of lithium salts into aluminum hydroxide $Al(OH)_3$, starting from gibbsite or bayerite polymorph, have been deeply studied [18,19,24,26–32] and the structures of the resulting

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compounds have been already well-described [17]. However, very few data are available on the solubility product of these materials. To our knowledge, only Matsuo et al. [13] reported a $LiAl_2(OH)_6OH.2H_2O$ solubility product of $K_s = 3{,}7.10^{-8}$ corresponding to reaction below.

$$[LiAl_2(OH)_6]OH.2H_2O + OH^- = Li^+ + 2Al(OH)_4^- + 2H_2O \qquad (1)$$

Finally, in the context of intermediate-level radioactive waste immobilization in a cementitious matrix, dihydrogen production by pore water and hydrates radiolysis is of critical interest for safety issues [33,34]. The radiolytic production rate of dihydrogen has to be assessed, which is made possible by knowing apparent hydrogen radiolytic yields $G(H_2)$ of each component of the matrix. However, no data is available for $LiAl_2(OH)_6OH.2H_2O$ hydrate which may occur in some cemented waste packages.

This work first aims at confirming the solubility product value of $LiAl_2(OH)_6OH.2H_2O$ provided by Matsuo et al. at 25 °C [13]. The second objective is to determine the radiolytic production rate of dihydrogen when $LiAl_2(OH)_6OH.2H_2O$ is submitted to external $\gamma$-irradiation. The consequence of LiOH and water intercalation in the gibbsite structure on the dihydrogen production rate is finally briefly discussed.

## 2. Materials and methods

### 2.1. Elaboration and characterization

Gibbsite (CAS n°21645-51-2, Sigma-Aldrich) was suspended into mixed lithium and sodium hydroxide solutions using a liquid/solid weight ratio of 40. Mixed lithium and sodium hydroxide solutions were prepared by dissolving lithium hydroxide and sodium hydroxide into decarbonated and deionized water. The lithium concentration increased from 0 to 500 mmoL/L whereas the sodium concentration decreased from 500 to 0 mmoL/L (Table 1). The initial total hydroxide concentration remained constant and equal to 500 mmoL/L in all runs. These concentrations and liquid over solid ratios made it possible to reach thermodynamic equilibrium within 9 months of experiment. Solutions and suspensions were prepared and sealed in a $CO_2$-free atmosphere to prevent the reacting medium from carbonation. During the whole set of experiments, suspensions were stored in a thermostatically controlled room at 25 °C.

Powder X-Ray Diffraction (PXRD) analyses were carried out on suspensions to avoid any drying of the samples. Each suspension was introduced in a capillary (diameter = 1 mm) after 7, 25, 180 and 270 days of stirring at 25 °C, and then flame-sealed. X-ray diffraction data were collected by using the X'pert pro diffractometer from Panalytical equipped with copper radiation ($\lambda = 1.5418$ Å) and by adopting the Debye Scherrer geometry (transmission mode). PXRD patterns were collected in the angular range $2\theta = 5–120°$ with a total counting time of 7 h per sample. Rietveld refinement was not possible because of the presence of a stacking fault in the $LiAl_2(OH)_6OH.2H_2O$ structure [17]. Therefore only Le-Bail refinement using Fullprof_Suite program was performed in order to follow the evolution of the unit cell parameters during the sorption experiments (Table 2).

Simultaneously, suspensions were filtered using cellulose membrane (0.45 µm pore size) after 7, 25, 180 and 270 days of stirring at 25 °C and liquid fractions were collected. The pH values of the supernatants were immediately measured using a high-alkalinity electrode (Mettler Toledo InLab Expert Pt1000 pH 0–14 T 0–100 °C) calibrated using two IUPAC pH buffers at pH 10.01 ± 0.01 (25 °C) and 12.40 ± 0.05 (25 °C). The chemical composition of solutions was determined using ICP-AES (Vista Pro Varian). The analytical errors were equal to ±5%. Solid fractions were rinsed 2 times by using isopropanol, dried in a controlled humidity chamber at 20 °C and 20% RH then collected prior the analysis. Solid fractions were characterized by thermogravimetric analysis using a TGA/DSC Netzsch STA 409 PC apparatus in nitrogen atmosphere with a heating rate of 10 °C/min up to 1000 °C.

### 2.2. $\gamma$-irradiation and gas analysis

Dried solid fractions collected after 270 days of experiment were $\gamma$-irradiated by using a $^{60}Co$ source experimental irradiator available

**Table 2**
Unit cell volume obtained by Le Bail calculations and apparent hydrogen radiolytic yield of the mineral fraction suspended during 270 days at 25 °C as a function of the initial lithium concentration (Li-Al-OH stands for $LiAl_2(OH)_6OH.2H_2O$).

| $t_{initial}$ | | Unit cell Volume (Å$^3$) | | G(H2) ( $\times 10^{-7}$ moL/J) | |
|---|---|---|---|---|---|
| [LiOH] | [NaOH] | Gibbsite | Li-Al-OH | Dose = 2.5 MGy | Dose = 5.0 MGy |
| 0 | 500 | – | – | 0.001 | 0.001 |
| 25 | 475 | 426.92 (1) | 338.62 (4) | 0.001 | 0.001 |
| 50 | 450 | 427.06 (1) | 338.62 (3) | 0.002 | 0.066 |
| 75 | 425 | 427.25 (2) | 339.67 (3) | 0.065 | – |
| 100 | 400 | 427.58 (2) | – | 0.074 | 0.016 |
| 125 | 375 | – | 339.90 (1) | 0.081 | 0.036 |
| 150 | 350 | – | – | – | 0.06 |
| 200 | 300 | – | 339.45 (1) | 0.1 | 0.049 |
| 250 | 250 | – | 339.68 (1) | 0.104 | 0.073 |
| 400 | 125 | – | 339.66 (1) | 0.113 | 0.087 |
| 500 | 0 | – | 339.70 (1) | 0.096 | 0.076 |

**Table 1**
Measured aqueous fraction compositions and corresponding calculated activity product (equation (9)) as a function of initial lithium ions concentration after 180 and 270 days of stirring at 25 °C – Concentrations are indicated between brackets and are expressed in mmol/L, Ionic strength I in mmol/L, normalized electrical imbalance N.E.I. in % and pH and $\log(K_s)$ are unit less.

| $t_{initial}$ | | t = 180 days | | | | | | t = 270 days | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [LiOH] | [NaOH] | $[Li^+]_{aq}$ | $[Al(OH)_4]_{aq}$ | pH(±0.1) | I(mol/L) | $\log(k_s)$ | N.>E.I.(%) | $[Li^+]_{aq}$ | $[Al(OH)_4]_{aq}$ | pH(±0.1) | L | $\log(k_s)$ | N.>E.I.(%) |
| 0 | 500 | <LD | 36 | 13.4 | 400 | – | 15 | <LD | 36 | 13.5 | 412 | – | 6 |
| 25 | 475 | <LD | 33 | 13.5 | 395 | – | 7 | <LD | 34 | 13.6 | 432 | – | 0 |
| 50 | 450 | <LD | 33 | 13.4 | 376 | – | 6 | 2.1 | 33 | 13.5 | 397 | −5.7 | −3 |
| 75 | 425 | 2.0 | 30 | 13.4 | 357 | −5.7 | 8 | 2.5 | 31 | 135−.5 | 387 | −5.6 | −11 |
| 100 | 400 | 3.0 | 28 | 13.4 | 338 | −5.5 | 7 | 2.4 | 30 | 13.4 | 342 | −5.6 | 7 |
| 125 | 375 | 5.6 | 25 | 13.4 | 323 | −5.3 | 6 | 2.3 | 27 | 13.4 | 334 | −5.7 | −4 |
| 150 | 350 | 5.5 | 21 | 13.4 | 303 | −5.4 | 5 | 1.9 | 17 | 13.4 | 307 | −6.1 | −1 |
| 200 | 300 | 35 | 8.2 | 13.3 | 274 | −5.4 | 12 | *41* | *7.7* | *13.3* | *263* | *−5.3* | *30* |
| 250 | 250 | 90 | 5.2 | 13.2 | 250 | −5.2 | 39 | *90* | *4.9* | *13.1* | *231* | *−5.2* | *69* |
| 400 | 125 | 235 | 3.7 | *13.0* | 233 | −4.9 | 77 | *236* | *3.4* | *12.8* | *213* | *−4.7* | *120* |
| 500 | 0 | 386 | 2.9 | *12.8* | 228 | −4.7 | 113 | *333* | *2.9* | *12.4* | *182* | *−4.4* | *153* |