Perlite for permanent confinement of cesium

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Abstract

We present the potential use of expanded perlite, a metastable amorphous hydrated aluminium silicate, as a permanent medium for the long-term confinement of cesium. The method requires simply a loading by mixing an aqueous cesium nitrate solution and expanded perlite at 300 K followed by densification by sintering. The formation of pollucite, $CsAlSi_2O_6$, a naturally occurring mineral phase, upon careful heat treatment is demonstrated by X-ray diffraction. Leaching tests on the resulting glass-ceramics reveal a very low Cs departure of 0.5 mg m^{-2} d^{-1}.

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1. Introduction

The generation of large quantities of environmentally unfriendly nuclear waste, for example those with long lived radioactivity, poses a great world-wide problem for now and the future. Ways of separating and storing these materials are of constant debate and promote the search for efficient methods of separation and finding containers for their safe storage for long term periods spanning hundred of years. One of the nuclides in question in the western countries is radioactive cesium. Our interest has been in finding suitable host for the storage of cesium and its decayed products. The present paper reports the use of perlite on a laboratory level for trapping natural cesium. Borosilicate glass, glass-ceramics, cesium-loaded zeolites and pollucite have been shown to be potential candidates for Cs storage. Pollucite, $CsAlSi_2O_6$, can accommodate up to 40 wt% Cs into its structure thus producing a highly dense waste form. Furthermore, the measured solubility of pollucite as well as the leakage of Cs from pollucite are three orders of magnitude less than those for silicate glasses [1]. Therefore, various synthetic methods have been considered for pollucite using self-propagating high-temperature synthesis (SHS) [2], reaction between gaseous Cs and fly ash [3], hydrothermal [4], arc melting technique [5], ion exchange in zeolites [6] and crystallization from a glass [7]. Moreover, pollucite is a naturally occurring mineral with a three-dimensional structure that contains and irreversibly traps Cs [8]. The resulting samples have been the subject of several characterizations in view of their possible application as waste form such as thermal expansion coefficient measurements [9], leaching tests [7], sinterability, effect of beta radiation effects [10] and radiogenic transmutation [11]. The possibility to obtain pollucite from zeolites [8] stimulates the research of other aluminosilicate minerals. These results are very encouraging and have driven us to search for other related materials and here, we focus on a metastable amorphous hydrated aluminium silicate, perlite.

Perlite with typical average chemical analysis 71–75 wt% SiO_2, 12.5–18 wt% Al_2O_3, 4–5 wt% K_2O, 1–4 wt% Na_2O and CaO, traces of metal oxides and 2–5 wt% water [12] is the naturally occurring mineral. However, perlite is mainly used in its expanded form which is obtained by rapid heating and quenching resulting in an increased porosity due to the removal of the trapped water. Expanded perlite is an ultra-light-weight material, that is fire resistant and acts as an excellent thermal and acoustical insulator. The open structure of expanded perlite can also be exploited for the insertion of waste mineral cations (for example: Cs) from aqueous solutions. Due to the strong excess of silicon compared to aluminum, the formation of a vitroceramics is expected with pollucite as the crystalline phase. The localization of Cs in pollucite will potentially decrease its leakage [5]. Finally, expanded perlite is a ready-to-use material with a reasonable cost. All these considerations stimulate the study of the use of perlite for the confinement of Cs [13].

2. Experimental

2.1. Synthesis

Expanded perlite was supplied by Thermal Ceramics de France and used as received. An aqueous cesium nitrate, $CsNO_3$ (Aldrich, 99%), solution was mixed with the expanded perlite in a 5:1

weight proportion. Different amounts of $CsNO_3$ were dissolved in a constant volume of water in order to achieve various Cs_2O/perlite weight ratios between 5 and 50 wt%. The resulting samples were then dried at 423 K to remove water. In order to check the influence of the porosity, similar samples have been elaborated starting from thoroughly ground powders of the expanded perlite. Dense pellets for the leaching tests have been prepared using different techniques: (1) pre-calcination at 1373 K for 1 h to reduce the sample volume, grinding, shaping into pellets and sintering at 1293 K for 1 to 3 h, (2) starting from ground perlite, direct sintering at 1293 K in a crucible with a small load, and (3) sintering using the flash technique. Samples were sintered at 1123 K for 5 min in a spark plasma sintering (SPS) furnace, Dr. Sinter 2080 (Sumitomo coal mining). Before sintering, expanded perlite powders were directly loaded into cylindrical graphite die with inner diameter of 8 or 20 mm and then put into the sintering chamber that was evacuated to 3 Pa. The control of the heating rate was made by a computer program system and the temperature was recorded by a thermocouple fixed on a small hole at the external surface of the graphite die. A pressure of 25 MPa was applied by manual operation and not released until the beginning of cooling stage. A constant heating rate of 100 K min^{-1} was applied during each sintering cycle. Moulding from the liquid was not possible due to its high viscosity even at temperatures as high as 1823 K.

2.2. Characterizations

Chemical analysis were performed by ICP–MS technique with a Plasma Quad ICP/MS instrument equipped with Meinhard nebulizer. Operating conditions were single ion monitoring at m/z 133; plasma gas: 14 ℓ min^{-1}, auxiliary gas: 1 ℓ min^{-1}, nebulizer gas: 0.75 ℓ min^{-1}. Cs solutions used for calibration were daily prepared on a mass basis by non-consecutive dilutions of a CPI stock certified solution (1 g ℓ^{-1} in Cs) with 2.5% nitric acid (Suprapur Merck). The leaching solutions were diluted 10 times with 2.5% nitric acid (Suprapur Merck) before analysis. TGA experiments were performed on a TA instrument under air at a 5 K min^{-1} heating rate. The leaching tests have been performed either in static or dynamic mode (Soxhlet apparatus) at 353 K with various S/V (Surface/Volume) ratios. X-ray diffraction patterns were collected on a Siemens D5000 diffractometer using monochromatized Cu Kα_1 radiation ($\lambda = 1.5406$ Å). SEM observations have been done on a Jeol 6700 F apparatus.

3. Results and discussion

3.1. Chemical analysis

In order to evaluate the reproducibility of the composition of perlite, chemical analysis have been performed on five samples received from the Sardinia quarry by Thermal Ceramics at four months intervals. As shown in Table 1, the chemical composition is quite consistent, the largest variation concerns Al_2O_3. Besides the other elements usually found in perlite, Al, Na, K and Ca, we also note the presence of a significant amount of iron. The whole content differs from 100% and it has been related to the presence of water and other minor elements.

Table 1.
Chemical analysis of perlite mineral as received from the quarry at four months intervals

Samples	SiO_2	Al_2O_3	K_2O	Na_2O	FeO	CaO
08/2000	74.4	11.23	4.66	3.32	2.64	0.65
04/2000	73.2	12.50	4.55	3.32	2.84	0.65
12/1999	71.5	13.45	4.76	3.15	2.96	0.64
08/1999	72.2	13.54	4.86	3.24	2.94	0.65
04/1999	73.8	10.60	4.70	3.20	2.80	0.64
Mean	73.0	12.26	4.71	3.25	2.84	0.65
Deviation %	1.9	13.5	3.4	3.1	7.0	1.5

The cesium content of samples heat treated at different temperatures between 873 and 1823 K indicates no Cs loss upon melting for all loading between 5 and 50 Cs_2O wt%. This means that Cs is perfectly trapped in the matrix.

3.2. Thermal analysis

A typical TGA trace is shown in Fig. 1 for a 27.7 wt% $CsNO_3$ (20 wt% Cs_2O) sample. At low temperature, a first weight loss, around 2–3 wt%, has been attributed to adsorbed water. The main weight loss takes place between 713 and 913 K and corresponds to the nitrate decomposition. Surprisingly, an increase of the decomposition temperature is observed with increasing initial $CsNO_3$ content. Moreover, the weight loss deviates from the value expected from the decomposition of $CsNO_3$ into Cs_2O. The observed value fits with the formation of a mixture of Cs_2O_3 and Cs_2O_4. At low $CsNO_3$ contents, the weight loss corresponds to the formation of Cs_2O_4 whereas the value expected for the formation of Cs_2O is observed for the 50 wt% Cs_2O sample. These results are perfectly reproducible. The fact that the nitrate is dispersed inside the pores may be a reason for the unexpected thermal behaviour.
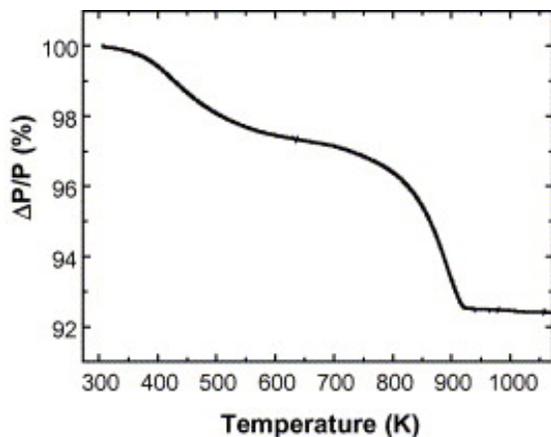

Fig. 1. TG-DTA traces of a 20 wt% sample.

3.3. X-ray diffraction

X-ray diffraction patterns, recorded on powders annealed at different temperatures and containing different amounts of Cs, reveal the crystallization of pollucite, $CsAlSi_2O_6$ (Fig. 2). The pattern is usually characterised by a high background and a broad hump around $2\theta = 25°$; the first is related to the presence of an amorphous phase and the second from poorly crystallised silicate. The presence of pollucite is evidenced by sharp peaks. Moreover, the presence of pollucite also depends on the Cs content and on the annealing time and temperature. To promote crystallization of pollucite, longer annealing times are needed with decreasing Cs content. For example, at 1373 K, 2–12 h are needed for 50 and 25 wt% Cs_2O, respectively. Furthermore, the effect of grinding perlite yields a decrease of the crystallization temperature; for example, for the 50 wt% sample, it is reduced to 973 K and requires only 2 h. Similar study performed on the sintered samples reveals that, for all Cs loadings, the diffraction lines of pollucite appear on the diffractogramms after 3 h sintering. This result has been explained by the fact that, inside the sintered sample, Cs ions can move and therefore yield the formation of pollucite. Indeed, the lowering of the viscosity allows such movements. It is no more the case inside the highly porous powder where Cs is confined in restricted areas and much longer time is needed to perform crystallization. Moreover, the thermal treatment at 1373 K before sintering can enhance the crystallization. If one considers the mean chemical composition, it appears that the formation of pollucite is restricted to samples with a Cs content around 25 wt%. For higher loadings, there is not enough Al to form pollucite. The 25 wt% sample has been annealed at 1373 K for 12 h and the resulting diffraction pattern has been compared with the corresponding JCPDS file No. 88–0055. No significant shift of the lines appears. This means that the other alkali cations in the original perlite have not been inserted (or at very minor levels) in the pollucite network.
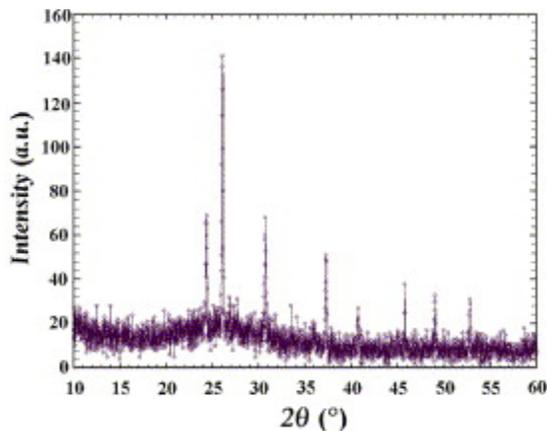

Fig. 2. X-ray diffraction pattern of 50 wt% sample calcined at 700 °C .

3.4. Sintering

The sintering temperature of 1293 K has been chosen as it yields a good densification without deformation of the pellets. At higher temperatures, the viscous flow promotes the deformation. After annealing, the colour of the samples turn from a dirty white to brown, in relation with the oxidation of the small amount of Fe^{2+} to Fe^{3+}. In view of a possible application, we have considered the possibility of a one-step sintering process, particularly avoiding the pre-calcination at 1373 K with intermediate grinding steps. However, it has been observed that sintering does not take place with the 50 wt% sample, in relation with the crystallization of pollucite at low temperature (973 K) that inhibits densification. The densification of both as received and grounded samples exhibit densities better than 96% of the flash values. However, the flash technique allows full densification.

3.5. Leaching experiments

Preliminary experiments performed on powdered samples yield a removal rate of Cs around a few ng m^{-2} d^{-1} at room temperature. Therefore, other experiments either on powdered or sintered pellets have been performed. The influence of the S/V ratio has been tested on a powder, 10 wt% Cs_2O annealed at 1293 K for 1 h, with a specific surface area around 1 m^2 g^{-1}, under static mode at 353 K. Different quantities of powders were inserted in a closed container with a constant volume of 80 ml water in order to achieve S/V ratios of 12.5, 125 and 250 cm^{-1}. 10 ml aliquots were then taken at regular intervals and replaced by the same volume of de-ionized water. As shown in Fig. 3, the removal rate of Cs is always very slow with values of 2–7 ng m^{-2} d^{-1} after 21 days or more. Moreover, the shape of its evolution with time is comparable to what is expected for a mechanism involving the formation of a surface gel. The values for the highest S/V ratio are significantly lower and are in agreement with an improved efficiency of the surface gel. A sintered pellet with 10 wt% Cs_2O has been cut in pieces and submitted to the same treatment at 353 K. One piece has been taken at regular intervals for SEM. Observations at regular intervals up to 72 days contact with water (Fig. 4) show the presence of white spots at the surface, whose size and shape are independent of time. EDX analysis of the Cs content at the surface of the samples reveals a constant value close to the expected 10% (Fig. 5).
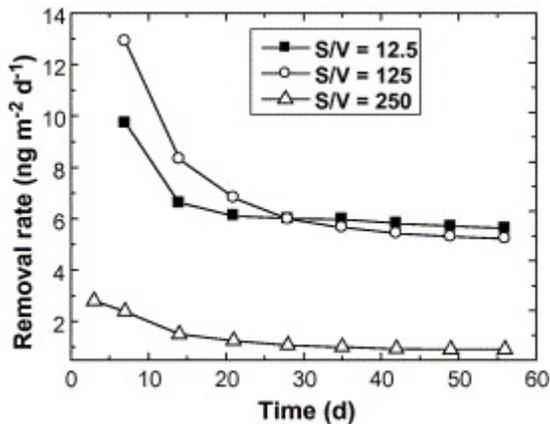

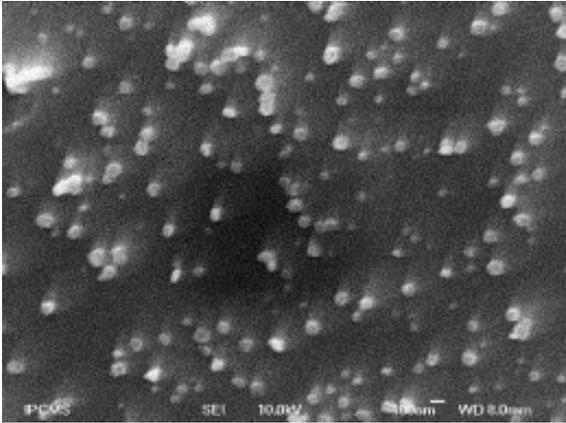Fig. 3. Powder leaching results on perlite charged by 10 wt% in Cs_2O.

Fig. 4. SEM observation on leached sintered sample after 64 days.
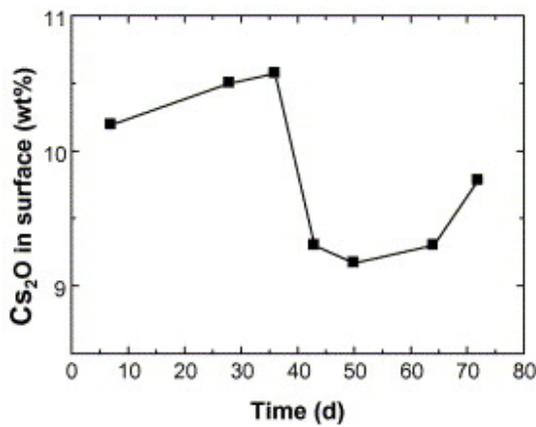

Fig. 5. EDX analysis of Cs content on leached sintered sample after 64 days.

Leaching experiments have also been performed on pellets either in static or dynamic mode. In static mode, for a pellet with 12 wt% Cs_2O, $S/V = 0.025$ cm^{-1} (only the geometric surface of the samples has been considered for working out the rate) at 353 K the removal rate of Cs rapidly decreases and reaches a constant value after 40 days. The estimated removal rate is 1.5 mg m^{-2} d^{-1} on the seventh day and 0.6 mg m^{-2} d^{-1} after 42 days. In dynamic mode, perlite pellets from both sintering processes (virgin or ground) were used and the experiments were performed with 450 ml ion-exchanged water with the sample surfaces being similar around 7 cm^2. Both samples give very similar results as shown in Fig. 6. Both processes resulted in very slow removal rates for Cs, with a time evolution in agreement with the surface gel model. The pH monitored on a daily basis reveals no changes from a value close to six for both samples and for the two processes.
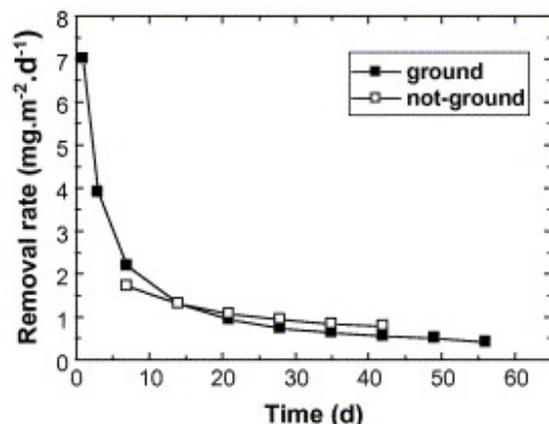
Fig. 6. Dynamic leaching test results on sintered samples.

4. Conclusions

The results give great promises of the use of perlite as a potential matrix for confining natural cesium. We, therefore, propose it as a possible candidate for radioactive waste. Its high stability, low removal rate of cesium in water and its abundance and lost cost are good characteristics. Furthermore, the non-toxicity of the mineral makes it ideal for the environment. The irreversible transformation to pollucite at high temperature and high densification achieved by sintering technique are additional bonuses. Current work in our group has extended the range of elements (Rb, Sr, Ba, Ni, Cd, Nd and Eu) that can be confined in perlite.

Acknowledgements

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