In or out: Setting a trap for radioactive iodine

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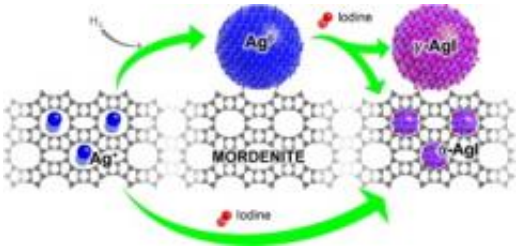

Porous mordenite is illustrated in the middle portion of the figure. Tiny particles of ionic silver (Ag+) are attached to the mordenite, as depicted by the three small blue spheres. Today's standard approach to capturing radioactive iodine begins with the reduction of the Ag+ particles using hydrogen gas (H2), resulting in neutral silver (Ag0—the large blue sphere at top center) embedded within the mordenite. When exposed to iodine gas (the tiny red spheres) the silver-laden mordenite forms different crystalline phases of silver iodide—depicted by the larger gamma phase (γ-AgI) particles upon the mordenite's surface, and the smaller alpha phase (α-AgI) confined within its pores.

Nuclear power plants produce a host of radioactive isotopes as by-products. One such radioisotope is Iodine-129 (^{129}I). With a half-life of nearly 16 million years, the ^{129}I produced by nuclear power plants will be sticking around for a long time. Because iodine plays a role in human metabolism, radioactive ^{129}I is especially dangerous if it escapes into the environment. Researchers utilizing the U.S. Department of Energy's Advanced Photon Source (APS) at Argonne National Laboratory have uncovered new information that might lead to improved long-term

storage of Iodine-I29.

For decades the nuclear industry has employed silver particles embedded within a mineral matrix to capture radioactive iodine gas. The silver and iodine combine to form silver iodide (AgI) nanocrystals. The researchers in this study, from Argonne and Sandia National Laboratories wanted to learn more about the microscopic structure of the AgI formed from iodine capture. To accomplish their goal they employed highly-intense x-rays produced at Argonne X-ray Science Division (XSD) beamline 11-ID-B of the APS to probe mineral samples containing silver iodide particles.

For this study, published in the Journal of the American Chemical Society (*JACS*), the group prepared powdered samples of a commercially produced mineral analog called mordenite, a type of zeolite. Zeolites encompass an array of porous minerals used extensively by industry as catalysts, molecular filters, and—of particular importance here—in radioactive waste remediation.

Mordenite laced with silver has long been used to capture radioactive iodine. According to Karena Chapman of XSD, lead author of the *JACS* paper, “No one was able to decipher the details of the capture mechanism on the molecular scale.” To uncover those molecular details, Chapman and colleagues turned to a technique called pair distribution function (PDF) analysis. The PDF experiment is conceptually very similar to x-ray powder diffraction. Used in laboratories all over the world, x-ray powder diffraction can analyze that materials possess crystalline structure, but exist as jumbles of smaller particles; for instance, the hundreds of crystalline grains found in a teaspoon of salt. In powder diffraction, x-rays travelling through a sample produce a distinctive pattern used to deduce the underlying crystalline structure(s).

For these particular materials, PDF is superior to standard powder

diffraction techniques. “Unlike powder diffraction, which analyzes only the position and intensity of the peaks in the pattern,” said Chapman, “PDF analyzes all the scattering, including diffuse scattering features in the so-called background. PDF provides information about the different interatomic distances within the material regardless of sample crystallinity or homogeneity.” Chapman also noted that the APS provides ideal conditions to carry out the PDF technique because “The APS is the best source of high-energy x-rays in the U.S., and the 11-ID-B beamline at the APS is the only dedicated PDF beamline in the U.S.”

A total of four samples of silver-laced mordenite were examined using PDF. Two of the samples held a mordenite-and-silver combination (the silver can bind to iodine). But the silver in those two mordenite samples differed: one held ionic silver (Ag^{+}), meaning that the silver atoms donated electrons to other types of atoms in the mineral. The other mordenite-and-silver sample was treated with heated hydrogen gas so that the silver was converted (or reduced) from the ionic form to the neutral (or pure metallic) form, called Ag^{0}.

The other two samples were identical to the first two, except that they were exposed to iodine gas, resulting in AgI nanocrystal formation within the mordenite. By subtracting-out the x-ray data from the samples lacking iodine, a differential PDF (denoted d-PDF) produced detailed molecular-scale information of the AgI particles themselves (i.e., excluding the mordenite matrix).

In nuclear waste remediation, radioactive iodine is trapped by mordenite impregnated with neutral silver (Ag^{0}) particles. The PDF data showed that after exposure to gaseous iodine, the Ag^{0}-and-mordenite sample formed AgI nanocrystals within the mordenite, as expected.

But two sizes of nanoparticles were revealed, each possessing its own crystalline phase, or form. The smaller alpha crystalline phase of silver

iodide (α-AgI) was trapped within the tiny pores of the mordenite and possessed sub-nanometer dimensions. By contrast, the larger gamma crystalline phase of silver iodide (γ-AgI) lay upon the mordenite's surface. These findings shed new light on how silver iodide particles exist within mordenite in present-day nuclear waste treatment.

What struck the researchers was the quite unexpected finding that the AgI nanoparticles found in the Ag^+ (ionic silver)-impregnated sample all possessed sub-nanometer dimensions, and were confined within the mordenite's pores. The researchers hypothesize that this new finding may provide an improved method for radioactive iodine capture and retention if a way can be found to permanently trap the toxic AgI within the mordenite's pores.

Chapman suggested that this research "shows the importance of studying materials on the molecular and atomic scales so as to optimize their desirable characteristics."

More information: "Radioactive Iodine Capture in Silver-Containing Mordenites through Nanoscale Silver Iodide Formation", *J. Am. Chem. Soc.* 132, 8897 (2010). DOI:10.1021/ja103110y

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