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Minerals and design of new waste forms for conditioning nuclear waste

Les minéraux et la formulation de nouvelles matrices de stockage pour les déchets radioactifs

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ABSTRACT

Safe storage of radioactive waste is a major challenge for the nuclear industry. Mineralogy is a good basis for designing ceramics, which could eventually replace nuclear glasses. This requires a new storage concept: separation-conditioning. Basic rules of crystal chemistry allow one to select the most suitable structures and natural occurrences allow assessing the long-term performance of ceramics in a geological environment. Three criteria are of special interest: compatibility with geological environment, resistance to natural fluids, and effects of self-irradiation. If mineralogical information is efficient for predicting the behaviour of common, well-known minerals, such as zircon, monazite or apatite, more research is needed to rationalize the long-term behaviour of uncommon waste form analogs.

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R É S U M É

Le stockage sûr des déchets radioactifs est un défi technologique majeur de l'industrie électronucléaire. La minéralogie est une base de réflexion pour élaborer les céramiques qui pourraient éventuellement remplacer les verres nucléaires dans un scénario de séparation-conditionnement. Les règles de la cristalochimie permettent de choisir les meilleures structures, et l'étude des occurrences naturelles des minéraux analogues permet d'estimer les futures performances de ces céramiques dans le milieu naturel pour des échelles de temps géologiques. Trois critères sont particulièrement concernés : la compatibilité avec le milieu géologique, la résistance aux eaux naturelles, et le comportement sous auto-irradiation. Toutefois, le raisonnement minéralogique ne prend tout son intérêt que pour les minéraux courants, dont le comportement est bien connu. Les performances des céramiques à base de zircon, de monazite ou d'apatite peuvent donc être bien évaluées par la minéralogie, alors que celles des matrices se basant sur des minéraux plus rares demandent un effort de recherche plus important pour rationaliser leur comportement à long terme dans le milieu géologique.

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1. The nuclear waste issue

Nuclear power plants worldwide produce annually several thousands tons of spent fuel. In some countries, spent fuel is considered as waste, but in other countries, like France, it is reprocessed to extract uranium and plutonium. Two groups of waste elements are obtained at this stage: minor actinides and fission products. Minor actinides are transuranic elements produced by one or several neutron captures on ^{238}U . There are isotopes of Am, Np, or Cm with half-life ranging from 2.1 Ma (^{237}Np) to 18 years (^{244}Cm). All are α emitters, with a decay scheme connected to the “natural” decay chains of U, Th, or Np. Minor actinides and their daughter elements are the main source radioactive hazard in nuclear waste. Fission products are nuclei resulting from the splitting of ^{235}U or other fissile elements. Some of them are radioactive (β emitters), with a half-life long enough to accumulate in the spent fuel. Those with short half-life disappear in few years during the cooling stage, but some will be present in waste for durations similar to minor actinides, notably ^{135}Cs (2.3 My), ^{99}Tc (210 000), and ^{129}I (15.6 Ma). The actual waste obtained after reprocessing is then a complex mixture of radioactive and non-radioactive nuclei, including some long-lived radioactive isotopes which must be stabilized in a safe and robust waste form. In France, this is a boro-silicate glass (R7T7), which has several advantages: it incorporates many different chemical elements, has a low surface-to-volume ratio, and can be made through a simple industrial process with 100% incorporation efficiency. Experimental studies and modelling have shown that R7T7 glass should be reasonably durable in geological environment (Vernaz, 2002; Vernaz and Dussossoy, 1992; Vernaz et al., 2001). The high resistance of R7T7 to leaching results mainly from the formation of a protective amorphous silica-rich layer. The main weakness of a glassy waste form is also well-known: fundamentally, a glass is a metastable material which tends to recrystallize, although this process can be very slow (Grambow, 2006; Grambow and Giffaut, 2006). Both devitrification and the formation of a protective amorphous layer are complex processes, which are difficult to model in a complex, radioactive, geological system, when very long time periods are considered (Grambow, 2006). At present, best estimates indicate that the dissolution rate of R7T7 immersed in water, after a short initial period at 1 g/m²/d, reduces by a factor of 10^4 in a maximum of few months (Vernaz et al., 2001).

2. Crystalline waste-forms

Crystalline waste-forms have been considered for a long time (Lutze and Ewing, 1988). Because crystals are more stable than glasses, ceramics are expected to be several orders of magnitude more durable than glasses. Moreover, as crystals are stable compounds with definite thermodynamics and kinetics properties, modelling and predicting the long-term behaviour of a crystalline waste form is expected to be more robust than for glasses (Oelkers, 2001). However, as crystals are usually produced as powders, a crystalline waste form must be a dense ceramic in order to reduce the surface-to-volume ratio.

Oxide ceramics consist of an ordered assemblage of atoms, linked by ionic-covalent bonding, in which oxygen is the main anion. A crude, but efficient model for oxides is to consider that ionic bonds are dominant, and that each ion is a rigid sphere with a definite ionic radius (Pauling's rules, Pauling, 1929). Each cation, (and most radioactive waste elements are cations with the exception of ^{131}I), is surrounded by anions. Because anions are bigger than cations, the crystalline structure is mainly a stacking of anions letting cavities filled by cations. The number of anions around cations, known as the coordination number, depends on the anion/cation radius ratio.

In nuclear waste forms, the radioactive element content should be limited to a few weight percent, in order to avoid an increase of the temperature, a fast destruction of the crystal net by radiation damage, and, for fissile elements, problems of criticality. Incorporation of a radioactive element in a crystalline structure is then a classical substitution problem: a minor element replaces a major element in the crystal lattice. Substitution rules for ions are by-products of Pauling's rules: (1) the radius of the substituting ion must be similar to that of the nominal ion, but actually depends also on the shape of the polyhedron and on the softness of the structure; (2) if the ion charge is not the same, it must be compensated by another substitution elsewhere in the structure. It is also empirically established that it is easier to replace an ion by a slightly smaller one than the reverse. These rules are now rationalized by recent experimental and theoretical evidence of a full relaxation of cationic sites around substituted elements (Juhin et al., 2008).

As a consequence of these rules, a given structure can accept only some specific substituted elements. It is then difficult to design a crystalline structure which could accommodate all the waste elements produced by spent fuel reprocessing. A specific waste form should be designated for each element, or at least for each group of chemically similar elements. A major consequence is that utilization of crystalline waste forms at an industrial level would require each element, or each group of chemically similar elements, to be selectively extracted from the spent fuel. This is a major technological challenge but considerable progress has been made on that subject, at least at the laboratory scale. Conditioning nuclear waste in crystalline forms is now a promising alternative solution to glassy waste-forms.

3. Performance criteria for crystalline waste-forms

Conditioning nuclear waste in glass has been proven to be a robust method even at industrial scale. If crystalline waste forms pretend to replace glass, it must constitute a very significant progress in all aspects, to counterbalance the difficulty of the separation. The criteria qualifying a crystalline structure as a nuclear waste form can be summarized as follows:

- ability to incorporate, in the crystal lattice, a significant amount of waste element;
- durability in natural fluids significantly higher than glass;

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