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ORIGINAL ARTICLE

Decontamination and solidification of liquid radioactive waste using natural zeolite

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Abstract This study is based on evaluation of solidification methods for low-level radioactive liquid using natural zeolite. In classical method, LLW is decontaminated using zeolite and after the process spent zeolite becomes radioactive waste. After decontamination process, zeolite waste is solidified using cement, sand and water. In this method; liquid radioactive waste was used instead of water, natural zeolite was used instead of sand/aggregate and cement was used for binding the mixture in solidification process. In this study, leaching properties and strength of the solidified waste form were investigated for both techniques. Effect of temperature on the radionuclide adsorption of the zeolite was determined to optimize the waste solution temperature for the plant scale operations. In addition, the effect of pH on the radionuclide uptake of the zeolite was determined to optimize the waste solution's pH for the plant scale operations. The advantages of this method used for the processing of LLW were discussed in this paper.

Keywords Decontamination · Solidification · Radioactive waste · Zeolite

Introduction

Generally the volume of liquid low-level wastes is relatively large and the specific activity is rather low when compared to other radioactive waste types. Ion exchange technology has been applied for many years in nuclear fuel cycle operations and other activities involving the treatment of radioactive liquids. Zeolite is used as ion exchange material in various stages of NPP: primary coolant (water) purification, treatment of primary effluents, treatment of fuel storage pond water, steam generator blow down demineralization, liquid waste and drainage water treatments, boric acid purification for recycling, condensate polishing (for nuclear power plants with boiling water reactors). Liquid low-level radioactive waste must be solidified for transportation and disposal. Generally water is partly removed from the liquid waste and the remaining material is immobilized typically using cement [1]. A wide range of ion exchange media is available for removing the contaminants from LLW [2]. These vary from low cost naturally occurring inorganic materials to expensive synthetic organic and inorganic engineered to remove specific ions. The well-known low cost materials are clay and natural zeolite. The chemistry of most ion exchange media has been extensively studied for the nuclear industry and for other waste treatment applications [3–6]. A wide range of materials is available for the ion exchange treatment of radioactive liquids [7]. These materials are available in a variety of forms, have widely differing chemical and physical properties and can be naturally occurring material like zeolite. Ion exchange materials can be categorized according to their suitability for different applications. The type of material to be used is selected based on its ability to remove impurities and undesirable ions under given pH. These materials are available in a variety of forms, have widely differing chemical and physical properties and can be naturally occurring or synthetic. To minimize disposal costs, in any process for the removal of radionuclide from a liquid waste it is important to minimize the volume of the secondary waste to be conditioned and disposed off in a final repository [8, 9]. The selection of an appropriate medium depends on the needs of the system. Generally low

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cost ion exchange media required large volumes. This leads to larger volumes of waste to treat and dispose.

Description

Distribution coefficient (K_d)

The distribution coefficient (K_d) for each radionuclide present in the solution can be used directly to calculate the amount of ion exchange medium that is needed to achieve a desired decontamination for a certain amount of liquid in a batch process. Under dynamic conditions, in which the ion exchange medium is used in a column, the distribution coefficient can be used to calculate the theoretical maximum capacity of the ion exchange bed. If the bed includes m kg of ion exchange medium, the theoretical maximum capacity of the ion exchange bed to purify a volume V can be calculated as:

$$V = K_d \times m \quad (1)$$

Ion exchange processes can be implemented in a variety of ways, including in batches, in columns, in continuous loops and, as part of, or in combination with, membrane processes [9]. Each technique has features that make it more or less suitable for specific applications. In this study, ion exchange process has been applied using the column. A measured quantity of the ion exchange medium is mixed with the liquid waste in a suitable container. The amount of media required and the rate of exchange can be determined by laboratory tests or by calculated using the following equation:

$$m = (D - 1)V/K_d \quad (2)$$

where K_d is the measured distribution coefficient, D is the required decontamination factor, V is the volume of liquid to be purified, m is the amount of the ion exchange medium needed to reach the required decontamination factor.

Materials

Natural zeolite used in this experiment was obtained from the Gordes location in western Turkey. The zeolite consists of clinoptilolite and k-feldspar. The cation exchange capacity of Gordes zeolite was determined to be about 70 meq/100 g. The chemical compositions were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-ES). The results are presented in Table 1.

Scanning electron microscopy (SEM) of Gordes zeolite is shown in Fig. 1. SEM is an important tool for microscopic analysis, since it is extensively used to study the particles size and shape of the materials.

Table 1 Chemical compositions of starting material (wt%)

Oxides	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	CaO
Gordes zeolite	63.74	11.80	1.66	1.18	0.51	2.46	1.86

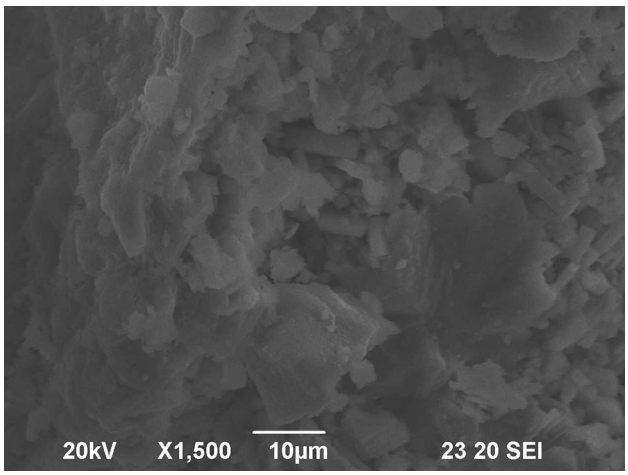

Fig. 1 SEM image of Gordes zeolite

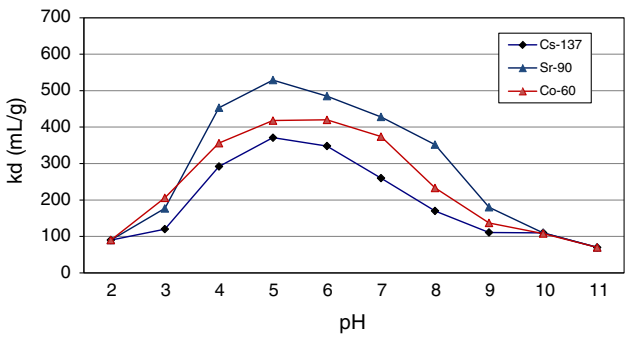

Fig. 2 Distribution Coefficients (K_d) at different pH levels

Optimal pH of natural Gordes zeolite is within 4–9, since they are soluble both in acidic and alkaline media. In general, a single ion exchange material is unlikely to be able to take up a particular radionuclide over the whole pH range. Effect of pH levels on the distribution coefficient (K_d) of the zeolite was determined to optimize the waste solution pH for the plant scale operations. Distribution coefficients at different pH levels are shown in Fig. 2.

Methods

Ion exchangers were prepared using exchange beads of size $-16 + 25$ ASTM mesh in the column. For ion exchange natural zeolite were prepared and loaded with column. The pilot plant scale column system was constructed of 5 L



Fig. 3 Ion exchange column

Table 2 Specific radioactivity of liquid radioactive waste

Radioactivity	Bq/L
Gross alpha	1×10^4
Gross beta	1×10^4
^{60}Co	8×10^3
^{137}Cs	9×10^3
^{90}Sr	9×10^3

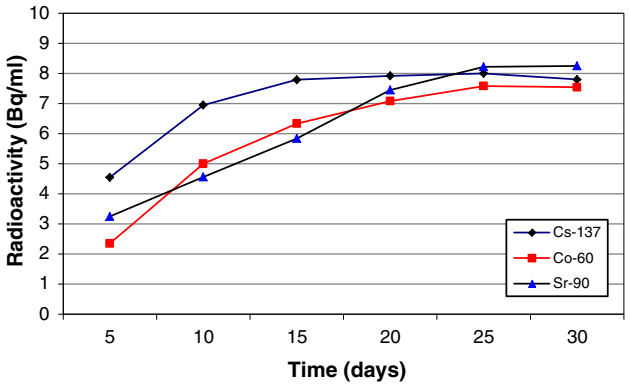

Fig. 4 Radioactivity versus time

capacity. 0.5 kg of exchange powder was equilibrated with 5 L of radioactive LLW. The most common uses of ion exchange media are in vessels or columns. In this study, the ion exchange medium zeolite is contained inside a steel pressure vessel, with an engineered inlet, outlet and a flow distribution system to allow liquid to percolate through the bed of the medium at a specified flow rate. Retention screens on the inlet and outlet prevent the medium from escaping into the process loop. A secondary circuit with unscreened drain and fill lines is used to remove the spent medium and fill the vessel with a new medium. The column was used with bed-type ion exchange media, zeolite, constructed in $-16 + 25$ ASTM meshes of sizes to meet the requirements of the system. Column operation was a semi-continuous process. Column system is shown in Fig. 3. In column operation, determination of the medium being spent was based on ionic breakthrough, which is the point at which the exit concentration of the iconic species being removed starts to increase sharply to some predetermined level.

In this method, multiple columns can be connected in parallel to prevent interruptions in the process to replace ion exchange media. In this application, while one set is in operation the other column is filled with a fresh medium. The frequency of such changeovers is governed by the capacity of the medium relative to the ionic strength and the flow rate of the liquid being treated. The capacity of the system is determined in bed volumes, which is the ratio of the volume of liquid treated to the volume of the bed of the exchange.

Liquid radioactive waste composition

Gross radioactivity values and specific radioactivity of radionuclide are measured in liquid radioactive waste and presented in Table 2. The measured pH level of liquid waste ranges between 8 and 10.

The liquid radioactive waste should have less than 1–2 g/L total dissolved zeolite content. Radionuclide should be present in a suitable ionic form. It was maintained by arranging the pH level of the liquid. Waste should not contain very small amounts of organic contaminants. According to test results, passed radioactivity from the column during the operation time is presented in Fig. 4. Decontamination factor (D) of each radionuclide was calculated by dividing initial radioactivity (AI) to final radioactivity (AF) of the liquid purified waste. Decontamination factors were determined between 240 and 780 depending on pH and temperature.

Effect of temperature on the radionuclide adsorption of the zeolite was determined to optimize the waste solution temperature for the plant scale operations. Adsorption percentages (%) at different temperatures are shown in Fig. 5.

Decontaminated liquid was discharged and spent zeolite waste was taken into in-drum mixer for solidification. Sand, cement and water were added into the drum. Water/cement ratio was taken as 0.5 for the first method. In the new technique, pH of liquid LLW was maintained at 5–6

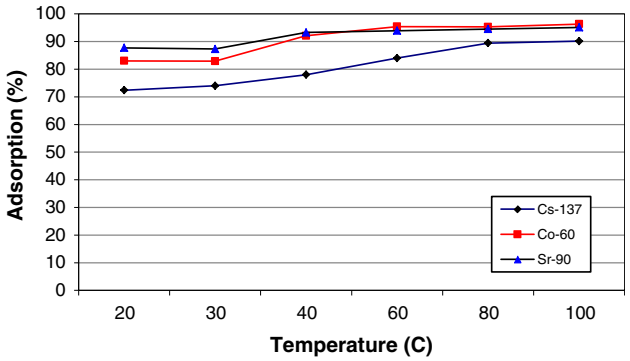

Fig. 5 Adsorption percentage (%) at different temperatures

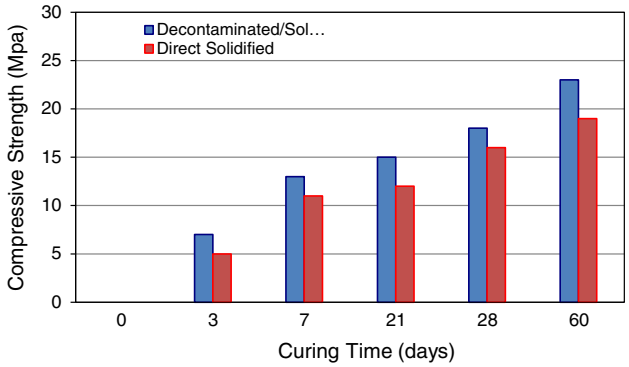

Fig. 7 Compressive strength of solidified samples

Table 3 Solidification mixture for two methods

Material	Decontamination/ solidification	Direct solidification
Waste	Spent zeolite (^{60}Co, ^{137}Cs, ^{90}Sr)	Liquid LLW (^{60}Co, ^{137}Cs, ^{90}Sr)
Cement	Portland (OPC)	Portland (OPC)
Sand/ aggregate	Sand	Natural zeolite
Water	Demineralized water	NA
C/W	0.5	0.5 (C/LLW)



Fig. 6 Solidification process

for cementation and then radioactive LLW was directly taken into drum without any decontamination. Natural zeolite was used as a sand/aggregate and zeolite with premixed cement was added into the drum. In this method no water is required because the liquid waste was taken into the drum without dewatering. A solidification mixture of these two methods is presented in Table 3. The mixing equipment is an in-drum mixer (Fig. 6).

The mixing of the waste with the cement and additives are performed on this equipment. The mixer is composed of two stainless steel screws which rotate in contrary directions. Mixing time is determined as 15 min for each method.

Results and discussions

The first-method test results at different pH levels show that maximum purification efficiency was achieved at pH 5 for Gordes zeolite. Real radioactive waste was used in this study and gross and specific radioactivity of radionuclide was measured by gamma spectrometric analysis. Mainly three radionuclides; ^{60}Co, ^{137}Cs and ^{90}Sr are available in LLW with 8–9 $\times$ 10^3 specific radioactivities. Passed liquid from the purification column was collected and analyzed during the operation time. The process effectively worked in first 5–10 days then the radioactivity breakthrough occurred. Decontamination factor (D) of each radionuclide at the beginning of the process was calculated in the range of 500–780. After 10 days D decreased according to zeolite ion exchange capacity. Adsorption results show that heat is positively effective on adsorption. Increasing the temperature in this purification column system was causing increasing of adsorption in range of 10–15 % for each radionuclide activity.

Compressive strength values of the first-method samples measured were higher than direct solidified sample values. The difference of these strength values was presented in Fig. 7. Leaching tests were applied on samples of two methods. Leach rates of two different process samples are determined. One is direct solidified sample the other is

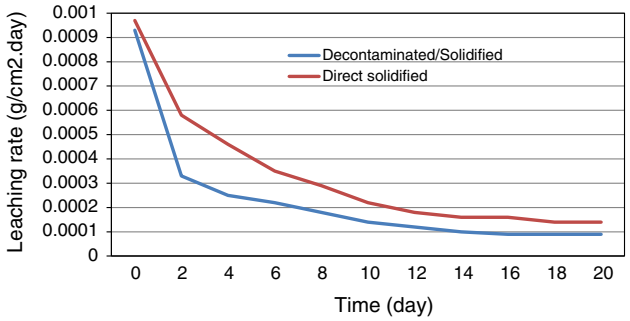

Fig. 8 Leaching rate of solidified samples

after decontamination process sample. Tests were applied on 28 days cured samples. Both leaching rates were based on ^{137}Cs radionuclide tests. Cylindrical samples were immersed into water and leaching amounts during the 20 days were determined for each method. Changing of leaching rate according to the time is shown in Fig. 8.

Conclusions

Decontamination of liquid radioactive waste is an important issue for minimization of operational waste treatment and disposal costs. After the decontamination process another form of concentrated radioactive waste remains. This radioactive waste is usually stabilized by solidification process. In this study two solidification methods were evaluated. First method includes two stages; decontamination and solidification. For this reason this method requires more time and investment. The second method, direct solidification, is a simple and economical method. The second method requires much shorter time for processing LLW. LLW was solidified using these two methods. After the processes different waste forms were produced. Integrity and leaching performance of these solidified waste samples were measured. Results show that solidification after decontamination produce a better form of solidified waste form. Compressive strength of two-staged solidification samples was also better. Besides, ion exchange capacity of zeolite is used effectively in this method because of the ion exchange column stage. Two-staged solidified waste forms were determined to be obviously long term safer than the direct solidified method samples. As a result high strength with low leach rate waste form production is the main advantage of this method. Disadvantages of this method are; not applicable for all types of LLW, requires technological background, expensive method and low capacity.

The direct solidification method can be applied easily for less hazardous liquid waste streams. Natural materials like zeolite and clay can be used in direct solidification method for liquid waste stabilization. This method is cost effective and time saving method with reasonable waste form product. Technically simple and less costly treatment methods are always attractive in waste management applications. In this study, investigations show that the results comply with good performance of cements reported in the literature [10]. This new solidification method could be acceptable for most of the liquid LLW types.

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