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Chemical mitigation of the transmutation problem in crystalline nuclear waste radiophases

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Certain deleterious effects on a solid nuclear waste form, though not yet quantitatively defined, could occur due to transmutations of the type $^{137}Cs^+ \rightarrow {}^{137}Ba^{2+}$ and $^{90}Sr^{2+} \rightarrow {}^{90}Zr^{4+}$ (of half-life, $t_{1/2}$, approximately 30 years in both cases). The relevant causes of such possible effects are the valence and size changes. In this paper, a chemical mitigation strategy is explicitly formulated: if the transmuting species can be incorporated in a multiple-cation host, in which one of the inert cations is a variable-valence transition metal, the valence-change aspect of transmutation can be mitigated by a complementary valence change of the transition metal ion. A generalized scheme is:

$$Cs^+R^{z+}O_{(z+1)/2} \xrightarrow{\beta^-} Ba^{2+}R^{(z-1)+}O_{(z+1)/2},$$

where R is a transition metal. The present work involved chemically simulating the transmutation and then attempting to find a Cs- or Sr-bearing single-phase host which would remain single-phase after the transmutation had occurred. Of several structures investigated, perovskite appears to be promising as the A-site can accommodate the approximately 20% size change which occurs when Cs decays to Ba. Ta and Nb were used as the variable-valence ions in the B-site. The application of the results to unpartitioned and partitioned nuclear wastes is discussed.

1. Introduction

The transmutation problem in a solid nuclear waste form derives from the fact that when a nuclide undergoes radioactive decay the newly-formed daughter may be a chemically-different species, having a different ionic size and/or valence. Thus, if the nuclide is chemically incorporated in crystalline solution in a waste form before transmutation, it may not be soluble in the same structure after transmutation has occurred. This may lead to the decomposition of this phase into two or more phases and the possible loss of mechanical integrity.

In typical commercial-power nuclear wastes, the most significant transmutations in the present context are

$$^{137}_{55}Cs^+ \xrightarrow{\beta^-} {}^{137}_{56}Ba^{2+} (t_{1/2} = 30\,\text{year}) \quad (1)$$

and

$$^{90}_{38}Sr^{2+} \xrightarrow{\beta^-} {}^{90}_{39}Y^{3+} (t_{1/2} = 29\,\text{year}) \xrightarrow{\beta^-} {}^{90}_{40}Zr^{4+} (t_{1/2} = 64\,\text{h}), \quad (2)$$

where $t_{1/2}$ is the half-life. For the latter series, the amount of Y^{3+} in secular equilibrium with Zr^{4+} is negligible.

In both these transmutation sequences, the ionic radii differences of the parent and daughter ions are about 30%. Although from the Hume–Rothery rules this size difference would inhibit solid solubility, there are some structures in which the ionic radius tolerance factor is substantial, for example the XII-fold A-site in perovskite. Perovskites of various chemistries are among the candidate crystalline radiophases in tailored ceramic formulations [1–4] for nuclear wastes.

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A mechanism for charge compensation is also required for both crystalline and glassy insulating solids. In the absence of such a mechanism, apart from electron or hole trapping at gross lattice defects, if transmutation took place at sufficiently low temperatures, preventing appreciable atomic diffusion, the lattice strains around transmuted (now mis-fitting) ions would eventually cause a smearing-out of the X-ray diffraction pattern in much the same way as does radiation damage, cold-work, or glass formation. The transmutation-induced departure from thermodynamic equilibrium would increase with time as transmutation continued: at moderate temperatues it would be a question of diffusion kinetics when phase decomposition would occur.

The present work was aimed at finding structures which could accommodate the parent and daughter nuclides in the same site: the idea was that the host should contain inert cations which could change valences to compensate for the transmutation-induced valence change. For example, with the $Cs^+ \rightarrow Ba^{2+}$ transmutation we would seek a refractory, insoluble crystalline solution of the type

$$Cs^{+}R^{z+}O_{(z+1)/2} \rightarrow Ba^{2+}R^{(z-1)+}O_{(z+1)/2}, \qquad (3)$$

where R is a transition metal cation. We will refer to this as a "chemical mitigation" strategy. Though the valence change problem has been widely commented on, to our knowledge an explicit approach to mitigation of the problem has not appeared in the literature.

Generally speaking, we would seek to incorporate only a relatively small amount of, for example, radiocesium in the host phase. Thus, we could incorporate the radiocesium in either a Cs-rich host, $CsRO_{(z+1)/2}$ or a Ba-rich host, $BaRO_{(z+1)/2}$.

Of course, another way of minimizing the problem of transmutation in crystalline waste forms is simply to dilute the radioisotopes in question, either on the atomic scale by crystalline-solution dilution with "cold" isotopes or on an approximately 1 μm scale by dilution of the waste solid with inert phases. In this paper, however, we focus on the "chemical mitigation" strategy outlined above.

2. Experimental procedure

The various Cs- and Sr-bearing phases were made up by sol–gel techniques developed and used routinely in these laboratories [5, 6]. The desired mixture of ions was first put into solution or sol. The sol was then gelled and dried, and the gel was then calcined at about 600° C to drive off nitrogen oxides (if starting with nitrate solutions). The calcines were cold-pressed and sintered at about 1100° C or vacuum hot-pressed, to consolidate and crystallize them. The structural characteristics of the preparations were investigated by powder X-ray diffraction analysis, using a standard diffractometer and graphite-monochromated CuKα radiation.

3. Results

3.1. $Cs \rightarrow Ba$

3.1.1. Iron pollucite

$CsFeSi_2O_6$ is the iron analogue [7, 8] of pollucite which is a favoured [1, 2] phase for Cs-fixation in some tailored ceramic waste form strategies. The stable equilibrium solubility of Ba in pollucite itself is said to be small, if not negligible [9]. We investigated the possible crystalline solution

$$CsFeSi_2O_6 \rightarrow (Cs_{1-x}, Ba_x)(Fe^{3+}_{1-x}, Fe^{2+}_x)Si_2O_6. \qquad (4)$$

Firing in air at 1050° C produced apparently phase-pure material for x up to 0.5. However, no lattice dilation was observed relative to $CsFeSi_2O_6$ and, although an expected contraction on replacing Cs^+ by Ba^{2+} could perhaps be off-set by an expansion on reducing Fe^{3+} to Fe^{2+}, it became clear that additional diffuse X-ray scattering, peaking near $d = 0.32$ nm, and increasing monotonically with x, was present in the diffraction patterns. Thus, some amorphous material was present in addition to iron pollucite. Materials heated in forming gas (5% H_2/N_2) at 1000° C to promote Fe^{2+} formation showed no lattice dilatation as evidence of crystalline solubility. Also, substituting Mg^{2+} or Zn^{2+} for the desired Fe^{2+}, so that air firing could be employed without iron valence uncertainties, did not change the situation.

3.1.2. $CsFeSiO_4$

A similar procedure to that in Section 3.1.1 was performed with $CsFeSiO_4$, but again no signs of crystalline solubility were observed.

3.1.3. Perovskite

Here the possible crystalline solution

$$(Ba_{1-x}, Cs_x)(Zr_{1-x}, [Ta/Nb]^{5+}_x)O_3 \rightarrow Ba(Zr_{1-x}, [Ta/Nb]^{4+}_x)O_3 \qquad (5)$$

was examined. Ta_2O_5 or Nb_2O_5 powders were used instead of solutions, but the rest of the cations were initially present as solutions; these were mixed with the powders and the specimen preparation was then performed as described above. Gallagher [10] studied the Nb option, not for the present reasons, and concluded that all the Cs was lost on firing at 1200° C in air. In the present work, the preparations were calcined briefly in air at 750° C and then fired in welded Pt tubes at about 1000° C.

The solubility of Cs in $BaZrO_3$ was found to be quite extensive. $(Ba_{1-x}, Cs_x)([Ta/Nb]_x, Zr_{1-x})O_3$ preparations were made up with $x = 0$, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1.0. Since the compounds $CsTaO_3$ and $CsNbO_3$ are not perovskite-structured [11–13], complete crystalline solubility was not expected. The solubility limits were found to be $x \simeq 0.5$ and 0.7 for Nb- and Ta-compensated materials, respectively. Some difficulties were experienced in preparing homogeneous solid solutions. Many preparations exhibited broad or split diffraction lines; the splitting or broadening was not due to deviations from cubicity. Regrinding and re-firing did not significantly change the observations. Compositional inhomogeneity was also observed in electron microprobe studies. The inhomogeneity is no doubt due to the use of the Ta_2O_5 and Nb_2O_5 powders instead of solutions, but was regarded as a minor problem in the present context. Assuming the lattice parameter of the perovskite phase to be linear with (Cs, Nb) or (Cs, Ta) addition, the lattice volume contraction was approximately 0.1 and 0.07% per respective percentage of (Cs, Ta) or (Cs, Nb) replacement of (Ba, Zr).

For a monolithic host containing an appreciable amount of ^{137}Cs or ^{90}Sr, the bulk temperature of the monolith may be several hundred degrees centigrade, depending on its size, thermal conductivity, etc. Thus, it is necessary to obtain leaching results at elevated temperatures. Simple hydrothermal experiments were made to check on the gross solubility or otherwise of the Cs-doped perovskite phase. Pure $BaZrO_3$ itself does not have especially good leach resistance [14]. No changes in the (broad) X-ray patterns of two of these preparations, $(Ba_{0.8}, Cs_{0.2})(Zr_{0.8}, Ta_{0.2})O_3$ and $(Ba_{0.8}, Cs_{0.2})(Zr_{0.8}, Nb_{0.2})O_3$ fired only briefly at 800° C were observed after finely ground powders were treated with de-ionized water at 300° C/300 bars for seven days using a 10:1 water/solid (wt/wt) ratio, the mixtures being sealed in welded Au tubes. After the hydrothermal treatment, it was found that about 20% of the Cs was in solution for both the Ta- and Nb-compensated materials. Powdered crystalline $(Ba_{0.6}, Cs_{0.4})(Zr_{0.6}, Ta_{0.4})O_3$ and $(Ba_{0.6}, Cs_{0.4})(Zr_{0.6}, Nb_{0.4})O_3$ preparations fired at 1100° C in welded Pt tubes were treated for seven days in de-ionized water at 400° C/300 bars, again using Au capsules and a 10:1 water/solid (wt/wt) ratio. Although no changes were observed in the X-ray patterns, solution analyses showed that nearly all the Cs was extracted into solution for the Ta-bearing material. In contrast, only about 2% of the Cs in the Nb-bearing material was extracted; the difference between the Ta- and Nb-containing materials was not expected and remains unexplained. Possibly the Cs was extracted but reprecipitated in the latter case. These experiments are by no means definitive or comprehensive but they do show that exposure to aqueous media at several hundred degrees centigrade does not cause very rapid disintegration or dissolution.

The thermal stability in open systems of these preparations was not particularly good: Cs volatility became a problem at temperatures above about 800° C for unconsolidated material. The volatility was detected by gravimetric measurements and by X-ray diffraction analysis, which showed the development of second-phase material.

In a "hot" system, there would seem little difficulty for the Nb- or Ta-forming tetravalent cations to compensate the Cs → Ba transmutation, as such cations (especially Nb^{4+}) are readily produced in a reducing atmosphere and the ionic sizes of Nb^{4+} and Ta^{4+} are not very different to that of Zr^{4+}. Indeed, perovskite-structured $BaNbO_3$ can apparently be prepared in a closed system [15].

In the present work, some powdered $Ba([Nb/Ta]_x, Zr_{1-x})O_{3+x/2}$ preparations were heated for several days in flowing 5% H_2/N_2 at about 850° C to see whether a $Ba([Nb/Ta]_x^{4+}, Zr_{1-x})O_3$ perovskite phase would be promoted by this particular set of reducing conditions. However, no difference in the phase assemblage was observed by X-ray diffraction analysis for preparations calcined at 600° C in air which were then heated in the reducing conditions above and the same calcines heated in air at 900° C for one day. Nor were any differences noted in the phase assemblages of materials fired initially in air at 1400° C to crystallize them before and after the above-mentioned heat-treatment in 5% H_2/N_2. Thus, conditions need to be rather more reducing than those employed here to form the $Ba([Nb/Ta]^{4+}_x, Zr_{1-x})O_3$ perovskite. The actual preparations studied were characterized by $x = 0.4$ for the calcines and $x = 0.2$ for the crystallized materials. After heat treatment, the preparations were mainly perovskite, but second-phase material was present.

3.2. Sr → Zr

3.2.1. *Anorthite*

The anorthite ($[Ca, Sr]Al_2Si_2O_8$) structure was investigated for Zr solubility, with attempted substitution of Fe^{2+} or Mg^{2+} in the Al^{3+} site. The transmutation sequence can be visualized as:

$$(Ca_{1-x}, Sr^{2+}_x)(Al_{1-y}Fe^{3+}_y)_2Si_2O_8 \rightarrow$$
$$(Ca_{1-x}, Zr^{4+}_x)(Al_{1-y}, Fe^{3+}_{y-x}, Fe^{2+}_x)_2Si_2O_8, \quad (6)$$

for $y \geqslant x$. However, no Zr solubility was detected by X-ray diffraction analysis for preparations fired in air at 1200° C.

3.2.2. *Yttrium iron garnet, $Y_3Fe_5O_{12}$*

The notional strategy was as follows: Sr solubility in the Y-site could be charge-compensated by adding Si^{4+} which would inhabit the tetrahedral Fe^{3+} site. On the $Sr^{2+} \rightarrow Zr^{4+}$ transmutation, charge compensation could take place via the transformation of two (octahedral or tetrahedral) Fe^{3+} ions to form Fe^{2+}. Again, Mg^{2+} was used as a substitute for Fe^{2+} ions and the calcines were sintered in air at 1200° C. In chemical terms, the sequence would be:

$$(Y_{1-x}, Sr^{2+}_x)_3(Fe^{3+}_{1-3x/5}, Si^{4+}_{3x/5})_5O_{12} \rightarrow$$
$$(Y_{1-x}, Zr^{4+}_x)_3(Fe^{3+}_{1-9x/5}, Fe^{2+}_{6x/5}, Si^{4+}_{3x/5})_5O_{12}. \quad (7)$$

From X-ray diffraction analysis evidence, only a small degree of Sr solubility was deduced ($x \leqslant 0.15$) and no Zr solubility was indicated.

3.2.3. *Oxides*

The rationale here was based on the ability of the fluorite structure to accommodate aliovalent ions. Cubic zirconia "stabilized" by CaO or Y_2O_3 is the best-known example. Such oxides were examined for crystalline solubility of Sr and Zr, the possibility being that the charge compensation problem would be taken care of through oxygen deficiency. For example, if A is a tetravalent cation such as Zr or Th, the transmutation process would be in the first instance

$$(A^{4+}_{1-x}, Sr^{2+}_x)O_{2-x}\square_x \rightarrow$$
$$(A_{1-x}, Zr_x)^{4+}O_{2-x} \text{ (mass balance)} \quad (8)$$

However, this equation is not charge balanced. To balance it, oxygen from the atmosphere would have to be picked up. Otherwise the material would form an uncompensated (p-type) semiconductor. The fluorite-structured oxide hosts examined were fluorite-structured ZrO_2, ThO_2, and CeO_2. Mixtured containing up to 20 mol% SrO were made up and reacted in air at 1200° C. None showed observable crystalline solubility (about 3 mol% was approximately the limit of detection of the X-ray technique) of both Sr and Zr. In view of the well-known extensive solubility of CaO and Y_2O_3 in ZrO_2 and ThO_2 this very limited (unobservable in the present experiments) solubility of Sr^{2+} is disappointing since $Sr_x, Zr_{1-x}O_{2-x}\square_x$ would have been favourable from the points of view of chemical insolubility and radiation resistance. Although considerably higher equilibration temperatures would have promoted solubility, such higher temperatures are probably not realistic for radwaste processing.

The sesquioxides Y_2O_3, La_2O_3, Nd_2O_3, and Gd_2O_3 were also examined. Here, a feature was that solubility of both Sr and Zr might be possible since the maximum valence difference of host and solute was only unity. Again, however, no observable solubility of either Sr or Zr was found in preparations fired at 1200° C.

4. Discussion

4.1. Crystal Chemistry

Analogues of aluminosilicate minerals such as pollucite or anorthite did not show promise as being structurally-tolerant to the transmutation of ^{137}Cs or ^{90}Sr, respectively, although metastable persistence of transmutation-induced solid solutions in these framework structures may be possible. In these structures, Fe^{3+} replacing Al^{3+} occupies tetrahedral sites and for chemical mitigation, Fe^{2+} needs to be formed. The existence of Fe^{2+} in these sites is known not to be favoured by crystal-field considerations. For example, in beryl and cordierite, in which both octahedral and tetrahedral sites are available for Fe^{2+}, Fe^{2+} occupancy of the octahedral site is strongly favoured [16, 17]. Such aluminosilicates, in which there are octahedral Fe^{3+} sites, could be worthy of further study. In the present work, natural crystals of cordierite showed considerable leaching and alteration in de-ionized water at 200 and 300° C, whereas a natural beryl crystal showed no such reaction. Natural beryls have been reported to contain more than 6 wt % Cs_2O [18]. Preparation may present special difficulties because of the toxicity of BeO, but this problem would probably be insignificant compared to the problem of that of the ^{137}Cs radioactivity.

Although perovskite looks promising for the $Cs \rightarrow Ba$ transmutation in the present context (a demonstration of the mitigation strategy rather than a recommended final "product") we have, as yet, found no material (admittedly from fairly limited studies) which would accommodate the $Sr^{2+} \rightarrow Zr^{4+}$ transmutation. Perovskite by itself would not be suitable as there would be a very high site preference energy for Zr^{4+} to exist in the VI-fold site rather than in the XII-fold site on which it would have formed by transmutation. In this absence of an atomic scale host, it was decided to explore an encapsulation strategy as one option. Perovskite-structured $SrZrO_3$ diluted into a ZrO_2 matrix was investigated. The two-phase ceramics were made by mixing Sr and zirconyl nitrate solutions, drying, calcining and vacuum hot-pressing at 1350° C. This mixture was chosen on the basis that both $SrZrO_3$ and ZrO_2 are not much affected by de-ionized water at lower temperatures up to 300° C [19, 20], although adverse effects can occur at lower temperatures in certain types of simulated groundwaters [19]. The transmutation product would be expected simply to be oxygen-deficient ZrO_2 in a compatible ZrO_2 matrix. The preparations containing 5 and 10 mol % $SrZrO_3$ in ZrO_2, however, showed alteration after treatment at 300° C and 300 bars in de-ionized water for 7 days; the crystalline $SrZrO_3/ZrO_2$ (wt/wt) ratio was reduced and there was development of an X-ray amorphous phase.

4.2. Relevance to radwaste

The relationship of the above results to the transmutation problem in partitioned or unpartitioned waste is now discussed. If ^{137}Cs and/or ^{90}Sr are partitioned from liquid waste streams or neutralized sludges, as for example at the Rockwell Hanford site, the crystal–chemical problem becomes fairly simple to deal with, along the lines put forward in the body of this paper. However, because of the approximately 30 year half-lives, the ^{137}Cs and ^{90}Sr will have virtually disappeared after a few hundred years. Hence, direct encapsulation in metal or ceramic containers of even very water-soluble $^{137}CsCl$ and slightly water-soluble $^{90}SrF_2$ becomes viable, as at Hanford, if no transportation in the public domain is necessary. However, if transportation is required it is probable that future legislation will specify that the isotope-bearing solid itself should be insoluble and refractory (for fire resistance in a transportation accident or sabotage); this is really the problem which the present experimental work addresses.

The chemical mitigation strategy, though simple in concept, does not appear to be widely applicable if thermodynamic stability of the transmuted material is required, although, as mentioned earlier, there might be a considerable degree of metastability of the transmuted material in a zeolite-like system such as pollucite. Such metastability cannot be studied by high-temperature synthesis or even low-temperature hydrothermal synthesis. The only available experimental methods in this case would be neutron-induced transmutation or "hot" isotope synthesis.

For ceramic crystalline waste forms [1–4], designed for relatively fresh commercial wastes, it is clear that for the full complement of radwaste ions plus various amounts of inert process chemical additives, building in the chemical mitigation strategy as an "equal partner" to the problems of leach resistance, thermodynamic compatibility, full-phase characterization and radiation stability would be very difficult. The best approach at present would seem to be, given the choice of similarly-performing radiophases, the one with the best likelihood of mitigation of the transmutation problem should be chosen. It must be emphasized that, in an upartitioned waste form, the ^{137}Cs and ^{90}Sr problems do not disappear when virtually all the ^{137}Cs and ^{90}Sr have disappeared; any changes in solubility or volume in the original Cs- and Sr-bearing radiophases will last as long as the waste form itself and will contribute to the total properties of the waste form.

Because the distribution of atomic co-ordinations in a glass is less well defined than it is in a crystal, a common assumption is that valence and size changes attendant upon radioactive transmutation will be more easily accommodated than in insulating phases. However, many glasses are more aptly described by a model of microcrystallites linked together by "amorphous" regions of different composition, i.e., a partial phase separation [21] rather than a more or less homogeneous assemblage of ions represented by a single radial distribution function. The higher the degree of phase separation in the glass the more similar will be the accommodation problem in the glass and the crystalline phases, but the problem will not vanish even if phase separation in the glass is negligible: the problem will be merely less obvious.

5. Conclusions

(a) A "chemical mitigation" method for transmutation resistance in crystalline radiophases has been put forward.

(b) If it is necessary that ^{137}Cs- and ^{90}Sr-bearing hosts derived from partitioned nuclear wastes remain refractory and leach-resistant for several hundred years, perovskite hosts (encapsulated for ^{90}Sr) would seem far superior to ^{137}CsCl or $^{90}SrF_2$ with respect to leach properties. Cs volatility would be just adequate, rather than outstanding, for fire resistance. Further work could no doubt suggest preferable alternatives.

(c) For ceramic hosts, it would seem at this stage to be extremely difficult to design for full mitigation, in the thermodynamic sense, of the transmutation problem, but the presence of inert transition-metal ions would add to the possibility of metastable mitigation.

(d) The only reliable solution to the transmutation problem would seem to be sufficient dilution, and further work is necessary to quantify "sufficient" dilution and its value in a total waste package. However, existing defense wastes are extremely dilute in radionuclides and transmutation problems in such solidified unpartitioned wastes would seem to be trivial.

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