# Some Consequences of the Radiation-Induced Transformations of $^{137}$Cs in Synthetic Hollandite-Type Phases

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Criteria for the safe immobilization of $^{137}$Cs in synthetic hollandite-type phases are reviewed with respect to chemical, crystallographic, and physical stability, including possible radiation damage, following $\beta$ decay of $^{137}$Cs$^{+1} \rightarrow \beta^- + {}^{137}$Ba$^{2+}$. Whereas synthetic preparations so far possess properties which offer some optimism that a relatively stable waste product is possible following changes in charge and ionic radius of the radioactive ions, this is by no means established. © 1987 Academic Press, Inc.

## Introduction

In the SYNROC (*1, 2*) and other (*3, 4*) proposals for the safe disposal of radioactive $^{137}$Cs, the hollandite phases (Ba, Cs)$_x$Al$_{2x}$Ti$_{8-2x}$O$_{16}$ (*2*) or cesium priderite Cs$_x$Al$_x$Ti$_{8-x}$O$_{16}$ (*3*) play "host" for $^{137}$Cs$^+$. This radioactive ion is hazardous because of its high activity, 30-year half-life, volatility at elevated temperatures, and tendency to form water-soluble compounds.

It should be appreciated that SYNROC, or any alternative synthetic ceramic preparation, will inevitably take the form of a multiphase assembly designed to incorporate a wide range of radioactive ions (*1*) and, hence, the following considerations of stability may in fact be convoluted with chemical and elastic interactions at interfaces (grain boundaries, etc.) between the different components. The following discussion is limited to the $^{137}$Cs$^+ \rightarrow {}^{137}$Ba$^{2+}$ transmutation. Clearly, the arguments presented should in principle be extended to the

multitude of other transmutations that will occur in the multiphase assemblages proposed for disposal of a wide range of radioactive ions (*1*). However, the present brief discussion highlights many of the practical difficulties and uncertainties involved. An in-depth study of this one relatively well-defined case will help focus attention onto the more general problem.

Kesson (*5*) made a detailed study of preparation conditions that lead to high leach resistance with respect to removal of Cs in deionized water, at room temperature. The essential conclusions were that Cs fixation is optimized if (i) well-homogenized precursor materials are used, which are first calcined at 650–800°C, to avoid Cs volatilization, and then hot-pressed at 1100–1250°C; and (ii) revised formulations of SYNROC (-E and -F) are used that incorporate a reservoir of rutile in their parent phase assemblage. It was stated that the products are characteristically rich in TiO$_2$ (rutile) and low in Al$_2$O$_3$

(alumina). $Cs^+$ was partially substituted for $Ba^{2+}$ in the hollandite phase. It has been established that the Ti-rich limit of the pure (Ba, Al)-hollandite phase $Ba_xAl_{2x}Ti_{8-2x}O_{16}$ has $x = 1.14$ (6). A careful study of the solubility of Cs in this phase showed that use of well-controlled preparation techniques led apparently to single-phase material, with a maximum Cs/Ba ratio of 0.4 (7).

Independent studies of titania-rich preparations ($x < 1.14$) showed that the hollandite phase coexists with $Ba_2Ti_9O_{20}$ (8) and related polymorphic forms. Introduction of Cs into these preparations gave two-phase mixtures of $Ba_2Ti_9O_{20}$ and $Cs_2Ti_5O_{11} \cdot nH_2O$ ($0 < n < 4$), depending on heat treatments (dehydration occurred above 200°C) (9, 10). The latter phase was not detected in earlier X-ray and neutron diffraction studies (2, 6) but was found, subsequently, in SYNROC-F (11). The fine-scale fibrous nature of this phase and some other distinctive characteristics are still under investigation in this laboratory.

Earlier (3) Fujiki et al. reported that Cs could be readily adsorbed and immobilized from aqueous solutions using crystalline hydrous titanium dioxide ($TiO_2 \cdot nH_2O$) fibers. Maximum cesium uptake, from a 0.1 $M$ cesium hydroxide solution, resulted in $Cs_2Ti_5O_{11} \cdot 4H_2O$. The absorbed Cs was then immobilized in a mineral-like phase of the hollandite structure, cesium priderite ($Cs_xAl_xTi_{8-x}O_{16}$, $1.5 < x < 2$), which was obtained by solid-state reaction of the hydrated cesium titanate with titania and alumina. The most leak-resistant immobilizer was produced by sintering the mixed phase of cesium priderite and rutile, and its cesium leachability in pure water was 4.88 $\times 10^{-9}$ g/cm²-day at room temperature. On this basis, the use of such a phase assemblage for $^{137}Cs$ immobilization was proposed (3).

It is the purpose of the present paper to examine further the logic of using either a mixed (Ba, Cs)-hollandite or a pure Cs

priderite phase for immobilization of $^{137}Cs$. Essentially, it is necessary to account for possible changes in structure, and in the phase assemblage overall, as $^{137}Cs$ decays to $^{137}Ba$ by $\beta^-$ emission. Some discussion of the transmutation problem has been given for crystalline phases in general (12), but consideration does not appear to have been given to the possible instability of specific (Cs, Ba) phases, when the charge and ionic radius of the $Cs^+$ cations change during the desired stable lifetime of the waste product, i.e., $\gg \tau_{1/2}$.

## Chemical, Crystallographic, and Physical Changes during Radioactive Decay

It is not necessarily a trivial problem to accommodate both $^{137}Cs^+$ and $^{137}Ba^{2+}$ in crystallographic sites that are electrostatically, mechanically, and chemically stable. Such stabilities need to be retained during several half-lives of $^{137}Cs$ (say 10 × 30 years = 300 years). Since the radioactivity will undoubtedly deposit energy locally (the ranges of 0.518 and 1.17 MeV $\beta^-$ will certainly be ≤1 mm), elevated temperatures may be expected within the waste container. Thus, both initial and final products are required to have compatible thermal expansivity characteristics.

### Chemical Changes

The $^{137}Cs^+$ component of hollandite may be taken as having the stoichiometry $Cs_xAl_xTi_{8-x}O_{16}$. Following radioactive decay, $^{137}Cs_xAl_xTi_{8-x}O_{16} \rightarrow \beta^- + [^{137}Ba_x Al_xTi_{8-x}O_{16}]^+$ yielding a positively charged species which would certainly be electrostatically unstable. The most economical electrostatic rearrangement required to revert to a neutral hollandite phase would appear to be the creation of trivalent titanium according to $Ti^{4+} + \beta^- \rightarrow Ti^{3+}$; overall the radioactive transformation would become, for example,

$$^{137}Cs_x^+ Al_x^{3+} Ti_{8-x}^{4+} O_{16} \rightarrow$$

$$^{137}Ba_x^{2+} Al_x^{3+} Ti_x^{3+} Ti_{8-2x}^{4+} O_{16}.$$
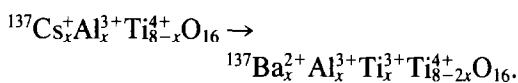
This requires direct replacement of $^{137}Cs^+$ by $^{137}Ba^{2+}$ *and* replacement of an equal number of $Ti^{4+}$ cations by $Ti^{3+}$. This requires trapping of $\beta^-$ particles, or local reduction by loss of oxygen or replacement of $O^{2-}$ by $OH^-$.

## Crystallographic Changes

$Al^{3+}$ and $Ti^{3+}$ may both occupy $[MO_6]$ octahedrally coordinated sites in the framework structure of hollandite. What remains to be established is (i) whether the final $Ba_x(Al_x, Ti_x^{3+}) Ti_{8-2x}O_{16}$ phase lies in a stable range of $x$, and (ii) whether it will intergrow coherently with pure Cs-hollandite, in the case of the priderite proposal (3), or will it stay within the solid solubility range of mixed (Ba, Cs)-hollandites, at the temperature and atmospheric conditions of disposal. Use of the latter preparation would appear to offer more control, in principle, of the elastic properties of the product, if necessary. It should be apparent that a mixed ($Al^{3+}$, $Ti^{3+}$)-hollandite phase may become chemically and mechanically unstable under oxidizing conditions, when $Ti^{3+} \rightarrow Ti^{4+} + e^-$, and it may be necessary to ensure reducing conditions in a metallic radioactive waste container or by inclusion of Ti metal.

## Physical Changes due to Radioactive Decay

This section concerns the possible effects on stability of radiation damage due to the 0.518- and 1.17-MeV electrons that are emitted by $^{137}Cs$ and by any recoil of the radioactive ions.

*Recoiling nuclei.* Conservation of momentum requires that the recoiling nuclei should have energies of 2 or 4.6 eV. These energies are of the same order as the formation energies of point defects in ionic solids, but less than the ~25 eV dis-placement energy. Thus, whereas some point defects may be produced by recoiling nuclei, cascades of defects, resembling fission tracks, are *not* likely to occur.

*β Particles.* The mechanisms of interaction for highly energetic electrons with ionic crystals have been reviewed recently (13). Electron energies in the mega-electron volt range will allow energy transfer to the crystal which will certainly exceed the knock-on displacement energy for Cs, Ba, Ti, Al, and O ions and thus ion displacement and even cascade damage may be expected. The extent to which this will produce permanent damage is strongly dependent on dose and dose rate, the availability of thermal energy for self-healing recombination mechanisms, and the availability of nucleation centers that may act as sinks for interstitial and/or vacancy defects, the primary components of displacement damage.

The possibility of being able to dilute the Cs content in the mixed (Cs, Ba)-hollandite would allow control of the density of point defects. What remains to be assessed is to what extent such point defects may aggregate and precipitate as extended defects, which might lead to mechanical instability (e.g., due to swelling). It may be that if the original waste form is relatively free of defects, then self-annealing (recombination) mechanisms will prevail over aggregation and precipitation.

A much more efficient radiation damage process in ionic crystals is a mechanism called "solid-phase" radiolysis (13). This has a very low threshold energy (<30 eV) and will occur repeatedly as the initial energy of a $\beta^-$ radiation is dissipated by inelastic scattered events. Radiolysis in alkali halides and silicates is believed to involve creation of anionic Frenkel pairs following exciton production (13). Typical energies involved are comparable with the band gap (say 5–30 eV). Radiolysis and other electron-induced radiation damage

effects have recently been reported for (Cs, Ba)-hollandite phases (14). Again, the degree of permanent damage in the form of extended defects will be dependent on the rate of recombination versus the rate of precipitation at existing interfaces and crystalline defects. It is difficult to assess this adequately, without a thorough study of the temperature dependence of extended defect formation, in a material closely simulating the proposed radioactive waste.

## Conclusions

The above discussion appears to offer some optimism for the use of hollandite-type phases for safe immobilization of $^{137}$Cs. Clearly, it is necessary to begin more pragmatic studies of such materials, including the following:

(i) Measurement of leach rates according to some agreed criteria: room temperature rates are clearly not sufficient; $\leq 100°C$ may be more appropriate.

(ii) The study of ceramic techniques necessary for preparation and quality control of bulk quantities of radioactive-waste simulated materials should be continued; in particular, techniques for the detection and elimination of the relatively unstable $Cs_2 Ti_5O_{11}$ and related hydrated cesium titanate phases should be critically evaluated.

(iii) Samples containing "hot" $^{137}$Cs should be prepared and stored where they may remain accessible for periods of, for example, 2, 4, 8, 16, and 32 years (at least), after which times both their macro- and microtextures should be carefully controlled by leach tests and optical and electron microscopy, as well as the other diffraction and chemical analysis techniques.

(iv) Controlled comparative studies of these and other proposed waste disposal materials should be carried out simultaneously.

Such a program of studies should be as widespread (international) as possible to avoid hasty, economically driven industrial developments, which may prove expensive, if not physically impossible, to reverse, should leakage problems arise in the future.

It is often reported that the waste-containing ceramic phases may be sealed in a durable canister and geologically isolated for ultimate safety. The above discussion, and I believe many researchers' experience, should emphasize that it is not a trivial problem to work safely with large quantities of $^{137}$Cs and that the real problem is to first place the radioactive ions safely into the canister. We have reported recently on identifying characteristics and thermal stability of hydrated cesium titanates, showing that careful electron microscopic analysis may be required to detect these phases (10, 15).

## Acknowledgments

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