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Durability and shielding performance of borated Ceramicrete coatings in beta and gamma radiation fields ☆,☆☆

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HIGHLIGHTS

- It incorporates all suggestions by the reviewers.
- Explanation to each new term is provided and suitable references are given.
- Sample identities have been streamlined by revising the text and the tables.
- Some figures have been redrawn.

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ABSTRACT

Ceramicrete™, a chemically bonded phosphate ceramic, was developed for nuclear waste immobilization and nuclear radiation shielding. Ceramicrete products are fabricated by an acid–base reaction between magnesium oxide and mono potassium phosphate. Fillers are used to impart desired properties to the product. Ceramicrete's tailored compositions have resulted in several commercial structural products, including corrosion- and fire-protection coatings. Their borated version, called Borobond™, has been studied for its neutron shielding capabilities and is being used in structures built for storage of nuclear materials. This investigation assesses the durability and shielding performance of borated Ceramicrete coatings when exposed to gamma and beta radiations to predict the composition needed for optimal shielding performance in a realistic nuclear radiation field. Investigations were conducted using experimental data coupled with predictive Monte Carlo computer model. The results show that it is possible to produce products for simultaneous shielding of all three types of nuclear radiations, viz., neutrons, gamma-, and beta-rays. Additionally, because sprayable Ceramicrete coatings exhibit excellent corrosion- and fire-protection characteristics on steel, this research also establishes an opportunity to produce thick coatings to enhance the shielding performance of corrosion and fire protection coatings for use in high radiation environment in nuclear industry.

1. Introduction

Chemically bonded phosphate ceramics (CBPCs) are a class of materials developed for nuclear waste immobilization and nuclear radiation shielding [1–5]. They are formed by an acid–base reaction between a sparsely soluble oxide and an acid phosphate solution at room temperature. When magnesium oxide (MgO) is used with a solution of mono potassium phosphate (KH_2PO_4), the ceramic formed by the reaction is known as Ceramicrete™. This product is used commercially with a range of fillers in structural materials applications. Oak Ridge National Laboratory developed stackable and storage stacks for storage of nuclear materials using 4 wt.% boron carbide (B_4C) in Ceramicrete [6]. This design is being used in US Department of Energy facilities and the commercial product that

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resulted from this work is called Borobond™ (visit http://www.ceradyne.com/products/nuclear/borobond.aspx, last visited March 10, 2015). It is used for neutron shielding for storage of nuclear fuels.

The focus of earlier projects [4,5] was on optimizing neutron-shielding capabilities of Ceramicrete. They established that 4 wt.% of B_4C is the optimal loading that can be used for neutron attenuation. This article assesses the feasibility of extending the application to include shielding of this formulation for β- and γ-rays.

Nuclear waste storage facilities, such as tank farms at Hanford in the United States [7] and wastewater contaminated storage areas in Fukushima, Japan [8], need a suitable containment material, which should satisfy several requirements. It should be impermeable to liquids, leach resistant to the stored liquids and sludge, and corrosion resistant to moderately acidic to highly alkaline solutions. All these properties, except corrosion resistance, have been tested on Ceramicrete in the past during investigation of immobilization of Hanford and Mayak (Russia) tank waste streams [1]. There are number of case studies on these properties summarized in Ref. [6], and the latest tests on liquid waste streams in Ref. [2]. In all these case studies, leach resistance of Ceramicrete to radioactive isotopes is demonstrated by the standard ANS 16.1 test [9] and durability against corrosion resistance of Ceramicrete and diffusion of individual matrix components is demonstrated by Product Consistency test [10].

Recently, one of the authors (ASW) and his colleague were granted a patent [11] for a CBPC coating that shows superior corrosion resistance of steel and fire-protection characteristics. This first ever all-ceramic coating is based on a pumpable and sprayable version of Ceramicrete. When applied as a coating on steel, it forms a passivation layer on the steel surface by chemical reaction with steel, imparting corrosion protection. The topcoat formed in the process protects the passivation layer and also protects steel from fire by acting as an excellent reflector of incident infrared radiation. Such a coating may have applications in containment of nuclear materials and waste streams that come in all forms, solids, sludge and liquids.

Protecting storage facilities from corrosion using Ceramicrete will require the coating that is durable in radiation environment. Conventional polymer based coatings cannot meet this requirement. In addition, if Ceramicrete is used to immobilize high level waste [1–3], it should also exhibit stability to radiation resulting from the immobilized waste. Therefore, there is a need to evaluate Ceramicrete for its properties to shield nuclear radiations and assess its durability in intense radiation field. In the process, because of versatility of Ceramicrete formulations, it can also be optimized for the shielding properties.

These needs exist in other waste management applications also. For the first approximately 300 years, the activity of spent fuel rods is dominated by β- and γ-rays. This was shown by National Energy Association [12] from a study on spent fuel from a PWR reactor. Their data shows that the fission products dose from the spent fuel was more than two orders of magnitude higher compared to the same from actinides, and the radiation by fission products remained higher for about 300 years. The same conclusion was drawn in another technical evaluation in Sweden, in which dominance of the relative activity of fission products from spent fuel from a power reactor at a burn-up level of 33 GWD/MTU [13]. Once the fission products have decayed sufficiently, the activity of actinides becomes and stays high over millions of years. Ceramicrete shields, which attenuate these radiations efficiently, can vastly improve the design of spent fuel storage casks.

The γ- and β-activity of spent fuels will keep increasing as modern power plants adapt to high burn-up fuels. Due to increased fission reactions in high burn-up fuels, the fission products level in the spent fuel will increase, and as a result, the β- and γ-dose will also rise. This was demonstrated at Oak Ridge National Laboratory by monitoring the radiations of spent fuel produced at different burn-up levels in an experimental PWR power reactor [14]. They show that when the burn-up level was increased from 7.79 Gwd/MTU to 47.25 Gwd/MTU, the ^{137}Cs content in the spent fuel increased from 280 g/TU to 1760 g/TU. This increase was almost linear. This proportionate increase of fission products in the spent fuel at elevated burn-up levels increases the β- and γ-doses resulting from the increased level of fission products. Storage of such fuels will require materials of superior shielding for characteristic energies of fission products. Use of suitably formulated Ceramicrete shields may fulfill this need.

In an earlier project [4], an alternative Ceramicrete composition was proposed to enhance β- and γ-ray shielding performance of Ceramicrete. The idea there was to use very inexpensive iron oxide in Ceramicrete as filler. If added in Ceramicrete in a large proportion, iron, with an atomic weight of 55.8, can be an effective shielding additive. This opens an opportunity to modify Borobond composition and produce a shielding material for all three radiations, viz., neutrons, β- and γ-rays.

Generally, β- and γ-ray attenuation coefficients depend strongly on the density of the shield used [15]. Lead and steel have high density and hence are preferred shielding materials. Steel, though is not as efficient as lead, is a comparatively low cost material. It is also a construction material. The down side of steel and several alloys used in nuclear power plants and waste containment systems, however, is that they are susceptible to environmental corrosion. The various mechanisms of corrosion in these materials in radiation fields are described in Ref. [16]. Among those, the most important one is neutron embrittlement, which causes steel and other alloys to lose their ductility when they are exposed to neutrons [17]. For long-term storage of nuclear materials or for extended operations of nuclear power plants, protection of steel and other alloys from accelerated corrosion as well as from accidental fires is a concern.

This challenge is addressed by using specialty steels and alloys and, wherever possible, conventional polymer coating products, such as epoxy for corrosion protection. While polymers are good at providing neutron shielding, their durability and performance in high-energy β- and γ-fluxes is poor. Furthermore, they cannot withstand high temperatures and their flash points are low. They are designed as coatings that physically protect metal surfaces from harsh environments, but do not passivate the substrates chemically. Because of the absence of a passivation layer, if such a coating is breached, a damaged part would corrode and the corrosion front would travel underneath the remaining coating. This is a phenomenon, known as osmotic blistering [18], lifts the coating at the edge of the damaged part and destroys the coating the rest of the coating eventually. If one can reduce nuclear radiations on steel and alloys using Ceramicrete type of shield, the corrosion issue will be vastly reduced.

The previous work [4,5], along with additional data reported in this paper, will show that the borated version of Ceramicrete provides good attenuation of neutrons. This paper, on the other hand, focuses on its ability to attenuate β- and γ-radiation and hence shows that all three radiations can be attenuated simultaneously. For this purpose, it assesses durability of the borated Ceramicrete in intense β- and γ-radiations. Optimized composition of Ceramicrete for shielding of all three radiations and its durability under intense radiations will help in designing suitable coatings useful in power plants and storage facilities of nuclear materials.

2. Materials and methods

The current study is done with borated Ceramicrete containing 4 wt.% B_4C in the total powder composition of the product for neutron attenuation, and an equal amount of dysprosium oxide