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Hydration of γ -Alumina in Water and Its Effects on Surface Reactivity

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The stability of γ -alumina suspensions in water has been investigated by long-duration experiments (1 day to 6 months). Several complementary methods were used to characterize the solid (acid–base titration and dissolution rate measurements, X-ray photoelectron spectroscopy, X-ray diffraction, gravimetric/differential thermal analysis, infrared spectroscopy, and scanning electron microscopy). It appears that γ -alumina, which is widely used as a model oxide in sorption experiments, thanks mainly to its high specific surface area and to the presence of aluminol groups on its surface, is progressively transformed to bayerite (β -Al(OH)₃). This transformation was characterized by an induction period of about 4 days, corresponding to the formation of a transient amorphous hydrated phase, followed by an increase in the bayerite concentration, which levels off after about 2 months. This transformation results in a dramatic decrease in the surface density of sites reactive to protons. Thermodynamical calculations predict the hydration reaction of γ -alumina leading to a more stable phase (bayerite, gibbsite, or boehmite). Since the surface reactivity and sorption properties of solids are factors controlling the transport of elements in water, it is necessary to take into account the stability of solids when modeling sorption experiments. These factors are important for the long-term prediction of the effectiveness of barriers placed around radioactive waste depositories.

1. Introduction

The surface properties and sorption behavior of metal oxides in aqueous media have been the subject of many investigations during recent years because they play an important role in the transport of ions in the environment, in such fields as geochemistry, oceanography, and pollution control.¹ Quantitative sorption data and modeling are necessary to predict the migration behavior of solute species. Several types of surface complexation models have been developed (1-pK, 2-pK, multisite complexation model, etc.) in order to calculate the thermodynamic equilibrium constants of the complexes formed between surface functional groups and adsorbed ions.^{1–4} They describe in different ways the acid–base reactions between surface groups and H⁺/OH[−] ions in solution. All models assume that an equilibrium is achieved at the oxide/water (or electrolyte) interface, which usually means that the hydroxylation of the surface by dissociative adsorption of water molecules is complete. This is the main reason for the “hydration” procedure, which is applied to oxides after synthesis at high temperatures (γ -alumina or cuprous oxide for example) or after fracture (quartz).⁵ The first step in this procedure is often washing with a base or an

acid,^{6,7} which speeds up hydration compared to an equilibration in a neutral medium.⁸ Without this washing, reproducible titration curves with γ -alumina suspensions are not obtained for up to one or several weeks.^{9,10} If the origin of this slow equilibration is the gradual hydroxylation of the alumina surface, the site density should increase with time until a constant value is reached. To our knowledge, there are no published data concerning such an evolution on γ -alumina in water. Another surprising fact is the assumed high stability of γ -alumina in suspension, since most of the articles dealing with the sorption properties of this oxide^{6,7,11} do not mention the possibility of transformations leading to oxo-hydroxide (AlOOH) or trihydroxide (Al(OH)₃). However, the presence of bayerite (β -Al(OH)₃) has been detected in 4-month-aged suspensions of γ -Al₂O₃ by Raman spectroscopy and X-ray diffraction¹² and in suspensions aged for 4–5 weeks by Fourier transform infrared (FTIR) spectroscopy.^{10,13} From these results, it is suspected that the change in the surface properties of γ -alumina during the hydration procedure is explained not only by the superficial hydroxylation but

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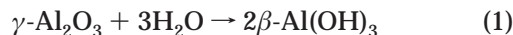
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also, or even essentially, by the formation of a new phase according to a reaction such as



Several studies^{10,12,13} have shown that this reaction leads to the formation of detectable amounts of bayerite after a few weeks, but the kinetics of this reaction and its consequences on the surface properties have not been thoroughly studied. Moreover, the location of the bayerite is not discussed, except in one case in which the alumina surface is assumed to be fully covered by an overlayer of bayerite.¹⁰ This remains an important question since the effect of bayerite formation on surface reactivity of γ -alumina might be negligible if the bayerite were to grow as isolated crystallites with a low total surface area.

In the present work, we have performed a detailed study of the process of hydration of γ -alumina and its influence on the reactivity of this oxide in water. Several complementary methods, including X-ray diffraction (XRD), electron microscopy, thermal analysis, infrared spectroscopy, photoelectron spectroscopy, and acid–base titration, have been used to characterize thoroughly the bulk and the surface of the samples. Through this approach, it was possible to define, to our knowledge for the first time, the kinetics of the evolution of the surface of γ -alumina in water and its reactivity.

2. Experimental Section

2.1. Chemicals and Solutions. γ -Alumina was manufactured by Merck (aluminum oxide standardized 90). Its crystal structure was checked by XRD, and a coherence length of ca. 3 nm was calculated with the Scherrer formula. Scanning electron microscopy showed that crystallites are agglomerated into particles of ca. $100 \pm 60 \mu\text{m}$ with cracks (Figure 4a). The specific surface area (Brunauer–Emmett–Teller (BET) method with N_2 adsorption) is $150 \text{ m}^2 \text{ g}^{-1}$. The fitting of sorption and desorption isotherms by t -plot excludes the presence of micropores ($<2 \text{ nm}$). Barrett–Joyner–Halenda (BJH) fitting indicates the presence of mesopores (60% of pore volume for pore diameters less than 6 nm and 10% between 20 and 80 nm). The measured surface area results essentially from the presence of mesopores. This result is in agreement with previous measurements which showed the presence of mesopores (ca. 4 nm) in transition alumina.¹⁴

Bayerite ($\beta\text{-Al}(\text{OH})_3$), used as a reference, was synthesized by precipitation from an aluminate solution with nitric acid at constant pH.¹⁵

Other substances used were HNO_3 and 0.1 M NaOH (Normadose, Prolabo), sodium nitrate p.a. (Prolabo), and deionized water (conductivity $> 16 \text{ M}\Omega$).

2.2. Hydration Procedure. Batches of 100 mg of alumina were stirred in 50 mL of 0.1 M NaNO_3 at 25°C for durations ranging from 1 day to 6 months.

2.3. Measurement of Solid Reactivity. The potentiometric titrations were performed using a Metrohm automatic system monitored by homemade software, with a combined Ag/AgCl–glass electrode (Metrohm) calibrated with disposable standard buffer solutions (Centipur, Merck). The test solution vessel was immersed in a water bath thermostated at $25.0 \pm 0.1^\circ\text{C}$ with a continuous flow of argon to prevent CO_2 uptake. All titrations were carried out in the presence of 0.1 M NaNO_3 as background electrolyte. The speed of the titrant addition (i.e., added quantity and equilibration time before reading) was gradually increased during the titration experiment from $0.1 \mu\text{mol min}^{-1}$ (pH of the suspension between 4.6 and 9.5) to $1 \mu\text{mol min}^{-1}$ ($\text{pH} < 3.5$ or $\text{pH} > 11$), since the stabilization of the potential measured by the glass electrode was faster for pH values far from the neutral range. This kinetics is probably related to diffusion in the mesopores. The same apparatus was used for dissolution

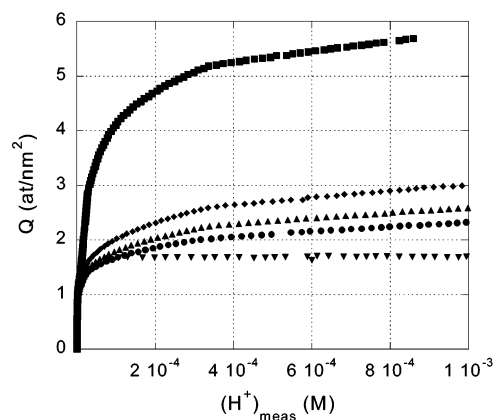


Figure 1. Adsorption measurements of protons on $\gamma\text{-Al}_2\text{O}_3$ by titration with nitric acid after various hydration times: 1 day (■), 8 days (◆), 15 days (▲), 1 month (●), and 6 months (▼). Variation of the surface charge Q expressed in sites per nm^2 , as a function of measured H^+ concentration in solution.

experiments at constant pH, in which the volume of nitric acid required to compensate the protons used up by alumina dissolution was recorded as a function of time.

2.4. Solid Characterizations. For solid characterization, the suspensions were filtered by $0.2 \mu\text{m}$ porosity membranes and the powders were dried in a desiccator in the presence of silica gel.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were simultaneously performed, using a Netsch STA409 apparatus. The heating speed was 5 K/min . X-ray diffractograms were recorded using $\text{Co K}\alpha$ radiation. Surface areas and pore distributions were determined by nitrogen adsorption and desorption, with a Coulter SA3100 area analyzer, after degassing for 12 h at 120°C . For high-resolution scanning electron microscopy (SEM), using a Leo DSM 982 Gemini instrument, the powders were deposited on a carbon ribbon and metallized with Pt/Pd. Infrared spectroscopy was carried out on a paste made by a mixture of the powder with “Fluorolube”, between two CaF_2 windows with a Perkin-Elmer 1720 spectrometer monitored by the Spectrum V2.00 software.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG CLAM2 analyzer with an unmonochromated aluminum X-ray source (Al $\text{K}\alpha$, 1486.6 eV). The samples were fixed on aluminum plates with silver lacquer. Peaks from silver and carbon were superimposed on the sample spectra, but the silver lacquer did not generate any oxygen peak. Curve fitting and decomposition were achieved assuming Gaussian peaks following Shirley background subtraction. Atomic concentrations were calculated from the peak areas using photoemission cross sections from Scofield.¹⁶

3. Results

3.1. Reactivity of γ -Alumina Suspensions. At the origin of this study was the observation of nonreproducible titration curves of γ -alumina. It seemed that the curves obtained depend on the duration of preliminary hydration time. We therefore decided to study systematically the influence of this factor.

γ -Alumina suspensions, which were hydrated for different times, were titrated by an acid or a base starting from the natural pH (ca. 7.8 whatever the hydration time). Varying of the hydration time results in a modification of the titration curves. The most striking effect is the decrease in site density deduced from the surface charge achieved for the highest or the lowest values of pH (saturation curves). As an example, acid saturation curves are shown in Figure 1 for several hydration times.

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The alkaline side (not shown) presents the same features. The surface charge is obtained from the titration curves, which represent the concentration of protons which have reacted with the surface ($[H^+]_{\text{react}}$) as a function of the actual proton concentration in solution ($[H^+]_{\text{meas}}$), after deduction of the “blank”, corresponding to the protons consumed in a solution without any suspension. In the 2-pK model, this value is equivalent to the MOH_2^+ concentration in the solid, since the MO^- concentration can be neglected in the most acidic pH region, the surface charge Q being calculated according to the following relation:

$$Q \approx [\text{MOH}_2^+] = [H^+]_{\text{react}} = [H^+]_{\text{tot}} - [H^+]_{\text{meas}} \quad (2)$$

where $[H^+]_{\text{tot}}$ is the proton concentration added during the titration, after deduction of the blank.

If $[H^+]_{\text{react}}$ reaches a plateau, all the MOH groups are assumed to be protonated and the limiting value corresponds to the site density. In the case of γ -alumina, the pH required for reaching a plateau is outside the stability range of the solid, and some protons are consumed by $\gamma\text{-Al}_2\text{O}_3$ dissolution. This is the reason for the constant increase in $[H^+]_{\text{meas}}$ above 4×10^{-4} M. A correction based on the consumption rate of protons involved in the dissolution of the solid has been applied, leading to a plateau at a value around 10% lower than the value measured at 4×10^{-4} M. Even without an accurate saturation value, it can be seen from Figure 1 that the site density decreases dramatically with the increase of hydration time.

To confirm the decrease in the reactivity, dissolution experiments at constant pH were performed. The volume of decimolar nitric acid added to maintain a pH value of 3.00 ± 0.01 in a γ -alumina suspension was plotted versus time (Figure 2A).

The first part of the curves corresponds to the fast decrease of the solution pH from ca. 7.8 to 3 (i.e., 0.60 mL considering an activity coefficient of 0.83 according to the Debye–Huckel equation) and to the quantity of acid required for the protonation of MOH surface groups. The speed of the latter reaction is limited by the diffusion process in the porous particles of γ -alumina, and its completion might require a time as long as 1 h, according to measurements of the dissolved amounts of aluminum. Once the proton consumption by these reactions becomes negligible, the slope of the curves corresponds to the dissolution rate. This value was calculated at $t = 2$ h, and the results are plotted in Figure 2B. This time was chosen since it was close to the duration of the titration experiments described above. It can be seen that the dissolution rate decreases for increasing hydration times. Both dissolution and protonation reactions are surface phenomena, and previous measurements¹⁷ already assumed that the dissolution rate depends on the site density.

3.2. Characterization of Hydration Products. The results presented above lead to the surprising conclusion that the surface reactivity decreases for increasing hydration time. Thus, the phenomenon which takes place during this step is not a simple hydroxylation (i.e., transformation of Al–O–Al bridges into Al–OH groups) of the anhydrous oxide surface. To help to understand the real behavior of $\gamma\text{-Al}_2\text{O}_3$ in water, its stability can be calculated from the thermodynamic constants of some chosen aluminum oxy-hydroxides (Table 1). Nordstrandite ($\gamma\text{-Al}(\text{OH})_3$) was not considered, due to its scarcer occur-

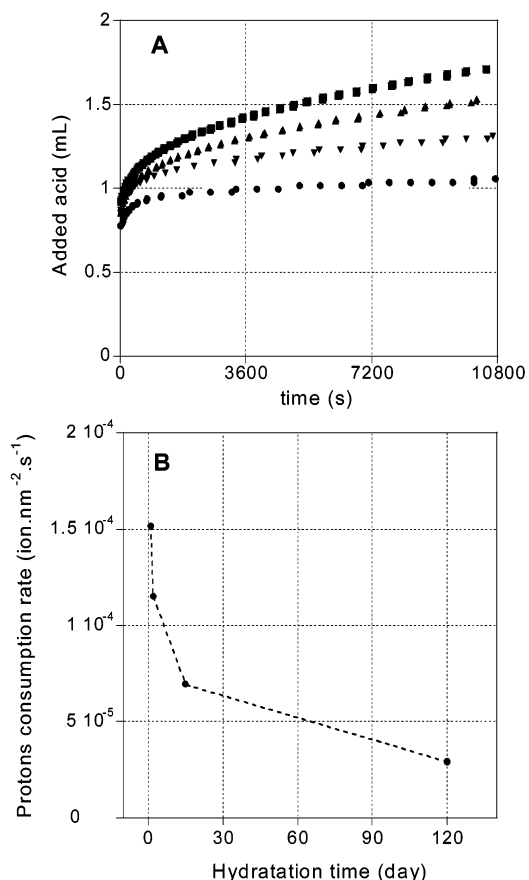


Figure 2. Dissolution experiment of $\gamma\text{-Al}_2\text{O}_3$ after various hydration times: 1 day (■), 2 days (▲), 15 days (▼), and 4 months (●): (A) volume of added acid to maintain pH at 3.00 ± 0.01 versus time and (B) dissolution rate measured at $t = 2$ h from the above curves.

Table 1. Thermodynamic Constants Used in Calculation

| species | paramineralogical name | ΔG_{298K} (kJ/mol) | reference |
|---|------------------------|-------------------------------|-----------|
| $\gamma\text{-Al}_2\text{O}_3(\text{s})$ | γ -alumina | −1564.2 | 18 |
| $\gamma\text{-AlOOH}(\text{s})$ | boehmite | −917.8 | 19 |
| $\beta\text{-Al}(\text{OH})_3(\text{s})$ | bayerite | −1149.8 | 19 |
| $\alpha\text{-Al}(\text{OH})_3(\text{s})$ | gibbsite | −1154.9 | 19 |
| $\text{H}_2\text{O}(\text{g})$ | | −228.6 | 20 |
| $\text{H}_2\text{O}(\text{l})$ | | −237.1 | 20 |

rence. The calculated free energies of hydration reactions of γ -alumina in water leading to the formation of bayerite, gibbsite, and boehmite are listed in Table 2. In previous works,^{10,12,13} bayerite and boehmite were identified in aged $\gamma\text{-Al}_2\text{O}_3$ suspensions. These observations are consistent with the negative free energies found for reactions leading to these products. Gibbsite was not identified in aged suspensions, whereas its formation is possible according to the thermodynamical results. This fact can be explained by the formation of the kinetic $\text{Al}(\text{OH})_3$ polymorph, as observed in the precipitation of bayerite from aluminate solutions^{21,22} or in the aging of amorphous alumina gels.²³ Another aluminum oxy-hydroxide, pseudoboehmite, is not

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Table 2. Thermodynamics of Hydration Reactions of γ -Alumina

| reaction | $\Delta G_{R,298K}$ (kJ/mol) | threshold water vapor pressure for hydration (Torr) |
|---|---------------------------------|--|
| $1/3 \gamma\text{-Al}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) = 2/3 \beta\text{-Al}(\text{OH})_3(\text{s})$ | -16.5 | 0.97 |
| $1/3 \gamma\text{-Al}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) = 2/3 \beta\text{-Al}(\text{OH})_3(\text{s})$ | -8.0 | |
| $1/3 \gamma\text{-Al}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) = 2/3 \alpha\text{-Al}(\text{OH})_3(\text{s})$ | -19.9 | 0.24 |
| $1/3 \gamma\text{-Al}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) = 2/3 \alpha\text{-Al}(\text{OH})_3(\text{s})$ | -11.4 | |
| $\gamma\text{-Al}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) = 2 \gamma\text{-AlOOH}(\text{s})$ | -42.8 | 2×10^{-5} |
| $\gamma\text{-Al}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) = 2 \gamma\text{-AlOOH}(\text{s})$ | -34.3 | |

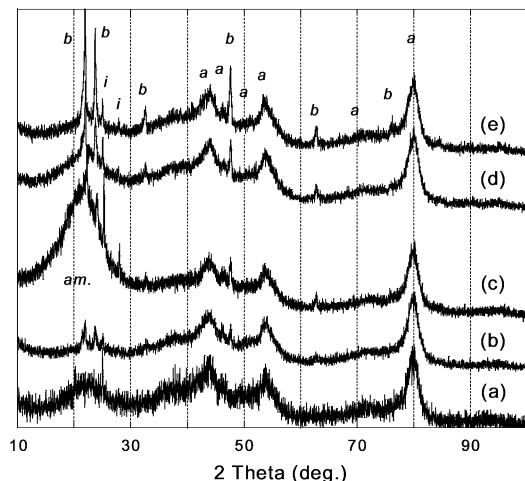


Figure 3. X-ray diffractograms of γ -alumina (a) as received and after various hydration times: (b) 4 days, (c) 10 days, (d) 16 days, and (e) 4 months. γ -Alumina (JCPDS 04-0880), bayerite (JCPDS 20-11), impurity, and amorphous phase are denoted as a, b, i, and am, respectively. Intensities of diffractograms were normalized against the strongest γ -alumina peak (located at ca. 80°).

considered in our calculations due to the lack of thermodynamical data. It was not observed in aged $\gamma\text{-Al}_2\text{O}_3$ suspensions, but its amorphous structure makes it difficult to identify and its formation cannot be excluded. The same calculations were carried out with gaseous H_2O , yielding a figure for the threshold water vapor pressure for the hydration of $\gamma\text{-Al}_2\text{O}_3$. This value is less than 1 Torr for the three oxy-hydroxides, which means that these hydration reactions could take place in ambient atmosphere, since the water pressure is 23.6 Torr for a relative humidity of 100% at 298 K.²⁰

3.2.1. XRD Analysis. To identify the products formed by the hydration process, X-ray diffractograms of samples after various times were recorded (Figure 3). For the as-received oxide, the diffractogram is consistent with γ -alumina and the large width of the peaks is explained by small mean crystallite dimensions. A narrow peak at ca. 25° (2θ) corresponds to an impurity coming from the sample conditioning for XRD. The diffractograms of three powders, hydrated for 4 days, 16 days, and 6 months, present the same general features, but several narrow peaks are superimposed. All these peaks correspond to reticular distances consistent with bayerite. Another interesting feature is the evolution of the diffractograms in the $15\text{--}25^\circ$ range. This region is characterized by a broad line which may be interpreted by the presence of an amorphous phase. This line is present in the initial γ -alumina. Its intensity is lower at approximately 4 days of hydration and then increases for the 16-day-hydrated

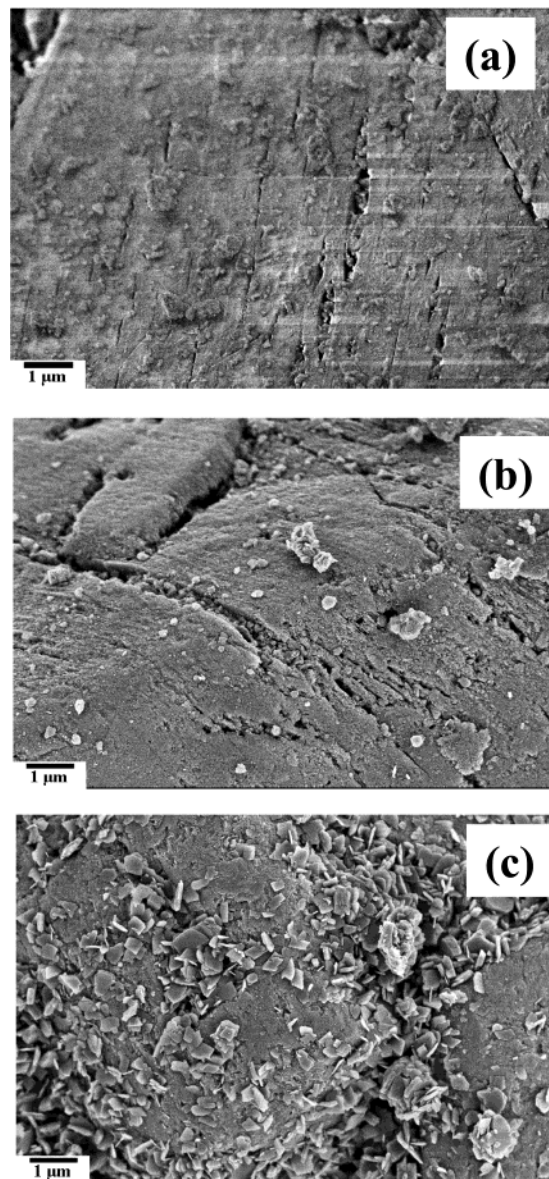


Figure 4. Scanning electron micrographs of γ -alumina (a) as received and after hydration during (b) 2 weeks and (c) 6 months.

sample, and finally, after 6 months its intensity is smaller than in the initial sample. Thus, a transient amorphous phase is present during a certain period of time, whereas a bayerite phase is seen by 4 days of hydration.

3.2.2. SEM Observations. The location of these new phases is an important question, since a total coverage of γ -alumina by bayerite would dramatically change the surface properties of the solid, whereas the formation of large bayerite particles with low surface area would have a lesser effect. SEM observations were therefore carried out on initial and hydrated samples (Figure 4). Scanning electron micrographs of as received γ -alumina show a flat surface with parallel slits. After a 2-week hydration, the

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Table 3. Results of XPS Analysis of Alumina and Bayerite

| sample | γ -Al ₂ O ₃ as received | γ -Al ₂ O ₃ after 15 days hydration | γ -Al ₂ O ₃ after 6 months hydration | bayerite |
|---|---|--|---|----------|
| O1s fwhm | 3.03 | 2.65 | 2.58 | 2.62 |
| O1s binding energy | 531.1 | 531.4 | 531.2 | 531.4 |
| Al2p fwhm | 2.42 | 2.32 | 2.44 | 2.24 |
| Al2p binding energy | 74.0 | 74.1 | 73.8 | 73.8 |
| O1s/Al2p ratio after correction by Scofield factors | 1.7 | 2.1 | 2.1 | 2.6 |

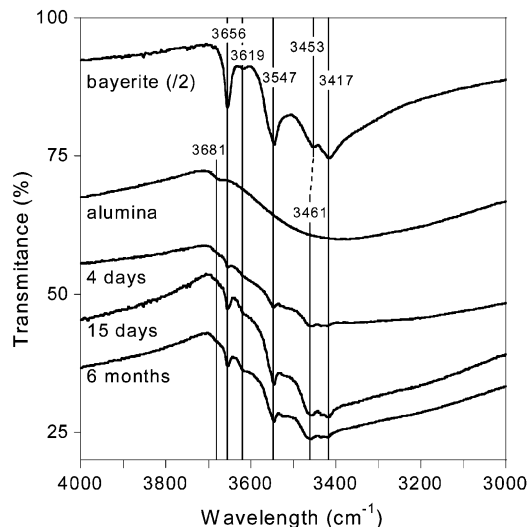


Figure 5. IR spectra of γ -alumina as received and after various hydration times and of synthetic bayerite. For better clarity, the spectrum of the 15-day-hydrated sample was decreased by 10% and $(T_0 - T)$ of the bayerite spectrum was divided by 2.

surface appears unchanged. A clear difference is observed for 6-month-hydrated samples, on which 0.5 μm wide platelets cover most of the initial γ -alumina surface. Whereas this shape is slightly different from the bayerite somatoids obtained by precipitation of aluminate ions at basic pH,²⁴ it can be assumed that the neutral pH of the suspension (about 8.5) has led to a faster β -Al(OH)₃ crystal growth in the *a* and *b* directions. From the SEM pictures, it looks like bayerite is present only as large particles, whose formation could be explained by a dissolution–precipitation mechanism, consistent with the disappearance of the amorphous phase in X-ray diffractograms (Figure 3).

3.2.3. Infrared Spectroscopy. The 3000–4000 cm^{-1} range (hydroxyl vibrations) of the infrared spectra of γ -alumina samples and bayerite is shown in Figure 5. As received γ -alumina presents only a broad line at 3681 cm^{-1} , attributed to H-bonded groups.²⁵ Five new lines appear for hydrated samples (Figure 5b–d) at 3656, 3619 (weak), 3547, 3461, and 3417 cm^{-1} . All these lines correspond to bayerite spectra²¹ (Figure 5e), but special attention has to be paid to the 3461 cm^{-1} line. This line is detected in our hydrated samples and was reported in synthetic bayerite.²¹ In our synthetic bayerite sample, it is replaced by a line at 3453 cm^{-1} . This shift could be explained by the presence of sorbed species (Na^+ , HCO_3^- , NO_3^- , etc.), since from analysis of bayerite samples with different specific surface area, Phambu²¹ has concluded that the line at 3461 cm^{-1} can be attributed to surface hydroxyl groups. The other lines would correspond to vibration of hydroxyl present in the bulk of the hydroxide.

The comparison of the intensity of the 3461 cm^{-1} line with that of the nearest band, that is, the 3417 cm^{-1} line, may yield some information about the specific surface area. Thus, the latter line is the stronger for synthetic bayerite²¹ with low specific surface area ($<5 \text{ m}^2/\text{g}$), whereas it is the weaker line for hydrated γ -alumina, indicating the formation of a high-area bayerite.

3.2.4. XPS Analysis. XPS results are listed in Table 3 for the three above-mentioned samples and for a synthetic bayerite. The calculated atomic O/Al ratio is 2.6 for the latter compound, lower than the theoretical value (3). As-received γ -alumina shows a lower ratio O/Al of 1.7, greater than the theoretical value (1.5). For both hydrated samples, an identical intermediate O/Al ratio (2.1) was found. These values indicate that the surface hydration of γ -alumina levels off after 2 weeks in suspension. The fwhm (full width at half-maximum) of the O1s peak is 2.6 eV for bayerite, consistent with previous studies,²⁶ and is attributed to the hydroxide groups. γ -Alumina shows a larger fwhm (3 eV). The fwhm's of O1s peaks of both hydrated samples are the same as for bayerite (2.6 eV), and it can be assumed that all the oxygen atoms at the surface of these samples belong to a bayerite-like phase (crystallized or amorphous). The broader O1s peak of as-received γ -alumina was decomposed into two contributions: a peak corresponding to a bayerite-like phase and an oxide phase. The fitting of the experimental curves was carried out with three fixed parameters: binding energy, fwhm of bayerite (531.3 and 2.6 eV, respectively), and a 2.2 eV fwhm for oxide. This latter value was chosen from previous studies on aluminum oxides.²⁷ The result of the decomposition is shown in Figure 6, along with O1s spectra of the 15-day-hydrated sample for comparison purposes. The best fit requires a contribution of the oxide phase of around 25% to the total peak area. To confirm that this broadening comes from the presence of the oxide phase, the Al2p spectra of as-received γ -alumina and a 15-day-hydrated sample were recorded (Figure 6). The Al2p fwhm of γ -alumina is only slightly higher (2.4) than the value found on hydrated samples (2.3 eV), indicating no significant broadening of the peaks in the as-received γ -alumina (such broadening is sometimes encountered with powdery samples in which each particle may get a different electrostatic charge during the measurement).

Thus, the oxide phase, initially present on the surface of γ -alumina, is no longer detected after 15 days in suspension. Considering the analysis depth of XPS (ca. 1–3 nm), this result indicates that the reactivity of the solid surface after 2 weeks in suspension is totally controlled by the hydroxide phase.

3.3. Quantification and Kinetics of the Hydration Reaction by DTA/TGA. **3.3.1. Analysis of Thermograms.** To quantify the hydrated phases for increasing hydration times, the samples were studied by DTA and

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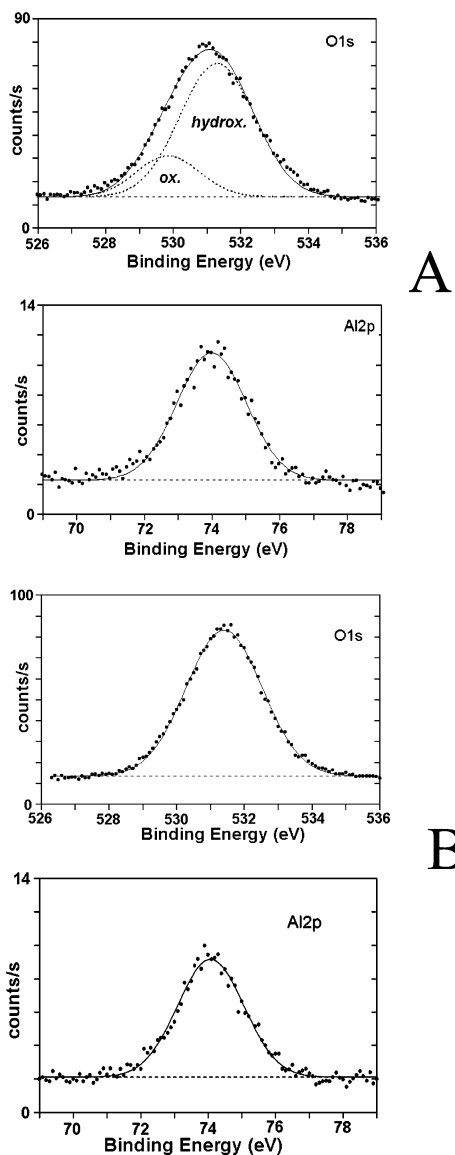


Figure 6. XPS spectra of γ -alumina (A) as received and (B) after a 15-day hydration time with contributions of oxide and hydroxide in the O1s peak of as-received γ -alumina denoted as ox and hydrox, respectively.

TGA (Figure 7). For pure bayerite, a single strong endothermic peak appears at 290 °C (Figure 7A), correlated with a large mass loss (Figure 7B). This temperature of dehydration is consistent with the 280–330 °C range quoted in the review by Alwitt.²⁴ The thermograms of hydrated γ -alumina (Figure 7A) present two endothermic peaks at about 100 and 260 °C (called peaks E₁ and E₂, respectively). For γ -alumina without hydration treatment, only peak E₁ is observed. The thermogram of γ -alumina after a 2-day hydration also presents peak E₁, but with an intensity 3 times higher. After an 8-day hydration, peak E₂ appears, and its intensity increases with increasing hydration time. Hydration has the opposite effect on peak E₁, whose intensity decreases between 2 days and 6 months of hydration, after an initial increase. Peak E₁, located at the boiling temperature of water, can be attributed to the desorption of physically adsorbed water.⁴ Peak E₂ is consistent with dehydration of bayerite formed in γ -alumina suspensions. The shift of the maximum intensity of the DTA peak from 290 °C for synthetic bayerite to 260 °C for alumina-supported bayerite could

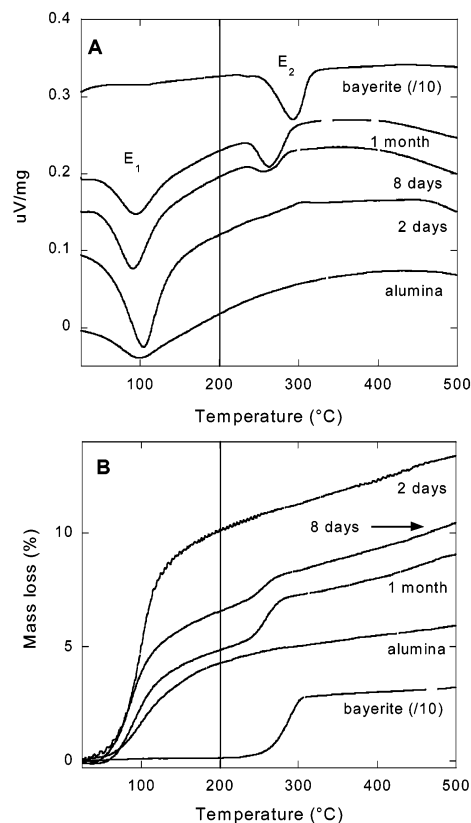


Figure 7. (A) Differential thermal analysis and (B) thermogravimetric analysis of γ -alumina as received and after various hydration times and of bayerite. DTA and TGA data of bayerite were divided by 10, and DTA curves of hydrated alumina samples and bayerite were shifted for better clarity.

be explained by a difference of granulometry, as observed for numerous ground materials.^{28,29} In Figure 7B, a mass loss is seen above 200 °C for all samples. Above this temperature, this feature can be produced by several phenomena: dehydration of bayerite if present, dehydration of an amorphous phase, or dehydroxylation of the surface of the oxide.

3.3.2. Interpretation of DTA/TGA Results. In Figure 8, the evolution of three experimental quantities is plotted against hydration time of γ -alumina: mass loss from 25 to 200 °C and from 200 to 1000 °C and area of the DTA peak E₂. The amount of bayerite is quantitatively related to the area of the DTA peak E₂ and can be measured after 8 days in suspension. Thus, an induction time greater than 2 days is required for bayerite crystallization; then the amount of bayerite increases between 8 and 30 days and levels off afterward. From the value of the peak area for pure bayerite, it can be calculated that the concentration of bayerite is about 6% after long-term hydration. The behavior of the physically adsorbed water (mass loss below 200 °C) is more complex. The quantity is initially low for nonhydrated samples and can be attributed to the adsorption of atmospheric humidity during storage. Then, it rises to a maximum for the shorter hydration times (i.e., 1 day), indicating that water has reached the interior of the pores. Then it decreases until the 15th day and levels off. According to the assumption that removed water is physically adsorbed in the pores, a decrease in the amount of water should correspond to a decrease in the

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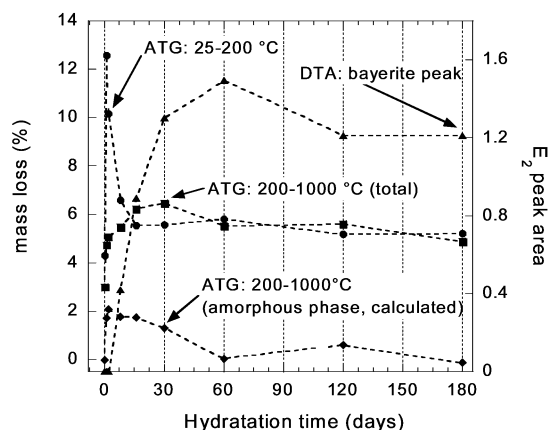


Figure 8. Evolution of area of peak E_2 (▲) and mass loss at 200 °C (●) and from 200 to 1000 °C (■), measured by DTA and TGA, respectively, with increasing hydration time. The mass loss between 200 and 1000 °C from the amorphous phase (◆) was calculated (see text for details).

available pore surface. This effect will be discussed later. Different behavior is observed for the mass loss between 200 and 1000 °C. The rate increases sharply during the first days, reaches a maximum after 1 month, and then decreases weakly and levels off after 2 months. This value includes the mass loss from bayerite dehydration: the previously calculated bayerite concentration of 6% in the sample would lead to a mass loss of 2%, whereas a value around 5% is found. The extra loss can be explained by the dehydroxylation of the surface since a loss of water of 3% corresponds to the loss of about 12 OH groups per nm^2 of a solid with such a specific area. We note that this figure is what is found for the initial γ -alumina, indicating that the surface is highly hydroxylated in the commercial product. Subtracting the mass loss assigned to bayerite dehydration and surface dehydroxylation from total mass loss between 200 and 1000 °C would lead to the mass loss assigned to the amorphous phase. This value is represented in Figure 7: starting from zero for the as-received sample, it jumps to 2% for the 1-day-hydration sample and then slowly decreases to zero after a 2-month hydration. This result is an additional hint of the presence of a transient amorphous phase during the first weeks of hydration, which then evolves into bayerite.

4. Discussion

As suggested by the different investigation techniques, hydration proceeds through several steps. The decrease in the quantity of physically adsorbed water, after an initial increase, as observed by TGA, may be explained by the formation of a new hydrated phase in the pores present in γ -alumina. This would lead to an increase of the solid volume, since the density of bayerite is lower than that of transition alumina (2.53²¹ and 3.65³⁰ g/cm^3 , respectively). From these data, the molar volume for the same quantity of Al atoms in the solid can be calculated for bayerite (31 mL/mol Al) and for alumina (14 mL/mol Al). Thus, this volume increase could partially stop up the pores and lower the volume available for physically adsorbed water. However, the specific area of our samples increases from 152 to 161 m^2/g after hydration for 10–15 days and to 166 m^2/g after a 6-month hydration. It is significant that similar behavior has been observed with “hydratable aluminas” (amorphous Al_2O_3 designed to transform rapidly into bayerite): the alumina only

partially transforms into bayerite without a change of surface area, and this effect was explained by pore filling.³¹ The decrease of the pore surface of γ -alumina might be compensated by the formation of microscopic bayerite platelets or of an amorphous phase.

The transient formation of an amorphous phase is detected by XRD with a maximum at about 10 days of hydration (Figure 3). This step corresponds to a specific mass loss detected by TGA/DTA (Figure 8). Concurrently with the formation of this phase, we observe the largest decrease in the reactive site density, which takes place within 8 days (Figure 1). As suggested by XPS, this phase may be an amorphous precursor of bayerite, whose formation, as discussed below, seems to be the main cause of the decrease in the site density. However, as early as 4 days after the beginning of hydration, crystalline bayerite appears, as seen by XRD (Figure 3), creating a detectable peak (E_2) in DTA after 8 days (Figure 8) and appearing as crystals of a few hundred nanometers after several months.

The formation of bayerite results in a large decrease in the reactivity, which can be explained with the help of the MUSIC interpretation of gibbsite ($\alpha\text{-Al}(\text{OH})_3$) behavior,³² since bayerite and gibbsite are composed of different relative stackings of the same unit layer. The coordination of hydroxyl groups for the various faces is the same for both polymorphs. The hydroxyl groups on the {001} face are all doubly coordinated, whereas the {010} and {100} faces present doubly and simply coordinated OH groups. Studies by acid–base titration,³² organic acid sorption,^{21,33} krypton adsorption,³⁴ and IR spectroscopy³⁴ have shown that the reactivity of gibbsite is dependent only on edge planes ($hk0$ faces) and that the basal face {001} can be considered as nonreactive to protons. The conclusions of these experiments can be transposed to bayerite, since both polymorphs have the same distribution of simply and doubly coordinated hydroxyl groups on the various faces. According to the micrographs of 6-month-hydrated γ -alumina, the bayerite crystallites have preferentially developed {001} faces, so that this new phase is probably mainly nonreactive, and the global site density will drop whereas the specific area increases. From this result, the validity of the determination of the site density on γ -alumina after hydration for a few weeks is doubtful. In fact, the values obtained by titration correspond to the reactivity of a surface composed by aluminum hydroxides, mainly bayerite. The real site density of pristine γ -alumina would be closer to the value determined after a short hydration, since this higher value means that hydroxylation has already taken place, as shown by the contribution of OH in the O1s peak by XPS and the mass loss after 200 °C in TGA. However, it is not possible to know if the surface is fully hydroxylated. A site density of about 5 OH groups per square nanometer is higher than previously measured values,⁴ but this behavior can be explain by highlighting the tetrahedral coordination of aluminum atoms at the surface of the oxide.³⁰ In octahedral coordination,³² doubly coordinated OH ions ($\text{Al}_2^{\text{VI}}\text{OH}^0$) can only be protonated at very low pH values ($\text{p}K_{2,2} = 0$) and deprotonated at high pH values ($\text{p}K_{2,1} = 12$). Thus, these groups can be considered as nonreactive and only singly coordinated OH ions ($\text{Al}^{\text{VI}}\text{OH}^{1/2-}$) could react in solution

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($pK_{1,2} = 10$). In tetrahedral coordination, the deprotonation of $\text{Al}^{\text{IV}}\text{Al}^{\text{VI}}\text{OH}^{1/4+}$ can take place, since the calculated $pK_{2,1}$ value would be 7.4.²⁵ For the same coordination, the $pK_{1,2}$ value of singly coordinated hydroxyl groups ($\text{Al}^{\text{IV}}\text{OH}^{1/4-}$) would be 4.4.²⁵ Thus, after a short hydration period, both the singly and doubly coordinated OH groups could be titrated. Afterward, the formation of an overlayer of bayerite (consistent with XPS results), whose {001} planes are nonreactive, will lower the mean site density.

5. Conclusion

Using several complementary investigation methods, we were able to characterize the process occurring during hydration of γ -alumina. This process consists essentially of the formation of bayerite, via a transient step corresponding to an amorphous phase. This process, whose kinetics has been established, has an important influence on the surface reactivity of alumina and hence on its sorption properties. The decrease in the density of sites reactive to protons is essentially explained by the low reactivity of the surface hydroxyl groups of bayerite. This study also shows that the often-recommended hydration procedure does not lead to a steady state of bayerite formation and to a stable surface site density: even after several months, no steady state of reactivity is achieved.

It is not excluded that a long-term evolution takes place through continuing formation of bayerite or even by another process, since bayerite is not the thermodynamically stable phase.

We have studied here a case in which the surface reactivity of a solid evolves with time. Since surface reactivity and sorption properties of solids are important factors controlling the transport of toxic and radioactive elements in water and porous media, one should take into account the stability of solids, and especially of their surfaces, when modeling sorption experiments. This is very important for the long-term prediction of the effectiveness of natural or artificial barriers placed around radioactive waste depositories.

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