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Radiation-induced microcrystal shape change as a mechanism of wasteform degradation

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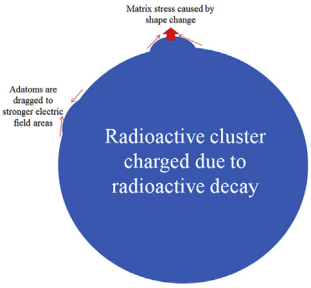
HIGHLIGHTS

- Mechanical destruction of waste-forms containing actinides (ceramics and crystals doped with ^{238}Pu) is overviewed.
- For the first time the damaging effects caused by electrical fields induced by the decay of radionuclides are recognised.
- Electrical field mechanism is an addition to recognised processes of matrix swelling and solid solution destruction.
- Mechanical self-destruction can only be detected after extended times which can be many years or even decades.
- To avoid potential damage the wasteform should be homogeneous and/or electrically conductive.

GRAPHICAL ABSTRACT



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ABSTRACT

Experiments with actinide-containing insulating wasteforms such as devitrified glasses containing ^{244}Cm, Ti-pyrochlore, single-phase La-monazite, Pu-monazite ceramics, Eu-monazite and zircon single crystals containing ^{238}Pu indicate that mechanical self-irradiation-induced destruction may not reveal itself for many years (even decades). The mechanisms causing these slowly-occurring changes remain unknown therefore in addition to known mechanisms of wasteform degradation such as matrix swelling and loss of solid solution we have modelled the damaging effects of electrical fields induced by the decay of radionuclides in clusters embedded in a non-conducting matrix. Three effects were important: (i) electric breakdown; (ii) cluster shape change due to dipole interaction, and (iii) cluster shape change due to polarisation interaction. We reveal a critical size of radioactive clusters in non-conducting matrices so that the matrix material can be damaged if clusters are larger than this critical size. The most important parameters that control the matrix integrity are the radioactive cluster (inhomogeneity) size, specific radioactivity, and effective matrix electrical conductivity. We conclude that the wasteform should be as homogeneous as possible and even electrically conductive to avoid potential damage caused by electrical charges induced by radioactive decay.

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1. Introduction

Understanding long-term behaviour of actinide-containing host-matrices under self-irradiation is crucial in ensuring safety of nuclear waste storage and disposal. An important aspect of long-term matrix integrity is the resistance of material against damage caused by radiation. Radiation-induced damage of crystalline structures is usually, although not always, accompanied by reduced chemical durability, swelling and crack formation in poly- and single-phase crystalline ceramics [1] as well as in devitrified glasses containing large volumes (30 wt%) of crystalline inclusions [2]. Under irradiation at room temperature (depending on cumulative dose and energy) the original crystalline structure may be (a) retained [3]; (b) converted into another type of crystalline structure [4]; or (c) amorphized (become amorphous or metamict) [1,5,6]. For example, the long-term stability and chemical durability of natural solid U-bearing Zr-silicate gel is assumed to be caused by two competing processes, first, crystallisation of the gel into U-doped zircon assisted by self-irradiation and, second, metamictisation of the crystallised zircon back to a gel-like state [7]. Extended experiments with actinide doped crystalline waste forms have however shown significant mechanical damage with crystal cracking within a decade of storage [1,2]. Self-irradiation of materials over very long time scales, measured in the hundreds and thousands of years in the case of immobilized nuclear waste, creates continuous excitations and long-lived defects, which evolve in a medium that is changing with time. Slowly occurring processes that have hitherto not been the focus of attention may also result in significant consequences for the retention capacities of nuclear wasteforms. For example, the irradiation of insulators (e.g. glass and ceramics) causes intensification of surface diffusion processes and may result in surface instability [8–11]. Furthermore, although the amorphisation of crystalline materials is the most evident result of irradiation, the primary irradiation effects in glassy materials are volume changes and viscosity diminution [12–14]. Wasteform tolerance to radiation effects is most important for higher activity wastes which typically utilise glassy and crystalline wasteforms as well as glass-composite materials (GCM's) which consist of both crystalline and glassy phases [15,16]. Radiation effects in these materials have been intensively investigated with many overview reports available see e.g. Refs. [1,17–19]. Moreover a Joint ICTP-IAEA Workshop on radiation effects in nuclear wasteforms and their consequences for storage and disposal was held in 2016 that involved experts in both experimental and theoretical (modelling) methods for radiation effects in materials to explore the potential of both experimental and theoretical/computational approaches to understand the consequences of irradiation of materials under extreme conditions, particularly focusing on long-term irradiation conditions envisaged for nuclear wasteforms containing long lived fission products and actinides. The following summaries on mechanical changes under self-irradiation in nuclear wasteforms briefly follow the reports presented at the Joint ICTP-IAEA Workshop [20].

Although radiation damage effects have been extensively examined in analogue minerals that naturally contain radionuclides and accumulate high doses of self-irradiation [1,5,6] the mechanisms of damage that cause alterations are not well understood. This paper aims after a brief summary of mechanical destruction effects observed to analyse an almost ignored mechanism of mechanical damage of non-conducting nuclear wasteforms caused by electrical fields [21] that are induced in the insulating materials by the decay of radionuclides. We will show that:

- This mechanism can eventually lead to nuclear wasteform destruction in conditions of non-uniform radionuclide distribution;
- The most important parameters that affect the matrix integrity are the radioactive cluster (inhomogeneity) size, specific radioactivity and effective electrical conductivity of matrix.

2. Nuclear wasteforms

Radioactive or nuclear waste is defined as waste that contains or is contaminated with radionuclides at concentrations or activities greater than established clearance levels [22]. It is a general safety requirement that waste packages shall be designed and produced so that the radioactive waste is appropriately contained both during normal operation and in accident conditions that could occur in the handling, storage, transport and disposal. Processing radioactive waste is applied to enhance safety by producing a wasteform that fulfils the acceptance criteria for safe processing, transport, storage and disposal. The wasteform is a component of the waste package and is defined as the waste in its physical and chemical form after treatment and/or immobilization resulting in a solid product prior to packaging. Radioactive and chemically hazardous constituents in the waste can be immobilized into a wasteform through two processes: (1) binding them into the material at atomic scale (chemical incorporation), or (2) physically surrounding and isolating the material (encapsulation).

A number of wasteform and container materials have been used for waste immobilization, including ceramic, glass, metal, cement, polymer and bitumen [1,15,16,23–30]. In practice the more durable materials are used to host longer-lived and higher activity waste. The choice of the wasteform depends on the physical and chemical nature of the waste and the acceptance criteria for the storage and disposal facilities to which the waste will be consigned. When selecting a wasteform material several factors should be considered which include the following key considerations [26,28,31]:

I. *Waste loading*: The waste form should be able to accommodate a significant amount of waste (typically 25–45 wt %) to minimize volume, thereby minimizing the space needed for storage, transportation and disposal.
II. *Ease of production*: Fabrication of the waste form should be accomplished under reasonable conditions, including low temperatures and, ideally, in an air atmosphere, using well established methods to minimize worker dose and the capital cost of plant.
III. *Durability:* The waste form should have a low rate of dissolution when in contact with water to minimize the release of radioactive and chemical constituents.
IV. *Radiation stability*: The wasteform should have a high tolerance to radiation effects from the decay of radioactive constituents. Depending on the types of constituents being immobilized, the waste form could be subjected to a range of radiation effects, including ballistic effects from alpha decay and ionizing effects from decay of fission product elements.
V. *Chemical flexibility:* The waste form should be able to accommodate a mixture of radioactive and chemical constituents with minimum formation of secondary phases that can compromise its durability.
VI. *Availability of natural analogues:* Since direct laboratory testing of the waste forms over the relevant time scales for disposal (typically 10^3–10^6 years) is not possible, the availability of natural mineral or glass analogues may provide important clues about the long term performance of the material in the natural environment, thereby building confidence in the extrapolated behaviour of the waste form after disposal.
VII. *Compatibility with the intended disposal environment:* The wasteform should be compatible with the near field