Effect of solution composition on the recrystallisation of kaolinite to feldspathoids in hyperalkaline conditions: Limitations of pertechnetate incorporation by ion competition effects.

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Abstract

The incorporation of pertechnetate (TcO_4^-) into feldspathoids produced by alkaline alteration of aluminosilicate clays may offer a potential treatment route for ^{99}Tc containing groundwater and liquors. Kaolinite was aged in NaOH to determine the effect of base concentration, temperature, and solution composition on mineral transformation and pertechnetate uptake. In all reactions, increased temperature and NaOH concentration increased the rate of kaolinite transformation to feldspathoid phases. In reactions containing only NaOH, sodalite was the dominant alteration product however, small amounts (6-15%) of cancrinite also formed. In experiments containing NaOH/Cl and $NaOH/NO_3$ mixtures, sodalite and nitrate cancrinite were crystallised (at 70 ^{o}C), with no reaction intermediates. The addition of SO_4^{2-} crystallised sulfatic sodalite at 40 & 50 ^{o}C, but at higher temperatures (60 and 70 ^{o}C) sulfatic sodalite transforms to vishnevite (sulfatic cancrinite). In experiments where a pertechnetate tracer was added (at ~1.5 μmols L^{-1}), only 3-5 % of the ^{99}Tc was incorporated to the feldspathoid phases. This suggests that the larger pertechnetate anion was unable to compete as favourably for the internal vacancies with the smaller OH^-, NO_3^-, SO_4^{2-} or Cl^- anions in solution, making this method likely to be unsuitable for groundwater treatment.

Introduction

There is a global legacy of contaminated land around nuclear facilities, specifically arising from leaking storage ponds and containers (Mon et al., 2005, Perdrial et al., 2011, Wang and Um, 2012). At the Sellafield nuclear facility, UK, approximately 20 million m^3 of soil may be contaminated, and ^{90}Sr, ^{137}Cs and ^{99}Tc have been identified as important contaminants (Hunter, 2004). In oxic environments, technetium is highly mobile in the form of its pertechnetate anion, TcO_4^- (Burke et al., 2005), and its half-life of 2.1 x 10^5 years (Szecsody et al., 2014) means that ^{99}Tc is particularly problematic. Hence there is a need for low cost, preferably non-invasive, techniques to be developed that might increase the pace of restoration at nuclear sites.

Kaolinite ($Al_2Si_2O_5(OH)_4$, (Grim, 1968) is commonly found in sediments and soils around nuclear sites (Huertas et al., 1999), and has a simple 1:1 sheet silicate structure (Bauer et al., 1998). Under alkaline conditions, kaolinite dissolves, releasing Al^{3+} and Si^{4+} into solution, leading to the formation of secondary feldspathoid and zeolite phases (Mashal et al., 2004, Qafoku et al., 2003, Zhao et al., 2004, Wallace et al., 2013). The exact phase precipitated depends on the solution composition, base concentration, Si:Al ratio and temperature (Deng et al., 2006b). Important features of the internal structure of these neo-formed minerals, such as cancrinite ($[(Ca,Na)_6(CO_3)_{1-1.7}][Na_2(H_20)_2][Si_6Al_6O_{24}]$) (Bonaccorsi, 2005), sodalite ($(Na_8Cl_2)[Si_6Al_6O_{24}]$) (Bonaccorsi, 2005) and vishnevite ($[(Na,Ca)_{6-x}K_x(SO_4)][Na_2(H_2O)_2][Si_6Al_6O_{24}]$) (Bonaccorsi, 2005), are channels and cages, which are known to selectively incorporate guest anions/cations (Deng et al., 2006b, Mon et al., 2005). Alkaline altered sediments are known to incorporate ^{90}Sr and ^{137}Cs (Choi et al., 2005, Choi et al., 2006, Chorover et al., 2008, Deng et al., 2006a, Mon et al., 2005, Wallace et al., 2013), however, there is no information available regarding the successful incorporation of ^{99}Tc, in the form of pertechnetate (TcO_4^-), into alkaline alteration products. Perrhenate (ReO_4^-) has been incorporated into sodalite (Dickson et al., 2014, Mattigod et al., 2006) and the incorporation of this negatively charged, tetrahedral anion may support the hypothesis that TcO_4^- could be encapsulated into similar phases. This work investigates alkaline alteration of kaolinite, particularly the effect of base concentration, temperature, and solution composition during aging, with a view to encapsulating ^{99}Tc, in the form of pertechnetate (TcO_4^-), into a range of neoformed phases. Thus, potentially providing a novel remediation treatment for land contaminated with ^{99}Tc.

Material and Methods

Materials:

Two natural kaolinite samples were used as supplied; kaolinite from Fluka Chemicals (Switzerland) and sample K-Ga 1b from the Clay Mineral Society (Chantilly, USA). Ammonium pertechnetate was obtained from LEA-CERCA (France). All other reagents (sodium hydroxide, chloride, nitrate and sulfate) were obtained from VWR international (USA).

Methods:

In all instances, aerobic batch experiments were carried out in sealed 50 mL polypropylene Oakridge tubes. Initial experiments suspended 0.4 g of dry kaolinite (Fluka) in 20 mL of NaOH solution (0.05 M, 0.5 M, 5 M), at room temperature (RT) or 70 °C in a temperature controlled oven (5 M NaOH only). The same solid-to-solution ratio was used in all subsequent experiments. Samples were shaken on a daily basis. At intervals of 1, 7, 14 and 35 days (RT), and 7 and 10 days (70 °C), tubes were removed from the oven. After cooling to RT, solid phases were extracted by centrifugation, at 6000 *g* for 10 minutes. The solid phase was washed four times with deionised water and dried, at room temperature, in a desiccator containing Carbosorb.

Effect of solution composition and temperature:

Temperature effects were determined when 0.4g dry kaolinite (Fluka) was aged in 20mL 5 M NaOH, for 10 days at 40 ^oC, 50 ^oC, and 60 ^oC. In order to investigate the effect of changing the anion composition on the alteration products formed, three additional basic (5 M NaOH) solutions were used that contained either 1 M NaCl, 0.5 M $NaNO_3$ or 4 M Na_2SO_4. Kaolinite (Fluka) was aged in the NaOH/Cl solution at 70 ^oC for 10 days. Kaolinite (K-Ga 1b) was aged in the NaOH/NO_3 solution at 40 ^oC, 50 ^oC, and 60 ^oC for 14 days and in the NaOH/Na_2SO_4 solution, at 40 ^oC, 50 ^oC, 60 ^oC and 70 ^oC for 10 days. Additionally, 7 day time series experiments were performed at 70 ^oC using kaolinite (K-Ga 1b) in NaOH, and kaolinite (K-Ga 1b) in the NaOH/Na_2SO_4 solution, with daily sample-sacrifice.

Pertechnetate sorption experiments

Four sets of triplicate experiment were performed where ammonium pertechnetate was added at tracer concentrations (1.5 μM) to each of basic solutions described above (i.e NaOH, NaOH/SO_4^{2-}, NaOH/NO_3^- and NaOH/Cl^-) prior to the addition of kaolinite (K-Ga 1b) and incubated at 70 ^oC for up to 72 days. At regular intervals, aqueous samples were separated by centrifugation and Tc activity determined by liquid scintillation counting on a Packard TriCarb 2100TR.

Sample characterisation:

The starting material and alkaline alteration end products were analysed by a number of complimentary techniques. Powder X-ray diffraction (XRD) using a Bruker D8 diffractometer. Samples (50-100 mg) were mounted on silicon slides and scanned between 2° and 70° 2θ. Rietveld refinement was carried out using TOPAS 4.2 software (Bruker) providing quantitative analysis of the crystalline phases. (For the results presented in this study, the errors were -/+10 % at the 50 % level (i.e. between 40-60 % present) and -/+1 % close to the limit of detection (e.g. at the 3 % level there was between 2-4 % present). N_2–specific surface area was measured using the BET method, with a Micrometrics Gemini V Surface Area Analyser, with samples degassed for a minimum of 19 hours, at RT, with nitrogen gas prior to analysis. Electron micrographs were produced using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) using a FEI QUANTA 650 FEG environmental SEM. Samples were mounted on a carbon pad and coated in platinum prior to analysis.

Results

Preliminary investigation of alkaline alteration of kaolinite in NaOH solutions.

There was no evidence of new phases in the XRD patterns (not shown) where kaolinite was aged in 0.05 M and 0.5 M NaOH at room temperature for 35 days. A partial phase transformation to sodalite (data not shown), occurred when kaolinite was aged in 5 M NaOH, however, kaolinite peaks were still dominant at day 35. XRD patterns (data not shown) for the aging of kaolinite in 5 M NaOH, at 70 °C, indicated that full transformation to sodalite had occurred after 10 days. Based on these results, 5 M NaOH and elevated temperatures were used in subsequent experiments.

Effect of time and temperature on the alkaline alteration of kaolinite in 5 M NaOH.

Kaolinite was aged over 7 days in 5 M NaOH at 70 ^{o}C. XRD patterns (figure 1A) show that the transformation from kaolinite to sodalite started after 1 day, evidenced by the sharp decrease in the main kaolinite (k) peak intensities and the formation of peaks from the neo-formed sodalite (s) and minor amount of cancrinite (c). Rietveld analysis of the day 1 and 2 samples indicated the presence of 8 and 15 wt% of cancrinite (figure 2A), respectively. By day 3, sodalite was the dominant phase, with only minor kaolinite peaks visible. There was no evidence of cancrinite after day 2. Throughout the next 4 days, the kaolinite peaks further reduced as the sodalite peaks increased, until only minor amounts of kaolinite were visible in the XRD patterns by day 7. Rietveld analysis (figure 2A) of day 7 samples quantified 81 wt% sodalite and 19 wt% kaolinite. BET (figure 4) analysis indicates an initial increase, from 12 to 16 m^2/g, in the surface area at day 1, followed by a consistent decrease in surface area up to day 6 (7-10 m^2/g).

Rietveld analysis of XRD data from 10 days experiments at lower temperatures (figure 6C) showed 80 wt% sodalite and 20 wt% kaolinite at 50 ^{o}C, and 24 wt% sodalite, 70 wt% kaolinite and 6 wt% cancrinite at 40 ^{o}C. This indicates that the rate of clay transformation increased with temperature.

Effect of time and temperature on the alkaline alteration of kaolinite in 5 M NaOH + 4 M Na_2SO_4

XRD patterns for kaolinite aged over 7 days, in 5 M NaOH and 4 M Na_2SO_4 at 70 ºC are shown in Figure 1B. We note sharp decreases in the kaolinite (k) peak intensies between the starting material and the 1 day aged sample. The decrease in the kaolinite peaks, and the appearance of small peaks at 13.9º and 24.4º 2θ was consistent with the transformation from kaolinite to sulfatic sodalite/vishnevite. Rietveld analysis (figure 2B) of the day 1 samples quantified the neoformed feldspathoids as 2 wt% vishnevite and 29 wt% sodalite. After two days aging, the XRD patterns (figure 1B) showed further reductions in the kaolinite peak intensities (k) together with increasing sulfatic sodalite peak intensities (s). Rietveld analysis (figure 2B) for the day 2 samples showed that sulfatic sodalite had increased to 62 wt%, vishnevite had increased to 2.5 wt% and kaolinite had decreased to 35.5 wt%. By day 3, peaks for vishnevite (v) increased in intensity (figure 1B,), and only minor kaolinite peaks were visible. Throughout the next four days, the kaolinite peaks further reduced and the sodalite/vishnevite (s/v) peaks became more prominent until only minor amounts of kaolinite were visible in the XRD patterns by day 7. After 7 days, Rietveld analysis (figure 2B) showed that sodalite had decreased to 24 wt%, vishnevite had increased to 53 wt% and kaolinite had decreased to 23 wt%. This suggested that the kaolinite transformed to vishnevite, via a sulfatic sodalite intermediate phase. No broad humps were observed in the XRD patterns at any time during the reaction indicating that there were no amorphous phases detected at any time during the transformations.

SEM images (figure 3) of the solid phases collected during the transformation show the kaolinite starting material and the sulfatic sodalite/vishnevite alteration product at day 2 and 7. The kaolinite starting material (figure 3A) comprised multiple layers of stacked hexagonal plates approximately 20-30 µm in size. The EDS spectra of kaolinite showed the presence of Al, Si and O, with the Al and Si peaks present at equal intensities. After 1 day of aging, the overall crystal morphology of the kaolinite had evolved (data not shown). An interlocking desert rose morphology, characteristic of cancrinite (Deng et al., 2006), was observed after 2 days (figure 3B). These crystallites were approximately 2.5 μm in diameter and contained O, Al, Si, Na, and S by EDS analysis, consistent with formation of sulfatic sodalite or vishnevite. By day 7, the sample crystal morphology comprised spheres of interlocking tabular crystals (figure 3C) with a diameter of ~3-5μm. BET (figure 4) analysis indicates similar change to those observed in the pure NaOH system with an initial increase (12 to 15 m^2/g) in surface area at day 1 followed by a consistent decrease in surface area up to day 6 (4-6 m^2/g).

XRD patterns (figure 5) in respect of the aging of kaolinite in 5 M NaOH and 4 M Na_2SO_4, at 70 ^oC for 10 days, showed the presence of sulfatic sodalite and vishnevite. Rietveld analysis (figure 6B) of a sample aged at 60 ^oC for 10 days quantified the phases to be 34 wt% sulfatic sodalite, 8 wt% kaolinite and 58 wt% vishnevite. After 10 days aging at 50 ^oC the reaction products were 69.5 wt% sulfatic sodalite and 30.5 wt% kaolinite. At 40 ^oC the reaction products were 36 wt% sulfatic sodalite and 64 wt%. This suggested that at lower temperatures kaolinite transforms to sulfatic sodalite, and to vishnevite at higher temperatures.

Alkaline alteration of kaolinite in 5 M NaOH + 1 M NaCl or 0.5 M $NaNO_3$

The addition of 1 M NaCl to the 5 M NaOH solution led (figure 5) to the transformation of kaolinite to sodalite after 10 days aging at 70 ^oC. In contrast XRD data shows that aging kaolinite in 5 M NaOH + 0.5 M $NaNO_3$ for 14 days at 60 ^oC (figure 5) led to the formation of nitrate-cancrinite. Trace amounts of kaolinite (figure

5) were still present after 14 days. Rietveld analysis (figure 6A) of the 14 day sample quantified the phases to be 98.5 wt% nitrate-cancrinite and 1.5 wt% kaolinite, which suggested that the kaolinite to nitrate-cancrinite transformation was almost complete after 14 days. Experiments were also carried out at lower temperatures and showed an increase in the amount of kaolinite remaining after 14 days (i.e. 8 wt% at 50 ^{o}C and 31 wt% at 40 ^{o}C). This indicates that the rate of transformation from kaolinite to nitrate-cancrinite increased as temperature increased, and no reaction intermediates were present.

Pertechnetate incorporation behaviour during phase transformation

The % ^{99}Tc remaining in solution (figure 7) during the aging of kaolinite in either 5 M NaOH, 5 M NaOH +1 M NaCl, 5 M NaOH + 0.5 M $NaNO_3$, or 5 M NaOH + 4 M Na_2SO_4, was very high, ~ 95-97 %, in all instances. This suggested that only a small uptake to solids (~ 3-5 % ^{99}Tc; figure 7, inset) occurred during the first 9 days of aging. Although these experiments continued for 72 days, no further uptake was observed.

Discussion

The end products which form during alkaline alteration of kaolinite vary depending on base concentration, temperature and solution composition. The lack of mineral transformation during the reaction of kaolinite in 0.05 M and 0.5 M NaOH, and partial transformation to sodalite in 5 M NaOH at RT, implied that there was a threshold concentration effect between 0.5 M and 5 M NaOH. Full transformation at higher [NaOH] is anticipated as the increased rate of a reaction is related to increases in base concentration. The rate of mineral transformation is also higher at higher temperatures (Mashal and Cetiner, 2010).

Our experiments showed that in 5 M NaOH, kaolinite started to transform to sodalite at 70 °C after 1 day, with only trace kaolinite remaining after 7 days. In previous work on feldspathoid precipitation from both kaolinite (Rios et al., 2009, Zhao et al., 2004) and Si-Al solutions (Deng et al., 2006b), amorphous and zeolitic intermediates were observed before sodalite and cancrinite precipitation. However, we did not observe these intermediate phases in our experiments.

Effect of solution composition on alteration product formation

It is thought that guest anions form ion-pairs with Na^+ ions in solution, inducing the nucleation and growth of the neoformed feldspathoid end-products (Zhao et al., 2004). As we have stated, the end products vary depending on which anions are present in solution (Choi et al., 2006), and incorporation of guest ions is likely to be size dependent. The anion-Na^+ ion pairs must be able to fit inside the cages and channels of the aluminosilicate minerals which grow around them (Barrer et al., 1968). In this study, the addition of sodium sulfate, sodium nitrate and sodium chloride produced end products of sulfatic sodalite/vishnevite ($[(Na,Ca)_{6-x}K_x(SO_4)][Na_2(H_2O)_2][Si_6Al_6O_{24}]$), nitrate-cancrinite ($Na_6[Si_6Al_6O_{24}]\cdot 2NaNO_3$) and sodalite ($(Na_8Cl_2)[Si_6Al_6O_{24}]$), respectively. The formation of nitrate cancrinite and vishnevite resulted in guest anion substitution of NO_3^- and SO_4^{2-} into the ideal cancrinite structure. The sodalite structure does not have the wide channels found in cancrinite, only cages. These cages contain a central anion, tetrahedrally bound to four cations. As the ideal sodalite structure has a central Cl^- anion, the formation of sodalite in the presence of sodium chloride is as anticipated (Barrer et al., 1974), (Zhao et al., 2004).

In the NaOH/NO_3^- system no reaction intermediates were observed for the transformation of kaolinite to nitrate cancrinite (figure 5). The formation of nitrate cancrinite in high NO_3^- experiments has been previously reported (Buhl et al., 2000, Zhao et al., 2004). In our experiments, the degree of reaction for the NaOH/NO_3^- system was more than any of the other systems tested, with 69, 92 and 98 wt% transformation from kaolinite to nitrate-cancrinite at temperatures of 40, 50 & 60 ^{o}C after 14 days.

Reaction pathway for the NaOH/SO_4^{2-} system

The transformation of kaolinite aged in NaOH/SO_4^{2-} has not been reported previously, therefore, this reaction pathway was studied in more detail. The XRD patterns (figure 1B) observed for the alteration products are similar to those for sulfate-cancrinite which was synthesised from aluminosilicate solutions (Deng et al., 2006b). The morphological changes, observed via SEM (figure 3), show blade-like spheres at day 2 which are similar to those which have been reported in the literature for cancrinite (Choi et al., 2005), however that reaction was performed at a lower base concentration, (0.01 M NaOH instead of 5 M) and for a longer time period (190 days compared to 7 days). The appearance of peaks for Na and for S in SEM-EDS analysis, which were not present in the starting material, support the formation of sulfatic sodalite/vishnevite. In summary, XRD, SEM, EDS and surface area evidence all suggest that the partial alkaline alteration of kaolinite started after 1 day of reaction.

Vishnevite (sulfate cancrinite) formation was observed after 3 days of reaction. Rietveld analysis (figure 6B) shows a gradual increase in the % vishnevite over days 4 to 7, to 53 %, with the amount of sulfatic sodalite decreasing to 24 % over the same period. This is consistent with the dissolution of sulfatic sodalite and the crystallisation of vishnevite. SEM images of the reaction products at day 7 (figure 3c) showed minor changes in morphology, in that the spheres were smaller and more tabulated, which is similar to other SEM images reported for cancrinite (Deng et al., 2006c). The smaller size of the day 7 spheres was reflected by a slight increase in the surface area indicating some dissolution of sodalite and recrystallisation to vishnevite. By 7 days 78 % of the original kaolinite had reacted producing vishnevite at 70 ^{o}C (via a sulfatic sodalite intermediate). The sodalite intermediate is more stable at lower temperatures evidenced by the lack of vishnevite at 40 and 50 ^{o}C.

Proposed incorporation of ^{99}Tc into alkaline altered clays

The potential incorporation of the technetium anion, pertechnetate (TcO_4^-), into cancrinite or sodalite has received some support from other authors (Mattigod et al., 2006, Dickson et al., 2014); however, the successful incorporation of technetium into feldspathoids has not yet been achieved. The results (figure 7) of the low concentration pertechnetate experiments showed only a very small ^{99}Tc uptake under any of the reaction conditions studied. Up to 5 % sorption of ^{99}Tc to alkaline alteration products was observed in all instances. Using sulfate to drive the reaction toward sulfate cancrinite did not produce any increased uptake over other anions such as chloride or nitrate (despite the analogous tetrahedral coordination of SO_4^{2-} and TcO_4^-). TcO_4^- is a relatively large anion (~2.5 Å), and in cancrinite ^{99}Tc is likely to have been incorporated into a channel rather than a cage due to size constraints. Sodalite does not have channels, so the incorporation of ^{99}Tc would have been into the cages. The low ^{99}Tc uptake could suggest that the large pertechnetate anion is unable to compete favourably for the internal sites with the smaller, and therefore more size appropriate, OH^-, Cl^-, NO_3^-, or SO_4^{2-} anions (~1.4, ~1.7, ~2.0 and ~2.3 Å respectively), at these low concentrations. The successful incorporation of ^{99}Tc into alkaline alteration end products such as cancrinite and sodalite could provide a substantial research contribution. However, very high concentrations of pertechnetate (and conversely low concentrations of other anions) are likely to be required to produce significant uptake of ^{99}Tc to alkaline alteration end products.

Conclusions

Kaolinite undergoes alkaline alteration in the presence of 5 M NaOH (both with and without Cl^-) at 70 ^oC to sodalite, to vishnevite if sulfate is present (via sulfatic sodalite at lower temperatures), and to nitrate cancrinite in the presence of nitrate. The rate of reaction was faster for the OH and OH/NO_3^- systems relative to the OH/SO_4^{2-} system. Up to 5 % ^{99}Tc tracer could be incorporated into these alkaline altered feldspathoids which is insufficient to consider alkaline alteration of clay minerals to be a remediation strategy for ^{99}Tc.

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Figures

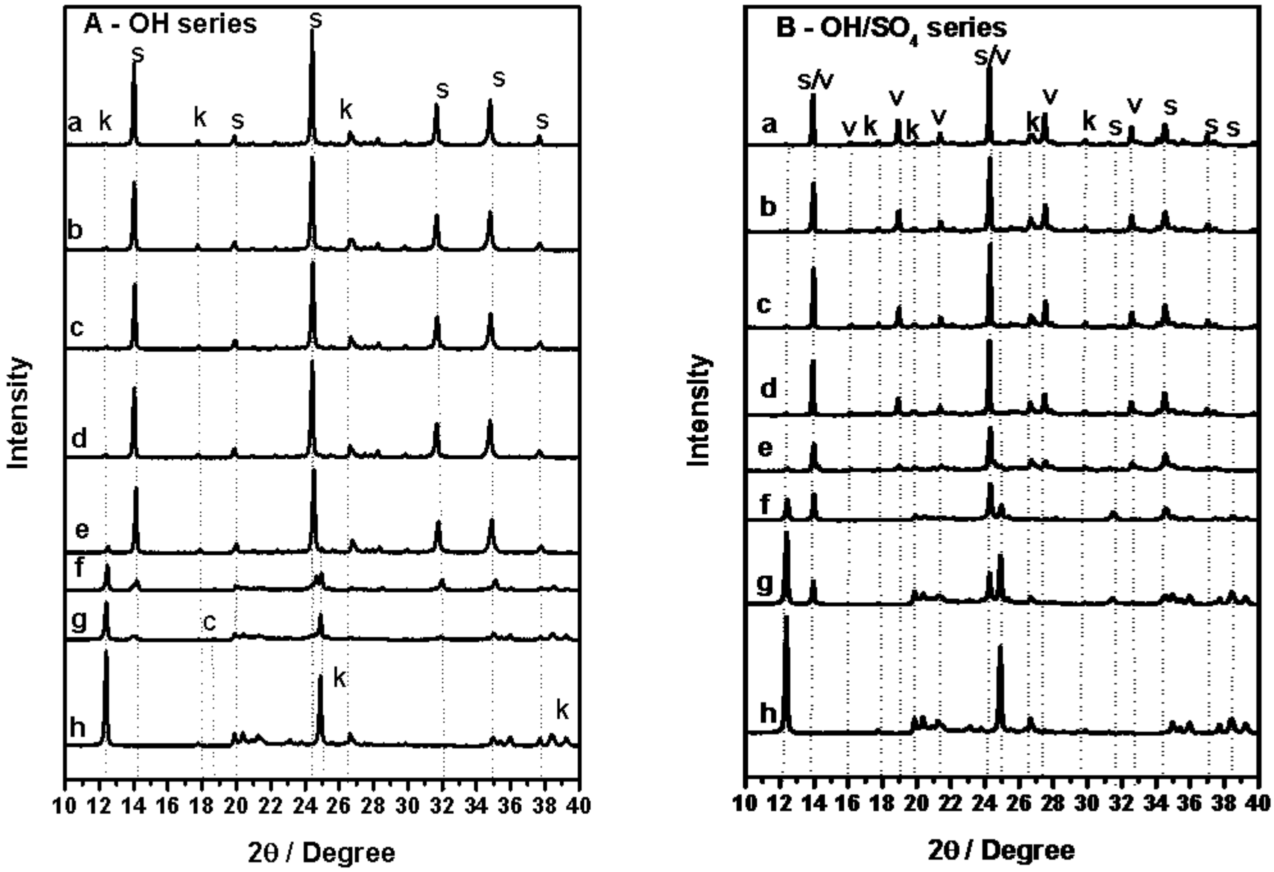

Figure 1: X-ray diffraction (XRD) patterns of kaolinite aged in 5M NaOH (A) and 5M NaOH/SO_4 (B) at 70^{o}C for a) 7 days, b) 6 days, c) 5 days, d) 4 days, e) 3 days, f) 2 days & g) 1 day. The XRD pattern of the kaolinite starting material is shown in h). Minerals are annotated as s (sodalite), k (kaolinite), v (vishnevite) and c (cancrinite).

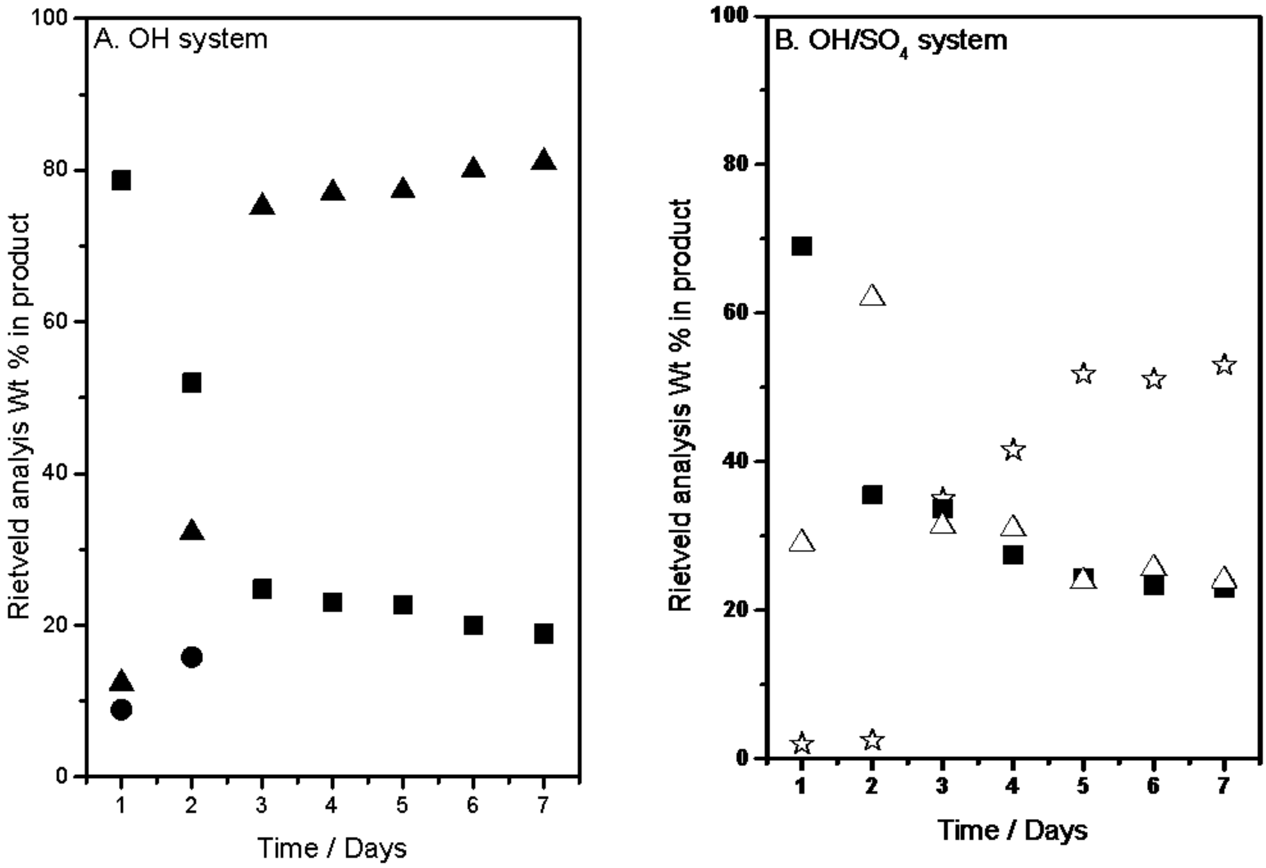

Figure 2: Rietveld analysis for kaolinite aged in 5M NaOH (A) and 5M NaOH/SO_4 (B) at 70°C for 7 days. Mineral Wt % are shown for kaolinite (squares), sodalite (triangles), cancrinite (circles) and vishnevite (stars). Muscovite impurity in the starting material not shown.

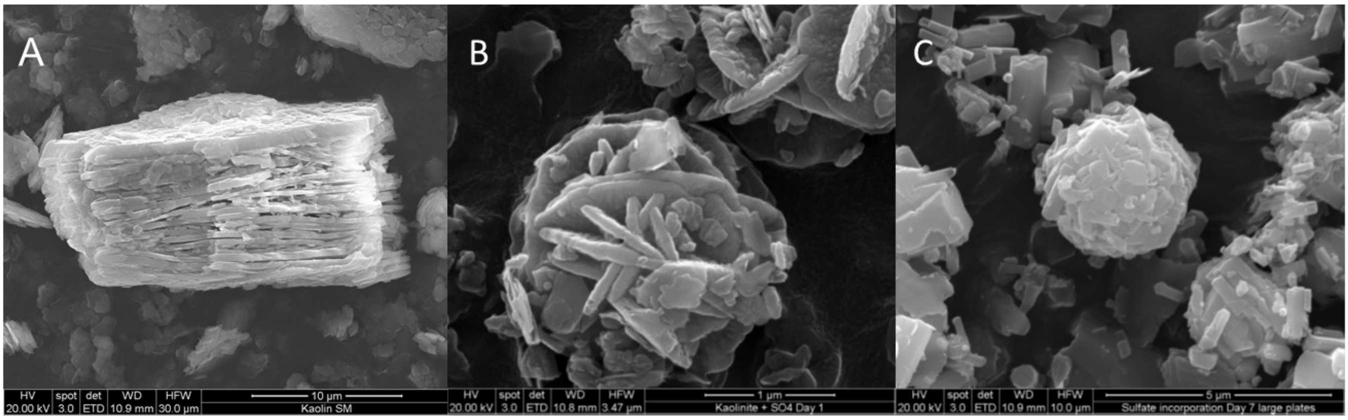

Figure 3: SEM images for kaolinite A) and the alkaline alteration product formed during the aging of kaolinite in 5M NaOH + SO_4 (4M) at 70°C for B) 2 days & C) 7 days.

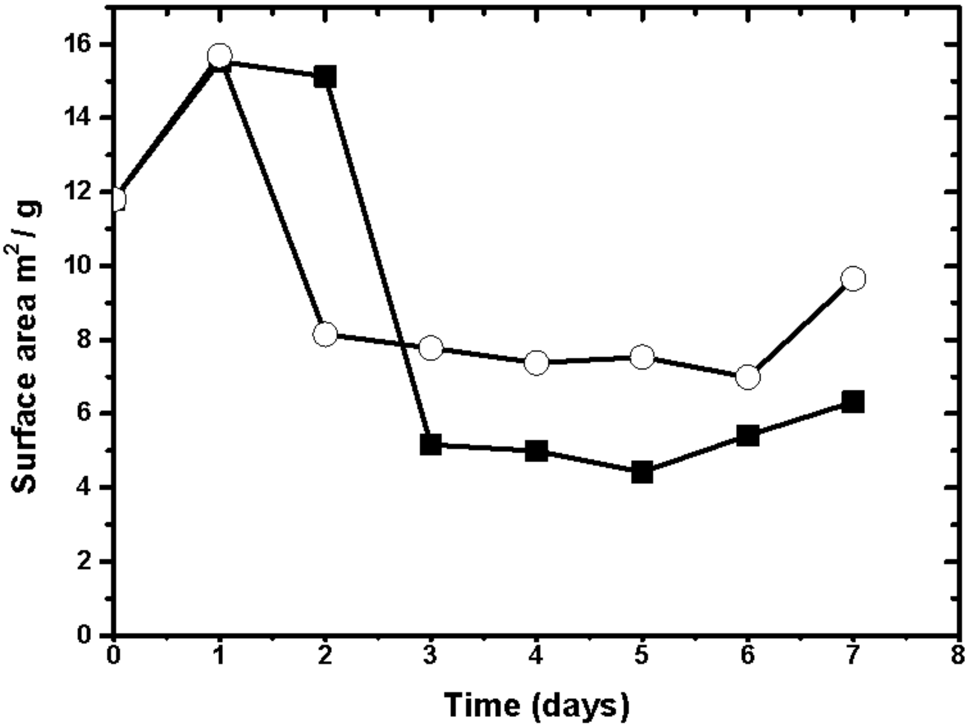

Figure 4: Changes in mineral surface area during the reaction of kaolinite in 5M NaOH (circles) and NaOH/SO_4 (squares) at 70°C for 7 days.

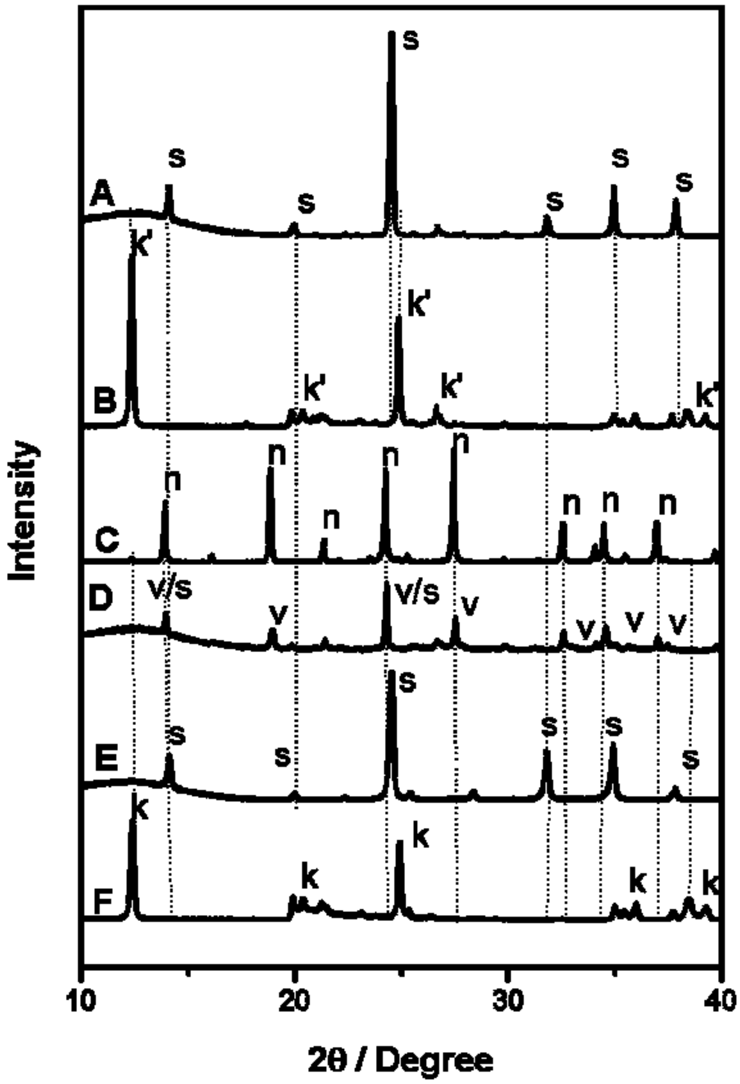

Figure 5: XRD patterns of (A) sodalite, annotated as s, the alkaline alteration product of (B) kaolinite (Fluka), annotated as k', aged in 5M NaOH + Cl at 70 °C for 10 day; (C) nitrate cancrinite, annotated as n, the alkaline alteration product of (F) kaolinite (K-Ga 1b), annotated as k reacted in 5M NaOH + NO_3 (60 °C, 14 days); (D) sulfatic sodalite/vishnevite, annotated as s/v the alkaline alteration product of (F) kaolinite (K-Ga 1b), annotated as k reacted in 5M NaOH + SO_4 (70 °C, 10 days) and (E) sodalite, annotated as s, the alkaline alteration product of (F) kaolinite(K-Ga 1b) , annotated as k reacted in 5M NaOH (70 °C, 10 days).

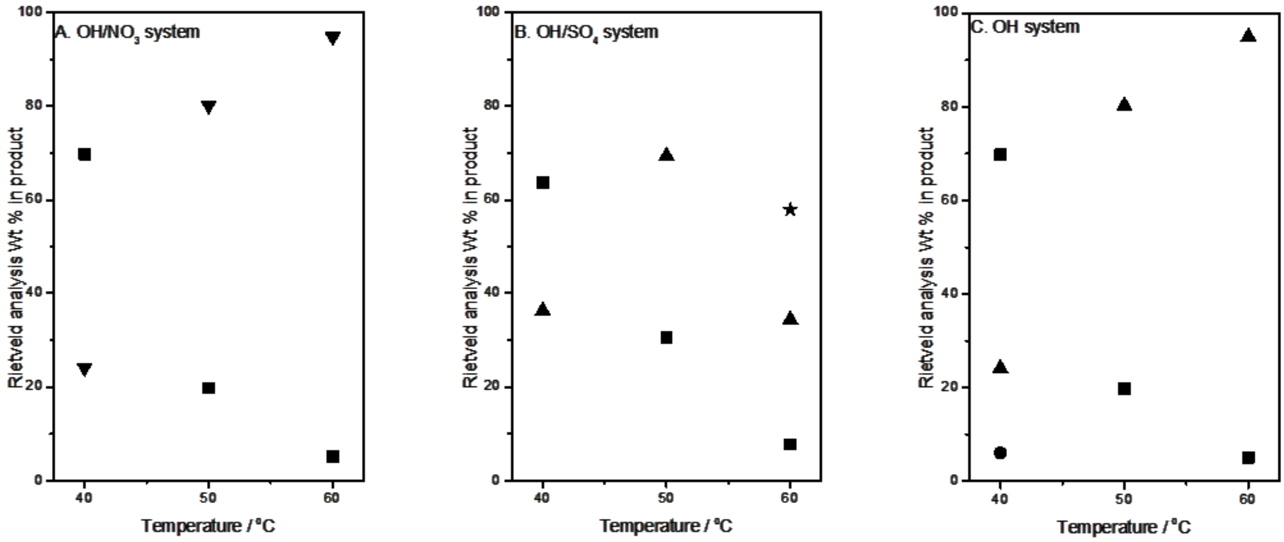

Figure 6: Rietveld analysis for kaolinite aged in A) 5M NaOH + NO_3 for 14 days at 40,50 & 60^oC. Mineral Wt % are shown for kaolinite (squares) and nitrate cancrinite (inverted triangles), in B) 5M NaOH + SO_4 for 10 days at 40,50 & 60^oC. Mineral Wt % are shown for kaolinite (squares), sulfatic sodalite (triangles) and vishnevite (stars) and in C) 5M NaOH for 10 days at 40,50 & 60^oC. Mineral Wt % are shown for kaolinite (squares), sodalite (triangles) and cancrinite (circles).

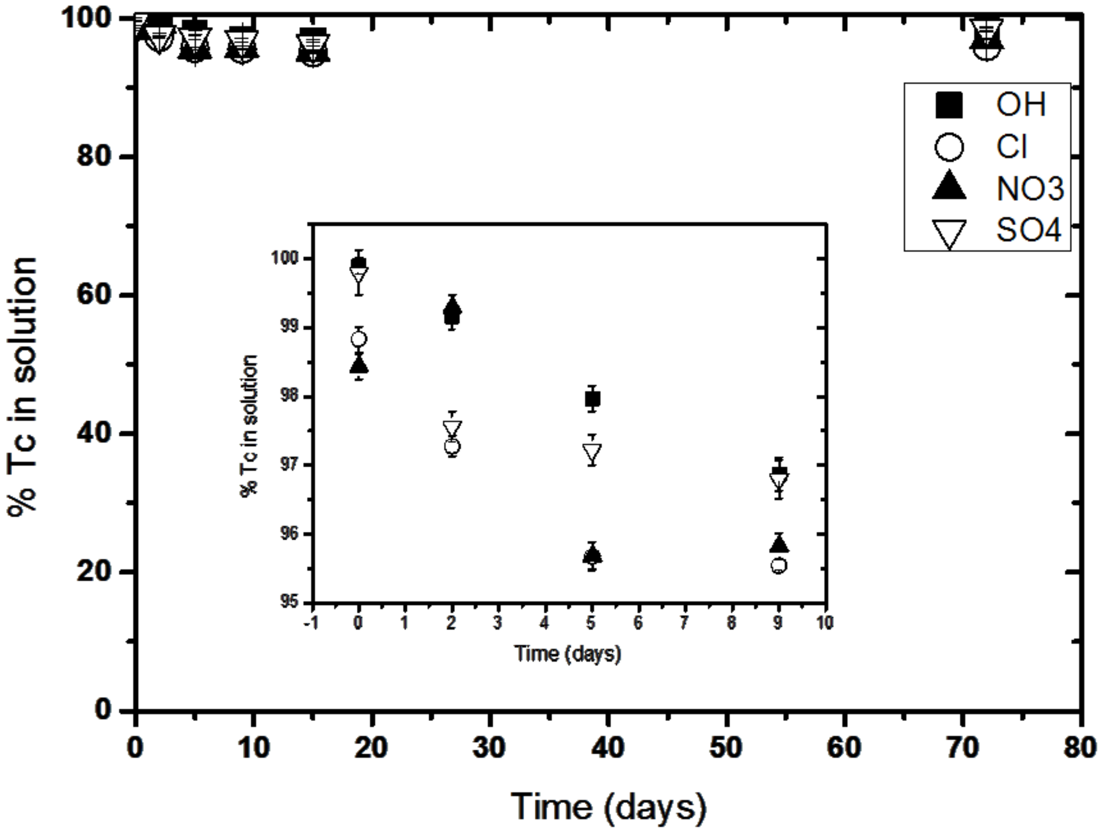

Figure 7: % ^{99}Tc (30 Bq/mL spike) in solution after aging kaolinite in 5M NaOH (squares), 5M NaOH plus Cl (circles), 5M NaOH plus NO_3 (triangles) and 5M NaOH plus SO_4 (inverted triangles) at 70ºC for 72 days.