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Removal of Cs Ions from Aqueous Solutions by Using Matrices of Natural Clinoptilolite and its Safe Disposal

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Abstract:

The possibility to use natural zeolite – clinoptilolite as a host material for radioactive Cs immobilization has been investigated. Cs-exchanged form of clinoptilolite which was prepared by treatment of clinoptilolite powder with 0.25 M CsCl solution was compacted. Both, powder and powder compact of exchanged clinoptilolite were thermally treated at 1200 °C. The XRPD analysis showed that Cs was successfully immobilized after heat treatment by formation of stable cesium dodecaoxo-alumopentasilicate in both, powder sample and compact. The newly formed compound showed satisfactory Cs ions retention during leaching test. The sintered compact showed somewhat better resistance to Cs leaching than the thermally treated powder. The compressive strength of sintered compact was close to 200 MPa which is more than enough for easy handling and safe storage.

Keywords: Cs disposal, Ion exchange, Clinoptilolite, Sintering, Leaching tests

1. Introduction

Cesium isotopes, which are the main fission products and major components of intermediate level radioactive wastes [1] belong to the most hazardous radiotoxic elements and present a serious environmental problem. Therefore, it is of significant importance to remove and safely dispose radioactive Cs from the waste streams. A multitude of storage materials have been studied, among which glasses, minerals, and glass-ceramic matrices [2, 3]. One of the most effective procedures consists of two steps: (1) removal of Cs cations by ion exchange and (2) suitable solidification treatment [4, 5]. Resins, which are organic exchangers, turned out poorly effective because they radiolytically decompose and have low thermal stability [5]. Zeolites, natural or synthetic, have successfully been proposed as valid alternative exchangers [6]. These aluminosilicate compounds show high resistance to radioactive irradiation [7] and high affinity for Cs cations [1, 8]. Natural zeolites such as mordenite, erionite, chabazite and clinoptilolite have already been taken into consideration for

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waste treatment [5, 9-11].

Among them, clinoptilolite $(\text{Na,K,Ca})_4\text{Al}_6\text{Si}_{30}\text{O}_{72}\cdot 24\text{H}_2\text{O}$ [12] has received considerable attention due to its high affinity to Cs cations and good thermal stability (600–800°C) [13]. This natural zeolite is a high-silica member of heulandite group with Si/Al ratio varying from 4.0 to 5.3.

One of the promising methods for trapping Cs radioisotopes into a zeolite framework is based on a thermal treatment of zeolite powder conducted after ion exchange. The main role of the treatment is to destroy zeolite structure and blocks Cs into a non-exchanging crystalline phase. [1, 14]

Bearing in mind that solid material is more convenient for handling and safe disposal than powder materials; the aim of this work is to transform Cs-exchanged clinoptilolite powder into stable ceramics by compaction and subsequent heat treatment (sintering). It will be shown that powder compaction and sintering improve Cs immobilization resulting in better resistance of solid ceramics to Cs leaching in comparison to heat treated powder.

2. Experimental procedure

2.1. Materials

Clinoptilolite sample used in this work was obtained from the Novakovići deposit (near Prijedor, Bosnia and Herzegovina). The Novakovići - clinoptilolite tuff is whitish colored, containing about 90% of zeolitic phase (clinoptilolite-heulandite), with additional quartz, feldspar and amorphous material (volcanic glass).

Preparation of Cs-exchanged clinoptilolite

Partially exchanged Cs^+ form of clinoptilolite was prepared after 5 successive exchanges from 0.25 M CsCl solutions (Cesium Chloride p.a., VWR AnalaR NORMAPUR®, min 99.5% CsCl) with the solid/liquid ratio 1/20. At the end of the exchange procedure, Cs-exchanged clinoptilolite was washed with distilled water and dried at 60°C before heat treatments. The powder was mechanically pressed under 60 MPa to obtain compacts with diameter of 10 mm and height of ~ 8 mm.

Heat treatment of Cs-exchanged clinoptilolite

Both, powder and powder compacts were heat treated at 1200 °C for 2h in air. Heating rate was 10 °C/min.

2.2. Methods

All samples were investigated by X-ray powder diffraction (XRPD). XRPD patterns were obtained on a Rigaku Ultima IV diffractometer, using a Cu tube operated at 40 kV and 40 mA. The diffraction data of samples were collected in 2θ the range of 4 to 65° using a count time of 1.0s and a step size of 0.02 of 0.02°, for routine phase analysis.

Semiquantitative elemental analysis of samples before and after ion exchange was performed by energy-dispersive X-ray spectrometry (EDXS), using an Oxford Instruments XMax SDD spectrometer coupled to a JEOL JSM-6610LV scanning electron microscope. An acceleration voltage of 20 kV and a probe current of 0.7 nA were used for sample excitation. The samples were coated with 15 nm layer of carbon prior to analysis.

The crystal morphology of the raw and Cs-exchanged clinoptilolite before and after the heat treatment was examined using a JEOL-JSM-5800LV scanning electron microscope

(SEM). Room-temperature compressive test of six samples was carried out by using 1185 Instron-type testing machine at a strain rate of 2 mm/min. The average value was calculated. Two end surfaces of the cylindrical samples were carefully ground to make parallel surfaces. The sintered compacts and heat-treated powder samples of Cs-exchanged clinoptilolite were left in contact with 25 ml of deionized water for 1h, 1 day and 7 days at room temperature. The cesium content in the liquid phase was analyzed using flame atomic emission spectroscopy (AAS Analyst 700/Perkin-Elmer) in order to determine the amount of released Cs ions.

3. Results and Discussion

After ion exchange, cesium-form of the zeolite was obtained, containing more than 25 wt. % of Cs⁺ ions. During the ion-exchange process, Cs⁺ ions moved through the pores and channels of the lattice and replaced exchangeable cations from clinoptilolite (mainly sodium and calcium). More than half of initial sodium and calcium ions were replaced with Cs⁺ ions as shown by semiquantitative EDXS analysis (Tab. I).

Tab. I EDXS analyses of clinoptilolite before and after Cs⁺ exchange.

| <i>Elements /wt. %</i> | Na | Mg | Al | Si | K | Ca | Fe | Cs | O |
|------------------------|-----------|-----------|-----------|-----------|----------|-----------|-----------|-----------|----------|
| <i>Before exchange</i> | 0.22 | 0.62 | 7.10 | 35.90 | 2.72 | 3.21 | 0.43 | 0.00 | 49.78 |
| <i>After exchange</i> | 0.08 | 0.25 | 5.68 | 27.95 | 0.65 | 0.30 | 0.40 | 25.68 | 39.00 |

Natural clinoptilolite is ubiquitously accompanied with quartz and feldspars, as confirmed by X-ray powder diffraction (Fig. 1a). In addition to crystalline phases, a certain amount of amorphous phase was also present. The exchange of Na, Ca and K ions with Cs in the zeolite structure results in formation of Cs-clinoptilolite. Fig. 1. indicates that XRD patterns of exchanged and starting zeolite are fairly similar due to similar structure of two zeolites. Although there is considerable peak overlapping, it is evident that the second strongest peak of starting zeolite, located at $2\theta = 9.71^\circ$ almost completely disappears while the intensity of peaks characteristic for Cs-clinoptilolite increase. This change is primarily due to the change in X-ray diffraction structure factors caused by introducing Cs into the crystalline structure [15].

XRD patterns of Cs-exchanged clinoptilolite after heat treatment at 1200 °C are presented in Fig. 2. It can be seen that new, stable crystalline phase is formed in both, sintered compact and heat-treated powder. The new phase, called cesium dodecaoxo-alumopentasilicate (Cs_{0.8}Al_{0.78}Si_{5.15}O₁₂), possesses CAS framework [16]. It is important to note that crystallization of Cs-aluminosilicate is faster in sintered compacts than that in heat-treated powder. It is quite expected knowing that powder compaction provides better contact between particles and therefore accelerate mass transport during heat treatment. It appears that temperature of 1200 °C is sufficiently high to promote crystallization of Cs-aluminosilicate without excessive evaporation of cesium.

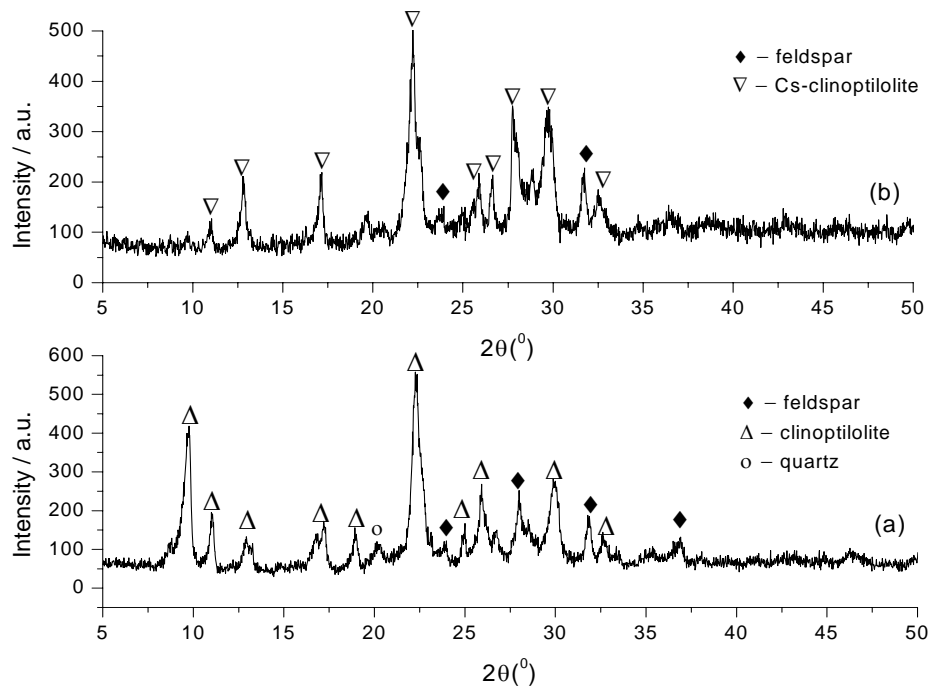


Fig. 1. XRPD of clinoptilolite a) raw and b) Cs-exchanged.

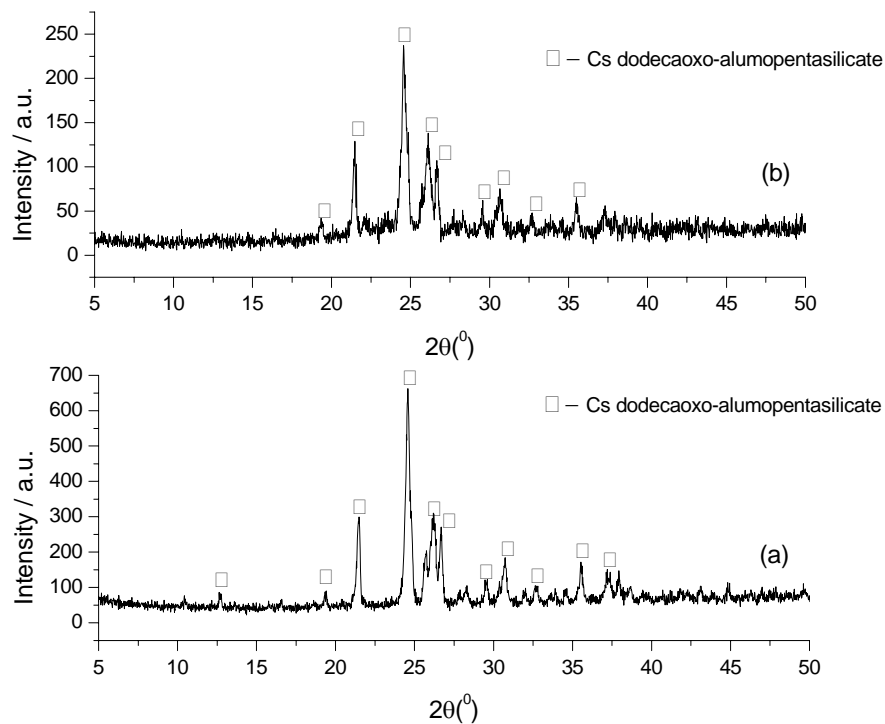


Fig. 2. XRD of Cs-clinoptilolite heated at 1200 °C for 2h: a) sintered compact and b) powder.

It is now of great importance to examine the effect of heat treatment on morphology of Cs-exchanged clinoptilolite. Fig. 3. compares the morphology of Cs-exchanged clinoptilolite before and after heat treatment.

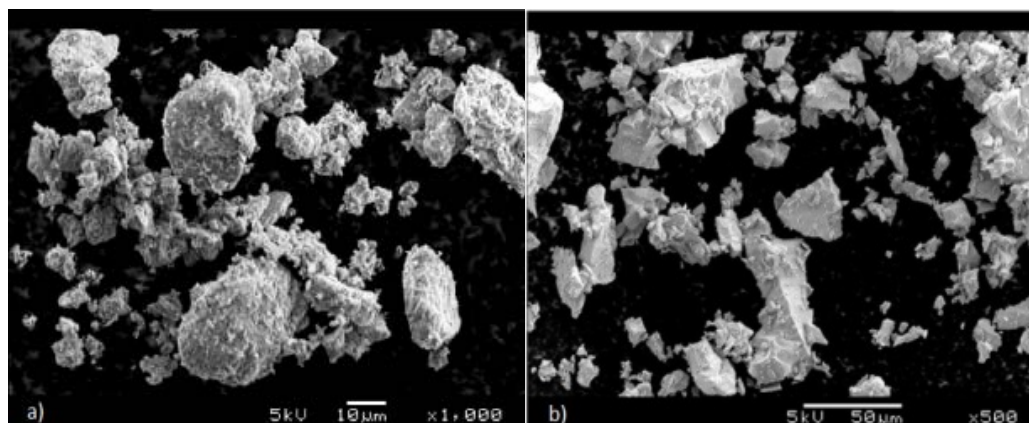


Fig. 3. SEM images of Cs-exchanged clinoptilolite a) before and b) after heat treatment at 1200 °C for 2h.

As can be seen in Fig. 3a, Cs-exchanged clinoptilolite consists of large agglomerates which can be more than 30 μm in diameter. These agglomerates are composed of fine particles with diameter less than 2 μm. It appears that sintering of these fine particles takes place during the heat treatment at 1200 °C which results in formation of hard, faceted agglomerates presented in Fig. 3b. This process is even more pronounced during heat treatment of sintered compacts. As expected, the compaction of powder brings particles closer and accelerates sintering. Fig. 4. shows fracture surface of sintered sample which is typical for brittle material. Both, transgranular and intergranular fracture modes were observed. It seems that large agglomerates show a tendency to form large grains during sintering. This is quite expected knowing the Cs-exchanged clinoptilolite powder did not undergo the procedure which is typical for fabrication of dense material. For example, one of the common steps in powder processing is milling which is normally used to break agglomerates and reduce particle size which normally leads to faster sintering process and thus higher density of sintered samples. However, milling of large amount of powder containing radioactive ions would be very inconvenient and expensive. Consequently, density of sintered compacts obtained in this study is relatively low but from the Cs storage point of view, high density is not essential. It is necessary to make sintered compacts with sufficient density and mechanical integrity which will allow safe handling and disposal of radioactive material. In order to characterize the mechanical integrity of sintered samples compressive strength was measured.

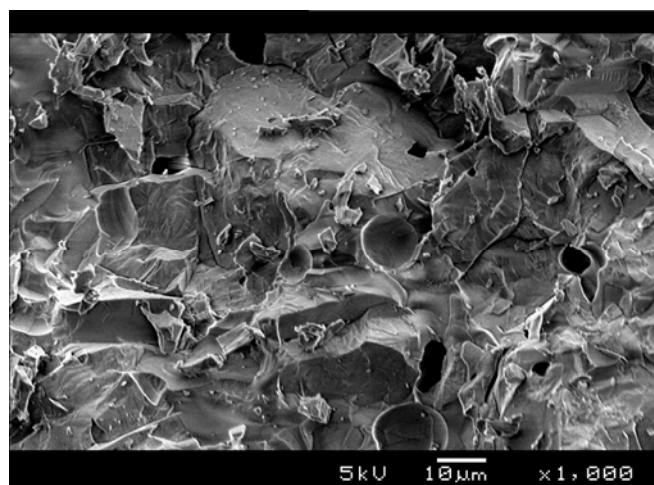


Fig. 4. Fracture surface of Cs-exchanged clinoptilolite.

After crushing of 6 sintered samples it was found that the average compressive strength is 190 ± 23 MPa. This value is far above the value necessary for easy handling. Based on our experience, machining of sintered samples with strength of 50 MPa was quite easy and without excessive chipping. It can be concluded that from the perspective of mechanical characteristics, Cs-exchanged clinoptilolite can be considered as a potential material for safe waste disposal.

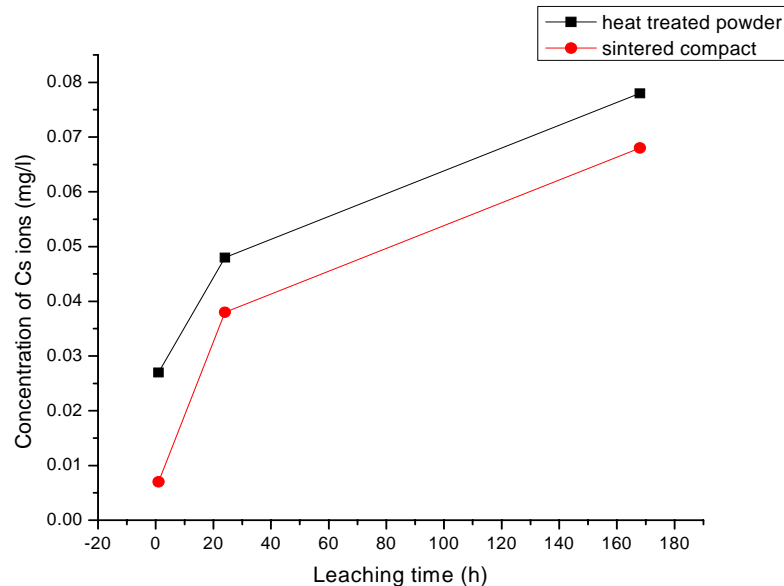


Fig. 5. Ion leaching (mg/l) of sintered compact and heat treated powder of Cs-exchanged clinoptilolite treated at 1200°C .

Ion leaching of sintered compact and powder sample of Cs-exchanged clinoptilolite treated at 1200°C is presented in Fig. 5. As the figure evidences, both samples show very low Cs ions release. The sintered compact shows better results releasing 10 percent less amount of Cs ions than the powder sample. After heat treatment, the Cs-exchanged clinoptilolite still contains some fraction of amorphous material due to relatively high ratio $\text{Si}/\text{Al} > 4$. It is believed that the released Cs ions probably come from the amorphous part of the sample since the Cs ions are adsorbed and not ionic exchanged. This study indicates that the thermal treatment of Cs-exchanged clinoptilolite enhances the retention capacity of exchanged Cs ions by trapping these ions inside the resulting crystalline structure.

4. Conclusion

The Novakovići - clinoptilolite tuff showed good selectivity for Cs and it was demonstrated that this natural, raw material can be suitable for Cs immobilization. Cesium-form clinoptilolite containing more than 25 wt.% of Cs^+ ions was obtained after ion exchanges. Both, powder compacts and powder of Cs-exchanged clinoptilolite recrystallized into new stable phase: cesium dodecaoxo-alumopentasilicate $\text{Cs}_{0.8}\text{Al}_{0.78}\text{Si}_{5.15}\text{O}_{12}$ after heat treatment at 1200°C for 2h. Powder compaction allowed formation of solid ceramic material which is much easier for handling than powder material. Furthermore, the sintered compacts with compressive strength of 190 MPa showed better resistance to Cs ion leaching than powder samples. It can be concluded that the obtained cesium aluminosilicate ceramic solid forms are promising candidate for the permanent immobilization and safe disposal of Cs radionuclides.

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Садржај: Испитивана је могућност коришћења природног зеолита-клинотилолита као материјала за имобилизацију радиоактивног цезијума. Цезијумски измењени клинотилолит, припремљен стандардном процедуром јонске измене са 0.25M раствора цезијум-хлорида, је био пресован. Оба узорка, како пресован тако и узорак у праху, су термички третирани на температури од 1200 °C. Рендгено-структурна анализа је показала да је цезијум успешно имобилисан након термалног третмана формирајући у оба узорка исту, цезијум додекаоксо-алумопентасиликатну фазу. Ново формирано једињење показало је задовољавајуће резултате у смислу задржавања цезијум јона током излуживања. Синтеровани узорак је показао нешто бољу отпорност на излуживање цезијума у поређењу са термички обрађеним узорком у праху. Компресиона чврстоћа синтерованог узорка износи близу 200MPa што је и више него довољно за лако руковање и безбедно складиштење.

Кључне речи: одлагање цезијума, јонска измена, клинотилолит, синтеровање, лужење
