

Treatment of radioactive liquid waste by sorption on natural zeolite in Turkey

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Abstract

Liquid radioactive waste has been generated from the use of radioactive materials in industrial applications, research and medicine in Turkey. Natural zeolites (clinoptilolite) have been studied for the removal of several key radionuclides (^{137}Cs , ^{60}Co , ^{90}Sr and $^{110\text{m}}\text{Ag}$) from liquid radioactive waste. The aim of the present study is to investigate effectiveness of zeolite treatment on decontamination factor (DF) in a combined process (chemical precipitation and adsorption) at the laboratory tests and scale up to the waste treatment plant. In this study, sorption and precipitation techniques were adapted to decontamination of liquid low level waste (LLW). Effective decontamination was achieved when sorbents are used during the chemical precipitation. Natural zeolite samples were taken from different zeolite formations in Turkey. Comparison of the ion-exchange properties of zeolite minerals from different formations shows that Gordes clinoptilolite was the most suitable natural sorbent for radionuclides under dynamic treatment conditions and as an additive for chemical precipitation process. Clinoptilolite were shown to have a high selectivity for ^{137}Cs and $^{110\text{m}}\text{Ag}$ as sorbent. In the absence of potassium ions, native clinoptilolite removed ^{60}Co and ^{90}Sr very effectively from the liquid waste. In the end of this liquid waste treatment, decontamination factor was provided as 430 by using 0.5 mm clinoptilolite at 30 °C.
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1. Introduction

Radioactive waste contains a variety of radionuclides and arises in a variety of physical and chemical forms. In Turkey, the amount of activity and waste volume of liquid wastes are relatively small. Despite of the low level radioactivity involved, there are many significant hazards that could arise as a result of inadequate management. Treatment of liquid wastes is needed to produce a waste product suitable for long term storage and disposal. The precipitation of liquid low level waste (LLW) was carried out to convert the waste to a more stable solid form and decrease its volume. Liquid waste was decontaminated at Çekmece Waste Processing and Storage Facility (CWPSF) by using natural zeolite as sorbent. In addition, precipitation and sorbent addition processes involve subsequent separation of a solid phase from a liquid one, and transfer of the solid phase

for immobilization. Previous studies showed that presence of additives (zeolite and kaolin) in the final cemented reduces long term leach rates and conserves mechanical strength due to the safety requirements [1,2].

Natural zeolites are volcanic minerals with unique characteristics. Their chemical structure classifies them as hydrated aluminosilicates, comprised of hydrogen, oxygen, aluminum and silicon, arranged in an interconnecting lattice structure. The arrangement of these elements in a zeolite crystal gives rise to a honeycomb framework with consistent diameter connecting channels that vary in size from 2.5 to 5.0 Å, depending on the type of zeolite mineral. This unique structure makes zeolites different from “other” aluminosilicates (kaolin, bentonite, etc.) due to the following special properties. Clinoptilolite is the most abundant member of the 48 minerals in the zeolite group. The mineral occurs in extensive deposits throughout the world. It has two-dimensional 8-ring and 10-ring channel structure with the largest cavity dimension measuring 4.4×7.2 [3]. Although more clinoptilolite is produced than any other zeolite mineral, most of the end use applications are construction aggregates,

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Table 1
Mineralogical analysis of zeolite samples

Mineralogical analysis	%
SiO ₂	65.28–75.38
Al ₂ O ₃	8.12–13.05
Fe ₂ O ₃	0.02–1.34
CaO	1.80–2.95
MnO ₂	0.01–0.03
K ₂ O	2.85–5.54
MgO	0.59–1.45
Na ₂ O	0.21–1.05
TiO ₂	0.05–0.15
ZnO	40–70 ppm
Ag ₂ O	3–6 ppm

building stone, soil additives and animal adsorbents. Only a very small percentage of these deposits are capable of producing high purity clinoptilolite suitable for ion exchange, and sorption applications [4]. In addition, clinoptilolite has been used for radioactive waste treatment for a long time [5,6].

Chemistry of clinoptilolite is (Na, K, Ca)_{2–3}Al₃ (Al, Si)₂Si₁₃O₃₆·12H₂O, hydrated sodium potassium calcium aluminum silicate. The low cost of natural zeolite makes their use attractive in water treatment applications. In this study, natural zeolites were used as sorbents. Sampling places of natural zeolite in Turkey comprised five zeolite deposits. Polatlı (Ankara), Bigadic (Canakkale), Saphane (Balıkesir), Gediz (Kutahya) and Gordes (Manisa). Clinoptilolite percentage of each zeolite sample is changed 75–98% depend on the sampling site. In addition of clinoptilolite, smectite is 5–10% and feldspar is 5–10%. Mineralogical analysis was determined by gravimetric and ICP techniques. Main minerals are shown in Table 1 and common properties of these natural zeolite samples are given in Table 2.

Natural zeolite has a high ion-exchange capacity and a particular affinity for heavy metal cations. It can absorb elements such as ¹³⁷Cs and ⁹⁰Sr and other radioactive isotopes from solution, and hold them in its three-dimensional crystal framework. Zeolite refers to a group of minerals that are basically hydrated calcium potassium sodium aluminosilicates in which the water is held in cavities in the lattice. The lattices are negatively charge and they loosely hold cations. Their ability to exchange one cation for another is known as their “cation-exchange capacity” or “CEC”. Total cation-exchange capacities in natural zeolites vary from 25 to 300 meq/100 g [7].

Sorption reversibility is another important parameter in waste management. In most of cases, sorbed radionuclides have to be recovered by a special treatment. If regeneration of sorbent is planned, solid–liquid interaction will be done by passing the liq-

uid through a bed of the solid. If discharge of sorbent is planned, in this case during the precipitation process mixing of the absorbent in the liquid will be done. For this purpose, sorbents are designed for regeneration and re-use. In this study, sorption reversibility of natural zeolites was not taken into account. After the treatment, zeolite sorbent was stored with its retained radioactivity and cementation applied on it for immobilization as final processing for disposal. At this stage, sorbent stability was important which affect both storage and disposal safety issues. Especially degradation of matrix and corrosion of container problems might occur. After precipitation, zeolite which remained in sludge was immobilized by cementation. By this way, liquid waste was immobilized in monolithic form before final disposal. Zeolite amounts in weight up to 10% of cement amount did not cause any weakness on the uniaxial compressive strength of cemented matrix. Small amounts of zeolite additives in cementation process does not cause any decrease on the strength of cementation matrix [8].

2. Materials and methods

Laboratory tests and plant processes were based on determination of several parameters for further applications. These are: determination of cation-exchange capacities and decontamination factor (DF) of each natural zeolite samples. In addition, selectivity and stability conditions of sorbent material were investigated. Cation-exchange capacity is a measure of the number of cations per unit weight available for exchange, usually expressed as milliequivalents per 100 g of material. Decontamination factor is dimensionless quantity and it is used to describe the ratio of contamination level before treatment to that after treatment. This factor is very useful for selection of suitable material as sorbent and commonly used in radioactive waste management applications [9]. 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 using the following equation:

$$K_d = (DF - 1) \times \frac{V}{m}$$

where K_d is the measured distribution coefficient, DF the required decontamination factor, V the volume of liquid to be purified and m is the amount of the ion-exchange medium needed to reach the required decontamination factor [10].

The liquid LLW contained four main radionuclides: ¹³⁷Cs, ⁶⁰Co, ⁹⁰Sr and ^{110m}Ag. Batch tests were applied on the samples of each zeolite deposits for these radionuclides. ASTM test method was used for determination of sorption properties of these samples [11]. Natural zeolite samples were used as sorbents and liquid radioactive waste was used as solution. Effect of contact time and initial concentration on the clinoptilolite was determined in conditions of (temperature, 30 °C; solid concentration, 10 g/L; agitation rate of 200 rpm). In addition, pH is an important parameter considering possible uses of the zeolites in the removal process. Selectivity is dimensionless quantity and it is used to describe the efficiency of removal of specific radionuclide in the presence of other materials (Table 3).

Table 2
Main properties of zeolite samples

Specific gravity (kg/m ³)	2150–2250
Apparent porosity (%)	39.4–44.2
Water capacity (%)	80–135
Thermal resistance (°C)	<700
Pore radius (nm)	0.4–1.2
Humidity (%)	2–8
Ion-exchange capacity (mol/kg)	1.2–3.5

Table 3
Parameters for test of the removal process

Test parameters	Value
Particle size (mm)	0.5–2.0
pH	6–13
Contact time (min)	40
Total initial activity (Bq/L)	8.45×10^5
Temperature (°C)	30

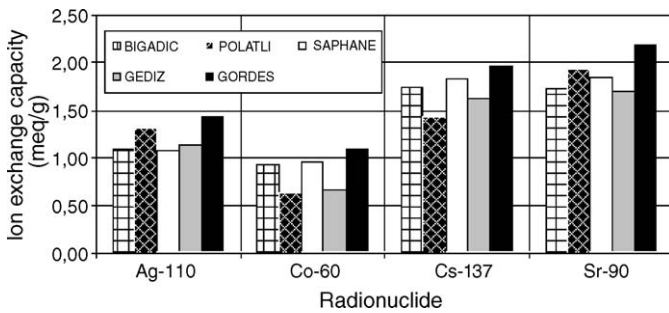


Fig. 1. Ion-exchange capacity on natural zeolites.

The batch ion-exchange capacities for: ^{137}Cs , ^{60}Co , ^{90}Sr and $^{110\text{m}}\text{Ag}$ are given in Fig. 1, where each point on graph represents the average values of five test results.

Sorbent effectiveness during precipitation process was verified by jar test. In this test method, five precipitation samples were prepared at different conditions (various additive amounts, different pH, etc.). One hundred and fifty millilitres of original liquid waste was transferred to each vessel. After stirring period, 24 h passed for settling. One hundred millilitres of clear liquid (supernatant) was taken for radioactivity analyze. Decontamination factors of each test were calculated. Decontamination Factors of samples for ^{137}Cs is given in Fig. 2. Precipitation conditions of the highest DF of test were taken for LLW treatment to the plant.

It was found that ion-exchange capacity of the natural zeolite is very good for ^{137}Cs at pH is about 10. The zeolite selectively removed ^{137}Cs isotopes through the process of ion exchange. Distribution coefficients vary from 3.75×10^3 to 4.45×10^3 mg/L in batch tests. Natural zeolite with low sodium content was selective sorbent for ^{137}Cs and $^{110\text{m}}\text{Ag}$. Concen-

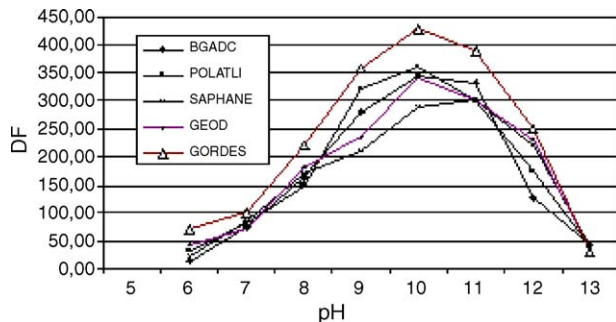


Fig. 2. Decontamination factors (DF) of natural zeolites for ^{137}Cs at different pH levels.

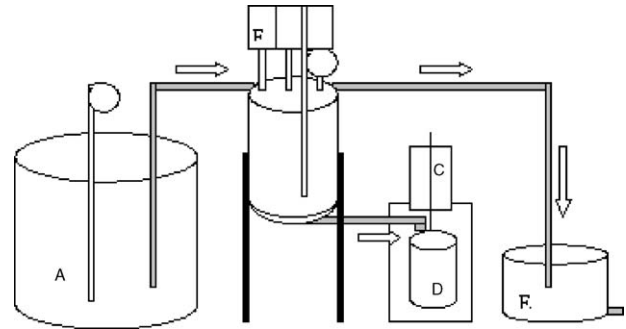


Fig. 3. Radioactive waste precipitation unit. (A) Waste collection tank, (B) precipitator, (C) in-drum cementation mixer, (D) drum, (E) clear liquid and (F) dosage tanks.

tration level of inactive salts in the solution was very effective on DF. Best results were taken by using 0.5 mm particle size of natural clinoptilolite.

2.1. Treatment of LLW

Liquid radioactive wastes at CWPSF has been collected and stored in storage tanks, pending treatment for interim storage. This liquid waste was classified as low level waste due to its radioactivity [12]. Total volume of this waste was 270 L and pH of the liquid waste was 9. Liquid waste was transferred from the collection tank to the precipitator for developing precipitation strategy. Then radioactive waste was pumped to precipitator for precipitation. At this stage, natural zeolite (particle size 0.5 mm) was added from dosage tanks and pH was increased to 10. Solution was mixed by using air jet mixer. After settling of the sludge the clarified solution was pumped to decantation tank. Clear liquid was released to environment due to its activity was less than release limits according to International Commission on Radiological Protection Risk Evaluations [13]. After precipitation, the radioactive sludge including additives was sent to in-drum mixer for cementation (Fig. 3).

3. Result and discussion

Liquid LLW at CWPSF in Turkey were purified to acceptable limits for discharge as the radioactive isotopes were held within the zeolite cage structure. The comparison of the ion-exchange properties of natural zeolites from five deposits in Turkey shows that Gordes zeolite is the most suitable sorbent for radionuclides for liquid waste treatment. In plant scale liquid waste precipitation application, decontamination factor of 430 was achieved for ^{137}Cs radionuclide activity (pH 10, particle size 0.5 mm). This type of zeolites can be used during chemical precipitation as an additive. Laboratory tests show that clinoptilolite has a high selectivity for ^{137}Cs and ^{90}Sr with distribution coefficients of order 10^3 (mL/g). The zeolites selectively removed cesium ^{137}Cs , ^{60}Co , ^{90}Sr and $^{110\text{m}}\text{Ag}$ isotopes through the process of ion exchange. According to laboratory batch tests, in the absence of potassium ions, native clinoptilolites could remove ^{90}Sr and ^{60}Co very effectively. The use of zeolites as sorbent was

not very effective when radioactive waste liquids contain high concentrations of inactive salts. Gordes zeolite was selectively removed ^{137}Cs isotopes from radioactive liquids at CWPSF. Clinoptilolite deposits in Gordes-Manisa/Turkey has prominent natural purity for commercial and industrial applications. Gordes zeolite's natural purity content based on its Si/Al ratio, cation-exchange capacity. Pure clinoptilolite, zeolite reserves in Manisa-Gordes/Turkey in excess of 5,000,000 tonnes. The permanent storage or disposal of the waste was facilitated by the inorganic and stable structure of the zeolite which can be encapsulated in cement. Zeolites reacted readily with cement thus allowing the radioactive waste to be entrapped and contained safely. Zeolites are physically robust and resistant to nuclear degradation, and they are less expensive than organic ion-exchange resins.

4. Conclusion

Liquid radioactive waste in Turkey were decontaminated (DF 430) by using natural zeolites as sorbents during precipitation process. By this process, radioactivity in liquid waste was held in zeolite sorbents. Natural zeolite without any pre-treatment can be used successfully as sorbent during precipitation process of liquid wastes. Significant properties of Turkish zeolites which were determined by this study are: they have high cation-exchange capacities and they have good selectivity in case of convenient precipitation conditions. Decontamination costs of liquid waste streams can be decreased by using natural zeolite as sorbent instead of other expensive chemical compounds.

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