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Scientists Study the Use of Fullerenes to Trap Actinides

Fullerenes are a new class of carbon molecules, the first truly molecular form of pure carbon yet isolated. Fullerenes consist of hollow cages composed of three-connected networks of carbon atoms. The name fullerene was chosen to honor R. Buckminster Fuller, the creator of the geodesic dome, and fullerenes are also known as "buckyballs." The most famous fullerene molecule, C_{60} or "buckminsterfullerene," has sixty carbon atoms arranged in the same geometry as the vertices of the seams on a soccer ball. Fullerenes and their discoverers, Richard E. Smalley, J. R. Heath, S. C. O'Brien, and Robert F. Curl of Rice University and Howard W. Kroto of the University of Sussex, England, were honored this fall by the 1996 Nobel Prize in Chemistry, eleven years after their discovery.

The cage-like structure of fullerenes can be used to encapsulate metal atoms on a molecular scale creating an endohedral
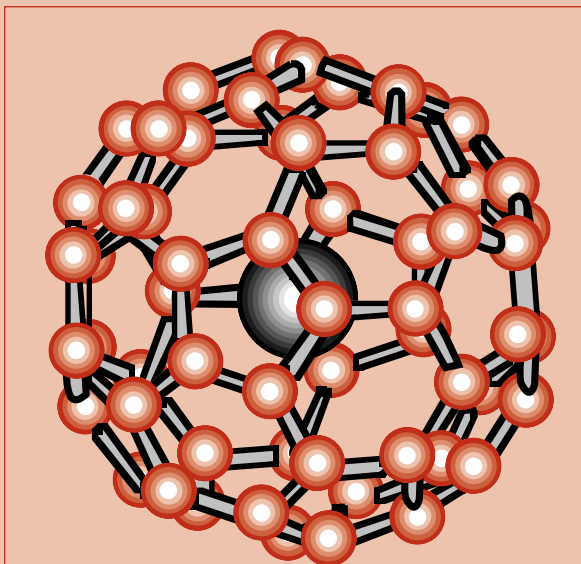

Figure 1. An idealized structure of U@C_{60}.* **The uranium atom in the center of the molecule is too large to fit through any of the holes in the five-membered and six-membered carbon rings that make up the fullerene cage. It is expected that the true structure of U@C_{60} will have the uranium atom off-center as the hollow within the cage is much larger than the uranium atom. It is also expected that the uranium atom will donate electrons to the cage and exist within the cage as an ion although the molecule as a whole will be uncharged.**

[*See Note p.2]

metallofullerene (a metal atom within a closed-cage fullerene). In fact, within a few days of the original realization that C_{60} may be shaped like a soccer ball, the first experimental indication was obtained that a metal atom can be put inside. Smalley writes, "For most observers on first learning of the proposed soccer ball structure of C_{60}, there often is an almost irrepressible urge to ask 'Can you put something inside?'" We asked, "Can you put an actinide inside?" Here was an opportunity to trap actinide atoms within one of the most stable molecules or clusters ever encountered and isolate it chemically from its environment.

The first application to occur to us was to use endohedral metallofullerenes as the basis for a superior waste form for actinides. An encapsulated actinide atom cannot escape from its fullerene cage—the holes in the cage are too small even for a helium atom to fit through. The problem of a stable waste form

Scientists Study the Use of Fullerenes to Trap Actinides *(continued)*

Collaborators on this project include **Michael D. Diener,** Rice University; and **Coleman A. Smith, James T. McFarlan and D. Kirk Veirs,** NMT-6.

is reduced to the simpler problem of the immobilization of the much larger and hydrophobic fullerene with the actinide trapped inside. In all conventional waste forms, metal ions have mobility and can be leached out of the matrix. The migration of a metal atom trapped within a fullerene is expected to be much lower because the whole fullerene must migrate for the trapped metal atom to move.

Our interest in this approach was stimulated in 1991 by a string of discoveries in fullerene science. The first and most significant discovery was made at the University of Arizona by Huffman and Krätschmer, who developed a method to produce macroscopic quantities of fullerenes in a carbon arc. Before this discovery was made, fullerenes were studied by sweeping the vapor created by an intense laser pulse, which had been focused onto a carbon target, into a sensitive mass spectrometer. The second discovery was the detection of fullerenes in Precambrian rock believed to be more than 600 million years old. Fullerenes thus appear to have been chemically stable in the environment for much longer times than those required for a plutonium waste form. The third discovery was of a uranium endohedral metallofullerene, $U@C_{28}$, whose efficiency of production was much greater than other endohedral metallofullerenes. The relative absence of empty fullerenes, the authors conclude, suggests that fullerene cages are to some extent actually nucleated in the gas phase around uranium atoms or ions. One could not only make actinide endohedral metallofullerenes, but the production efficiency was much higher when the metal was an actinide than it was for other metals.

Investigations of endohedral metallofullerenes have been plagued by low production efficiencies, sensitivity of the endohedral fullerenes to air, and a lack of separation methods to isolate a pure product. The last difficulty arises from the fact that endohedral fullerenes, with the single exception of $M@C_{82}$, are insoluble in all solvents. We have built a carbon arc apparatus for the production of actinide metallofullerenes under anaerobic conditions. We have developed a sublimation method for the separation of metallofullerenes from the "soot" produced in the carbon arc and, by careful control of the temperature, have accomplished separation of metallofullerenes from empty fullerenes. A thin film can be made by subliming fullerenes onto a target. Certain carbon atoms can be removed preferentially by sublimation at relatively low temperatures, leaving the metallofullerenes in the soot. The $U@C_{60}$ is sublimed after the empty fullerenes have been removed from the soot by raising the temperature by just a few degrees. The ability to produce relatively pure films of metallofullerenes will allow the investigation of their chemical and physical properties.

Safe production and manipulation of actinide-containing fullerenes has been demonstrated using anaerobic handling techniques. Sublimation of empty and endohedral metallofullerenes has proved its utility as a technique for separation of fullerenes into cage-size groups. This allows the preparation of films containing only C_{60}, C_{70}, and $M@C_{60}$ as well as films greatly enriched in higher fullerenes relative to C_{60} and C_{70}. The temperatures required for sublimation of $M@C_{60}$ indicate that its enthalpy of vaporization is a few kcal/mol higher than C_{60}, the likely result of stronger interactions between $M@C_{60}$ and its environment in the soot.

[*Note on nomenclature: A molecule identified as a fullerene always has a closed-cage structure. Endohedral metallofullerenes are written as $M@C_X$ where M is the metal, @ indicates that the metal is inside the fullerene cage as opposed to being bound to the outside of the cage, and X indicates that the fullerene cage is composed of X carbon atoms.]

Guest Editorial

High-Level Policies Impact Stewardship of Excess Plutonium

On March 1, 1995, President Clinton announced the withdrawal of 200 metric tons of fissile materials from the United States' nuclear weapon stockpile, declared that this material was excess to the U.S. nuclear security and defense needs, and publicly committed that these excess materials would never again be used for nuclear weapons. This excess fissile material includes 38.2 metric tons of weapons-grade plutonium in addition to a total of approximately 14.3 metric tons of fuel-grade and reactor-grade plutonium. Thus, based on U.S. government nonproliferation policies, the U.S. presently has a nominal 50 metric tons of "excess plutonium," which it must manage and dispose of in the future. (Note that this 50 metric tons is approximately one-half the total plutonium inventory currently existing at Department of Energy (DOE) sites and within assembled nuclear weapons in Department of Defense—DoD—custody).

The developing nonproliferation policy of the U.S. government, along with the changing roles and responsibilities of the various DOE program offices, will have major impacts on how the DOE will manage the excess plutonium inventory in the future. In turn, these developing policies, along with guidance and recommendations for materials management from cognizant DOE program offices, will significantly impact how Los Alamos will be required to manage and control its excess weapons-grade plutonium inventory. This is important to Los Alamos because of the various programmatic activities that require either excess or defense-related plutonium. For example, the DOE Office of Defense Programs underwrites work at TA-55 (the Plutonium Facility) to develop the capability to manufacture small quantities of "war reserve" plutonium pits as part of the Stockpile Stewardship and Management Program. At the same time, Los Alamos is developing pit-disassembly technologies (i.e., ARIES) for dismantling the *excess* pits in the DOE inventory. This work is performed under the auspices of the DOE Office of Fissile Materials Disposition (MD). Furthermore, Los Alamos is also working on technologies associated with the development of mixed oxide nuclear reactor fuel to make it possible to burn plutonium in nuclear reactors, should that option be chosen for disposal by DOE/MD. To make the situation even more complex, the DOE office of Environmental Management is evaluating the possibility of having Los Alamos stabilize and process various plutonium-containing residues from Rocky Flats as part of the recommendations of the Defense Nuclear Facilities Safety Board (DNFSB) 94-1 Program. The plutonium in the residues at Rocky Flats has also been declared excess to national security needs by the DOE.

In preparation for President Clinton's nonproliferation policy statement in 1995, the DOE and DoD performed an exhaustive review of exactly what fissile materials will be required to meet future U.S. national security needs. One result of that review was the identification of excess-plutonium-containing items that make up the 38.2 metric tons of excess weapons-grade plutonium at the various DOE facilities. This review identified specific plutonium pits in DOE custody at the Pantex Plant and at Rocky Flats, as well as excess pits in weapons that are currently in DoD custody and are awaiting return to the DOE for dismantlement. Since the President has declared that this plutonium has been permanently withdrawn from the nation's nuclear weapon stockpile and will never again be used for national security programs, it is prudent to ask the following questions: How do we ensure that the President's stated nonproliferation policy will not be compromised since TA-55 uses both excess plutonium items and defense-related plutonium items? Will additional controls and/or inventory accounting procedures be required for the plutonium removed from excess pits during ARIES prototype development to ensure confidence that the plutonium will not be used in defense-related activities? Will it be necessary for all excess plutonium at Los Alamos to be physically segregated from the

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> **"We must be confident that defense-related programs are not placed in jeopardy because of the high-level nonproliferation policies coming out of DOE Headquarters."**

plutonium used in pit fabrication and other defense-related projects? If so, how would this be implemented at TA-55 and at what cost in terms of facility space, duplication of processing facilities, and additional materials control and accountability, etc.? Will the DOE allow excess plutonium to be substituted for national security plutonium as well as vise versa? If so, how will the DOE provide assurance to the public and to special interest groups that excess plutonium is not being reused for national security purposes after the President has publicly stated that it has been permanently withdrawn from such use? These are important questions that must be addressed adequately by DOE and Los Alamos nuclear materials managers from the perspectives of operations, logistics, and politics.

President Clinton's nonproliferation policies also give rise to a second major issue of interest to Los Alamos—the voluntary submittal of excess plutonium by the U.S. to the International Atomic Energy Agency (IAEA) for inspection, as promised by the President. Most recently, on September 17, 1996, the U.S., Russia, and the IAEA held a trilateral meeting concerning IAEA verification of fissile material originating from weapons. Consequently, the DOE has decided to make international safeguards of U.S. excess fissile materials a routine factor in its planning and budgeting. It has recommended that 15.4 metric tons of excess plutonium being stabilized in the DNFSB 94-1 Program should be made available for IAEA inspection. It has also recommended that a long-term plan for safeguarding U.S. excess fissile material should be coordinated with the IAEA, and it is currently taking action to develop an implementation plan and to evaluate the potential availability of plutonium that can be offered for IAEA safeguards. This last action includes consultations between the DOE Office of Nonproliferation and the DNFSB 94-1 stabilization program as to how, where, and when this material should be placed under inspection.

As a result of this planning, excess plutonium residing at Los Alamos could conceivably be made available for IAEA inspection in the future. Plutonium removed from excess pits during ARIES prototype development and demonstration would be especially politically attractive in this regard. Much of the weapons-grade plutonium being stabilized at TA-55 under the DNFSB 94-1 Program is not considered excess but is required for the development and demonstration of pit fabrication. Therefore, DOE and Los Alamos managers must jointly evaluate any impacts on defense-related activities at TA-55 if any plutonium stabilized under the DNFSB 94-1 Program is considered for IAEA safeguards. We must be confident that defense-related programs are not placed in jeopardy because of the high-level nonproliferation policies coming out of DOE Headquarters. In addition, excess plutonium at Los Alamos must be adequately controlled, readily identifiable, and available for off-site shipment for long-term storage, disposition, or placement under IAEA safeguards, should the policy makers decide to implement any of these actions.

Future institutional, operational, and programmatic issues associated with managing the excess and defense-related plutonium at Los Alamos are complex, and the process to address these issues must be carefully thought out and effectively managed. It must ensure that U.S. nonproliferation policies are adhered to through adequate control and accounting of excess plutonium as defense-related activities at TA-55 proceed. It is important that Los Alamos managers are aware of the political nonproliferation policy decisions being made in Washington while also being cognizant of how these policies may impact plutonium operations at TA-55. Clearly a renewed and increased institutional attention to the management and control of nuclear material inventories will be required to meet the changing Los Alamos role and mission into the next millennium.

Robert G. Behrens

Editorial
On the Disposal of Plutonium

Looking forward to the dawn of a new century and the second millenium, the Actinide Research Quarterly (ARQ) requested and was granted an audience with Dr. Actinide to talk on the subject of plutonium, the "element of this century."

ARQ: For over 50 years the nuclear nations of this world were engaged in the race to produce plutonium for their nuclear weapons stockpile, which, we are told, helped maintain world peace based on the insane dogma of mutually assured destruction (MAD). With the end of the Cold War we are now rushing toward finding ways of disposing of what's called "excess plutonium" from retired nuclear weapons. What are your thoughts on this element that you are all too familiar with in the universal element chart (our discovery number 94)?

Dr. Actinide: A quite natural sequence of events although on occasions I was quite concerned about the madness that prevailed among some of you living through the dawn of your nuclear age.

ARQ: In addition to this urgent desire to dispose of plutonium, the following concerns seem to be of paramount importance: preventing theft and proliferation of nuclear weapons, protecting the public and environment from contamination, and if economically feasible, using plutonium as a viable energy source to fuel further progress.

Dr. Actinide: Admirable concerns for the human species and the world's citizens, indeed.

ARQ: But the problem of disposing of plutonium is compounded because plutonium now appears mixed in many different things. Besides, plutonium present in our environment now presents a contamination hazard.

Dr. Actinide: The dispersion of plutonium is as natural as can be. Contamination is in the eyes and minds of humans. Undo the mixing if that's what you wish to do. However, I would expect that you should not spread plutonium any more than you've done already by such silly activities as exploding it in the atmosphere or dumping it in your ocean.

ARQ: The most commonly suggested solutions to plutonium disposal fall in one of the following categories: burying it, glass-logging it, burning it, mixing it, and storing it.

Dr. Actinide: Such a cacophony of nonsense. You introduced it into the world; now that you have it, learn to live with it.

ARQ: One of the important concerns we have associated with any of these disposal scenarios is waste generation. More so than with any other human activity, the handling of radioactive materials inevitably increases waste.

Dr. Actinide: Remember all elements are radioactive on the Creator's time scale, some more so than others. It is nature's law that the total energy of the universe is conserved. Energy can neither be created nor destroyed. An element such as plutonium, a form of this energy, cannot be destroyed at will. Some of you may argue that an element undesirable to human species can be transformed to a more desirable form. But remember also that you do not control the outcome of such transformation of the elemental stuff.

ARQ: Yes, we know that we live in an environment of natural radioactivity and, therefore, it is unnatural to think of a "radiation-free" environment. For example, the world oceans contain, although diluted, the largest amount of uranium, another element of your superb expertise. We never hear anyone suggesting that we should clean up the ocean of its radioactivity. There's also cosmic radiation and radiation in the buildings we work in and live in, the food we eat, the air we breathe.

Dr. Actinide: That's right. You are a product of the earth, this wonderful place we live in. Plutonium also is here to stay with you and your children. The prudent thing for you to do is to manage and safeguard it properly so that you can draw from it more benefit than harm.

ARQ: Dr. Actinide, you'll grant that's easier said than done....

Dr. Actinide: Almost everything is. Among all things created, ironically for humankind, plutonium may turn out to be one of those elemental magnets that makes human beings all come together and cooperate to find a lasting solution to this uniquely human problem. That's the challenge.

Kyu C. Kim

The ideas presented in this editorial are the author's and do not necessarily represent the opinion of Los Alamos National Laboratory, the University of California, the Department of Energy, or the U.S. Government.

Fabrication of Zircon Leads to a Pu Stabilization Alternative

Background and Research Objectives

Zircon, because of its well-known, long-term durability (~10^9 years) in the geologic environment, has been proposed as a host medium for storage of Pu and other actinides recovered from dismantled nuclear weapons. Much is known about the structure of this single-phase mineral and its homologs (e.g., Hf, Th, Pa, U, Np, Pu). It is clear that zircon-type orthosilicate structures can accommodate
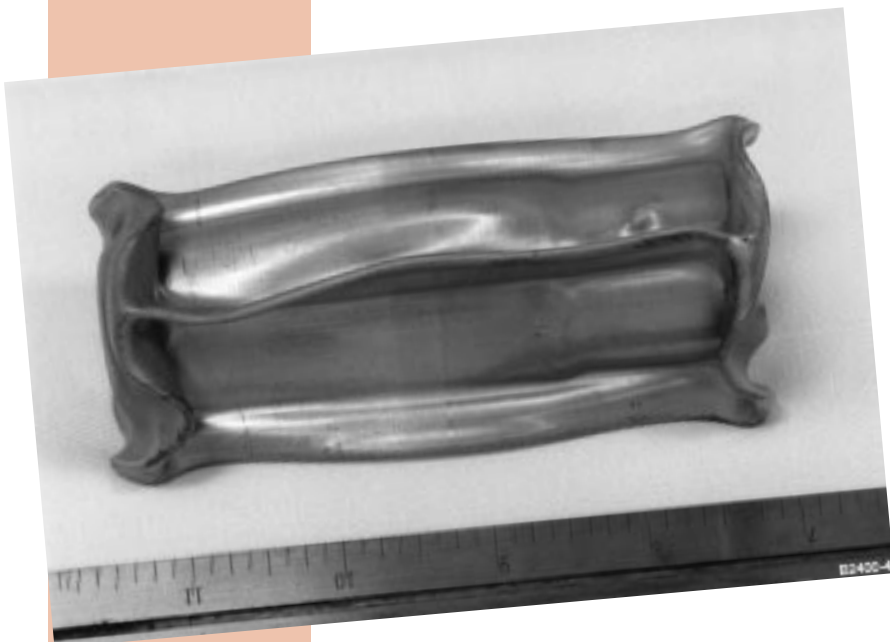

Figure 2. The tantalum container after the first HIP run. This figure shows that the welds are intact, and the body of the container remains in good condition after 2 hours at 1450°C and 4000 psi.

metal cations having radii both smaller and larger than that of the Zr ion in zircon. Natural zircon has been found to contain approximately 5000 ppm of U and Th. Some of the cations found in natural zircon (e.g., Gd, Hf) are strong absorbers for thermal neutrons. Laboratory-scale samples of zircon doped with up to 10 wt % of Pu have been prepared for conducting accelerated tests on the effect of radiation damage on the structure, property changes, and phase stability in simulated geological conditions (by W. J. Weber at the Pacific Northwest National Laboratory). Furthermore, small samples of pure $PuSiO_4$ have been prepared (by C. Keller in Karlsruhe, Germany), which suggests that it is possible to substitute Zr with more than 10 wt % of Pu. From the point of view of nuclear waste minimization, it is desirable that the

upper limit of Pu solubility in zircon be determined. While exploring the potential for increasing the Pu loading in zircon, we need to investigate the issues of criticality safety so that the optimum waste form can be determined.

Various methods for synthesizing laboratory quantities of zircon have been investigated. However, simultaneous application of high temperature and high pressure to enhance the solid-state reaction has not been attempted, especially for zircon doped with large quantities of Pu. With the existing equipment, such as hot presses and 'hot isostatic presses in the Plutonium Facility, LANL is in a good position to develop the technology for large-scale fabrication of Pu-bearing zircon and, therefore, to provide the nation with an alternative method for disposing of nuclear materials. The success of this work will allow us to address the technical problems related to short-term and long-term storage of nuclear materials recovered from weapons. The results of this effort will enhance TA-55's capabilities in solving plutonium disposition problems.

In this work we set out to obtain the following information, essential to large-scale fabrication of Pu-bearing zircon: 1) the process parameters for large-scale fabrication of zircon with desirable Pu-loading and 2) the solubility limit of Pu in zircon. What we learn will be important from the standpoint of minimizing waste volumes. This article presents the results of the first study.

Scientific Approach and Accomplishments

Since the main objective of this work was to investigate the feasibility of large-scale fabrication of Pu-bearing zircon, it was of utmost importance to be able to achieve this goal without releasing contamination to the work environment. Therefore, the approach taken in this work was to use the synthesis of zircon to explore potential problems in the containment of materials during processing. Furthermore, since PuO_2 is thermodynamically less stable than ZrO_2, the processing parameters developed for the synthesis of zircon would be applicable to those for Pu-zircon.

The process used was hot isostatic pressing (HIP). The equipment provides high temperature in the reaction chamber through resistively heated graphite heating elements. It provides high pressure by compressing inert argon gas supplied from gas cylinders to the reaction chamber. The hot press is capable of attaining temperatures up to 2000°C and pressures up to 30,000 psi. The material to be "hipped" is contained inside compressible containers, typically fabricated from thin metals, and is compressed with equal force from all directions.

For hipping zircon, a container made of refractory metal that melts at high temperature is desirable. However, most metals are thermodynamically unstable, (and more so at higher temperatures), with respect to the formation of their oxides. Since the starting materials for zircon are oxides, the oxidation of the container materials is inevitable unless some sort of barrier (inner container) is provided to separate the reaction mixture from the metal container. But this inner container must also be compressible as well as chemically inert to the reaction mixture.

In anticipation of fabricating Pu-zircon in PF-4, the LANL Plutonium Facility, some schemes need to be developed for packaging the reaction-mixture/container assembly. First, the powder mixture has to be loaded into the inner container inside a glove box. Then, for safety reasons, the container has to be assembled and sealed without the use of excessive heat. Thereafter, this inner container will be transferred from a glove box into the "cold" outer metal container in an introductory hood while the outer container is maintained free of contamination. The metal container will then be welded in a separate "cold" tungsten/inert gas (TIG) welding hood. Finally, the outer container has to maintain its integrity after the processing; otherwise the process equipment contained inside the hood will be contaminated.

Based on these criteria, tantalum was chosen for the outer container, and quartz the inner one. Tantalum was chosen based on its high melting point of 3017° C, its availability, and its relative ease of welding. The choice of quartz was based on the known phase behavior of the ZrO_2/ SiO_2 system. The phase diagram of this system indicates that zircon does not form any compounds with SiO_2 in the temperature range of interest. Furthermore, quartz softens at temperatures above 1200°C and, therefore, can be compressed. Nevertheless, the potential for reactions among Ta, ZrO_2, and SiO_2 still exists. Based on this containment system, the range of temperature, pressure, and time were explored to provide a reasonable processing scheme.

Results and Accomplishments

The tantalum container was compressed as expected, the welds were intact in all cases, and the quartz joint held together in one piece. The product was monolithic. The results from x-ray powder diffraction showed that 30 lines were observed in the starting material, and that almost all lines can be assigned to either monoclinic-ZrO_2 or SiO_2 (quartz). In the first HIP run, 39 lines were observed in the product. Out of the 39 lines, 25 are assignable to zircon, 11 are due to monoclinic ZrO_2, and only 3 are due to SiO_2 (cristobalite). However, the 3 strongest lines are due to ZrO_2 and SiO_2. This indicates that zircon begins to form in approximately 2 hours of reaction time, but the reaction is nowhere near completion. The other samples from all products showed almost identical patterns and relative intensities. This indicates that the extent of reaction did not differ significantly for reaction times ranging from 2 to 8 hours. A more quantitative analysis is necessary using x-ray diffraction on samples that are mixed with standard reference material. Further product material characterization by chemical, analytical, and metallographic techniques are underway.

Principal investigators are **Kyu C. Kim,** NMT-DO, and **John Y. Huang,** NMT-6. Others contributing to the project are **Patricia L Serrano and Mark A. Williamson,** NMT-6; **Mary Ann Reimus, Gary H. Rinehart, Christina M. Lynch, Paul Contreras, and Paul Moniz,** NMT-9; **Stanley Pierce,** MST-6; **Rudolph Fernandez,** NMT-4; **McIlwaine Archer and Richard G. Logsdon,** MST-7; and **Luis A. Morales,** NMT-5.

Zircon-and-Quartz Containers May Be Used to Stabilize Plutonium for Disposal *(continued)*

Under the high-temperature and high-pressure conditions employed in this work, hundred-gram batches of ZrO_2/SiO_2 mixture began to react and form zircon in approximately 2 hours. Considering the thermodynamic stability of PuO_2 relative to ZrO_2 (i.e., PuO_2 has less negative
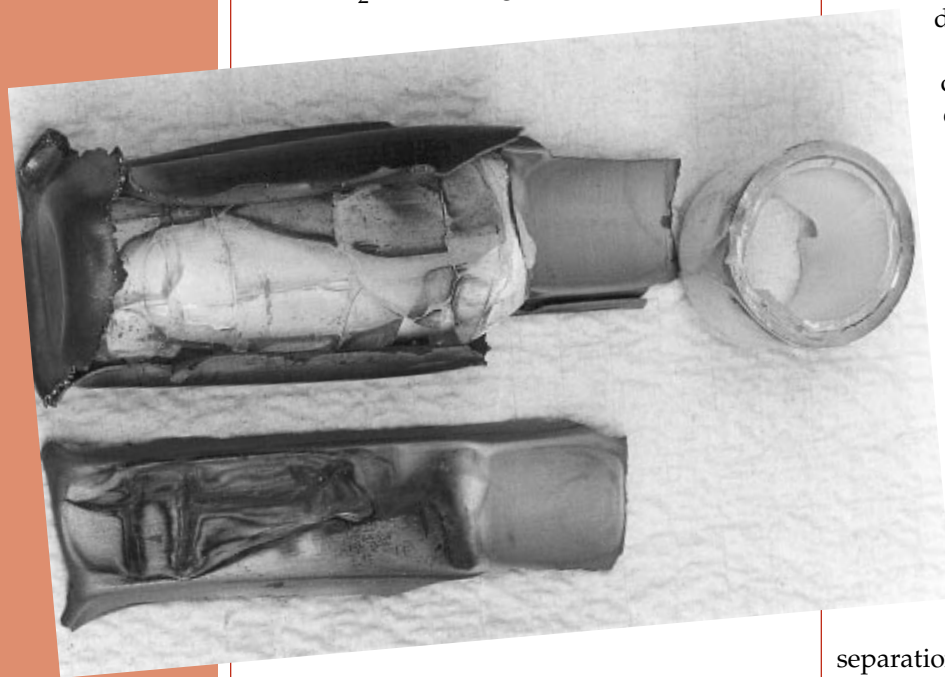

Figure 3. Cut-up view of a tantalum container after processing. The figure shows that the quartz joint holds together. The quartz container has broken into pieces and can be separated from the product.

standard Gibb's free energy of formation than ZrO_2), it is expected that the fabrication of Pu-bearing zircon will be accomplished more easily than the fabrication of zircon alone. The result of this preliminary work indicates that it is feasible to fabricate large quantities of Pu-zircon; however, further developmental work is necessary.

This work revealed potential container problems that could be encountered at the developmental stage and suggested practicable solutions. The quartz inner container, the glass sealant, and the tantalum outer container all showed expected behavior. The process developed for joining quartz parts with the use of a special glass sealant, as an alternative to high-temperature fusion, inside glove boxes is an innovative approach that is applicable to other operations in the Plutonium Facility. The containment system allowed the reaction mixture to be compressed isostatically. The separation of final products from the container materials was not difficult. The reactions between tantalum, SiO_2, and ZrO_2 could be prevented by providing a sacrificial barrier between the inner and the outer containers. Clearly, further developmental work is needed to establish a safe process for large-scale fabrication of Pu-bearing zircon.

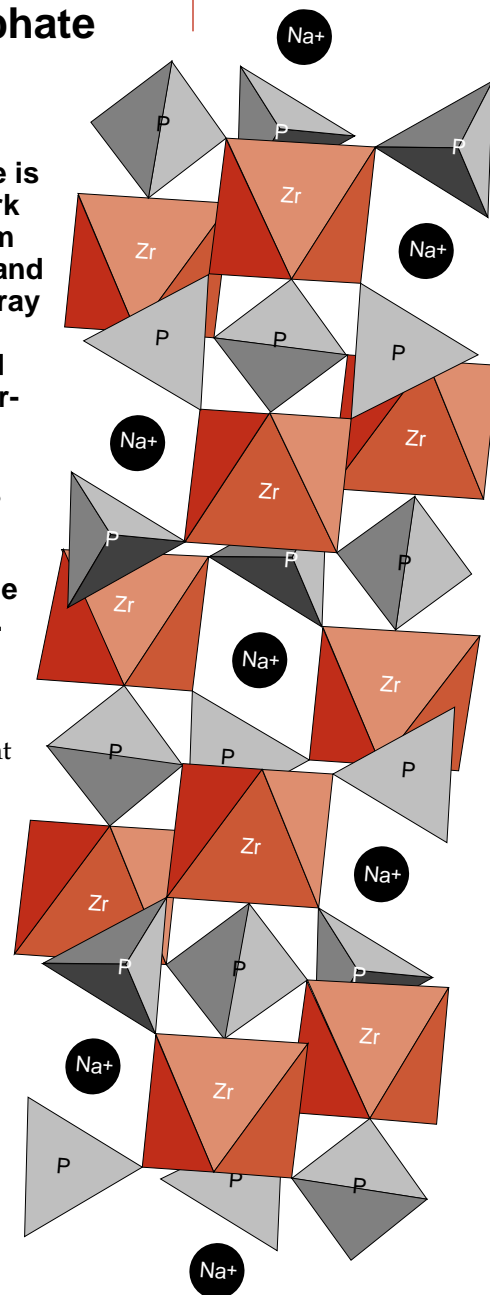# Ph.D. Thesis Explores Sodium Zirconium Phosphate (NZP) Waste Forms for Actinide Disposal

The disposal of high-level radioactive wastes generated during the reprocessing of spent fuel rods from nuclear reactors to recover the actinides is an ongoing problem for the DOE, costing billions of dollars. These wastes include defense wastes currently stored at a number of locations such as the tank farms at Hanford and the underground storage bins at the Idaho National Engineering Laboratory (INEL). Wastes generated during the reprocessing of civilian nuclear reactor spent fuel rods (before a 1977 moratorium on reprocessing initiated during President Carter's administration) are stored at the West Valley reprocessing facility (Western New York Nuclear Service Center) in West Valley, NY. These wastes represent millions of gallons of liquids and tens of thousands of cubic meters of solids; at INEL alone over 2200 m³ of unconsolidated solids remain.

Chemically and radiologically, reprocessed wastes are extremely complex. They contain fission products, residual actinides, cations from the dissolution of metal fuel rod containers, anions from acids used in the dissolution process, alkali salts employed for the purposes of neutralization, and a variety of organic sequestering agents. To reduce their volumes and to stabilize their chemistries, reprocessed commercial wastes in liquid form are often converted to solid form by drying and calcining them at temperatures below 600°C. During the calcination step, the wastes decompose into amorphous mixtures of chemically inert oxides; volatile reaction products are driven off. The solid products or *calcines* are characterized by moderate to high leachability and must be converted to chemically stable forms before they are disposed of.

Neither commercial nor defense high-level wastes are uniform or well-characterized. As a result, the development of waste forms that are suitable for the immobilization of reprocessed high-level calcines has continued to

Figure 4. The NZP structure is a three-dimensional network of interconnected zirconium octahedra (red polyhedra) and phosphorous tetrahedra (gray polyhedra). The structure accommodates cesium and strontium ions in large interstitial cavities occupied by sodium ions in the parent structure. Fission products and residual actinides substitute for zirconium as essential constituents of the three-dimensional network.

challenge the waste management community. In response to this challenge, researchers have proposed a variety of waste forms including noncrystalline, crystalline, and multiphase materials. Each of these materials possesses unique capabilities and deficiencies. For example, noncrystalline waste forms such as the borosilicate-based glasses are relatively insensitive to fluctuations in waste stream composition, and the process used to prepare such materials is reliable and straightforward. Industrial-scale processing of borosilicate-based waste forms is in place and has been demonstrated at the Defense Waste Processing Facility (DWPF) at the Savannah River Defense Plant. However, borosilicate-based glasses are thermodynamically unstable and are susceptible to uncontrolled crystallization under some repository conditions. Such materials lack the thermal and mechanical stability possessed by crystalline waste forms.

Ph.D. Thesis Explores Sodium Zirconium Phosphate (NZP) Waste Forms for Actinide Disposal *(continued)*

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Unfortunately, operations at the DWPF have been repeatedly delayed because of a combination of public relations issues and technical barriers. This delay has led to renewed interest in research on alternate waste forms. Scientists in the waste management community have continued to propose, synthesize, and characterize novel waste forms. Notable among these waste forms is sodium zirconium phosphate ($NaZr_2(PO_4)_3$ or NZP), a crystalline material that can accommodate the chemical complexity of high-level wastes.

The three-dimensional skeletal structure of NZP, as shown in Figure 4, allows the accommodation of cations of various sizes and oxidation states on three distinct crystallographic sites; in fact, the NZP structure may accommodate *all* of the chemical species associated with reprocessed, commercial, high-level waste calcines. Uranium, thorium, neptunium, and plutonium occupy the zirconium site in the parent structure. Cesium and strontium are accommodated on interstitial sites typically occupied by sodium. The substitution of sodium, zirconium, or phosphorous by fission products or actinides results in a structural isotype referred to as [NZP]. A wide variety of cations have been inserted into the NZP structure. It may accommodate approximately two-thirds of the ionic species of all known elements.

The [NZP] compounds permit the incorporation of all of the ions present in reprocessed, commercial, high-level waste calcines into crystalline waste forms whose resistance to dissolution and retention of [NZP] constituents is remarkable. Cursory studies indicate that the [NZP] materials are highly resistant to radiation damage. As crystalline waste forms, [NZP] compounds offer inherently low leach rates for single phases, negligible coefficients of thermal expansion, and the ability to immobilize high concentrations of waste in high-density

phases. This latter characteristic of [NZP] waste forms renders these materials promising candidates for the disposal and consequent reduction of large volumes of wastes containing significant quantities of nonradioactive constituents; plant operation, storage, and disposal costs decrease with decreasing waste volume. In this regard, crystalline waste forms, such as [NZP], offer a notable economic advantage over the less dense borosilicate-based glasses.

The ease of processing [NZP] waste forms is an additional feature that makes these materials attractive alternatives to other potential waste forms, such as SYNROC (synthetic rock), a multiphase waste form. The [NZP] materials may be synthesized by solid-state reaction of mechanically-mixed, coprecipitated, or hydrothermally prepared powders. Such [NZP] powders may be cold-pressed and sintered in air at moderate temperatures (600-1350°C); however, modifications of these techniques would be required for the industrial-scale production of [NZP] waste forms.

Some [NZP] compounds with waste loadings as high as 40 wt % have been prepared with simulated nonradioactive, reprocessed, high-level waste calcines by the author at The Pennsylvania State University; however, the preparation of [NZP] waste forms with actual reprocessed high-level waste calcines has not been demonstrated. A methodology has been developed and tested that allows one to determine appropriate batch formulations for several waste compositions. The batch formulations take into account site and charge balance so that the final product is phase-pure, *i.e.,* amorphous and undesired phases are absent. Future work at LANL will include the preparation of actinide-loaded samples, their characterization, and a comprehensive study of their behavior under repository conditions.

Publications, Presentations, and Reports
(October 1996–December 1996)

Journal Publications

M. D. Diener, D. K. Veirs, and S. S. Eaton (Univ. of Denver), "An Empty Fullerene Donor, C74," submitted to *J. Amer. Chem. Soc.*

M. D. Diener, C. A. Smith, and D. K. Veirs, "Anaerobic Preparation and Solvent Free Separation of Uranium Endohedral Metallofullerenes," submitted to *J. Chem. of Matr.*

Conference Presentations

K. M. Axler and M. H. West, "Process Modeling and Development for Treatment of Uranium-Contaminated Solid Wastes," The Second International Symposium on Extraction and Processing for the Treatment and Minimization of Wastes, Phoenix, AZ, October 27, 1996.

S. M. Dinehart, K. A. Qubat-Martin, D. W. Gray, V. A. Hatler, and S. W. Jones, "Radioactive Source Recovery Program: Responses to Neutron Source Emergencies," Hazwaste World/Superfund XVII, Washington, D.C., October 15–17, 1996.

H. L. Nekimken, N. G. Pope, J. M. Macdonald, R. A. Bibeau, B. G. Gomez, D. J. Sellon, "Case Study for the Evaluation and Selection of Man-Machine Interface (MMI) Software," Fall 1996 Instrument Society of America Meeting, Chicago, IL, October 7–10, 1996.

The following were presented at The 1996 Training Resources and Data Exchange (TRADE) Conference, Anaheim, CA, November 19–21, 1996: M. A. Stroud, "Pollution Prevention and Waste Management Performance Improvement at the LANL Plutonium Facility" and T. L. Binder, "Dressing Up With Somewhere To Go—Radiological II Practical Exercises at the LANL Plutonium Facility."

L. A. Avens, K. K. S. Pillay, and S. M. Dinehart, "The 94-1 Core Technology Research and Development Program," The American Nuclear Society International Meeting, Washington, D.C., November 11–15, 1996.

T. O. Nelson, D. E. Wedman, and H. E. Martinez, "Electrolytic Methods for the Decontamination of Metal Surfaces," 23rd national Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACCS), Kansas City, Missouri, September 29–October 4, 1996.

The following were presented at the American Nuclear Society/European Nuclear Society 1996 International Conference and Embedded Topical Meetings, Washington, D.C., November 10–15, 1996: H. T. Blair, K. M. Chidester, and K. B. Ramsey, "Fabrication of Mixed Oxide Fuel Using Plutonium from Dismantled Weapons"; K. M. Chidester, C. A. Beard, and H. T. Blair, "Fabrication of Mixed-Oxide Nuclear Fuel in Support of the Parallex Project"; and K. B. Ramsey and K. M. Chidester, "Fabrication of Non-Fertile and Evolutionary Mixed Oxide Fuels."

H. T. Hawkins and B. E. Scheetz (Pennsylvania State University), "Preparation of Monophasic Sodium Zirconium Phosphate [NZP] Radiophases: Potential Host Matrices for the Immobilization of Reprocessed Commercial High-Level Wastes," Proceedings of the Materials Research Society 1996 Fall Meeting, Boston, MA, December 2–6, 1996.

E. Garcia, J. A. McNeese, V. R. Dole, and W. J. Griego, "Vacuum Distillation Separation of Pyrochemical Residue Salts," 16th Pyrochemical Workshop, St. Charles, Illinois, October 28–31, 1996.

C. A. Smith, M. D. Mayne, K. Rodriguez-Cales, J. C. Baiardo, and T. R. Mills, "Hydrochloric Acid Recycle: Chloride Crystallization and Acid Reconcentration by Gas Phase Membrane Separation," 2nd Annual SERDP Symposium, Tyson's Corner, VA, November 20–22, 1996.

M. A. Williamson, "The Chemistry of Fluid Fuel Nuclear Systems," 16th Annual Pyrochemical Workshop, St. Charles, IL, October 28–31, 1996.

Reports

F. N. Schonfeld and R. E. Tate, "The Thermal Expansion Behavior of Unalloyed Plutonium," LA-13034, October 1996.

M. A. H. Reimus and J. E. Hinckley, "General Purpose Heat Source: Research & Development Program Radioisotope Thermoelectric Generator/Thin Fragment Impact Test," LA-13220, November 1996.

D. D. Padilla, L. A. Worl, F. C. Prenger, and D. D. Hill, "Magnetic Roll Separation of Sand, Slag, and Crucible," Final Fiscal Year 1996 94-1 R&D Project Report LA-CP-96-262, November 1996.

K. W. Fife, C. W. Hoth, and J. B. Nielsen, "Nuclear Materials Stabilization and Packaging End-Of-Year Status Report," LA-13238-MS, November 1996.

NEWSMAKERS

NMT Division welcomes a new scientific member. Dr. **Dane Spearing** recently graduated from Stanford University with a Ph.D. in geology and a minor in materials science. Much of Dane's doctoral research involved examination of the mechanisms and dynamics of displacive phase transitions in a number of minerals and ceramics using nuclear magnetic resonance spectroscopy and x-ray diffraction. Dane will be working with **John Huang** (NMT-6) on the synthesis and characterization of zircon as outlined in his postdoctoral research proposal.

As part of the NMT Division Review process, the following Extenal Advisory Committee members visited the division during this quarter to get familiarized with the division projects to be reviewed in March 1997: Dr. **Rohinton Bhada** of the New Mexico State University (10/2/96), Dr. **Gregory Choppin** of the Florida State University (10/16/96), Dr. **Robert Uhrig** of the University of Tennessee (10/16/96), Dr. **Todd LaPorte** of the University of California-Berkeley (11/21/96), and Dr. **Darryl DesMarteau** of Clemson University (12/17/96).

Professor **Alexandra Navrotsky** of Princeton University visited NMT Division on October 4 and presented a seminar on "Thermodynamics of Glasses and Crystals Related to Actinides Immobilization and Confinement."

Plutonium Futures The Science

Call for Papers

A formal Call for Papers has been issued for "Plutonium Futures—The Science," a conference to be held at the Hilton in Santa Fe, NM, on August 25–27, 1997. Authors are encouraged to submit summaries of papers describing work that is new, significant, and relevant to plutonium and actinide science. Topics include separations, transuranic waste, isotopes/nuclear fuels, detection and analysis, materials science, novel plutonium/actinide compounds and complexes, and environmental and biosphere chemistry. The conference program Chairs must receive these summaries by March 24, 1997. The summaries will be printed in a conference transactions document. The Call for Papers and other conference information is available by visiting the World Wide Web at http://www.lanl.gov/PuConf97, sending e-mail to puconf97@lanl.gov, or calling 505-667-8663. The conference is sponsored by Los Alamos National Laboratory in cooperation with the American Nuclear Society.