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One-step immobilization of cesium and strontium from alkaline solutions via a facile hydrothermal route

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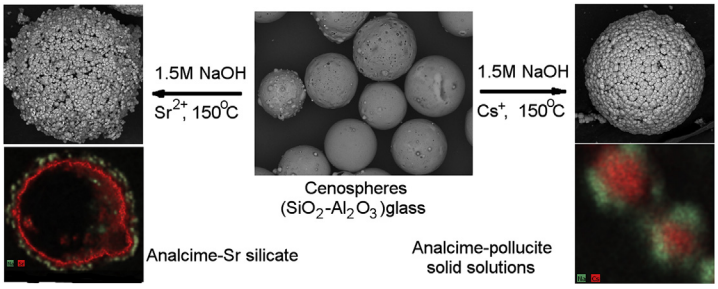
HIGHLIGHTS

- Analcime-pollucite solid solutions crystallize as host phases immobilizing Cs^+.
- Cs^+ and Sr^{2+} were immobilized by hydrothermal treatment of coal fly ash cenospheres.
- Sequestration of Cs and Sr from alkaline solutions was 90–99%.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrothermal treatment of coal fly ash cenospheres (Si/Al = 2.7) as a glassy source of Si and Al was carried out in 1.5 M NaOH at 150 °C in the presence of Cs^+ and Sr^{2+} to study the possibility of Cs^+ and Sr^{2+} immobilization in mineral-like compounds. Systems Na_2O-H_2O-$(SiO_2$-$Al_2O_3)_{glass}$, Na_2O-Cs_2O-H_2O-$(SiO_2$-$Al_2O_3)_{glass}$ with Cs^+/Na^+ ratios of 0.05 and 0.5, and Na_2O-SrO-H_2O-$(SiO_2$-$Al_2O_3)_{glass}$ with Sr^{2+}/Na^+ ratios of 0.25 and 0.025 were under study. Structure, composition and morphology of solid products were characterized by PXRD, SEM-EDS and STA methods. In the Cs^+/Sr^{2+} free systems the deep crystallization of cenosphere glass takes place resulting in hollow polycrystalline analcime microspheres. Microsphere solids including phases of ANA topology (analcime, pollucite or analcime-pollucite solid solutions) and Cs^+/Sr^{2+} silicates are produced as Cs^+ and Sr^{2+} immobilized forms in the Cs^+/Sr^{2+} bearing systems. The degree of Cs^+ and Sr^{2+} recovery from alkaline solutions was 90–99%.

1. Introduction

Alkaline high level solutions are produced at nuclear fuel reprocessing plants as a result of neutralization of initially acidic waste solutions with sodium hydroxide [1,2]. The typical neutralized alkaline wastes are tank waste supernatants in the United States at DOE sites (Hanford, Savannah River, Oak Ridge) having the

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actual NaOH concentration of 0.75–7 M [2,3]. Radioactive hydroxide solutions are also generated when decommissioning fast neutron reactors utilizing liquid sodium or a sodium-potassium blend as a coolant of a primary circuit [4]. Large quantities of spent metallic sodium are treated using a water based process resulting in 10–30 M sodium hydroxide. The largest contribution to the sodium hydroxide waste activity is provided by isotopes of cesium (^{137}Cs, ^{134}Cs) and, in lesser but remarkable extent, ^{90}Sr.

One of the management strategies of sodium hydroxide effluents is aimed at minimization of alkaline waste activity before their final processing by selective removal of radionuclides using a solid/liquid extraction technique based on an ion-exchange process [4–7]. Decontaminated sodium hydroxide solution of a low level activity, cesium loaded solids (organic and inorganic ion-exchangers) and/or stripped Cs matter are produced as secondary radioactive wastes which are subject to conversion into final chemically stable solid forms by cementation, ceramization or vitrification processes. The technical problem for ^{137}Cs and ^{90}Sr removal from sodium hydroxide solutions is the high sodium concentration in the wastes. Dilution and/or neutralization of sodium hydroxide solutions are often required to provide the efficient extraction of the radionuclides by ion exchangers [4].

A hydrothermal synthesis *in situ* of cesium and strontium bearing aluminosilicate minerals under highly alkaline conditions is reported as a promising approach to low-temperature fixation of ^{137}Cs and ^{90}Sr [8–11]. According to [10,11], pollucite, $CsAlSi_2O_6$, having the framework topology of zeolite analcime (ANA), $NaAlSi_2O_6 \cdot H_2O$ [12,13], was a target host phase to immobilize cesium by hydrothermal conversion of Cs-clay and Cs-zeolite complexes at 200 °C and 300 °C, respectively, imitating the treatment of the ^{137}Cs polluted soil around the Fukushima nuclear power plant. Hydrothermal treatment of Sr-loaded zeolites at 300 °C/300 bar resulted in Sr fixation in the structure of feldspar $SrAl_2Si_2O_8$ [9]. In this context, the hydrothermal processing of ^{137}Cs and ^{90}Sr bearing sodium hydroxide waste in the presence of aluminosilicate additives can be a facile method to scavenge the radionuclides ^{137}Cs and ^{90}Sr from the initial alkaline solution and to immobilize them in mineral-like feldspar- and feldspathoid-based matrices. This approach makes it possible to minimize both the alkaline solution activity and amounts of the secondary radioactive wastes as well as to treat other Cs waste, e. g. Cs traps or Cs raffinates, in the mixture with the sodium hydroxide effluents. The limited quantities of radioactive alkaline solutions can be treated as a batch process using an autoclave reactor [4].

A wide range of aluminosilicate materials has an appropriate composition to play a role of a pollucite forming precursor. Among them are available natural and technogenic raw materials which are reported to transform into the ANA phases under hydrothermal alkaline conditions, such as clay minerals (Si/Al = 1.4–2.1) [10,11,14], natural zeolites (Si/Al = 5.0) [11], natural clinker (Si/Al = 2.5–3.0) [15], quartz syenite (Si/Al = 3.7) [16], coal fly ash (Si/Al = 1.6) [17], coal fly ash cenospheres (Si/Al = 2.7) [18] and volcanic glass perlite (Si/Al = 4.6) [19]. The hydrothermal conversion of crystalline aluminosilicates into analcime or pollucite takes place at 200 °C and higher temperatures whereas the use of amorphous aluminosilicate glass (cenospheres [18], sodium aluminosilicate glass [20]) facilitates the crystallization of analcime at 150 °C.

For now, owing to the composition and sphere shaped morphology, coal fly ash cenospheres have been shown to be the promising material for making microsphere sorbents of radionuclides ^{137}Cs and ^{90}Sr from aqueous waste and their accommodation in pollucite and Sr-anortite based ceramics via the sorption-crystallization method [21,22]. Direct conversion of Cs salt/cenosphere composites (35 wt. % Cs_2O) into glass-crystalline compounds incorporating about 50 wt. % pollucite can be realized by thermal treatment at temperature of not above 750 °C [23]. Much earlier such possibility has been shown for zeolite type sorbents exactly at same temperature [24].

In this paper, we report a facile hydrothermal route to immobilization of cesium and strontium from sodium hydroxide solutions in ANA based solids at 150 °C starting from coal fly ash cenospheres as a glassy source of Si and Al, characterization of their

Table 1
Chemical and mineral composition (wt. %) of the initial cenosphere material.

Elements in terms of oxides								Si/Al	Crystal phases			Glass phase, wt.%
SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	MgO	K_2O	TiO_2		quartz	mullite	calcite	
67.6	21.0	3.0	0.9	2.2	1.8	2.8	0.2	2.7	3.4	0.8	0.5	95.4

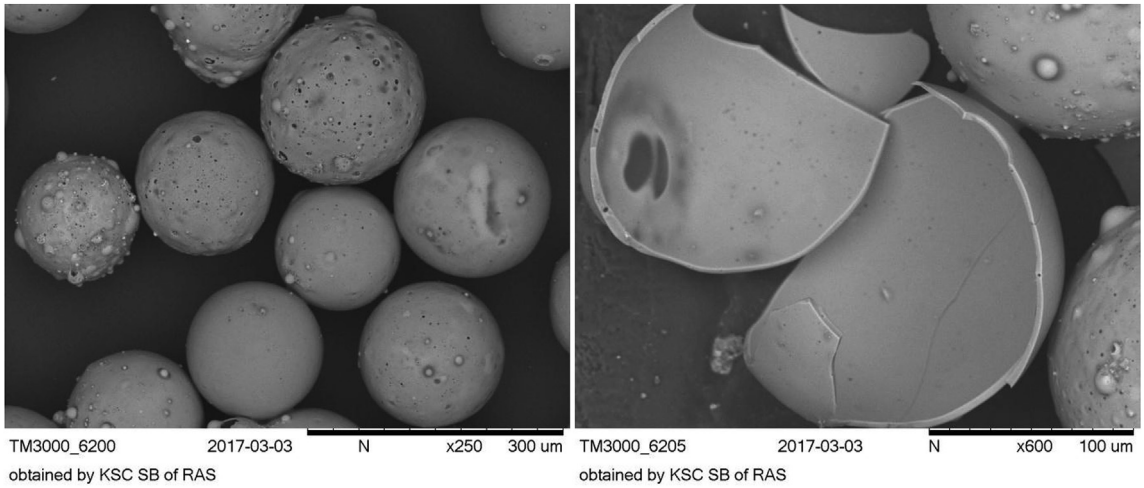

Fig. 1. SEM images of the initial cenosphere material: intact globules; (b) broken globule.