

# Locking away toxic metals into tiny holes

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Toxic and radioactive metals left over from the nuclear fuel cycle are of primary concern to the health of humans and the environment. Why? Because as the uranium from the reactor core ‘burns’, it decays to other elements, and leaving a pile of toxic material. Most of these remaining elements are still radioactive, and of particular concern are cesium (Cs) and strontium (Sr), which have the highest level of radioactivity in the waste. [Check out this HBO show by John Oliver](#), in a hilariously disturbing portrayal of America’s nuclear waste problem, he accurately points out many issues that never seem to go away.

I am deeply concerned by the nation’s nuclear waste problem, and I spent a great deal of my career finding ways to safely separate highly radioactive elements, and securely store them for as long as thousands of years. [A recent paper I published](#) looks into how the mineral gaidonnayite (pronounced: gay-don-NAY-ite), a hydrated sodium zirconium silicate, is surprisingly good at absorbing those toxic metals.

So how are we currently dealing with all this nuclear waste? There are many ways. The above video from the Last Week Tonight television show discusses some methods, and [here is another overview](#). However a lot depends on the nature of the waste and state/federal regulations. Some waste is stored in [cooling ponds on site](#), some is put into large [containers and buried](#), in the past some was [dumped in the ocean](#) – and the list goes on. In nearly all of those cases, the waste is treated as whole, without regard to what’s actually in the waste itself. However, many feel that high-level (highly radioactive) radioactive waste (including strontium and cesium) should be separated from low-level radioactive waste (like rare earth elements and other less toxic substances) so that waste can be stored more efficiently, or even recycled. Since we don’t have a [permanent storage facility](#) for nuclear waste in the United States, it is imperative that the most dangerous aspects of the waste are treated so they do not enter the environment and become [biologically available](#).

To tackle this problem, I turn to an important class of minerals that have been explored for [waste storage in the past](#). These are the naturally occurring [zeolites](#) and related [microporous minerals](#). These minerals act like natural molecular sponges; they are porous on the molecular scale (microporous), and can absorb elements from a liquid into the solid crystal. This process occurs spontaneously in nature, and has likely been going on for [billions of years](#). When these microporous materials start to absorb the element from the liquid, they also have to release back into the liquid, an element that already resides in the crystal. It’s an exchange process. Think of a dish sponge that has been colored green by food dye. If you want to wash off the green dye, you have to replace the dye with fresh water.

That physical exchange process in the sponge example is similar to what happens in the micro-pores of zeolite crystals, but the crystals’ atomic structures are made in ways that makes them selective for just a few molecules/elements (unlike the sponge, which can absorb all kinds of liquids). Minerals like zeolites



Figure 1: Image of gaidonnayite, a hydrated sodium zirconium silicate mineral, taken by the [RRUFF project](#). A very rare mineral found only in a few places on Earth, but very easy to make in the lab.

can't absorb all elements all the time, and certain microporous minerals are better at exchanging particular elements. The trick is finding the right match for the element that you want to selectively absorb, or modifying the mineral to make it work.

Gaidonnayite has small pores, so it wasn't expected to be able to exchange a large metal like cesium (having the largest diameter of all the known elements – [sans francium](#)). It was thought that the pores were too small to allow a large atom to move into them. However, I knew that gaidonnayite would have a desirable advantage. Other researchers have found that it (and similar zirconium silicate minerals) could resist the damaging effects of high radiation doses for thousands, or perhaps millions, of years. Therefore, gaidonnayite would be a good mineral to use because of its stability, if a way could be found to actually get the radioactive elements into it.

In the end, I made it work! But I had to modify the material a little bit from the natural state. Gaidonnayite did absorb cesium when hydrogen, the smallest of all elements, occupied the crystal prior to exchanging in the cesium. **But how does the smallest atom help capture the largest atom?** When I investigated the details of how the exchange process took place, I found some interesting interactions between water molecules already in the structure and hydrogen atoms that I introduced artificially.

The first step is to get the hydrogen in the crystal. It's easy – you just have to wash the mineral with a little bit of acid. Even a strong vinegar would likely be enough to prepare the mineral for the exchange treatment, but I used about 1% hydrochloric acid. The hydrogen spontaneously replaces the sodium in the crystal, and now the mineral is primed for cesium exchange. It's that simple.

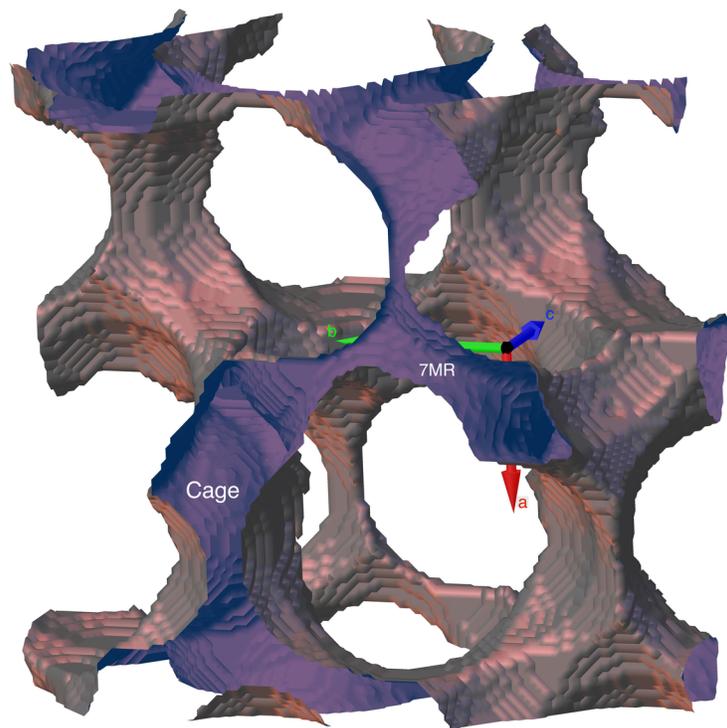


Figure 2: A internal mold view showing the pores/tunnels in gaidonnayite, with some of the tunnels shown in cross-section. The inside of the tunnels/cages are shown as purple, the outside is shown in tan colors. There are large cages where atoms, like cesium and sodium, can be held; however there are bottlenecked tunnels between these cages (labeled as 7MR), which make it hard for atoms to move around unless hydrogen is there to prop open tunnels and relieve the bottleneck. Made with OLEX2, (Celestian et al., 2019).

When hydrogen is in the crystal, it forces the water molecules in the tunnels to adopt a unique bonding geometry that remarkably forces the tunnels to expand. In the case of porous tunnel structures like gaidonnayite (and other minerals we have studied), hydrogen forces the water molecules that are already in the tunnels to adopt a chain-like pattern (sometimes called quantum water wires), which has a linear pattern because the tunnels are linear. The resulting water wires expand the tunnels just enough to accept an unusually large atom.

For gaidonnayite, it turns out that cesium could now get in.

Once the tunnels are propped open, cesium is allowed to rapidly enter the crystal. After a cesium atom enters the tunnel, the hydrogen atoms is pushed out, and the tunnel closes behind it. This locks in the cesium inside the crystal. It's entombed – and cannot get back out – even when we try to wash the mineral with acid and other substances!

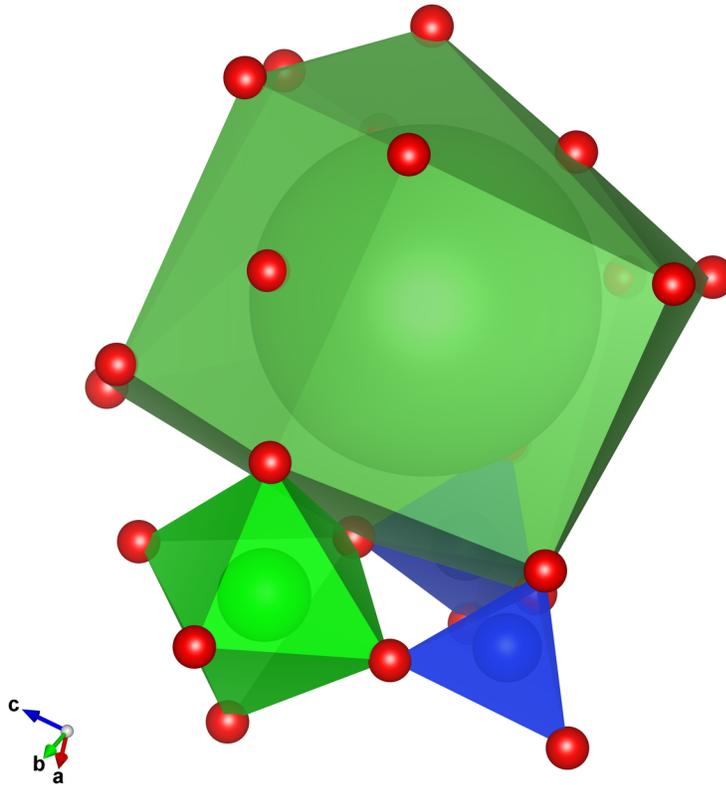


Figure 3: Illustration of cesium (dark green) trapped in a cage of gaidonnayite. The tunnels leading to these cages are small, and are usually inaccessible to large metals, like cesium, unless hydrogen is present. Red is oxygen, blue is silicon, light green is zirconium, dark green is cesium (Celestian et al., 2019).

Being able to selectively lock toxic elements inside the crystals, and have them safely stored in the crystals for the long-term, is a big advancement. This process can separate the high-level waste from the low-level waste efficiently, and also keep the toxic elements locked away from interacting with the environment or living organisms. Because gaidonnayite has no known toxicity to humans, there could be interesting ways to use it to absorb cesium, when other methods of safe containment, or soil/water remediation, fail. I am currently looking for more minerals that are selective for other radioactive elements.

It will be worthwhile to test this process in the real world and to see how it compares to other methods of waste separation. While the natural gaidonnayite mineral is super rare, it can be synthesized in the lab, and **it's really easy to make a bunch of it**. Even though policymakers cannot agree on a location to store spent nuclear fuel, I am hopeful that this research (and the work of other researchers, [see review here](#)) will encourage politicians, the nuclear industry, and other community stakeholders to make progress toward limiting potential ecological disasters by sequestering away the most harmful parts of nuclear waste.

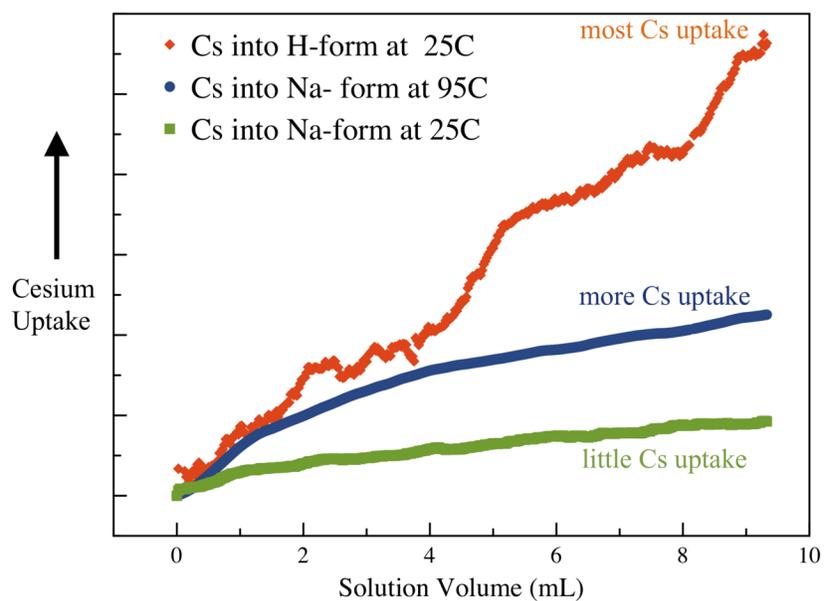


Figure 4: Putting hydrogen into gaidonnayite was an important step for enhancing cesium uptake and selectivity. This is an example of the gaidonnayite performance for cesium exchange at three different conditions as measured by Raman spectroscopy. Raw mineral (green), heated mineral (blue), hydrogen-bearing mineral (orange) (Celestian et al., 2019).

## References

In Situ Cs and H Exchange into Gaidonnayite and Proposed Mechanisms of Ion Diffusion. (2019). *Inorganic Chemistry*, 58(3), 1919–1928. <https://doi.org/10.1021/acs.inorgchem.8b02834>