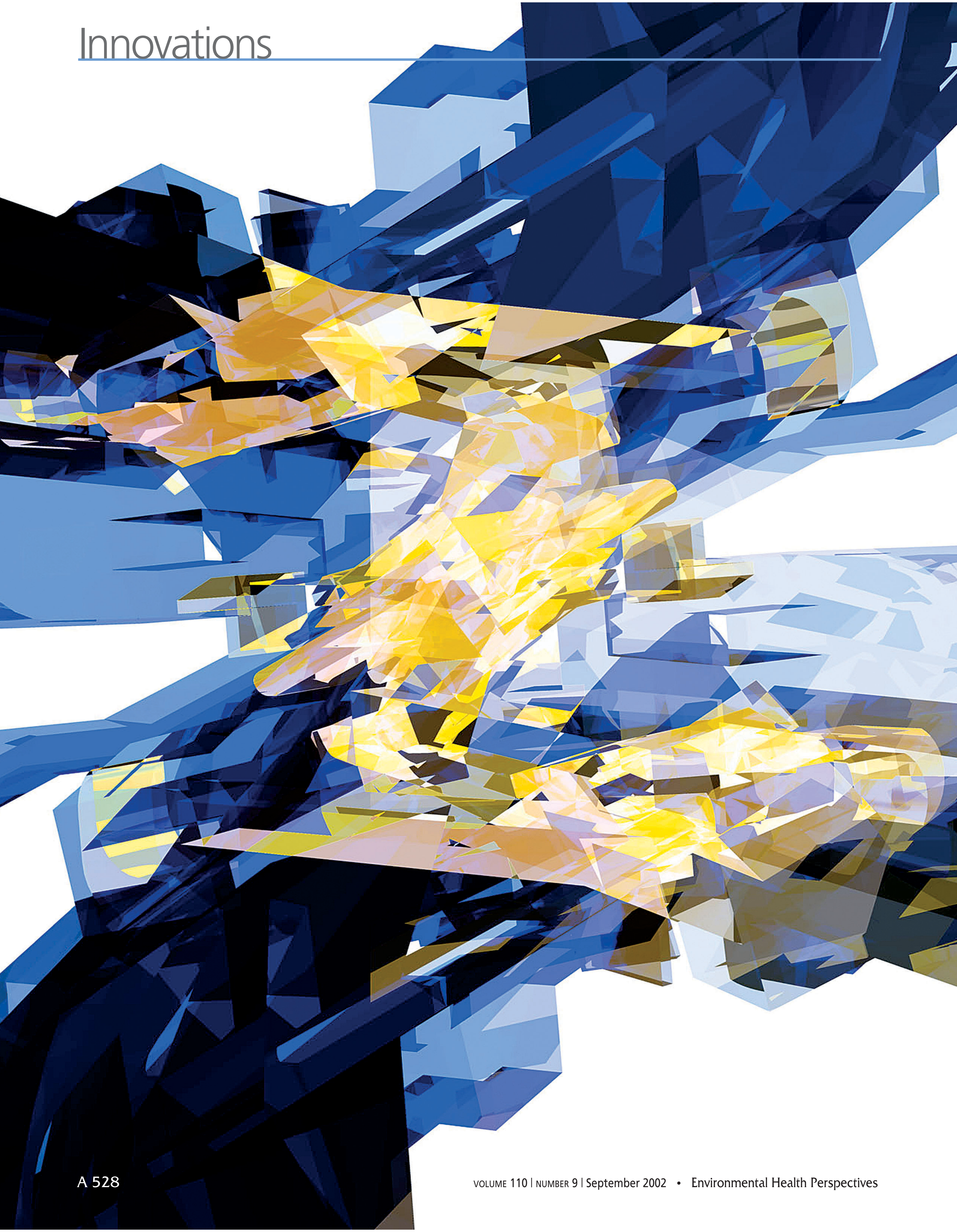


MIGHTY MICA

Synthetic Clay Remediates Radium

Radium is a serious contamination problem in many areas of the United States. A naturally occurring decay product of uranium, radium can break down into radon gas, a highly carcinogenic, colorless, odorless gas. Because it is highly water soluble, radium travels easily into groundwater in areas where it occurs more plentifully in the bedrock. Once in the body, it reacts much like calcium; bonding with bones, it can cause anemia, cataracts, bone cancer, and death.

As problematic as it is, radium is not unbeatable. Sridhar Komarneni, a professor of clay mineralogy at the Pennsylvania State University College of Agricultural Sciences and the university's Materials Research Institute, was part of a team including Naofumi Kozai, a visiting scientist from the Japan Atomic Energy Research Institute, and William Paulus, a master's degree recipient now with General Motors, that investigated a group of specialized synthetic clays with a particular affinity for substances such as radium and strontium. In research published in the 12 April 2001 issue of *Nature*, the team showed that one particular synthetic clay, known as Na-4-mica, not only targets radium ions for removal from water but also immobilizes them, offering the promise of a safe and effective way to clean up this radioactive waste.

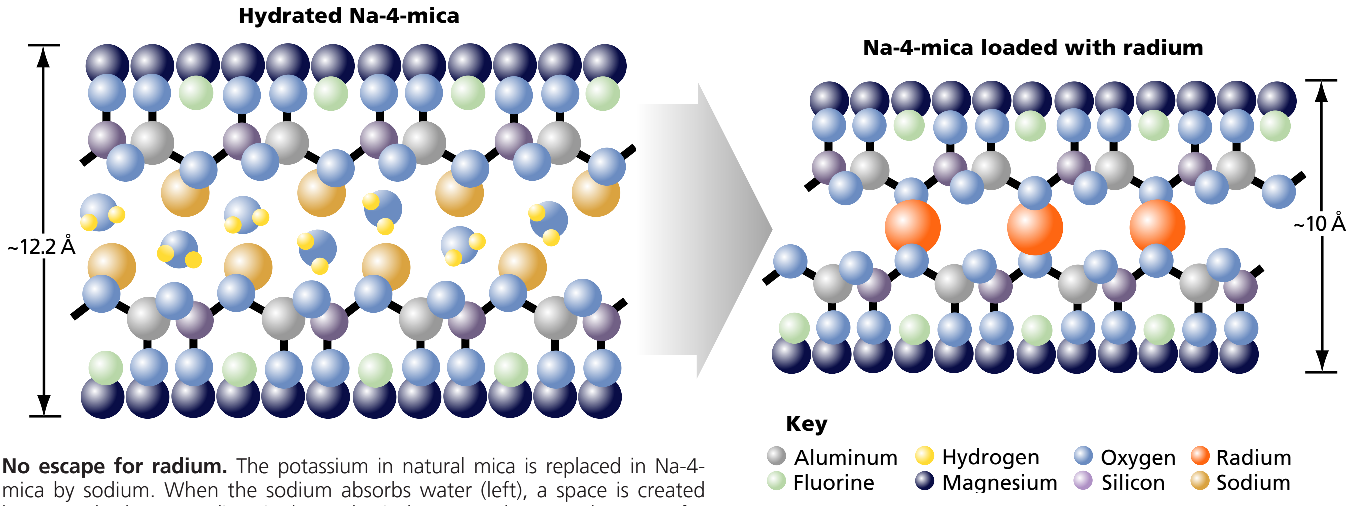
A Swell Idea

The U.S. Environmental Protection Agency has set drinking water limits for two of the most common isotopes of radium, radium-226 and radium-228, at 5 picocuries (pCi)/L combined. In addition, soil concentration limits for radium-226 in uranium and thorium mill tailings have been set at 5 pCi/g for the first 15 centimeters of soil, and 15 pCi/g below that depth. However, according to Komarneni, many parts of the United States still have a significant radium contamination problem, particularly the Southwest, where large amounts of uranium are mined, and points throughout the eastern United States, where coal and phosphate processing produce tailings that contain radium.

"Areas like Pennsylvania, which have a known radon problem, will also have radium in their soils, and perhaps in their water supplies," Komarneni says. "At least twenty-five water systems in Wisconsin have had problems with radium in their drinking water."

Enter the "swelling micas." This group of synthetic clays, of which Na-4-mica is only one, were originally developed expressly for water treatment. They expand as they absorb metal ions, then collapse, sealing the metals inside. Na-4-mica is formed by combining kaolinite, a soft clay mineral used in the ceramics industry, with magnesium oxide in sodium fluoride at a temperature of 890°C. The resulting product has natural mica's sheetlike structure and brittle composition, but the space between the layers, Komarneni says, is a slight 0.28 nanometers wide, which makes it very selective for smaller ions such as radium.

Na-4-mica has much the same composition as natural mica, containing aluminum, silicon, and magnesium. But natural mica



No escape for radium. The potassium in natural mica is replaced in Na-4-mica by sodium. When the sodium absorbs water (left), a space is created between the layers. Radium is then selectively attracted as a replacement for the sodium (right), and a strong electrostatic bond effectively locks the radium into place. (Not to scale.)

also contains potassium ions, which sit in hexagonal holes in the mineral's layers, superimposed upon one another, bonding the sheets tightly together. This "closed" structure makes natural mica a poor ion exchange medium, says Komarneni. In Na-4-mica, however, each of these potassium ions is replaced by two sodium ions. The sheet structure of the Na-4-mica is offset to accommodate the two sodium ions, creating a space for radium. According to Komarneni, it's this difference that makes Na-4-mica ideal for removing radium.

In theory, the new structure, with its offset layering, selectively attracts radium as a replacement for the sodium ions. The electrostatic energy of the added radium ions creates a shifting effect that helps realign the layers atop each other. The resulting strong electrostatic bond between the negatively charged mica and the positively charged radium ions effectively locks the radium into place. This bond, Komarneni says, can typically only be broken by exposure to extremes of pH; because such extremes are rarely found in nature, the clay offers a promising long-term storage solution for radioactive waste.

While still in its early stages, Komarneni's research indicates that Na-4-mica has a strong affinity for both radium and strontium, and can absorb approximately 20% of its own weight in those elements. So one gram of clay could theoretically clean hundreds of liters of water. Tests of whether it is possible to increase that capacity are still ongoing.

Once the clay is saturated with contaminants, it can be removed and sealed in a conventional hazardous waste facility if the radiation level is low enough, or encased in more secure storage if the level is higher, with the Na-4-mica serving as a backup to the steel containers and other reservoirs used to store such waste. Komarneni notes, however, that thanks to the strength of the bond between the clay and the contaminants, less extreme, and thus less expensive, storage methods can be used for radioactive waste.

The Promise of Clay

The clay has been tested with solutions of varying concentrations of sodium chloride and radium chloride, with a focus on both measuring rate of radium uptake and establishing that the clay would not take up sodium at the expense of radium. Testing several different synthetic and naturally occurring clays, Komarneni found that Na-4-mica performed the best, removing better than 95% of the radium from test solutions.

Na-4-mica was also tested at the Hanford Nuclear Plant site in Richland, Washington, by Komarneni and scientists at Pacific Northwest National Laboratory to address concerns about strontium migrating into the nearby Columbia River. Clark Carlson, who was a Pacific Northwest senior research scientist at the time, says a number of different ion exchange materials were tested for strontium removal capabilities.

"We used a high-potassium simulated [nuclear reactor] waste, which we spiked with strontium-90," Carlson explains. The team batch-tested clays by mixing 0.1 g clay with 5 mL waste, left it to sit for 72 hours, then filtered out the material and analyzed the solution by radioactive counting and mass spectrometry. Na-4-mica effectively removed 99% of the strontium in the test batches.

Komarneni says Na-4-mica could be used to remediate groundwater in a number of ways. To clean up a plume containing radium, for example, remediators could dig a trench and line it with the clay. The radium-containing water would pass through the trench, and the radium would bond with the clay while the purified water, spiked only with enviromentally benign amounts of the displaced sodium, flowed onward. Or ponds could be lined with the clay to prevent radium from leaking into groundwater. Additionally, he says, the clay could be pelletized and used in a conventional ion exchange column.

Suggested Reading

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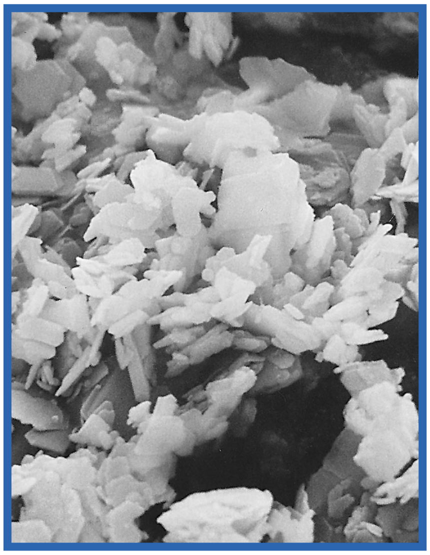
The use of kaolinite makes Na-4-mica less expensive to produce than other swelling micas made with gels or oxides. Kaolinite costs about 20¢ per pound, compared to about $2 per pound for gels and about $1 per pound for oxides. Komarneni estimates the total cost for Na-4-mica at just $2 per pound of clay manufactured.

According to Komarneni, the material is also environmentally safe to produce. "I think the only issue is possibly some slight volatilization of fluorine [which can cause lung damage]," he says, "but you could minimize that with scrubbers or by doing the process at lower temperatures." And Na-4-mica is environmentally preferable to current technologies, which involve stripping out radium with tremendous amounts of sodium—about a billion times more sodium ions than the radium ions to be stripped.

Komarneni says it's possible to recycle the clay by using sodium or potassium to leach out the radium or strontium, but that the low material cost makes it far more practical to manufacture fresh clay than deal with heavily contaminated solutions. However, he adds, this recyclability bodes well for the clay's use as a recovery system for more valuable substances, such as copper.



The crystal trap. One gram of Na-4-mica could theoretically clean hundreds of liters of water contaminated with radioisotopes.

It is, however, not a perfect solution, Komarneni admits. "It depends upon the other ions competing for those spaces in the clay," he explains. For example, Na-4-mica has an even greater affinity for copper than for radium or strontium. So if the waste contained a lot of copper, the mica would take up the copper at the expense of the radioactive elements. But these are not insurmountable problems. In the case of copper-contaminated waste, Komarneni says, "you could address that issue by increasing the pH of the copper-containing solution to around six and precipitating out the copper."

"I think Komarneni's clay does show great promise, and could work well in a barrier system as well," Carlson says. However, he adds, that presupposes that regulators would be willing to leave contaminated, albeit contained, material in place, which hasn't been a well-received approach to date.

"It's not the perfect solution for all circumstances," Komarneni says. "You have to know the circumstances and conditions under which you're using it. For example, you wouldn't want to use it as part of a treatment for acid mine drainage [with its extremes of pH]. But I do think it provides a viable, cost-effective solution to a very real problem."

Lance Frazer

Sridhar Komarneni