

X-RAY AND NEUTRON STUDIES OF THE OPTIMISED SYNTHESIS, THE STRUCTURE AND THE TRANSFORMATIONS INVOLVING NOVEL ION EXCHANGERS

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A combination of X-ray and neutron techniques can be used to elucidate the often rather complex structures of ion-exchangers - materials designed to trap and remove certain chemicals from an aqueous environment.

The sheer number of sites worldwide contaminated by industrial and military waste represents a major environmental and public health concern. For example, approximately 40,000 uncontrolled waste sites have been reported to U.S. federal agencies. About 1,300 of these have made it to the National Priorities List of

sites for remediation. The US experience is not unique.

In those cases where the toxic materials are transported in anionic or cationic forms, inorganic ion exchangers can be used to replace benign ions in the crystalline lattice for contaminant ions,

thereby limiting availability of these toxins to the biosphere [1]. In favourable instances the inorganic ion exchanger occurs naturally, can be mined and applied directly. For example the zeolites, naturally occurring aluminosilicate minerals possessing pores and channels of molecular dimensions, are well known ion exchangers. One of the most abundant, and therefore cheap, naturally occurring zeolites is the mineral clinoptilolite, which is commonly used for ammonia control and sorption in animal feed, fish tanks and kitty litter. It also happens to have a strong affinity for ^{90}Sr and ^{137}Cs , and is used routinely to treat radioactive effluent [2]. Unlike ion exchange resins, which are susceptible to radiation damage, the zeolites sequester the strontium and caesium over long periods. Clays, layered aluminosilicates, are also commonly used to treat contaminated soils and to sequester contaminants [1].

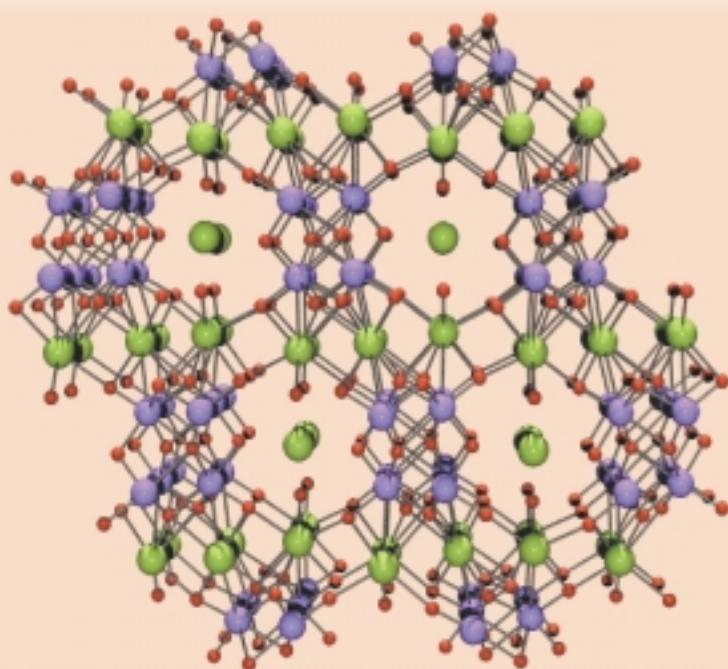


Fig. 1: Structure of $\text{Na}_{16}\text{Nb}_{12.8}\text{Ti}_{3.2}\text{O}_{44.8}(\text{OH})_{3.2}\cdot 8\text{H}_2\text{O}$ (SOMS-1) determined from a $5\times 5\times 8\ \mu\text{m}^3$ twined crystal. Large green balls are octahedral framework sodium cations, purple spheres are Nb/Ti sites and red spheres are oxygen.

The naturally occurring materials suffer from some disadvantages, including low capacity and a tendency to release contaminants if environmental circumstances such as pH are altered. The zeolites, and indeed the other mineral ion exchangers, are inspirational however when we seek fertile synthetic territory to explore for materials with these desirable ion exchange properties. The general formula $A^{x+z}[\text{Si}_{1-y}\text{T}_y\text{w}+\text{O}_2] \cdot m\text{H}_2\text{O}$ with $z = (4-w)y/x$, summarises the composition for most silicate zeolites. The framework cation sites substituting for silicon in the formula for quartz (SiO_2) are designated T; these cations, with typical valence $w = 3$ (Al^{3+}), are tetrahedrally coordinated by oxygen. The symbol A is used for possible charge balancing cations occluded in the regularly spaced pores and channels. Conventionally the ion-exchange capacity, determined by the Si/T ratio, has been maximised in aluminosilicate zeolites by producing materials with low Si/Al ($x\text{SiO}_2 + 1-x\text{Al}_2\text{O}_3 + 1-x(\text{A}_2\text{O}) \rightarrow (\text{Si}_2x\text{Al}_{2-2x}\text{O}_4)^{(2-x)} \cdot (2-x)\text{A}$). Unfortunately this limit is 1.0 and so the capacity for the aluminosilicates is limited.

Strategies designed to increase the ion exchange capacity include lowering the valence of the substituting “T-atom” in the formula above, increasing the number of anions in the framework by introducing octahedrally coordinated cations, and combinations of these two. Both strategies lead to new materials with increased capacity and selectivity [3,4]. In the first instance the substitution of Li^+ for Si^{4+} increases capacity and leads to other unusual properties including ion conductivity [3,5]. In the second instance, our collaborators T. Nenoff and M. Nyman at Sandia National Laboratory found inclusion of Ti^{4+} , although it does not decrease cation charge in the framework, does boost the anion content because of its octahedral coordination, and this requires extra charge-balancing cations in the pores and channels. Crystal structures, determined from the combined use of synchrotron X-ray diffraction from microcrystals (2 – 10 μm on edge) and neutron diffraction from powders, reveal that both strategies come together in the SOMS crystalline inorganic molecular sieves (Figure 1) developed at Sandia. In this instance a framework of octahedrally coordinated $\text{Nb}^{5+}/\text{Ti}^{4+}$ and Na^+ is formed, which is selective for removal of strontium from acidified solutions and in

the presence of such benign cations as Na^+ , Mg^{2+} and Ca^{2+} . Part of the sodium in the structure is exchangeable, and it also serves to decrease the total cation charge in this anion-rich framework. This results in increased cation exchange capacity, in a manner analogous to the principles observed in the Li-silicates [3].

It is important to determine accurate crystal structures for the materials resulting from the syntheses inspired by the strategies outlined above. This completes a feedback loop involving synthesis, ion exchange properties and structure and provides a basis for rationalising the functionality of the exchangers and for the development of new ones. Many of the structures of interest involve atoms of widely varying X-ray scattering powers, Li and Cs in the case of the Li-silicates for example [3]. They also crystallise from gels at low temperatures and so are often kinetically stabilised phases. This leads to samples that are mixtures of phases crystallising in fine hair-like crystal bundles. Structural studies have therefore relied heavily on synchrotron radiation, to both screen and collect useful diffraction data on microcrystals for determination of framework connectivity, and on neutron diffraction to provide the positions of light atoms either in the channels (Figure 1) or in the framework [3]. Time-resolved synchrotron X-ray powder diffraction is invaluable also since it allows us to observe directly the phases crystallising during a hydrothermal synthesis. Information from these studies can immediately be implemented in larger batch processes to prepare the single phase samples required for meaningful neutron diffraction, property and spectroscopic measurements.

The pressure to make the search for selective ion-exchangers more rational and efficient requires further development of time-resolved techniques. Along with wide-angle diffraction, this includes interrogating the crystallising gels with both SAXS and SANS to determine the incipient behaviour that leads to the formation of open materials rather than dense phases. Subtle changes in the starting materials chosen for synthesis often lead to quite different products. Some experiments in this area have begun (see for example [6]) and the joint use of X-ray and neutron diffraction on the same sample is clearly a priority in the future. ■

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