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Review

# Vitreous and crystalline phosphate high level waste matrices: Present status and future challenges

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ABSTRACT

Vitrification is currently the most effective process for immobilization of nuclear waste. However, ubiquitous borosilicate glass is not suitable for immobilization of nuclear waste from advanced reactors such as Fast Breeder Reactors (FBR) because solubility of many compounds/elements existing in the spent fuel in borosilicate glasses is quite poor. In order to possess a viable immobilization strategy for wastes arising from advanced reactors, alternatives to borosilicate glasses such as phosphate glasses, glass-ceramics and crystalline waste forms are being investigated. This review aims to provide an overview of nuclear waste immobilization employing phosphate-based glasses, glass-ceramics and crystalline ceramic hosts, focusing on structure and properties that make these new matrices suitable for the challenging task of waste immobilization.


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## Introduction

Nuclear energy is an important requirement for many developing countries, where the high energy density of nuclear power makes it cost effective in the medium term. Simultaneously, nuclear power avoids the large emission foot print of conventional fossil fueled power generation, and the attendant environmental impact. However, the wastes produced during nuclear power generation are environmental hazards [1], leading to somatic as well as genetic effects in the living being [2]. Therefore, the safe implementation of nuclear power is hinged on safe containment/

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management of nuclear wastes. The most common waste management protocols are delay and decay; dilute and disperse or concentrate and contain approaches [3], the last being best suited for the long-lived nuclides present in high-level waste (HLW). The concentrate and contain approach requires the selection of a suitable inert host matrix for immobilization of radioactive waste. The selected matrix should exhibit long-term thermal, chemical and mechanical stability under deep geological repository conditions [4]. A suitable host must also exhibit high leach and radiation resistance with flexibility toward homogeneous accommodation of different radio nuclides. Among them actinides (Np, Pu, Am, Cm) are the most dangerous high-level waste constituents, referring to radiotoxicity, and have the longest half-lives; thus storage is required for periods up to 500,000 years. Many glass, crystalline ceramic, glass-ceramic and composite based host have been proposed to meet these requirements (Table 1) [5].

Despite this, identifying a suitable waste host involves often conflicting parameters for selection of materials and processes (simplicity, reliability and benign technology). For instance, high waste loading requires glasses with a $T_g > 500\,^{\circ}C$. However, this leads to high fusion temperatures with the attendant risk of volatilization of waste cations [6]. The de-facto HLW immobilization matrices are primarily silica and/or borosilicate glasses partly owing to a combination of properties such as the ability to accept a large number of different waste cations, matured and established processing technology, outstanding durability and well characterized structure [7]. However, borosilicate glasses also have inherent limitations which limit their utility as universal HLW matrices. Solubility of some actinides, sulphates and halides in borosilicate glasses is poor. Additionally, advanced reactors such as fast breeders produce a larger amount of high Z elements in the waste stream, which are difficult to immobilize in conventional brosilicate glass matrices. Further, achieving adequate chemical durability allied with low melting temperatures to minimize volatility issues with some elements (Cs, Ru, Tc and Mo) [8].

**Table 1**
Candidates considered for immobilizing HLW.

| System | Host |
|---|---|
| Glass | Silicate; aluminosilicate and borosilicate<br>Phosphate, e.g. sodium aluminium phosphate; iron lead phosphate; iron phosphate |
| Ceramics | Alumina; aluminosilicates and zeolites<br>Titania; titanates, zirconates<br>Synroc (synthetic rock—hollandite, perovskite, zirconolite and rutile)<br>Zirconia; zircon and zirconolite<br>Calcium and lanthanide phosphates<br>Sodium zirconium phosphate, NZP<br>Monazite<br>Apatite, whitlockite<br>Britholite (silicate–phosphate apatite)<br>Crichtonite |
| Glass-ceramics | Celsian based barium aluminosilicates<br>Fresnoite based barium titanium silicates<br>Diopside based calcium magnesium silicates<br>Sphene based calcium titanium silicates<br>Zirconolite based<br>Basaltic glass-ceramics<br>Gadolinium titanate based<br>Phosphate based (apatite, monazite) |
| Cements | Silicate based<br>Phosphate based ('ceramicrete')<br>FUETAP concrete (formed under elevated temperature and pressure)<br>Geopolymers<br>Calcium sulphoaluminate |

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Overall an important problem related to enhancing safety of the nuclear fuel cycle is the improvement of existing waste forms and the search for alternative matrices for immobilization of radioactive waste; exhibiting superior properties compared to commercial glass based waste forms. One of the most commonly promoted alternatives is the use of poly-phase ceramics as waste hosts/matrices. The concept of using ceramics for radwaste immobilization was first introduced in early 1953 by Hatch [9]. There exist several ceramic phases exhibiting superior chemical durability compared to borosilicate glasses. For instance, SYNROC [10] (Titanate based ceramics) is stable in wet environments at 300 °C temperature while borosilicate glass exhibits poor chemical durability even below 100 °C temperature. However, in keeping with the topic of this paper, we do not delve into SYNROC in this review, instead referring the interested reader to the bibliography [11–14]. High chemical durability and resistance to radiation damage is also a hallmark of phosphate based ceramics such as monazite, zircon and apatite [5,6]. Further advantages include high waste loading, particularly actinide solubility allied to excellent thermal and mechanical stability.

Phosphate ceramics or glasses for the storage of nuclear waste were first studies in 1970 [15,11,16]. Since then, phosphate-based matrices have been extensively studies due to their low processing temperature coupled with high chemical durability [17]. The main advantages of phosphate waste form over established borosilicate glasses are: (i) Higher degradation resistance in geological fluid, (ii) Enhanced tolerance to radiation damage, (iii) Ability to incorporate large amount of actinides in there structure, (iv) Moderate solubility for actinides and rare earth [18]. While the previous statements are true for phosphate waste forms in general, it may be mentioned that ceramic waste forms have not been widely adopted and commercial processing of ceramic waste forms is not well established. The high melting points of ceramics precludes melt processing like glasses, and more complex techniques such as hot pressing, or hot isostatic pressing, to name a few, are being envisaged for these materials [19,20]. While glasses and crystalline ceramic materials have properties that are attractive for waste immobilization, a hybrid between these, namely glass-ceramics are also being investigated as potential waste hosts [21]. Glass-ceramics are polycrystalline materials prepared by controlled heat treatment of parent glasses [22]. In addition to an easy manufacturing process, glass-ceramic matrices are more tolerant to variation in the waste composition due to the presence of glassy and ceramic phases. For example, leaching of lanthanide elements can be reduced using glass-ceramic matrices, as the major crystalline phases accumulate the elements that precipitate in the stable glass matrix.

While there are many excellent reviews available highlighting the potential of glass and ceramic waste forms, most of these are not focused on the emerging area of phosphate based waste forms. This article presents a review of phosphate waste forms for the immobilization of HLW, in term of composition, structure, processing method and recent results.

## Immobilization in phosphate-based glass matrices

Glass-type materials have been suggested as suitable for HLW as well as for high-actinide waste streams due to the capability of their random network to accommodate ions with variable charges and radii. Other advantages of glass waste forms encompass: existing production technology with high-levels of radioactivity (transferred from electric melting of industrial glasses) and an acceptable level of chemical durability. Glasses being viable immobilization matrix, we began our review with phosphate