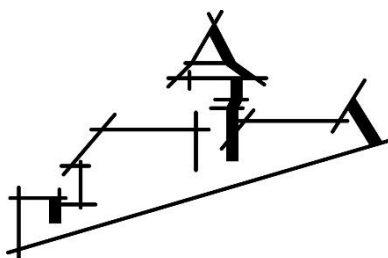


PROGRESSIVE TRENDS IN COORDINATION, BIOINORGANIC, AND APPLIED INORGANIC CHEMISTRY



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Comparison of kaolinites from different sources

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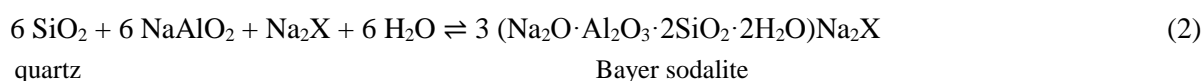
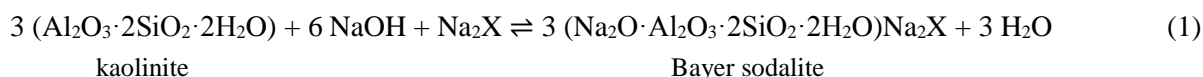
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The Bayer process is a well-established technique in the alumina industry for the recrystallization of Al(OH)₃ from bauxite. The dissolution of clay minerals during this process, and the subsequent formation of the so-called desilication product (DSP) are major technological issues in the Bayer process, due to cost and the behavior of this material in the bauxite residue. In order to gain more detailed fundamental understanding of the DSP-formation, designing suitable apparatus for the investigation and selection of the optimal model compounds is of primary importance. Accordingly, the aim of our work was to develop and test an apparatus for examining the dissolution kinetics of kaolinites obtained from various suppliers. In our experimental work, inductively coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy (SEM), energy-dispersive X-ray analysis (SEM-EDAX), X-ray diffractometry (XRD), Fourier-transform infrared spectroscopy (FT-IR), and surface/textural measurements were used to characterize the reactants and to analyze the products. These results are the first steps for us in understanding the mechanism of the dissolution of kaolinite and the subsequent formation of the DSP.

INTRODUCTION

The production of aluminum involves two main processes: the Bayer process and Hall-Héroult electrolysis. The first step of the Bayer process is the extraction of gibbsite, boehmite or diasporite from the aluminum-bearing bauxite ore. The bauxite is digested in a hot solution of sodium hydroxide, which leaches aluminum from the bauxite's other mineral constituents, such as compounds of silicon, iron, and titanium. The aluminum is then precipitated in the form of aluminum hydroxide, Al(OH)₃, which in the next step is calcined to form alumina, Al₂O₃. In the Hall-Héroult process, the alumina is dissolved in a molten bath of cryolite (Na₃AlF₆). Molten aluminum is obtained from the melt by electrolysis, which is an extremely energy consuming step [1].

During the extraction of alumina, it is essential to isolate the reactive silica, which dissolves in caustic soda and partly precipitates as the desilication product (DSP, which primarily consists of sodalite or cancrinite, both zeolite-like structures). The process may be described by the following equations:



where X stands for a mixture of aluminate, carbonate, sulfate, and smaller amounts of other anions present in the bauxite or in the process liquor. The rate of the reaction increases with increasing digestion

temperature. Bayer sodalites usually depart from the process with the red mud, but their formation causes major caustic and alumina losses. Moreover, high silica levels induce scaling in the heat exchangers and pipes, and result in poor product quality. In the industry, material and energy savings are crucial, hence technological innovations are needed, for instance, improved red mud separation techniques [2].

The formation of the desilication product can be studied by monitoring the silica concentration in the Bayer liquor during kaolinite dissolution. A typical C_{Si} vs. time profile upon kaolinite dissolution and the subsequent DSP formation is shown in Fig. 1. As it can be seen, in the first few minutes the silica concentration increases as the kaolinite dissolves. Once a certain concentration of silica is reached the concentration begins to decrease, together with the onset of the formation of the DSP. The final part of the kaolinite dissolution curve is shown as a mirror image of the drop of silica concentration [3].

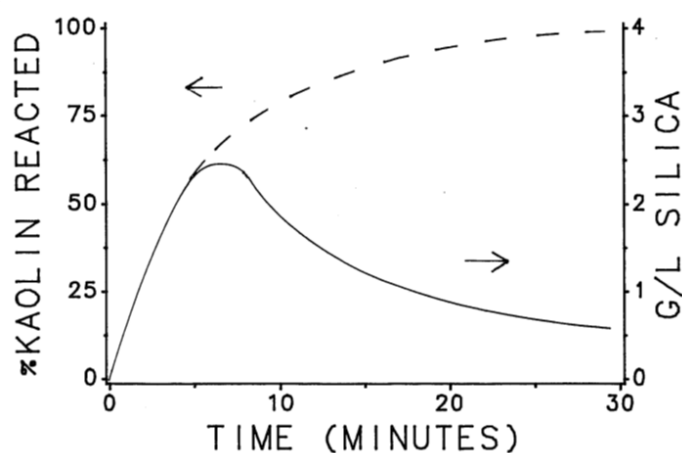


Figure 1. The variation of the silica concentration (schematic figure) as a function of time during the kaolinite dissolution–DSP precipitation process [3].

There are many attempts to control the formation of the DSP and the dissolution of the kaolinite with several additives or by changing the experimental conditions [4]. For example, Whittington *et al.* examined the effects of the heating rate (desilication to digestion) and the forms in which the reactants (CaO, gibbsite, two types of kaolin samples, and the spent liquor) were added to the system. They concluded that the DSP formation was highly affected by the form of the reactants and the sources of kaolin and also by the heating conditions [5, 6].

The current contribution is aimed at the general examination of the desilication process under laboratory conditions, including the planning and the optimization of a feasible apparatus that is suitable for studying the dissolution of kaolinite and formation of DSP, as well as identification of the most suitable type of kaolinite for studying the kinetics of reactive silica dissolution-DSP formation.

EXPERIMENTAL PART

Reagents and solutions

Irregular aluminum shots (99.9%, Alfa Aesar) and 9 M sodium hydroxide solutions were used to prepare the industrial composition Bayer liquors. The NaOH used for the spent liquor was diluted from a 50 % w/w NaOH solution, prepared by dissolving NaOH pellets (a. r. grade, VWR) in continuously stirred Milli-Q water (Merck Millipore Milli-Q) applying a reflux equipped with a CO₂ trap. The resulted liquor was filtered through 0.45 µm PTFE membrane while a CO₂ trap was used. Appropriate portions of the caustic solution were diluted to obtain 1 M NaOH stock solutions, which were standardized by HCl solution. The 1 M stock solutions of the acid were made by volumetric dilution of ≈ 37 % w/w HCl (a. r. grade, VWR) and they were standardized with using KHCO₃ solution [7].

During the measurements sodium silicate solution (extra pure, Merck), kaolinites from different sources (Alfa Aesar (USA), Sigma-Aldrich (USA), Zettlitz (Germany), Georgia KGa-1B (USA), and Eckalite 1 from Imerys Minerals (Australia), anhydrous sodium sulphate (99.92 %, Molar Chemicals), and anhydrous sodium carbonate (99.9 %, VWR) were applied.

Apparatus and equipment

Inductively coupled plasma spectroscopy with radial configuration (Thermo Scientific iCAP 7400 ICP-OES DUO spectrometer) was used for the determination of silica concentration in the Bayer liquor samples. These were diluted and acidified with HCl *prior to* the measurements.

Powder X-ray diffraction (XRD) patterns of the dried sodalites (DSPs) and the initial kaolinites were registered on a Rigaku Miniflex II instrument in the range of $2\theta = 4\text{--}70^\circ$ with 4 °/min scan speed, using CuK α ($\lambda = 1.5418 \text{ \AA}$) radiation. The reflections were assigned with the help of the JCPDS (Joint Committee of Powder Diffraction Standards) database. The average primer crystallite sizes were calculated by the Scherrer equation from the first reflections of the materials prepared [8].

The dried DSPs and the kaolinites were studied by Fourier-transform infrared (FT-IR) spectroscopy (JASCO FT/IR-4700 spectrophotometer). The applied resolution was 4 cm⁻¹ and 256 scans were accumulated for each spectrum. The spectrometer was equipped with a DTGS detector and ATR accessory. On the normalized curves, the structural attributes of materials were investigated in the 4000–500 cm⁻¹ wavenumber range.

The textural parameters of the kaolinites were mapped by N₂ adsorption-desorption techniques on a Quantachrome NOVA 3000e instrument. The materials were degassed at 300°C for 1 h in vacuum, to remove surface-adsorbents. The specific surface areas were determined by the Brunauer-Emmett-Teller equation from the adsorption branches, to calculate the average pore sizes and total pore volumes, the Barrett-Joyner-Halenda (BJH) method was used from the desorption branches.

The morphologies of the sodalites and the kaolinites were examined by scanning electron microscopy (SEM, Hitachi S-4700 type II) at various magnifications and acceleration voltages. A few nm of conductive gold-palladium alloy film was sublimed onto the surface of the samples in order to avoid charging. The microscope was equipped with energy dispersive X-ray (EDX) analysis detector (Röntec QX2 spectrometer with Be window) for measuring the elemental composition and distribution.

RESULTS AND DISCUSSION

The first step of our work was the preparation of an appropriate model solution with accurately known component concentrations. For the measurements, the following aluminate solution (modeling a spent process liquor) was employed: $[\text{NaOH}]_{\text{T}} = 4.5 \text{ M}$, $[\text{Al(III)}]_{\text{T}} = 1.9 \text{ M}$, $[\text{Na}_2\text{SO}_4]_{\text{T}} = 0.05 \text{ M}$, $[\text{Na}_2\text{CO}_3]_{\text{T}} = 0.20 \text{ M}$. To this model solution, either water-glass solution (with accurately known NaOH and Si(IV) concentrations) was added to set the initial concentration of Si(IV) in the solution to 5.0 gL^{-1} expressed in terms of SiO_2 or kaolinite with an initial concentration of 23 gL^{-1} .

An equipment was then designed and implemented in which the kinetic measurements were possible to be carried out. The tests were performed in a 280 mL PTFE vessel and the temperature of the Bayer liquor was 95°C (using silicon oil bath). The PTFE vessel was placed in a custom made, jacketed hard glass jar, in which the heat transfer was facilitated by glycerol. The target temperature was found to be reached within an hour and it was found to be constant within $\pm 0.5^\circ\text{C}$, over several hours. The evaporation loss over a period of 8 hours was checked gravimetrically and it was found to be about 1 %. The main target of these measurements was to establish conditions which result in reproducible C_{Si} vs. time profiles.

During the scouting experiments, water glass was added to the reaction mixture and the concentration of the dissolved silica was monitored as a function of time. The results of three parallel measurements are shown in Fig. 2. from which the equilibrium concentration of silica and the reproducibility of the kinetic runs can be obtained. It is also clear from these graphs, that in the initial period of the measurement, a transient phase is seen, that is, upon water glass addition, the formation of a precipitate was observed, which redissolved after a few minutes. The fall of Si(IV) concentration, which onsets at *ca.* 60 min reaction time is associated with the formation of DSP, as it was confirmed by XRD measurements (not shown).

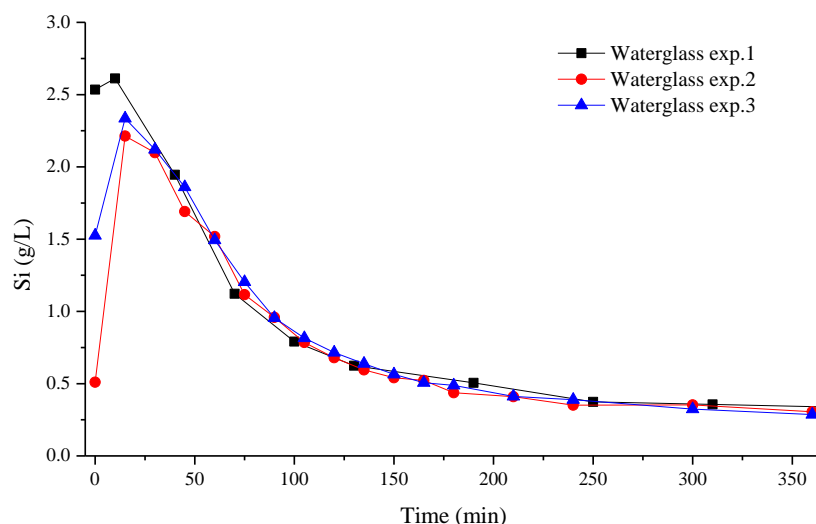


Figure 2. Variation of silica concentration (expressed in terms of $[\text{Si(IV)}]$) as a function of time from three independent measurements, upon adding water glass to the aluminate solution at 95°C . The Si-content was determined by ICP–OES. For the composition of the aluminate solution, see Experimental part.

For studying the dissolution-precipitation kinetics of kaolinite, an experimental protocol identical to that shown in Fig. 2. was used, but the silica was added to the system in form of kaolinite (23 gL^{-1}). The solid kaolinite samples were first characterized by various techniques for structural comparison. The powder XRD traces of the five kaolinite samples are depicted in Fig. 3. Diffraction patterns typical for kaolinite were observed in all samples studied (identified with the help of JCPDS card no. 14–0164), though their intensities were slightly different. The primer particle sizes were very similar (23 nm), except for the samples from Georgia and from Australia, where the primary particle sizes were found to be somewhat bigger (36 and 29 nm).

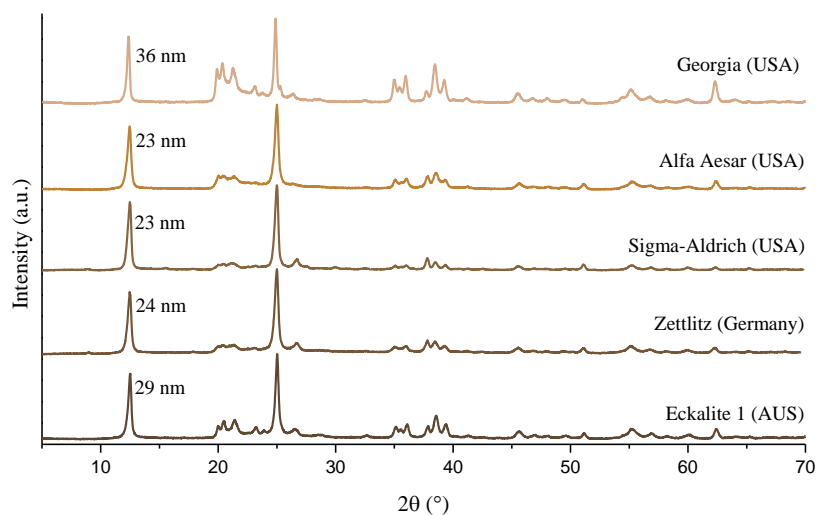


Figure 3. Powder XRD traces of the kaolinites from different sources. The primary particle size of the kaolinites obtained from the Debye-Scherrer equation is also shown.

The Fourier Transformed–Infrared (FT–IR) spectra of the initial kaolinite samples from the five different sources are also very similar (Fig. 4.). Only minor differences can be observed in some particular spectral regions, but these are commensurate with the experimental uncertainty.

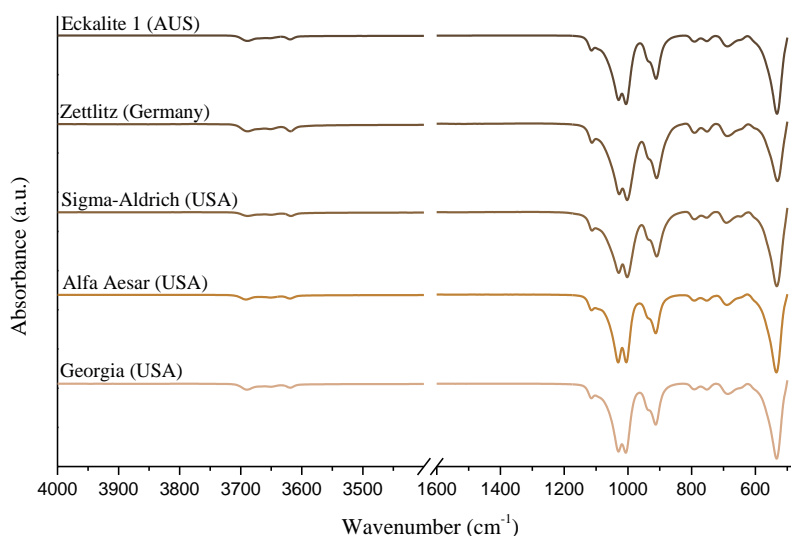


Figure 4. FT–IR spectra of the kaolinites from different sources.

The SEM images of the various kaolinite samples were found to be also very similar and exhibited amorphous structures irrespective of the source. These images attested, that the primary particles form aggregates with various sizes and morphology; some examples are shown in Fig. 5.

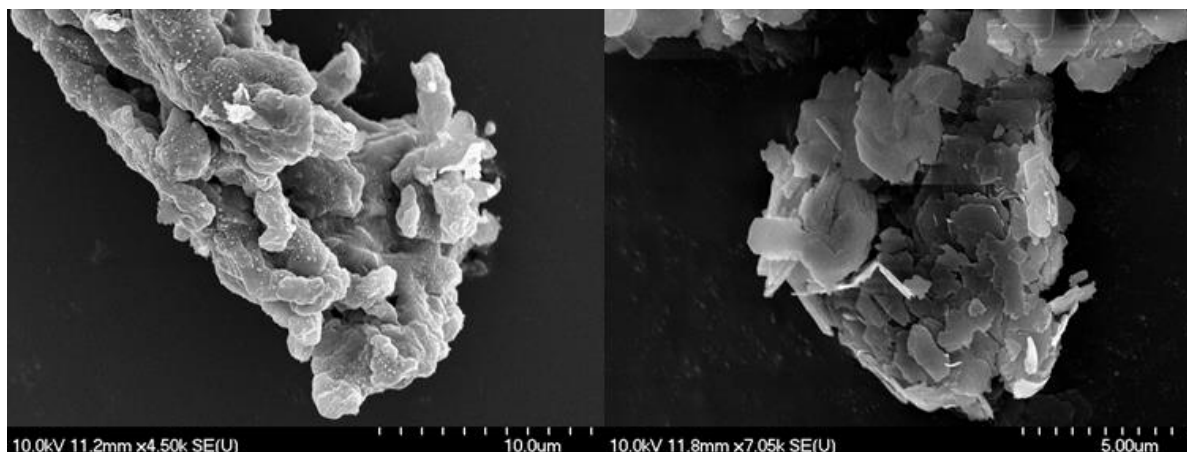


Figure 5. SEM images of the kaolinite samples from Zettlitz (left) and from the Sigma-Aldrich (right).

The chemical compositions of the samples were measured *via* SEM–EDX. These measurements proved that the Eckalite 1, Sigma-Aldrich and Alfa Aesar kaolinite samples have composition identical to that provided by the supplier on the Certificate of Analysis. The composition of the remaining two samples (from Zettlitz and Georgia) was not known. The composition of the kaolinite sample from Georgia was similar to that of the Alfa Aesar, however, the one from Zettlitz appeared to contain somewhat more impurities (up to *ca.* 1 at%). From the SEM-EDX measurements, it can be stated that the main component of the samples was kaolinite, and the contribution of the other components (impurities) was very small.

The dissolution kinetics of the kaolinites from different sources was studied at 95°C, using the model spent process liquor. A typical digestion experiment was run for 360 minutes and samples were taken in every 30 minutes and prepared for the ICP–OES measurements immediately after cooling (Fig. 6.)

The results are somewhat surprising, as the kinetic behavior of the various kaolinites shows a marked dependence on the source. These differences cannot be explained in terms of the data obtained for the structure or chemical composition of these specimens and cannot be explained by the previous solid phase measurements, they behaved differently as presumed (Fig. 6.). The Australian Eckalite 1 and the kaolinite from Alfa Aesar showed some similarity, they reached the maximum silica concentration within a half an hour. However, the same for the samples from Zettlitz and from the Sigma-Aldrich required more than an hour.

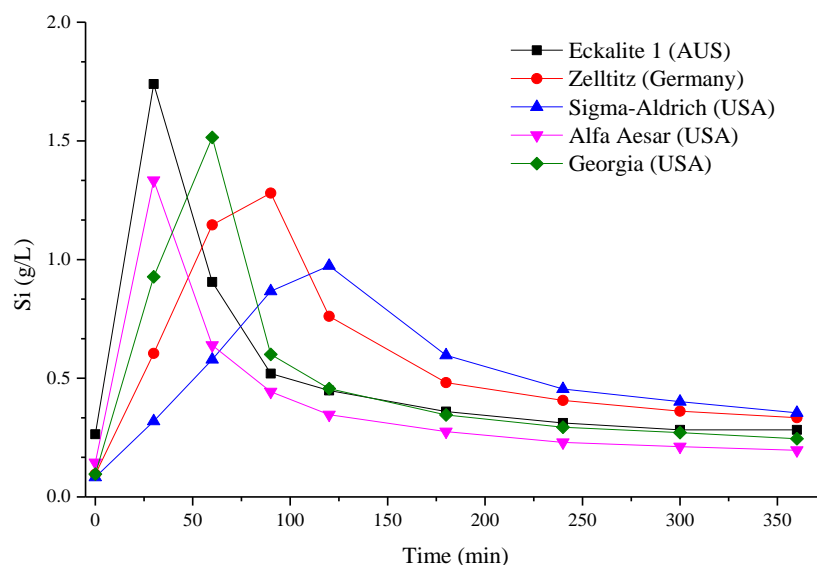


Figure 6. The dissolution of kaolinites from different sources followed by the precipitation of sodalite, monitored through the variation of silica the concentration as a function of time. The dissolved silica concentration was determined by ICP–OES.

Table 1. The textural parameters and Hinckley indices of the kaolinite materials.

Materials	Hinckley index	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Predominant pore radius (Å)
Georgia	0.90	12.1	0.034	19.2
Alfa Aesar	0.56	16.2	0.047	15.5, 19.1
Sigma-Aldrich	0.93	7.8	0.027	19.3
Zettlitz	0.85	15.4	0.046	19.3
Eckalite 1	1.24	15.6	0.053	19.1

The dissolution rates of the solids are frequently related to their crystallinity, amorphous phases show faster dissolution due to their low lattice energies. The Hinckley index serves as crystallinity index in the literature of kaolinites (Table 1) [9]. Interestingly, the highest and lowest indices were found to correspond to kaolinites that showed similar dissolution kinetics.

All kaolinites showed similar textural features, they had Type IV isotherms with H3 hysteresis loops according to the IUPAC classification [10], due to their mesoporous surface with around 4 nm diameter pores (Table 1). The highest specific surface areas and total pore volumes were found for the Eckalite 1 kaolinite and the one from Alfa Aesar, while the lowest values belonged to the kaolinite from Sigma-Aldrich. From these data, the key to the observed variations in the dissolution kinetics may be the difference in the textural parameters of the kaolinites.

The solid products obtained by the end of the kinetic runs, allowing 360 min digestion time, were separated from the mother liquor, washed with Milli-Q water, dried at 60°C and were examined *via* XRD and FT–IR. The XRD traces are shown in Fig. 7.

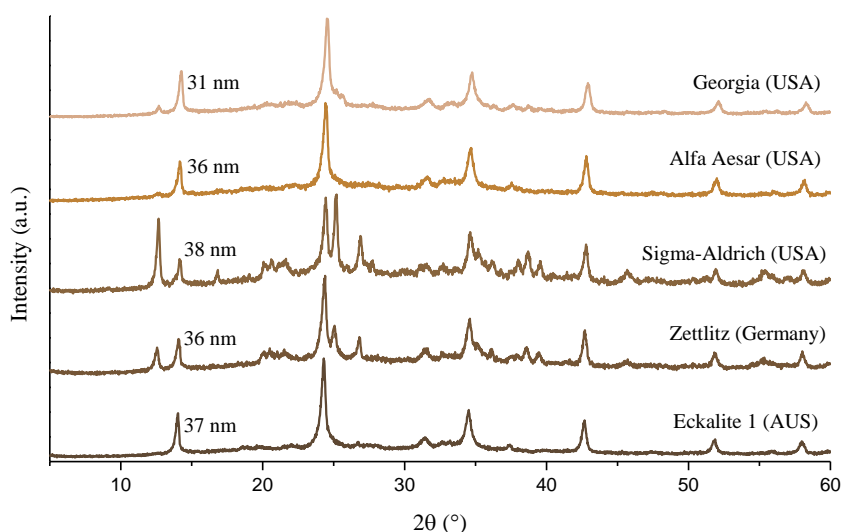


Figure 7. Powder XRD races of the solid products obtained at the end of the kinetic runs, allowing 360 min digestion time. The primary particle sizes of the sodalite are indicated on the graphs.

The typical diffractograms of sodalities are well detectable in Fig. 7.; on the basis of JCPDS card no. 74-1736 and 15-0469, a mixture of sulphate and carbonate containing sodalities is present. These patterns confirm the results obtained from the solubility tests (Fig. 6.) The wt% distributions of the kaolinite and sodalite phases were calculated from the integrated reflection intensities and are shown in Table 2 [11].

These differences can be also noticed in the FT-IR spectra (Fig. 8.) On the spectrum of the specimens obtained from the digestion of kaolinites from Zettlitz and from the Sigma–Aldrich there are some IR absorption peaks, which do not appear on the spectra of the other three samples (*e.g.*, at 912 and 535 cm^{-1}), they correspond to the unreacted kaolinite.

Table 2. The distribution of various crystal phases at the end of the digestion process.

Materials	Kaolinite (wt%)	Sodalite (wt%)
Georgia	13	87
Alfa Aesar	10	90
Sigma-Aldrich	48	52
Zettlitz	25	75
Eckalite 1	<5	>95

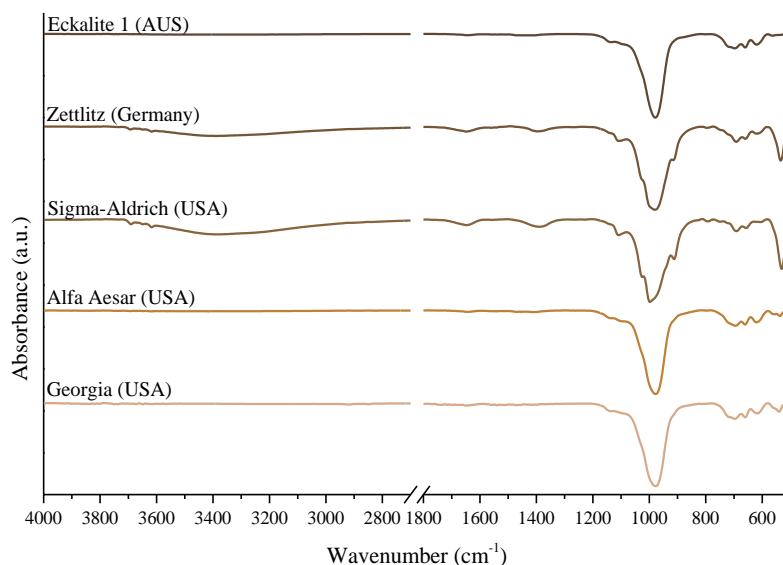


Figure 8. FT-IR spectra of the solid products obtained at the end of the kinetic runs, allowing 360 min digestion time.

Based on the SEM images of the solid products obtained at the end of the digestion (Fig. 9.), all the sodalites are lepispheres, with structures reminiscent of a ball of yarn [12].

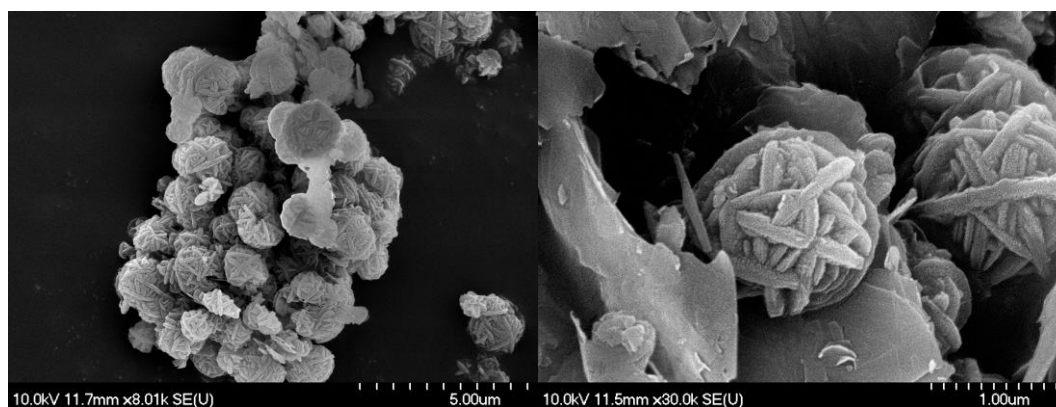


Figure 9. The SEM images of the solid products obtained at the end of the digestion of kaolinite from Georgia (left) and from Zettlitz (right).

CONCLUSION

The dissolution precipitation kinetics of kaolinites under conditions typical of the Bayer desilication process was studied. We found that kaolinites obtained from various sources behave in a markedly different way, in spite of the fact, that their structure, primary particle size, composition, morphology and crystallinity did not show any appreciable difference.

The investigation of textural parameters attested that specific surface area values are in direct correlation with observed dissolution behavior, but further experiments are needed for the identification of all parameters that are responsible for these differences. Such experimental work is currently in progress.

ACKNOWLEDGEMENTS

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