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Accelerated chemical aging of crystalline nuclear waste forms

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ABSTRACT

Nuclear waste disposal is a significant technological issue, and the solution of this problem (or lack thereof) will ultimately determine whether nuclear energy is deemed environmentally friendly, despite significantly lower carbon emissions than fossil fuel energy sources. A critical component of any waste disposal strategy is the selection of the waste form that is tasked with preventing radionuclides from entering the environment. The design of robust nuclear waste forms requires consideration of several criteria, including: radiation tolerance, geological interaction and chemical durability; all of these criteria ensure that the radionuclides do not escape from the waste form. Over the past 30 years, there have been numerous and thorough studies of these criteria on candidate waste forms, including radiation damage and leaching. However, most of these efforts have focused on the performance of the candidate waste form at $t = 0$, with far less attention paid to the phase stability, and subsequent durability, of candidate waste forms during the course of daughter product formation; that is, the chemical aging of the material. Systematic understanding of phase evolution as a function of chemistry is important for predictions of waste form performance as well as informing waste form design. In this paper, we highlight the research challenges associated with understanding waste form stability when attempting to systematically study the effects of dynamic composition variation due to in situ radionuclide daughter production formation.

1. Introduction

Despite renewed interest in nuclear energy to address both the world's increasing energy demands and man-made climate change, several obstacles are preventing its expansion. These include construction costs of new plants, proliferation risk, safety concerns and nuclear waste disposal. Of these issues, nuclear waste disposal will benefit the greatest from future technological advances. Furthermore, the waste problem is quite possibly also the largest obstacle to wider acceptance of nuclear energy, and a solution could enable the so-called "nuclear renaissance" [1]. Recently, President of the United States Barack Obama established a Blue Ribbon Commission (BRC) to address "America's Nuclear Future" to specifically consider issues related to the back end of the fuel cycle. Findings from the BRC final report support the development of one or more geologic repositories and continued research and development to eventually allow for more sustainable fuel cycle options [2]. In this paper, we focus on the waste form component of a comprehensive nuclear waste strategy, and are motivated by the conclusion of Ringwood et al.'s classic 1979 Synroc paper [3] – "If our society is to take advantage of the potential benefits of nuclear power, there can be no excuse for any policy which does not use the most advanced technology to safeguard future generations from the attendant dangers of nuclear waste. It can hardly be claimed that immobilisation of radwaste in borosilicate glasses, currently favored by the nuclear power establishment, satisfies this requirement." That is, the waste form is the front line of waste immobilization, and is the material where the radionuclides are introduced (and confined) on an atomic scale. Ceramics are closer to thermodynamic equilibrium than glass [4], and should have greater stability over the long periods required to encapsulate the waste [5]. However, continued research is required to improve our understanding of ceramics as waste forms, especially for complex waste streams. Several research topics are discussed in this paper.

There are many different types of radiological waste, which are typically categorized according to their activity. Although our focus in this paper is on radionuclides produced by fission in civilian reactors, many of the challenges described also pertain to military and other types of radwaste. Here, we further assume that spent fuel has been reprocessed, which not only may lead to significant decrease of volumetric load in geologic repositories (via recycle of actinides e.g. in fast reactor transmutation fuel) [6], but also allows for the consideration of customized waste forms for particular isotopes (though reprocessing does increase proliferation

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concerns). Ultimately, the approach of waste form customization will prevent an unoptimized singular waste disposal strategy for radionuclides with drastically different physical and chemical properties. For example, Cs-137 has a half-life of 30 years, while Tc-99 has a half-life of 200,000 years; clearly, there is an opportunity to considered tailored waste forms for isotopes with such disparate time scales. Nevertheless, reprocessing is a separate issue (see, e.g. [7]), encompassing factors from whether to reprocess at all, to what degree spent fuel should be reprocessed.

The focus of this paper is not an in depth analysis of fuel cycles (for which readers are directed elsewhere [8,9] and references therein), but rather, the effect of transmutation of radionuclides to chemically distinct daughter products on waste form stability and the resultant challenges associated with the encapsulation of isolated fission products in ceramic waste forms. Due to the technical challenges associated with this problem, the a topic of transmutation has received limited attention during the past 30 years of waste form development. We posit that improvements in waste form performance will lead to increased confidence in their long-term durability, thus enabling consideration of closed fuel cycles in the future. We begin with a brief review of recent and traditional crystalline waste form development activities before outlining a combined experimental and theoretical approach to accelerated chemical aging studies of ceramic waste forms. We subsequently discuss a number of technical challenges encountered when attempting to understand the effects of transmutation on ceramic waste form stability, with the ultimate goal of employing that improved understanding to design robust waste forms.

2. Survey of waste form development activities

The performance requirements of waste forms have dictated research in areas such as the extent of radionuclide incorporation (since it is advantageous for the waste form to accommodate as many radionuclide species as possible) [10], thermodynamic stability to ensure leaching resistance [11] and amorphization resistance to self-irradiation [12]. Since we limit this paper to the consideration of radiation effects, we will not consider leaching resistance and radionuclide incorporation further. (However, we acknowledge that radiation effects may influence both radionuclide incorporation and leaching resistance. Readers interested in a more detailed description of crystalline waste form development and selection based on radiation damage, leaching and radionuclide solution are directed elsewhere, as such topics have been reported extensively and need not be repeated here [12–18].) In the following subsection we provide a cursory overview of radiation damage, and subsequently introduce a less-examined aspect of radiation-induced changes to the material: the chemical aging of the material (i.e. compositional variation) with time due to daughter product formation.

2.1. Radiation damage

The effects of radiation expose the wasteform to a variety of chemical and physical processes which depend on the decay mode of the radionuclide, which governs the radiation damage spectrum, including species, energy, type of particles emitted, and so forth. These can be broadly classified into three distinct aging processes: alpha/ion beam damage, beta/electron beam damage and chemical evolution. All three of these processes compromise the stability/durability of the waste form, accumulating over time scales inaccessible to experiment.

The most studied mechanism is the radiation damage cascade associated with alpha decay. Momentum conservation dictates that the alpha particle receives around 98% of the *Q*-value (typically 4–6 MeV), while the recoiling daughter nucleus receives around 70–100 keV. The daughter nucleus travels on average several tens of nanometers through the solid, disrupting thousands of atoms in the local vicinity. The alpha particle travels much further than the daughter, of order several microns, generating additional damage due to ionization from electronic stopping along the trajectory and creating additional damage cascades from nuclear stopping near the end of range. Although the range of the alpha particle is longer, the damage volume from a daughter recoil is much greater. Further effects include chemical doping, since the transmuted daughter is chemically distinct from the parent, and gas accumulation which follows from neutralization of the alpha particle to form helium. The extent to which the host phase recovers from and accommodates these highly disruptive process is a key predictor of its stability. For ceramic wasteforms it is particularly desirable for the host phase to resist radiation-induced amorphization, since a loss of crystallinity implies an increase in the structural volume which in turn facilitates cracking and aqueous attack [13].

A number of studies have focused on the radiation tolerance, defined as crystalline stability under irradiation, of potential waste form candidates. One method to determine the effects of alpha-decay on candidate waste forms is to dope them with actinides such as ^{238}Pu, ^{239}Pu or ^{244}Cm. For example Farnan et al. found from nuclear magnetic resonance (NMR) experiments that when zircon ($ZrSiO_4$) is synthesized with ^{239}Pu, the damage produced during an α-decay event is significantly greater than expected from previous studies [19]. A similar method is used to understand the fundamental mechanisms of nuclear weapons aging for lifetime assessments [20,21].

Although zircon has been considered as a model waste form, its stability has been shown to be less than sufficient for a robust waste form [22]. A material system that has received significant attention is $A_2B_2O_7$ pyrochlore. In these systems, ion-beam irradiations have been used as a simulant for α-decay to examine the damage accumulation and phase stability of pyrochlores as a function of irradiation dose and spectrum, as well as pyrochlore chemistry. Originally focused on titanate pyrochlores, these studies have resulted in a number of proposed criteria for the stability of complex oxides under irradiation and thus new compositions and even crystalline structures for consideration as waste forms. These criteria include the enthalpy of formation of the oxide [23], the relative tendency towards atomic disorder [24], and empirical correlations based upon the bonding characteristics of the oxide [16]. These studies have identified zirconate pyrochlores as a radiation-tolerant alternative to the titanates, but have also suggested other crystalline structures, such as the $A_4B_3O_{12}$ δ-phase, that might exhibit exceptional properties [25,26]. Often, these experiments have been accompanied by atomistic simulations in an attempt to reveal fundamental insight on the defect-related phenomena, which is again similar to the approach pursued by aging studies for nuclear weapons, e.g. [27]. However, in the context of the current review, complex oxides materials have received relatively little attention with regards to leaching or radionuclide incorporation experiments.

Beta and gamma decay affect the waste form much less dramatically than does alpha decay. The key difference is that electrons, positrons, neutrinos and photons have far less mass than a helium nucleus and accordingly remove around 99.999% of the kinetic energy. There are three primary effects associated with beta and gamma radiation: (i) recoil of the daughter nucleus during decay, (ii) displacement of atoms elsewhere in the waste form via interactions with beta particles, and (iii) radiolysis due to ionization. The first effect, recoil of the daughter, can be as low as several eV; the recoil is easily computed for two-body decays (electron capture and γ emission), but is non-trivial for three-body process (β^+/β^- decay). Often the daughter recoil is less than the threshold displace-