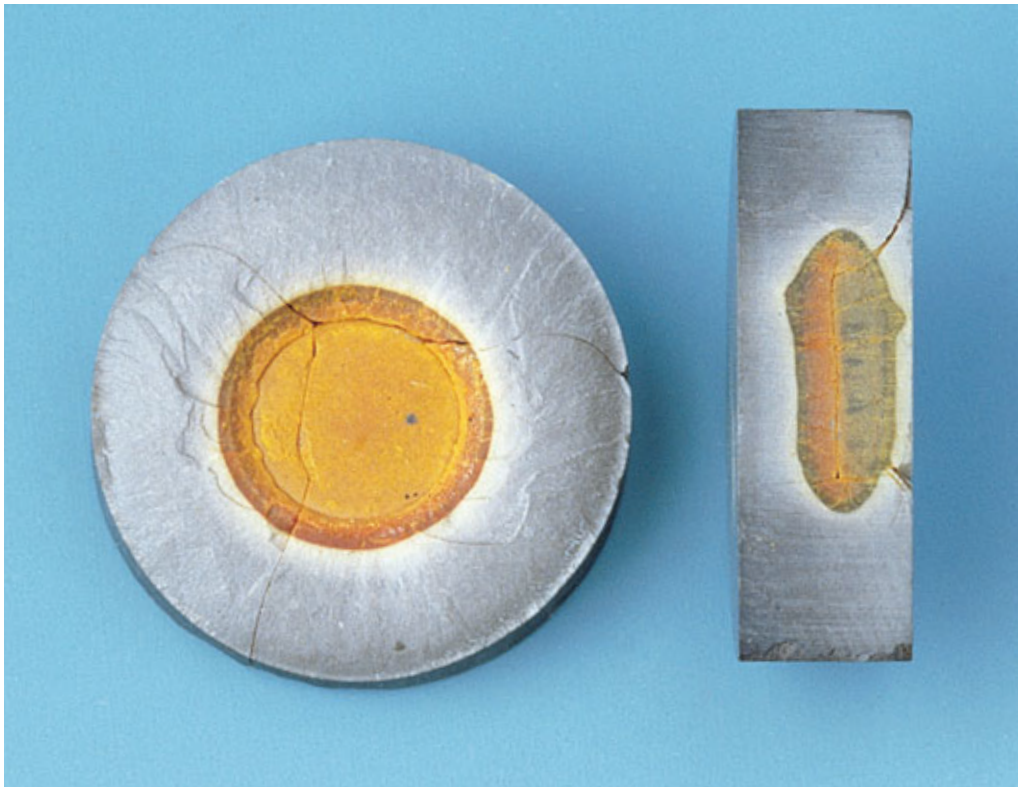
TAILOR-MADE MATRICES FOR LONG-LIVED RADIONUCLIDES

Once extracted from the general waste flow as small quantities of pure products, long-lived radionuclides (minor actinides, iodine, and cesium) can be given very special treatment. CEA and CNRS (French National Center for Scientific Research) have developed ceramic or glass/ceramic matrices adapted to each category of radionuclide obtained from the advanced separation processes. They have demonstrated the feasibility of these matrices and tested their performance. It now remains to demonstrate their suitability for an industrial process.

Matrices adapted for each category of long-lived radionuclide resulting from advanced separation processes are being developed. Apatites, capable of selectively incorporating iodine, cesium, and actinides, are the subject of in-depth research. Shown here are cross-sections of a composite iodo-apatite ceramic (core).



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Optimizing radionuclide conditioning

Since 1978, borosilicate glass has been considered in France, and in other countries such as the United States, the United Kingdom, Japan and Russia, as the reference industrial **matrix** for **conditioning** solutions of **fission products** (comprising more than thirty chemical elements!) resulting from spent-**fuel reprocessing** operations (see *Waste vitrification: more than one string to its bow*). For advanced separation processes, it is planned to extract **minor actinides** (neptunium Np, americium Am, and curium Cm) from the waste flow, as they represent the highest **radiotoxic inventory** after plutonium Pu (see box C, ***Radiotoxicity of spent fuel***), and certain long-lived fission products (iodine I, cesium Cs, technetium Tc). Thus, after only a few centuries of radioactive decay, the radiotoxic inventory of vitrified-waste **packages** will have fewer harmful effects than the uranium ore from which they came (see *Long-lived radionuclides partitioned at will*). Separated long-lived **radionuclides** exist in a well-known, chemically pure form. It should therefore be possible to place them in a specially adapted matrix, and research teams are now developing specific matrices that are capable of incorporating the radionuclide in question into their structure and offering improved performance compared with existing conditioning. This research work can be divided into two parts: firstly, possible materials liable to be suitable for conditioning must be found and, secondly, their performance in terms of **containment** capability and resistance to internal and external hazards must be demonstrated (see box G, ***Conditioning, a vital phase***). In addition, the possibility of manufacturing these materials industrially must be demonstrated. This work is conducted as part of the **Nomade** research group set up by CEA and CNRS, involving more than fifty laboratories, EDF, and Cogema.

Mineral species, known in nature for their selective-insertion capabilities with respect to certain radionuclides and their stability over time, are potential candidates for use in conditioning these separated radionuclides. CEA is exploring the use of apatites to condition iodine, cesium, and **actinides**, and zirconolite and hollandite for conditioning actinides and cesium respectively. It is also conducting research into titanate or phosphate ceramics or metal matrices for conditioning technetium(1). Results obtained so far show that these matrices have high incorporation capabilities (7% by mass for I; 5% for Cs; and

(1) The CNRS is developing other types of matrix, including monazites and TPD (thorium phosphate-diphosphate) for actinide conditioning.

10% for actinides), and at the same time, offer good chemical stability performance, about two orders of magnitude better than current conditioning solutions.

Apatites, specific matrices for iodine, cesium, and actinides

Many chemical elements make up the structure of apatite compounds (box 1). For this reason, several chemical **formulations** are defined for conditioning I, Cs, and **trivalent** minor actinides.

The iodo-apatite $Pb_{10}(VO_4)_{4.8}(PO_4)_{1.2}\mathbf{I}_2$ is obtained through a solid-state reaction of PbI_2 and $Pb_3(VO_4)_{1.6}(PO_4)_{0.4}$. This iodine-rich core is then coated with a layer of $Pb_3(VO_4)_{1.6}(PO_4)_{0.4}$ during a sintering(2) stage at a pressure of 25 MPa and a temperature of 700 °C, to form a composite ceramic. The aqueous-alteration resistance of iodo-apatite proves to be very similar to that of natural fluoro-apatites, in the region of 2×10^{-3} g/m²/d, under alteration conditions in a strongly renewed medium and at 90 °C.

Inserting Cs into the apatite structure has also been examined. *Abinitio* atomistic modeling (see *A "master key" to chemical separation processes*) has guided the choice of the chemical formula, which was confirmed by laboratory synthesis tests. Lattice energy(3) calculations show that Cs^+ has a strong affinity for fully phosphated apatites such as $Ca_8Nd\mathbf{Cs}(PO_4)_6F_2$, and much less affinity for britholites (silicate apatite) with a nominal formula of $Ca_7Nd_2\mathbf{Cs}(PO_4)_5(SiO_4)F_2$.

Actinides have a strong affinity for fluoroapatite monosilicate (britholite). This mineral has been found in the vicinity of natural **fission** reactors, dating back more than one thousand million years, on the Oklo site in Gabon. This site has been exposed to intense internal irradiation doses due to alpha (α) **self-irradiation** ($> 3 \times 10^{22}$ α/m³) and intense external doses induced by fission neutrons ($> 10^{21}$ neutrons/cm²). In the laboratory, britholite monosilicate, formula $Ca_9\mathbf{Nd}(PO_4)_5(SiO_4)F_2$, where the neodymium ion Nd^{3+} simulates the presence of the minor actinides Am^{3+} and Cm^{3+}, is synthesized by solid–solid reaction and natural sintering at 1,400 °C (box 2). Resistance to α self-irradiation, a particularly important property for actinide containment matrices (see box G, ***Conditioning, a vital phase***), was assessed on synthetic britholite using external radiation sources. The Nuclear Spectrometry and Mass Spectrometry Center (CSNSM) at Orsay used a 320-keV (1.5×10^{13} ions/cm²) Pb^{2+} ion beam, and a

(2) Heat treatment aimed at forming ceramic from precursors.
(3) Cohesion energy of the crystal lattice, i.e. the energy required to break the lattice and infinitely separate all the atoms.

1 The three mineral families studied

Apatites. The term "apatite" refers to a family of chemical compounds with the formula $Me_{10}(XO_4)_6Y_2$, where Me is a **divalent cation** (calcium Ca^{2+}, lead Pb^{2+}, barium Ba^{2+}, etc.), XO_4 is a trivalent **anion** (phosphate PO_4^{3-}, vanadate VO_4^{3-}, silicate SiO_4^{4-}, etc.), and Y is a monovalent anion (fluorine F^-, chlorine Cl^-, hydroxyl OH^-, bromine Br^-, etc.). Apatites all crystallize in the hexagonal system, of which the unit cell is a straight prism with a hexagonal base. Naturally occurring apatites, generally $Ca_{10}(PO_4)_6(F,OH,Cl)_2$ (figure a), have high **chemical durability** in a slightly alkaline aqueous medium. They are thermally stable and withstand radiation damage.

Hollandite. The general formula of hollandite is $A_2B_8O_{16}$ where A is monovalent or divalent, and B has a valence between 2 and 5. In nature, there is a whole range of minerals that crystallize in this structure. The difference between them lies in the chemical elements inserted as a substitute for titanium Ti in the B-site: hollandite (manganese Mn totally substituted for Ti), priderite (iron Fe^{3+}), henrymeyerite (iron Fe^{2+}), redledgeite (chromium Cr), ankangite (chromium Cr, vanadium V), etc. In the structure considered, the A-site is occupied by Ba^{2+} and Cs^+ (cesium ion), and the B-site by Al^{3+} (aluminum ion), Ti^{3+}, and Ti^{4+}.

Zirconolite. The generic formula of zirconolite is $Ca^{2+}Zr_x^{4+}Ti_{(3-x)}^{4+}O_7$ where $0.8 < x < 1.35$ (figure b). It is able to accommodate **lanthanides**, hafnium Hf and tri- and tetravalent **actinides** by insertion into the calcium Ca and zirconium Zr sites. Charge compensations are then ensured by substituting trivalent cations (Al^{3+}, Ti^{3+}) in the titanium Ti^{4+} site. This is the main phase of Synroc, a polycrystalline material proposed by ANSTO (Australian Nuclear Science and Technology Organization) for the **containment** of **fission product** solutions. This mineral phase was selected on the basis of studies of similar natural materials where significant cation substitution occurs. For example, naturally occurring zirconolites in Sri Lanka, dating back 550 million years, contain up to 20% by mass of thoria ThO_2 (and some of them 14% uranite UO_2), equivalent to 8×10^{19} total α disintegrations per gram. Though amorphized, they have nonetheless withstood the alteration processes of their natural environment.

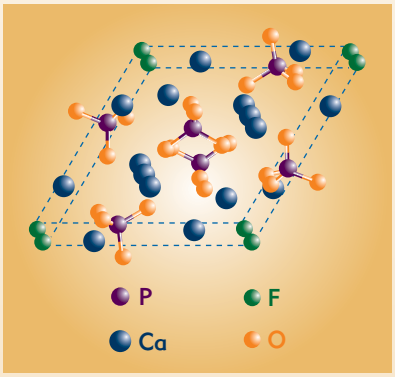

Figure a. Projection on the base plane of the $Ca_{10}(PO_4)_6F_2$ apatite hexagonal unit cell.

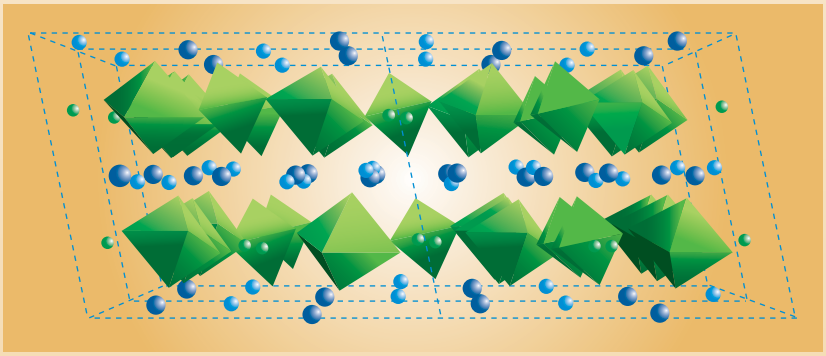

Figure b. Stereographic projection of the unit cell of 2M-monoclinal polytype zirconolite. In a monoclinal system, the unit cell is an oblique prism with a rhomboid base. Calcium Ca is shown in dark blue, zirconium Zr in pale blue, and titanium Ti in green.

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Ceramic matrices, developed for conditioning long-lived radionuclides, obtained through sintering processes.

160-keV (3.2×10^{15} ions/cm^2) He^{2+} ion beam to simulate the effect of α **recoil nuclei** and α particles respectively. Pb^{2+} ion impacts on britholite lead to defects and metamictization or amorphization of its crystalline structure. The accumulation of defects leads to total loss of structural periodicity in all three dimensions. A partial defect annealing process through He^{2+} ions, during which the crystalline structure is recovered, has been revealed (figure), even at low temperature (< 100 °C).

Hollandite, a specific matrix for cesium

Hollandite (box 1) is a compound derived from the quadratic(4) structure of rutile TiO_2. It is capable of inserting Cs into a lattice of channels that are parallel with the crystallographic axis *c*, formed by octahedral chains $[(Ti,Al)O_6]$. The selected compound is $BaCs_{0.1}Al_{1.5}Ti_{6.5}O_{16}$. It is synthesized by an alkoxide process and pressure-assisted sintering at 1,200 °C (box 2). The first chemical durability tests confirm good resistance to aqueous alteration (alteration rate of about 10^{-2} g/m^2/d under alteration conditions in a strongly renewed medium and at 100 °C).

Zirconolite, a specific matrix for actinides

This mineral structure, found relatively rarely in nature, defines a rich family of many polytypes. Tri- and tetravalent actinides and lanthanides enter the structure up to high concentration values (several tens of per cent by mass of oxide), following substitution rules depending on their valence (box 1). The formulation of zirconolite was selected in cooperation with ANSTO (Australian Nuclear Science and Technology Organization). Two synthetic processes have been defined (box 2). The first is a ceramization process during which powders are synthesized by the alkoxide process and natural sintering at 1,400 °C. The second is a pro-

(4) Crystalline system in which the unit cell is a square-based straight prism.

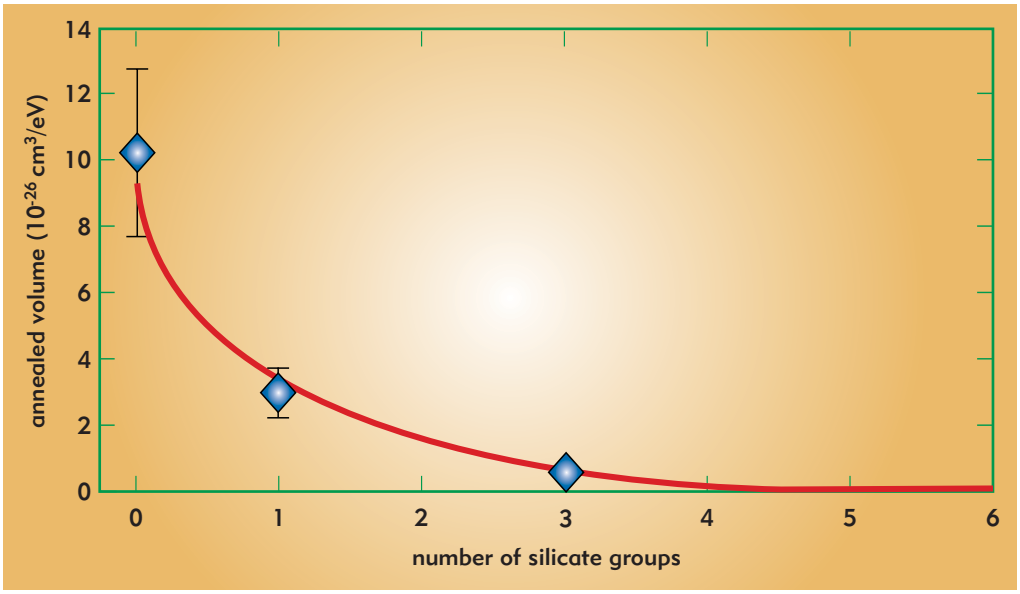

Figure. Curve showing α annealing efficiency in britholite versus the number of silicate groups (SiO_4) substituted for PO_4 groups. Partial annealing decreases in inverse proportion to the number of PO_4 substituted.

Theory of ceramic synthesis

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Britholite synthesis for conditioning actinides. The chemical reaction between the various solid compounds (Nd_2O_3, CaF_2, $CaCO_3$, SiO_2, $Ca_2P_2O_7$) leads to mineral-phase precursors, including neodymium Nd, which simulates the presence of an actinide. These precursors are subjected to heat treatment at 1,500 °C (calcination), then ground. The resulting powder undergoes uniaxial pressing, then sintering at 1,400 °C for 6 hours.

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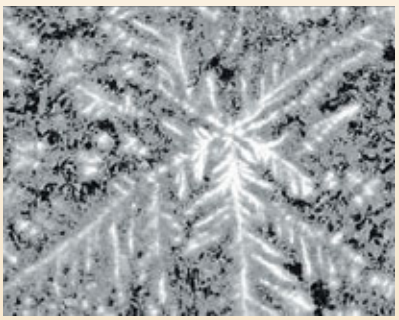
Uniaxial, pressure-assisted sintering device for ceramic synthesis.

Hollandite synthesis for conditioning cesium. The first step is the **hydrolysis** of organometallic compounds (alkoxides of aluminum Al and titanium Ti). Cesium Cs (the element to be inserted) nitrate and barium Ba nitrate are then added, after which the mineral-phase precursors undergo heat treatment at 750 °C (calcination) to obtain oxides. Metallic titanium is added to these oxides then the mixture is finely ground. The resulting powder undergoes pressure-assisted sintering at 1,250 °C, 21 MPa for five hours.

Two zirconolite synthesis processes for conditioning actinides. The first step of the ceramization process is the hydrolysis of organometallic compounds (alkoxides of aluminum Al, titanium Ti, and zirconium Zr). Calcium Ca nitrate and **lanthanide** Ln (the element to be inserted, simulating the presence of an actinide) nitrate are then added. The mineral-phase precursors are then dried and subjected to heat treatment at 750 °C (calcination) to obtain oxides, which are then ground. The resulting powder undergoes uniaxial pressing at 14–40 MPa, then natural sintering at 1,400 °C for 4–96 hours.



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Zirconolite matrix, after incorporating lanthanides, obtained using the melting–crystallization process.

The melting–crystallization process consists in melting a mixture of mineral phase precursor oxides (TiO_2, CaO, Nd_2O_3, Al_2O_3, ZrO_2) in a cold crucible heated by direct induction to a temperature of 1,700–1,800 °C. Neodymium Nd, the lanthanide to be inserted, simulates the presence of an actinide. Fractionated crystallization takes place during the cooling period.

cess for melting oxides at high temperatures (1,700–1,800 °C) in a cold crucible. In spite of its impact on the microstructure of the material, the grain size obtained by ceramization is ten times as fine, so does not modify the resistance of the material to aqueous alteration. The aqueous-alteration kinetics of zirconolite are very slow at the beginning, over a wide pH (2–10) and temperature (less than 300 °C) range. Furthermore, during alteration tests under static conditions simulating the long term, the alteration rate instantly drops to values below the detection limit. Alteration is probably stopped by the formation at the reaction interface of a very fine, insoluble, decalcified titaniferous film, from 1–10 nm thick (1 nm = 10^{-9} m), also containing Zr and lanthanides.

From scientific to technical feasibility

Started in 1994, this research and development program focusing on the search for high-performance materials for optimized long-lived radionuclide conditioning has already resulted in the selection of a set of specific mineral matrices for iodine, cesium, and the actinides, based on laboratory feasibility criteria as well as chemical durability. The laboratory experiments, backed up by models of structures and properties, have created an "ID card" for these matrices, demonstrating their scientific feasibility. By 2006, their technical feasibility will be demonstrated, providing the deciding authority with the data required for selecting the best management scenario for long-lived radioelements.

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