

## Zeolite – Salt Occlusion: A Potential Route for the Immobilisation of Iodine-129?

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### ABSTRACT

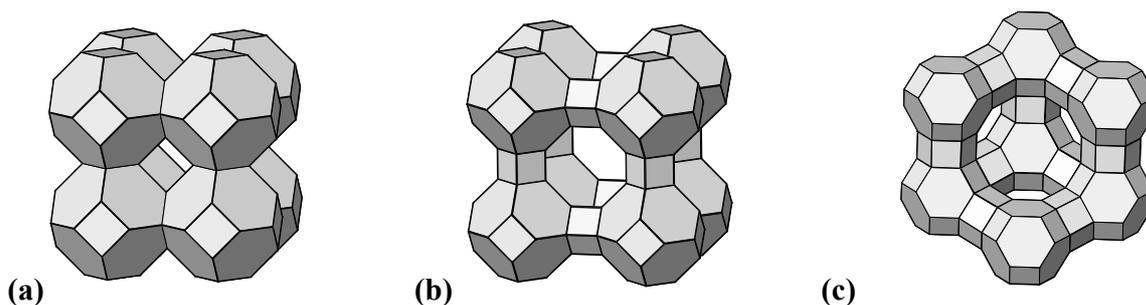
Reactions of zeolite Na-A with AgI, and the sodium, copper and lead forms of zeolites A, LTA, X and Y with NaI, have been examined as possible starting routes to the long term immobilisation of iodine-129. Heating the salts in air, at 500°C, with the sodium forms of the zeolites leads to the formation of occlusion products, where the iodide salt migrates into the zeolite pores. Detailed studies of the Na-A / 5AgI complex indicate it has a uniform distribution of Na, Si, Al, Ag and I, and is thermally stable to ca. 750°C, where there is a substantial weight loss as iodine is released. *In situ* powder X-ray diffraction studies have been used to monitor the occlusion reaction at 400°C, and show that the occlusion product decomposes to produce a single crystalline phase at 800°C prior to further decomposition at 850°C to a mixture of nepheline and elemental silver.

### INTRODUCTION

The long term immobilisation of iodine-129 arising from nuclear fuel reprocessing operations is a complex challenge. Secure containment of iodine-129 (half life 15.7 million years) is difficult to assure, due to the volatility of elemental iodine, the corrosive nature of iodide salts and the propensity for the displacement of iodide-129 by other anionic species in ground waters. At present, therefore, the preferred route for disposal of iodine-129 is through discharge to the ocean where dilution ensures minimal exposure to mankind. However, future regulatory decisions to reduce discharges to the marine environment may require the development of an inexpensive process for the safe and effective long term immobilisation of iodine-129.

We are exploring the occlusion of metal iodide salts into zeolite hosts as a potential route to the immobilisation of iodine-129. The occlusion of a metal (iodide) salt into a suitable zeolite host affords a nano-composite material in which the constituent cations and anions of the salt are dispersed within the microporous channel network of the host zeolite [1]. Effective sequestration of iodine-129 during reprocessing operations may be achieved by precipitation from the Dissolver Off-Gas liquor, using AgNO<sub>3</sub> [2]. The AgI thus formed may be converted to NaI by washing with NaOH in the presence of a suitable reductant, thereby regenerating Ag, if required [2]. Occlusion of AgI or NaI into a suitable aluminosilicate zeolite affords a primary wasteform

suitable for further elaboration. For example, calcination of an iodide salt occluded zeolite under ambient or isostatic pressure may yield iodo-sodalite,  $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{I}$ . This phase has been proposed as a durable waste form for the immobilisation of iodine-129 by several authors, as reviewed by Taylor [2]. Alternatively, encapsulation of an iodide salt occluded zeolite in a low melting glass, by sintering at ambient pressure, may afford a dense and durable glass-composite wastefrom. Previous work, with the aim of forming nano-composite materials with novel opto-electronic properties, demonstrated that AgI can be occluded into zeolites mordenite, ZSM-5 and zeolite Y [3, 4]. Here, we report our survey of the occlusion of AgI into zeolite A ( $\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]\cdot 27\text{H}_2\text{O}$ , Na-A) and the occlusion of NaI into zeolites Na-A, ZK-4 ( $\text{HNa}_7[\text{Al}_8\text{Si}_{16}\text{O}_{48}]\cdot 27\text{H}_2\text{O}$ , Na-ZK4), X ( $\text{Na}_{86}[\text{Al}_{86}\text{Si}_{106}\text{O}_{384}]\cdot 264\text{H}_2\text{O}$ , Na-X), Y ( $\text{Na}_{56}[\text{Al}_{56}\text{Si}_{136}\text{O}_{384}]\cdot 264\text{H}_2\text{O}$ , Na-Y), and the Pb- and Cu-exchanged versions of A, ZK-4, X and Y. The common framework topologies of zeolites A / ZK4 and zeolites X / Y, together with that of sodalite,  $\text{Na}_3\text{Al}_3\text{Si}_3\text{O}_{12}$ , are shown in Figure 1. The small face sharing  $\beta$ -cages characteristic of sodalite are linked through double four ring and six ring units in zeolites A / ZK4 and zeolites X / Y, respectively, to produce larger cages. The effective diameter of the alpha cage in zeolites A / ZK4 is 11.4 Å, with access restricted by 8-ring windows of approximately 4.2 Å diameter. The supercages in zeolites X / Y are ~13 Å in diameter, with access restricted by 12-ring windows of ca. 7.4Å diameter. In comparison, the effective diameter of the iodide anion is 4.4Å.



**Figure 1.** Framework topologies of (a) Sodalite, (b) Zeolites A / ZK-4 and (c) Zeolites X / Y.

## EXPERIMENTAL

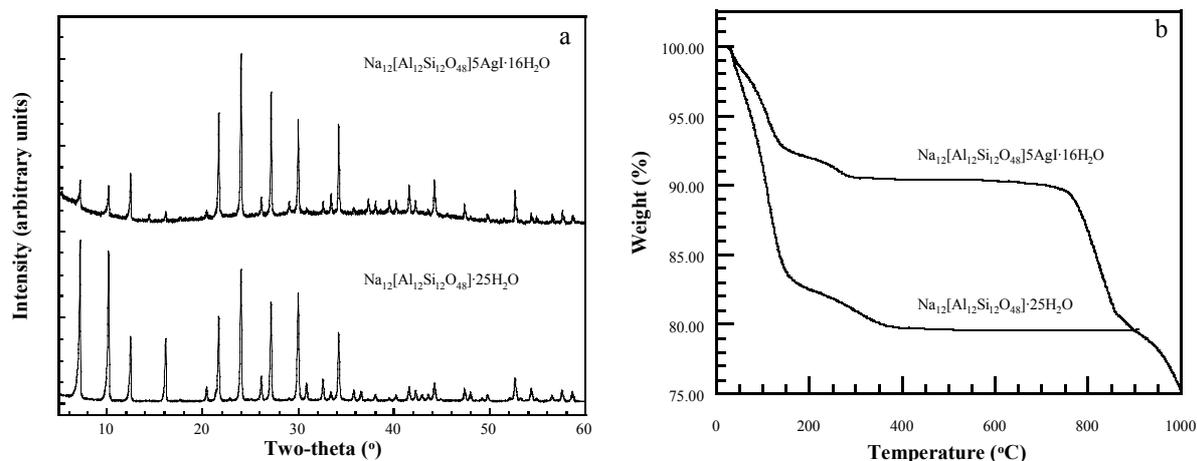
Samples of Na-A were supplied by UOP Ltd. or prepared by standard methods [5], Na-ZK4 with a Si/Al of ca. 2.0 was prepared by standard methods [6] and Na-X and Na-Y were purchased from Aldrich Chemicals. Exchange of extra-framework Na cations was achieved by stirring the appropriate zeolite with a 0.1M solution of Pb or Cu nitrate or acetate for 3 days, changing the solution every day. The exchanged zeolites were then thoroughly washed with de-ionised water before drying at ca. 60°C. Occlusion reactions were performed by first mixing appropriate quantities of polycrystalline zeolite and AgI or NaI, with an agate mortar and pestle. This intimate mixture was heated at a rate of 1°C min<sup>-1</sup> to 200 - 500°C, for 12 - 48h, in air. A slow ramp rate was employed to minimise dealumination and thus partial collapse of the aluminosilicate framework.

Room temperature powder X-ray diffraction data (XRD) were acquired using a Philips PW-1410 diffractometer or a Bruker D5000 diffractometer (Cu-K<sub>α</sub> radiation). High temperature powder X-ray diffraction data were acquired in air using the Bruker diffractometer equipped with an Anton Parr HTK1200 high temperature stage. Scanning Electron Microscopy (SEM)

studies were undertaken using a JEOL JSM-5600 SEM coupled with a PGT Energy Dispersive Spectroscopy (EDS) system. Specimens were prepared by applying a light dusting of material to carbon pads followed by carbon coating. Thermal analysis data were acquired using a TA Instruments Differential Scanning Calorimeter (DSC) and a Perkin Elmer Pyris 1 Thermogravimetric Analyser (TGA).

## RESULTS AND DISCUSSION

**Occlusion of AgI into Na-A.** The occlusion of AgI into Na-A was examined using a sample of UOP material. Powder XRD indicated this material to be single phase Na-A (Figure 2a) with a water content of 25 molecules per formula unit determined by TGA (Figure 2b). Samples from a master batch of Na-A and AgI mixed in a 1:5 molar ratio, were heated at 200°C, 400°C, 500°C for 12 - 48h in air. Whereas the diffraction pattern of the sample heated to 200°C for 12h appeared identical to that of the original mechanical mixture of AgI and Na-A, the AgI reflections in the samples heated to 400°C and 500°C for 12h were significantly reduced in intensity and subtle changes in the low angle reflections attributed to the zeolite phase were apparent. No AgI reflections were observed in the diffraction pattern of the sample heated to 500°C for 48h and all reflections could be indexed on the basis of a cubic unit cell with  $a = 24.530(2)\text{\AA}$ , characteristic of the Na-A framework. However, the intensities of the low angle reflections were significantly different from those of the Na-A starting material, see Figure 2a, indicating a change in the nature of extra-framework species, consistent with AgI occlusion.

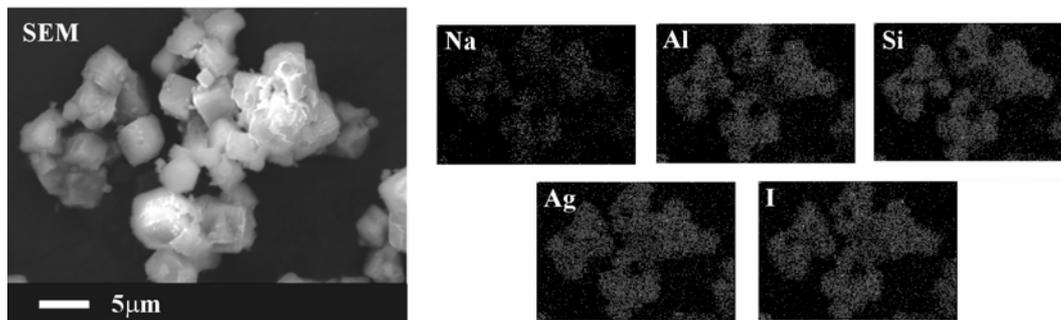


**Figure 2.** a) Powder diffraction patterns and b) Thermogravimetric analysis of  $\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]\cdot 25\text{H}_2\text{O}$  (Na-A) and the AgI occlusion complex prepared by heating at 500°C for 48h.

A sharp endotherm at 149°C was apparent in the DSC data of the mechanical mixture of AgI and Na-A, characteristic of the  $\alpha / \beta$  phase transition of AgI. This endotherm was also observed in the DSC data of samples heated at 200 - 500°C for 12h, although the intensity of this feature diminished with increasing reaction temperature. In contrast, the endotherm was not present in the DSC data of the sample heated to 500°C for 48h, indicating the absence of free crystalline AgI in this material, consistent with the XRD data.

Taken together, the combined XRD and DSC data suggest partial occlusion of AgI into the Na-A framework in samples heated at 400°C and 500°C for 12h, with full occlusion achieved

after heating at 500°C for 48h. The absence of super-cell reflections from the powder diffraction data indicate a random distribution of  $\text{Ag}^+$  and  $\text{I}^-$  ions within the Na-A framework. TGA indicated that volatilisation of AgI at 500°C was negligible (<0.02 wt%), in agreement with the thermodynamic data reviewed by Taylor [2]. SEM revealed the cuboidal morphology of the Na-A particles to be retained on occlusion of AgI and X-ray dot mapping confirmed a homogeneous distribution of Na, Al, Si, Ag and I, in these crystallites, Figure 3. The occlusion of AgI within Na-A crystallites was also confirmed from TEM and EDS analysis of thin sections splintered from crushed crystallites.



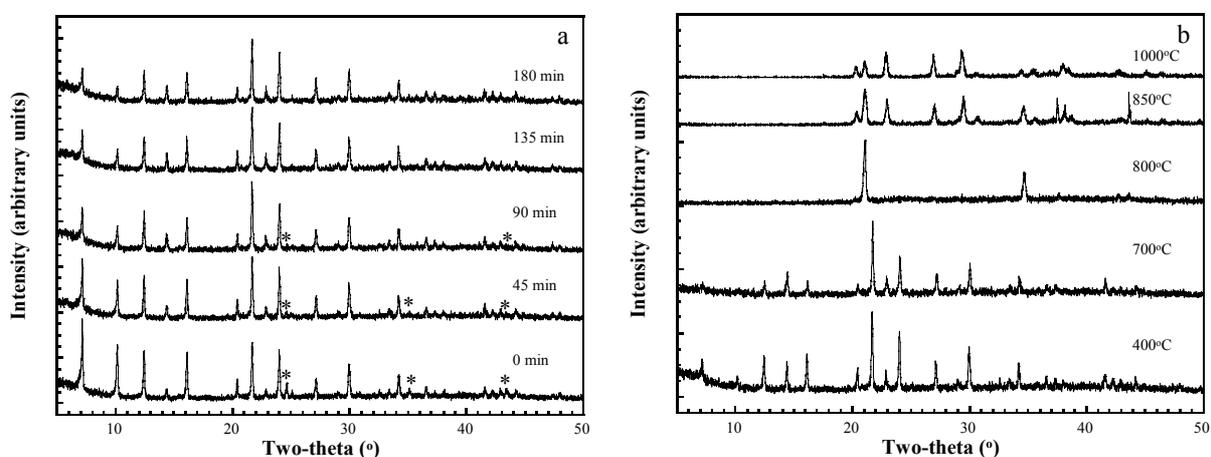
**Figure 3.** SEM image and X-ray dot maps of  $\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]\text{5AgI}\cdot\text{16H}_2\text{O}$  crystallites.

The thermal stability of the fully occluded Na-A / 5 AgI material, prepared by heating at 500°C for 48h, was studied by TGA and powder XRD. TGA of the occluded material to 1000°C revealed two weight loss events, Figure 2b. The first event, occurring between room temperature and 270°C, is attributed to the loss of zeolitic water. Assuming the occlusion of 5 AgI molecules per formula unit, the occluded phase was found to contain 16 water molecules per formula unit. Each AgI ion-pair thus displaces two zeolitic water molecules. For comparison, the occlusion of  $\text{NaNO}_3$  into Na-A is reported to lead to the displacement of ca. two zeolitic water molecules per occluded  $\text{NaNO}_3$  ion-pair [1]. The second event, arising at 750°C is attributed to the loss of iodine from the occluded zeolite both as  $\text{I}_2$  and AgI. Powder XRD of the product of this heat treatment revealed the presence of an amorphous phase,  $\text{NaAlSiO}_4$  (nepheline),  $\alpha\text{-SiO}_2$  and Ag. SEM / EDS analysis of this material revealed only a trace amount of iodine to be present.

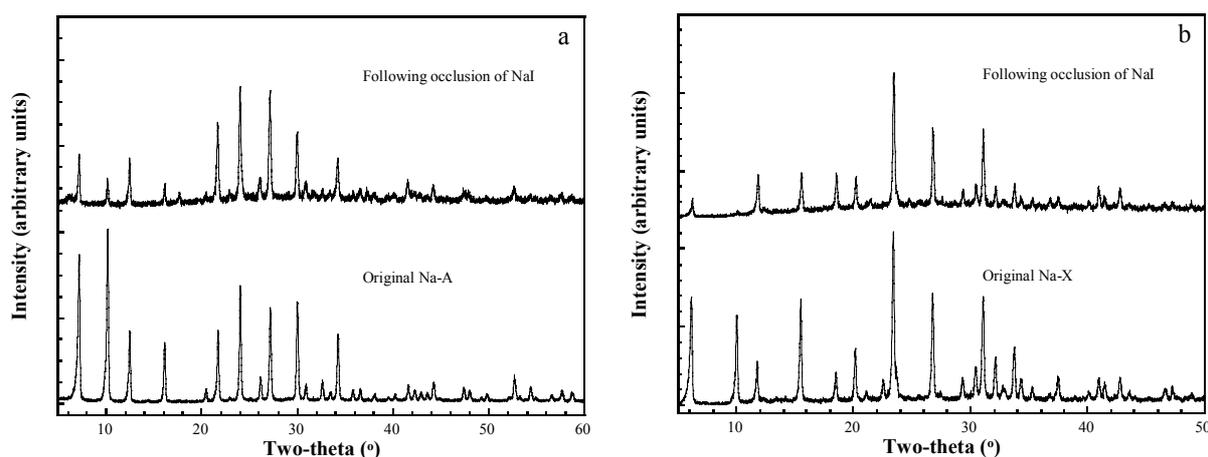
An *in-situ* high temperature powder XRD study of the occlusion process has also been carried out in air using a Na-A / 5 AgI mixture. The sample was heated to 200°C, monitored for 12 hours, heated to 400°C, monitored for 12 hours, heated to 500°C, monitored for 12 hours, then heated to 600, 700, 800, 850, 900, 950 and finally 1000°C. Upon heating to 200°C, small changes in the relative intensities of the zeolite peaks were observed, consistent with dehydration, and the AgI transformed to the cubic  $\beta$ -form. Upon heating to 400°C, the peaks for  $\beta$ -AgI disappeared over a 2-3 hour period, and the relative intensities of the zeolite peaks changed significantly, Figure 4a. Further heating, Figure 4b, led to complete collapse of the zeolite framework at 800°C to form a simple cubic phase, and by 850°C the sample was a mixture of  $\text{NaAlSiO}_4$  and silver metal.

**Occlusion of NaI into zeolites.** The occlusion of NaI into Na-A and several other zeolites has also been examined using a 1:4 molar ratio of zeolite:salt at 500°C for 24 hours. The products were characterised by powder XRD. The zeolites that were used were the sodium forms of A, calcined ZK-4, X and Y, and the Cu- and Pb-exchanged forms of all but Cu-A, which could not

be successfully prepared. For the sodium forms of these zeolites, complete occlusion of the NaI occurred based on the absence of any reflections associated with NaI in the products, and changes in the relative intensities of the zeolite peaks, Figure 5. For the copper forms of the zeolites, immediate reactions occurred as soon as the zeolite was ground together with NaI at room temperature. The Cu-exchanged forms of the zeolites were light blue, and the mixtures changed colour to green. There was also an obvious release of iodine vapour. After heating, these samples contained a mixture of zeolite and CuO. For the lead forms of the zeolites, reactions occurred at room temperature upon grinding, indicated by a change in the colour of the sample from white to yellow. However, there was no noticeable release of iodine vapour. After heating, there was little change in the relative intensities of the zeolite peaks, but all of the samples contained a significant amount of amorphous material. Further work is required to determine the nature of these products and whether or not any occlusion has occurred. We note, however, that there is no evidence in the X-ray patterns of any lead oxide or iodide.



**Figure 4.** a) In situ XRD of Na-A and AgI at 400°C,  $\beta$ -AgI reflections are denoted with an asterisk; b) Sequential powder diffraction patterns of the reaction of Na-A and AgI at 400, 700, 800, 850 and 1000°C.



**Figure 5.** XRD patterns of the a) Na-A and b) Na-X, and the occlusion compounds produced after heating with 4 molar equivalents of NaI at 500°C for 24 hours.

## CONCLUSIONS

Heating the sodium form of zeolite A with AgI, or the sodium forms of zeolites A, LTA, X or Y with NaI, to 500°C leads to the successful occlusion of the iodide salt into the zeolite pores. Detailed studies of the reaction of Na-A with AgI show that the product has a uniform distribution of Na, Al, Si, Ag and I in the crystallites, and is thermally stable to ca. 750°C. *In-situ* powder XRD shows that the occlusion reaction occurs over hours at 400°C, and the occlusion product does not change substantially with further heating prior to decomposition. At 800°C, the product contains a single crystalline phase, at 850°C this further decomposes to a mixture of nepheline (NaAlSiO<sub>4</sub>) and elemental Ag. The encapsulation of AgI occluded Na-A in a low melting point glass matrix, with the aim of producing a durable glass-composite material, should not, therefore, involve a processing temperature in excess of 700°C, to avoid the decomposition of the occlusion complex. The Cu-exchanged forms of these zeolites react with NaI upon mixing at room temperature and reduce the iodide to elemental iodine. The Pb-exchanged forms also react at room temperature based on colour changes, but without apparent release of iodine. The exact nature of these products is still unknown.

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