

# THE CRYSTALLIZATION OF HECTORITE CLAY AS MONITORED BY SMALL ANGLE X-RAY SCATTERING AND NMR

K. A. Carrado\*, L. Xu, S. Seifert, D. Gregory, K. Song, R. E. Botto  
Chemistry Division 200, Argonne National Laboratory  
9700 South Cass Avenue, Argonne, IL 60439

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## ABSTRACT

We have probed the 48-hr crystallization of a magnesium silicate clay called hectorite. Small angle x-ray scattering (SAXS) at the Advanced Photon Source using aliquots ex situ has revealed that data is consistent with ex situ XRD, TGA, AFM, and IR data in that all these techniques see clay crystallites beginning to form in the first few hours of reaction. Tetraethylammonium (TEA) ions are used to aid crystallization and become incorporated as the exchange cations within the interlayers.  $^{13}\text{C}$  NMR shows that 80% of the final TEA loading is accomplished in the first 10 hrs.  $^{29}\text{Si}$  NMR displays a visible clay silicate peak after just 1 hr. In addition, the first in situ study of clay crystallization of any kind was performed by in situ SAXS. Results are consistent with the ex situ data as well as showing the sensitivity of SAXS to sol gel reactions occurring on the order of minutes.

## INTRODUCTION

The mechanism of formation of clays is of interest because of the use of synthetic layered silicates as heterogeneous catalyst supports and in various other technological applications. We have probed the crystallization of a magnesium silicate clay called hectorite by several ex situ (samples isolated after progressive crystallization times) techniques. For complete crystallization, heating for 48 hours at 100°C is needed. However, several techniques have revealed that significant clay growth occurs in the first few hours of hydrothermal treatment. Evidence of clay peaks in XRD occurs after just 4 hours of hydrothermal treatment, and  $\text{Mg}(\text{OH})_2$  is no longer observable by XRD after 14 hours; observable changes in DTG and IR occur at about 4-6 hours as well [1]. From AFM results [2], Ostwald ripening is apparent in this system in certain time frames. Most noticeably at 4 hours but still at 8 hours, nucleation of the clay crystallites is occurring. Between 8 and 14 hours, the nucleation is complete, as evidenced by the unimodal distribution of lengths and heights in the 14 hour sample. At times longer than 14 hours, particles appear to simply coalesce and form substantially larger aggregate particles. We have now exploited both small angle x-ray scattering (SAXS) and solid state NMR to access different size regimes, length scales, and timeframes, to add information to the overall scenario of a clay crystallization mechanism.

## EXPERIMENTAL

The typical method for in situ hydrothermal crystallization of organo-hectorite clays is to create a 2 wt% gel of silica sol, magnesium hydroxide sol, lithium fluoride, and organic in water, and to reflux for 2 days. Complete details can be found elsewhere [1-3]. Reagents were purchased from Aldrich. The organic of choice for crystallization studies is tetraethylammonium chloride (TEA). Precursor clay gels are of the composition:



to correlate with the ideal hectorite composition [4] of  $\text{Ex}_{0.66}[\text{Li}_{10.66}\text{Mg}_{5.34}\text{Si}_8\text{O}_{20}(\text{OH},\text{F})_4]$ , where Ex = exchangeable cation (Ex = Li, TEA from this gel). A typical (scaled-down) reaction begins by dissolving 0.72 mmol of TEA in water and adding 4.8 mmol LiF with stirring. Separately, 24 mmol  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  is dissolved in water and mixed with 32 ml of 2 N  $\text{NH}_4\text{OH}$  to crystallize fresh  $\text{Mg}(\text{OH})_2$ . Prior to use, this brucite source must be washed several times with water to remove excess ions. It is then added wet to the organic-LiF solution. This slurry is stirred for about 15 minutes before addition of 0.036 mol silica sol (Iudox HS-30,  $\text{Na}^+$ -stabilized, 30%). This mixture is refluxed for up to 48 hr then centrifuged and the products are washed and air-dried. Small aliquots for ex situ time-resolved studies are removed at various times during the crystallization.

The SAXS instrument was constructed at ANL and used on the Basic Energy Sciences Synchrotron Radiation Center CAT undulator beamline ID-12 at the Advanced Photon Source [5,6]. For ex situ powder studies, the same powders as were used for the NMR analyses were sprinkled onto and sealed in scotch tape "cells". For the ex situ gel studies, wet aliquots were concentrated (via centrifugation) and transferred to 1.5 mm quartz capillaries. The SAXS data were collected in 5 minutes exposures (scans). Controls of pure silica and brucite sols (diluted to appropriate concentrations) were also run in

capillaries. For the in situ study, a small portion of unreacted clay gel was transferred to a 1.5 mm quartz capillary and sealed (the gel was first pre-concentrated by 75%). This capillary was placed in a home-built furnace assembly such that the gel was directly in the beam path. Temperature was computer-controlled; scanning began at 70°C, which took only 3-4 minutes to reach. Within 5 minutes the temperature had reached 100°C and held at  $\pm 1^\circ\text{C}$  for the duration of the run. SAXS data were collected in 2 min scans divided by 5  $\mu\text{sec}$  for the first 2 hrs, then as 10 min scans for the remaining 10 hrs. Monochromatic x-rays at 10.0 keV were scattered off the sample and collected on a  $19 \times 19 \text{ cm}^2$  position sensitive two-dimensional gas detector. The scattered intensity has been corrected for absorption, scattering from a blank capillary containing only water (or scattering from blank scotch tape for the powder studies), and instrument background. The differential scattering cross section can be expressed as a function of the scattering vector  $Q$ , which is defined as:  $Q = 4\pi (\sin \theta) / \lambda$ , where  $\lambda$  is the wavelength of the x-rays and  $\theta$  is the scattering half angle. The value of  $Q$  is proportional to the inverse of the length scale ( $\text{\AA}^{-1}$ ). The instrument was operated at a sample-to-detector distance of 67.0 cm to obtain data at  $0.04 < Q < 0.7 \text{ \AA}^{-1}$ . Mylar windows were used because mylar does not have diffraction peaks in this  $Q$  range.

NMR data were acquired on a Bruker Advance DSX-200 spectrometer operating at a  $^{13}\text{C}$  Larmor frequency of 50.3 MHz. A Bruker 7mm MAS probe and a simple  $90^\circ$ -pulse-acquire experiment was used for all experiments. Sample spinning was maintained at  $4000 \pm 2 \text{ Hz}$ . Data were acquired in the presence of proton decoupling with proton power set to 80 kHz. The  $90^\circ$ -pulse times were 6.5 and 7.0  $\mu\text{s}$  for  $^{13}\text{C}$  and  $^{29}\text{Si}$ , respectively. Recycle delays were 3 and 200 sec for  $^{13}\text{C}$  and  $^{29}\text{Si}$  experiments respectively. The number of transients recorded were 2400 and 128 for  $^{13}\text{C}$  and  $^{29}\text{Si}$  spectra, respectively. All spectra were referenced to TMS. Hexamethylbenzene was used as a secondary reference for  $^{13}\text{C}$  spectra, and TKS was used as a secondary reference for  $^{29}\text{Si}$  spectra [7]. All samples were packed to the same level in the rotor. However, because of variations in density, the sample weight varied from 114 to 153 mg. Thus, the data points in Figure 4 were normalized by weight. No attempt was made to normalize the spectra in the stacked plot (Figure 3).

## RESULTS AND DISCUSSION

Results from SAXS using aliquots ex situ show, first, that data for both isolated dried powders and the wet gels are consistent with each other. This has implications for SAXS sample preparation in that, for convenience, either form (wet or dry) can be used. Figure 1 shows the data from the gels. Scattering from the starting material silica sol (seen at about  $0.08 \text{ \AA}^{-1}$ ) gradually disappears as the clay crystallizes and scatters in the basal spacing region ( $0.4 \text{ \AA}^{-1}$ ,  $15 \text{ \AA}$ ). This phenomenon is visibly evident at about 6 hrs. High background levels in this high- $q$  region that are probably due to brucite scattering (as seen in the control sample that was measured) disappear sooner, between 1 and 4 hrs. This data is consistent with ex situ XRD, TGA, and IR data in that all these techniques see clay crystallites beginning to form after about 4 hrs of reaction.

In addition, the first in situ study of clay crystallization of any kind was performed by in situ SAXS. These data are shown in Figure 2 with only a few representative curves displayed. Results are consistent with the ex situ data. There is background scatter in this high- $q$  basal spacing region well past the 4 hr point in at which it disappears for ex situ samples. It is suspected that this is due to the overall weak intensity of the signal due to a low concentration of clay in the beam (note the low intensity at  $q = 0.04 \text{ \AA}^{-1}$ , especially as time progresses).

Tetraethylammonium (TEA) ions are used to aid crystallization, and they become incorporated as the exchange cations within the interlayers. Figure 3 displays the  $^{13}\text{C}$  NMR plots of several powder aliquots with the methyl and methylene peaks of TEA clearly growing in with time. In fact, this technique is so sensitive that in as little as 30-60 minutes there is enough TEA incorporation to be visible. A plot of the normalized signal (by weight) with reaction time shows that 80% of the final TEA loading is accomplished in the first 10 hrs (see Figure 4), after which the incorporation occurs at a much slower rate. This is in agreement with AFM results [2], where Ostwald ripening is apparent in this system only in certain time frames. Most noticeably at 4 hours but still at 8 hours, nucleation of the clay crystallites is occurring. Between 8 and 14 hours, the nucleation is complete, as evidenced by the unimodal distribution of lengths and heights in the 14 hour sample. At times longer than 14 hours, particles appear to simply coalesce and form substantially larger aggregate particles.  $^{29}\text{Si}$  NMR displays a visible clay silicate peak after just 1 hr, which increases as the silica peak decreases up to 48 hrs (figure not shown).

## CONCLUSIONS

The  $^{13}\text{C}$  NMR data presented here has allowed us to nearly pinpoint the time at which clay crystallites stop nucleating and begin to simply accrete and coalesce. Previous AFM studies had indicated that this occurred between 8 and 14 hours for the hectorite system. After 10 hours,  $^{13}\text{C}$  NMR shows that 80% of the TEA has been incorporated in a linear fashion. This may mean that just one mechanism is active during the early stages of nucleation and crystallization. Between 10 and 14 hours there is a clear break in the NMR data of TEA uptake, after which AFM has shown that primarily agglomeration of particles is taking place. The SAXS data are in agreement with all other methods in terms of visible tracking of clay nuclei. The in situ SAXS data, since they are in agreement with ex situ data, confirm that vital information is not lost by isolating aliquots at various times for analysis. In addition, careful analysis of these SAXS curves in the future should yield information on changes occurring on the timescale of minutes.

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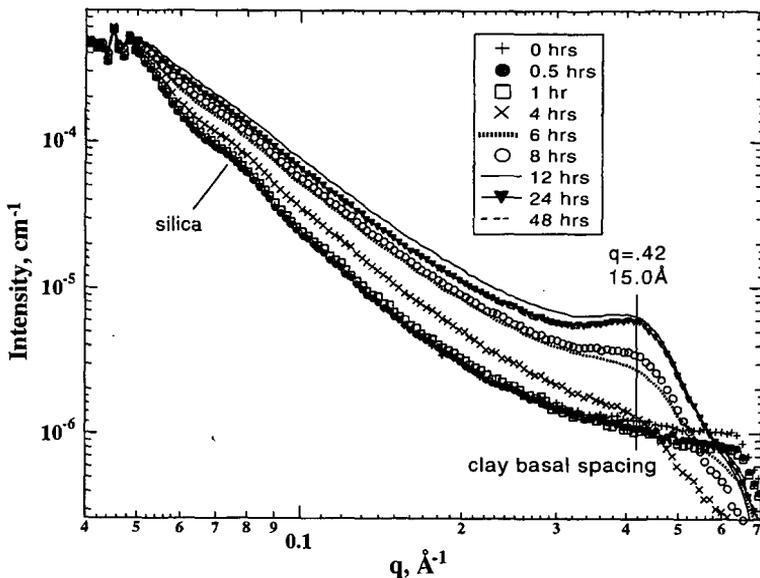


Figure 1. SAXS of ex situ synthetic TEA-hectorite gel aliquots taken at various times indicated in the legend.

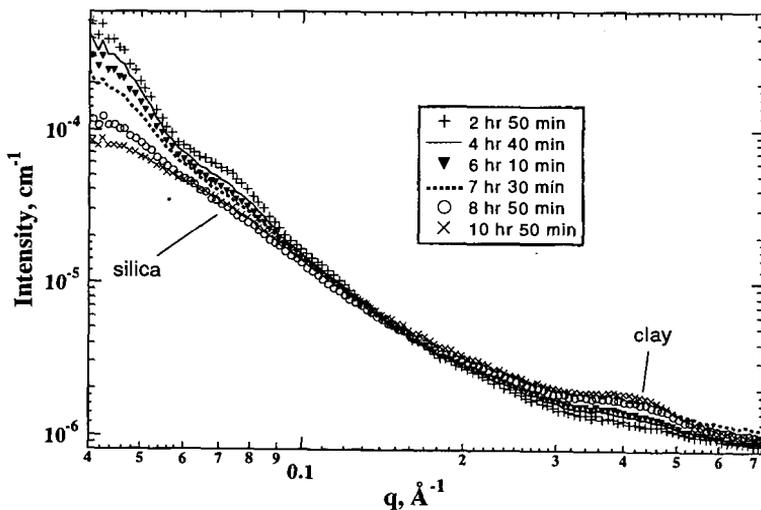


Figure 2. SAXS of in situ TEA-hectorite gel during crystallization at early stages. Only a few selected plots are shown for clarity as detailed in the legend.

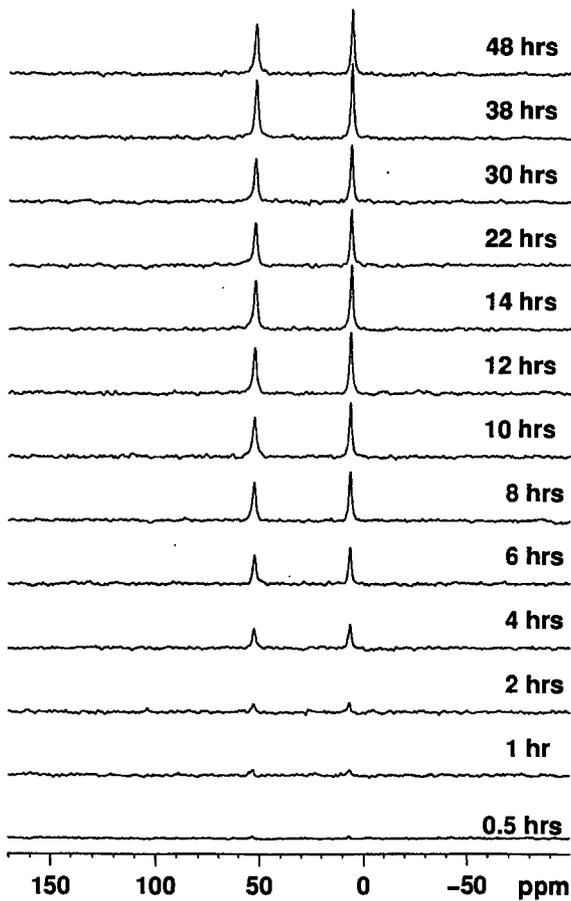


Figure 3. Solid state  $^{13}\text{C}$  NMR of the  $\text{CH}_3$ - and  $-\text{CH}_2$ - TEA peaks during crystallization of TEA-hectorite (ex situ).

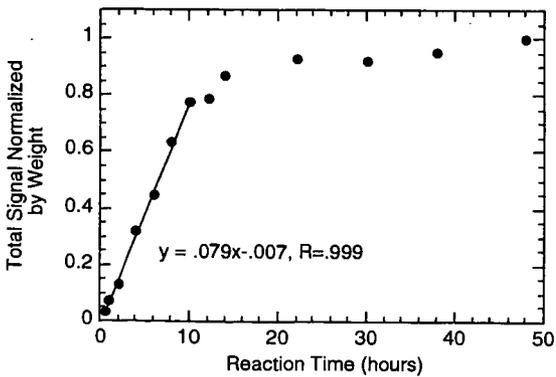


Figure 4. Correlation of TEA  $^{13}\text{C}$  NMR signal intensity vs. reaction time during the crystallization of TEA-hectorite.