



Self-propagating high-temperature synthesis of CeO₂ incorporated zirconolite-rich waste forms and the aqueous durability

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Abstract

Zirconolite-rich Synroc waste forms were rapidly synthesized by self-propagating high-temperature plus quick pressing (SHS/QP) using Ca(NO₃)₂ as the oxidant and Ti as the reductant. 2M-zirconolite (CaZrTi₂O₇) was produced as the major phase with perovskite (CaTiO₃) and pyrochlore (Ca₂Ti₂O₆) as minor phases. As the surrogate of tetravalent actinide nuclides, up to 50 at% CeO₂ was incorporated to substitute the Zr site of zirconolite. The weight fraction of zirconolite decreases gradually while the perovskite proportion increases when the CeO₂ addition is promoted. Ce was mostly incorporated into the Ca sites of perovskite and Ca₂Ti₂O₆ pyrochlore, rather than the assumed Zr site of zirconolite. The Ce-bearing Synroc waste form exhibits high hydrothermal stability. The MCC-1 leaching test shows the normalized leaching rates (42 d) of Ca and Ce are 0.49 g m⁻² d⁻¹ and 9.47 × 10⁻⁶ g m⁻² d⁻¹.

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1. Introduction

The immobilization of high-level waste (HLW) radionuclides from the reprocessing of spent nuclear fuel from commercial or military reactors is an international challenge that has occupied much attention over the last decades [1,2]. Conventionally, HLW was immobilized by vitrification into borosilicate or phosphate glasses [1–4]. The disadvantage of vitreous waste forms is their metastable nature. The solidified waste forms readily devitrify when subjected to the action of water and steam at elevated temperature and pressure, which may well be encountered by the vitrification bodies after burial in geological repositories [4–6]. Devitrification in these conditions can cause a drastic increase in effective surface area and leachability of dangerous species. Thus, the waste forms' long-term stability and safety can hardly be guaranteed using

glass as the host phase of long-lived nuclides. Moreover, the low solubility of actinides in glass matrix is another limitation [7]. Highly stable crystalline matrices, such as glass-ceramics and monophasic or assemblage of ceramics, have been developed for the long-term disposal of HLW [3,4,8–11]. Synroc, which is mainly composed of multiple crystalline minerals, such as zirconolite (CaZrTi₂O₇), pyrochlore (A₂B₂O₆X), perovskite (CaTiO₃), hollandite (BaAl₂Ti₆O₁₆), rutile (TiO₂), spinel (AB₂O₄), nepheline (KNa₃(AlSiO₄)₄) etc, was recognized as promising host material for HLW immobilization [12,13]. From the isomorphism substitution theory, radioactive nuclides can be incorporated into the crystal structure of above-mentioned mineral phases, which significantly promotes the long-term stability and waste loading of target waste forms [14–16].

Zirconolite is one of the most important constituent mineral phases in Synroc formulation. Because of its polymorph crystal structure, zirconolite holds the capability to accommodate various cations in a wide range of valence and ionic radius, such as rare-earths, actinides, alkaline earth ions and smaller cations like transition metal ions [17–22]. In addition, zirconolite demonstrates high leaching resistance, excellent thermal

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Table 1
Weight percentage of the raw SHS reactants.

Sample number	Weight percentage of reactants (wt%)						Total (wt%)
	Ca(NO ₃) ₂ ·4H ₂ O	CaO	ZrO ₂	CeO ₂	Ti	TiO ₂	
CNC-0	19.47	9.25	30.48	0	17.75	23.05	100
CNC-1	19.23	9.14	27.10	4.21	17.55	22.77	100
CNC-2	19.01	9.03	23.81	8.31	17.34	22.50	100
CNC-3	18.78	8.93	20.58	12.33	17.14	22.24	100
CNC-4	18.57	8.82	17.44	16.24	16.94	21.99	100
CNC-5	18.36	8.72	14.37	20.07	16.75	21.73	100

and radiation stability [23–26], which make it widely recognized as the major phase for safety immobilization of actinide nuclides. From previous studies, zirconolite-rich Synroc waste forms were mainly synthesized from the following two routes [20,27,28]: (1) liquid phase synthesis (such as hydroxide and sol-gel methods) and (2) solid state reaction. Muthuraman et al. [29] have proposed another facile synthesis approach, self-propagating high-temperature synthesis (SHS), for the management of nuclear wastes. As an exothermic chemical reaction, the combustion of SHS reactants can be sustainably propagated after ignition [30]. Compared with conventional solid state reaction, SHS leads to high temperature and reaction speed, as well as low energy consumption, low cost, simplified equipment requirement and convenient handling [31].

Recently, we have explored the SHS preparation of zirconolite waste forms using CuO and MoO₃ as the oxidants with Ti as the reductant [32]. To get highly densified specimen, hydraulic quick pressing (QP) was introduced into the SHS process. Silica sand was utilized as the heat insulator and pressure transmission medium. Consolidated zirconolite-rich specimens were readily obtained within several minutes. In this study, zirconolite-rich Synroc waste forms were prepared by SHS/QP using Ca(NO₃)₂ as the oxidant and Ti as the reductant. As the simulation of tetravalent actinide nuclides [33–35], up to 50 at% CeO₂ was doped to replace the Zr site of zirconolite. The aqueous durability of solidified Ce-bearing waste form was investigated according to the standard MCC-1 static leaching test [36,37].

2. Experimental details

All samples were prepared from SHS approach using Ca(NO₃)₂·4H₂O, CaO, Ti, TiO₂ (anatase), ZrO₂ and CeO₂ with purity higher than 99 wt% as the raw materials. Ca(NO₃)₂·4H₂O was employed as the oxidant with Ti as the reductant. As the surrogate of tetravalent actinide nuclides, varied CeO₂ additions (0 at%, 10 at%, 20 at%, 30 at%, 40 at% and 50 at%) were incorporated to substitute the Zr site of zirconolite (numbered as CNC-0, CNC-1, CNC-2, CNC-3, CNC-4 and CNC-5, respectively). The designed SHS reactions are written as follows with *x* value varied from *x* = 0 to 0.5:

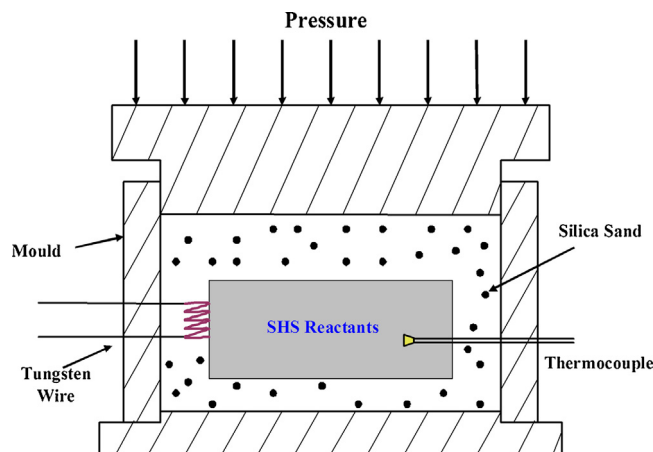
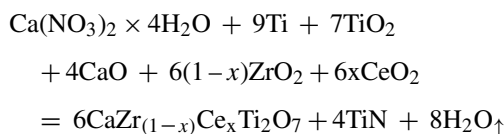


Fig. 1. Schematic diagram of the designed SHS/QP process.

Ce-bearing zirconolite were designated as the target phases. Meanwhile, TiN was designed as the by-product as the *N* element in Ca(NO₃)₂ was assumed to react with Ti. The compositions of raw SHS reactants are listed in Table 1. About 20 g of designed powder charges were mechanically ground and completely mixed in agate mortar. After desiccation at 90 °C for 3 h, the homogeneously mixed powders were pressed at 20 MPa using Φ 25 mm stainless mould, which resulted in cylindrical green bodies with relative density lower than 65%.

The SHS process was conducted as illustrated in Fig. 1. 40–70 mesh silica sand was employed as the heat insulator and pressure transmission medium. Before pressure exertion, the reaction temperature of CNC-0 was measured by a W/Re 5/26 thermocouple placed at the center part of the green body. The temperature tendency was recorded by a paperless recorder connected with the thermocouple. After the temperature measurement, a new sample was employed for subsequent SHS and compression process. The bottom of stainless mould was covered with silica sand and the preformed green bodies were embedded into the silica sand. The reactants were subsequently ignited by a tungsten wire, which was located at one side with tight contact of the pellets. The tungsten wire was heated by a direct current of about 50 A. The SHS reactants were ignited and combusted instantly under the high temperature radiation of tungsten wire. After about 30 s delay of combustion completion, the red-hot samples were compressed at 40 MPa by a hydraulic press with 60 s dwelling time. The whole combustion and densification process takes not more than 5 min.

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