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An experimental study on Sodalite and SAP matrices for immobilization of spent chloride salt waste

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HIGHLIGHTS

- Sodalite and SAP were evaluated as confining matrices for chloride salt waste.
- Addition of glass frit enhances the matrix retention capability.
- SAP matrix blended with glass frit exhibited the best confining performances.
- Sodalite and SAP with glass frit are comparable with similar matrices in the literature.
- SAP process produces a little amount of secondary active waste containing Cl-36.

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ABSTRACT

In the frame of Generation IV reactors a renewed interest in pyro-processing of spent nuclear fuel is underway. Molten chloride salt waste arising from the recovering of uranium and plutonium through pyro-processing is one of the problematic wastes for direct application of vitrification or ceramization. In this work, Sodalite and SAP have been evaluated and compared as potential matrices for confinement of spent chloride salt waste coming from pyro-processing. To this aim Sodalite and SAP were synthesized both in pure form and mixed with different glass matrices, i.e. commercially available glass frit and borosilicate glass. The confining matrices were loaded with mixed chloride salts to study their retention capacities with respect to the elements of interest. The matrices were characterized and leached for contact times up to 150 days at room temperature and at 90 °C. SEM analyses were also performed in order to compare the matrix surface before and after leaching. Leaching results are discussed and compared in terms of normalized releases with similar results reported in literature. According to this comparative study the SAP matrix with glass frit binder resulted in the best matrix among the ones studied, with respect to retention capacities for both matrix and spent fuel elements.

1. Introduction

The recovering of energy-producing elements such as uranium and plutonium from spent nuclear fuel, which is in line with Generation IV reactors concept, can be performed by pyro-chemical processing [1,2]. According to a procedure developed by the Argonne National Laboratory, the actinides and fission products are extracted by electrodeposition in a molten chloride salt medium (LiCl-KCl, 59-41 mol% eutectic composition) at 500 °C [3–5]. This process generates chloride salt wastes contaminated by fission products, containing alkali-metals and alkaline-earths, such as Cs, Ba, Sr and some rare-earths. The so obtained molten salt waste, which mainly consists of metal chlorides, cannot be subjected to conventional solidification processes, such as vitrification and ceramization, due to chloride volatility and low compatibility with silicate glass [6].

Therefore, in order to condition chloride salt waste coming from

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pyro-processes different methods and immobilization matrices have been considered and assessed for their leaching behavior and their capacity for retention of volatile elements [7,8]. Two possible alternatives can be adopted to manage this kind of waste: i) development of specific ceramic matrices such as mineral phases capable of immobilizing chlorides or ii) dechlorination of the fission products to allow incorporation into glass [9].

Processing of ceramic waste forms with the aim at confining chloride salt wastes coming from pyro-processes can be performed at high temperatures (up to 850 °C) and under high pressures (up to 25000 psi) according to a procedure named hot isostatic pressing (HIP) [10–14]. More recently, an alternative procedure for processing ceramic waste forms under ambient pressure, called Pressureless Consolidation (PC) was developed at the Idaho National Laboratory [12,15].

Sodalite, a naturally occurring aluminosilicate mineral containing chlorine, is among those mineral phases considered as potential immobilization matrices for chloride salt wastes [16,17]. Various synthesis methods to obtain sodalite-based matrices have been developed and optimized, i.e. starting from Zeolite 4A (used for preliminary decontamination of the salt by ion-exchange) [18,19] or direct synthesis from silica and sodium aluminate reagents [20] or from kaolinite through metakaolinite and nepheline [15,21,22]. Some authors of the present work compared two different methods to synthesize sodalite in order to condition the chloride salt waste: i) starting from kaolinite through nepheline and ii) starting directly from silica and sodium aluminate. The obtained products were fully characterized in order to determine the best synthesis method. The characterization tests revealed that synthesis from kaolinite through nepheline was by far the best synthesis method, with a high yield of sodalite, provided that rigorous conditions are followed. In particular, the preparation of pellets of reagents under argon atmosphere, followed by heating at 800 °C in an oven for not less than 100 h, is necessary to obtain a good product [22].

Past research activities were also conducted by the present authors to demonstrate the feasibility of sodalite synthesis, from kaolinite through nepheline, via the Pressureless Consolidation (PC) process proposed by Idaho National Laboratory [15,23]. Moreover, characterization and leaching studies were performed both on pellets and powders of sodalite blended with glass [19,23–26].

The Korea Atomic Energy Research Institute (KAERI) proposed an immobilization matrix for chloride salt wastes, termed SAP, consisting of SiO_2, Al_2O_3 and P_2O_5 [27,28]. This matrix, synthesized by a conventional sol-gel process, is able to stabilize volatile salt wastes due to the formation of metal aluminosilicates, aluminophosphates and phosphates, generating chlorine gas [29]. Glass can be added to the SAP matrix as a chemical binder giving rise to higher disposal efficiency and to a lower volume of waste compared with other immobilization matrices [27,30]. A recent evolution of SAP, the glassy wasteform U-SAP, shows even better performances with respect to other SAP wasteforms [31,32].

The present paper illustrates and summarizes the research activities performed by the present authors, focused on a feasibility study regarding Sodalite and SAP ceramic wasteforms for conditioning chloride salt waste and compares experimental leaching results with results from the literature regarding similar wasteforms. To this end, Sodalite and SAP were synthetized and characterized both in pure form and mixed with different glass matrices, i.e. commercially available glass frit and borosilicate glass. The confining matrices were loaded with chloride salt wastes in order to study their retention capacities with respect to the elements of interest. To achieve this, leaching tests at different temperatures were performed up to 150 days in order to systematically study the behavior of the obtained Sodalite and SAP based matrices. Collected data were then analyzed and compared, in terms of normalized releases after 7 days at 90 °C, with similar leaching results from the literature.

The paper is organized as follows: the second section 'Experimental' briefly describes the synthesis conditions, matrix preparations and characteristics of the performed leaching tests and of the parameters adopted to quantify leaching behavior. Characterization and leaching results obtained in this work are reported in Section 3. In Section 4 'Discussion' the normalized release values measured in this study are compared with equivalent literature results and discussed. Finally, Section 5 concludes the paper.

2. Experimental

2.1. Matrix synthesis

2.1.1. Sodalite-based matrices

Several sodalite ($Na_6(Li,K)_2[(AlO_2)_6(SiO_2)_6]Cl_2$) samples were prepared according to a two-step synthesis, through nepheline ($NaAlSiO_4$) from kaolinite ($Al_2Si_2O_7$), previously tested and optimized by some of the present authors [22,23]. Sodalite based matrices blended with glass were prepared by mixing and milling at room temperature the following reagents in the reported proportions in weight: 66.3% nepheline (NE), 25.0% glass and 8.7% simulated chloride salt waste (CSW). The simulated chloride salts were composed of lithium and potassium chlorides (eutectic composition) and a mixture of chloride salts of Rb, Sr, Cs, Ba, La and Nd (Table 1). The powder samples, kept under slight pressure, were introduced into a furnace and treated at 500 °C for 1 h in order to allow any residual moisture to evaporate, and then kept at 925 °C for 7 h [1,23]. Two series of samples were prepared with two different types of glass, namely commercially available glass frit (GF) and borosilicate glass (BG) (Table 2). The so-obtained sodalite-based matrices were fully characterized by X-ray diffraction, FT-IR, SEM-EDS and thermogravimetric analyses and results have already been reported in literature [22–24]. In the following discussion sodalite samples are indicated with the abbreviation SOD, while the sodalite samples blended with glass frit (GF) or borosilicate glass (BG) and loaded with chloride salt waste (CSW) are indicated as CSW.SOD.GF and CSW.SOD.BG, respectively.

2.1.2. SAP-based matrices

SAP matrix, SiO_2-Al_2O_3-P_2O_5, was synthesized by a conventional sol-gel process developed by Korea Atomic Energy Research Institute [25,27–29,33]. The so-obtained SAP was reacted with lithium and potassium chlorides in the eutectic composition (LiKCl.SAP) in the salt/SAP ratio of 1:2, 1:3 and 1:4, at increasing temperatures

Table 1
Composition of the simulated chloride salt waste loadings.

Chloride	CSW.SOD.GF CSW.SOD.BG	CSW.SAP	CSW.SAP.GF CSW.SAP.BG1 CSW.SAP.BG2	LiKCl.SAP.BG
	Wt%	Wt%	Wt%	Wt%
LiCl + KCl	7.802	29.50	20.65	23.33
RbCl	0.066	0.167	0.117	
CsCl	0.066	0.833	0.583	
$SrCl_2$	0.066	0.167	0.117	
$BaCl_2$	0.066	0.333	0.233	
$LaCl_3$	0.301	0.333	0.233	
$NdCl_3$	0.301	1.000	0.699	
$CeCl_3$		0.667	0.466	
$PrCl_3$		0.333	0.233	
Total	8.668	33.33	23.33	23.33