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The study on preparing absorbent of potassium nickel hexacyanoferrate (II) loaded zeolite for removal of cesium from radioactive waste solutions and stable solidification method for those spent absorbents

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Abstract: The development of cesium selective adsorbent is urgent subject for the decontamination of intermediate and high level water from nuclear facilities especially in nuclear accidents. For the selective adsorption and stable immobilization of radioactive cesium, K-Ni- hexacyanoferrate (II) loaded zeolite (FC-zeolite) (synthesized zeolite of Hanoi University of Science and Technology) were prepared by impregnation/precipitation method. The ion exchange equilibrium of Cs^+ for composites FC-zeolite was attained within 5 h and estimated to be above 97% in Cs^+ 100mg/l solution at pH: 4-10. Ion exchange capacity of Cs^+ ions (Q_{max}) for FC-zeoliteX was reached 158.7 and 98.0 mg/g in pure water and sea water respectively. Those values for FC-zeolite A was 103.1 and 63.7 mg/g. Decontamination factor (DF) of FC-zeolite X for ^{134}Cs was 149.7 và 107.5 in pure water and sea water respectively. Initial radioactivity of ^{134}Cs ion solution infect to decontamination factor. KNiFC-zeolite X after uptaked Cs (CsFC- zeolite X) was solidificated in optimal experimental conditions: Mixing CsFC-zeolite X with additive of $Na_2B_4O_7$ (5%), temperature calcined 900^{o}C for 2h in air. Solid forms was determined some of parameters: Cs immobilization, mechanical stability, volume reduction after calcination (%) and leaching rate of Cs^+ ions in solution.

Keywords: *Removal of Cs, Treatment of cesium from radioactive waste solutions.*

I. INTRODUCTION

Large amounts of high level aqueous wastes have been generated during nuclear fuel cycle operation, nuclear industry and especially in nuclear accidents such as Chernobyl, Fukushima NPP-1. These liquid radioactive wastes contains high radioactivity of ^{137}Cs. Hence to ensure the protection of human health and the environment from the hazard of these wastes, the development of effective and selective methods for removal of radioisotope cesium is urgent and important subject.

Among various inorganic ion-exchangers exhibiting high selectively to Cs^+, insoluble Potassium nickel hexacyanoferrate (II) (KNiFC) have been employed for the removal of ^{137}Cs in the treatment of nuclear waste solutions. However, the KNiFC are very fine crystals and have low mechanical stability; that tend to become colloidal in aqueous solutions and seem to be unsuitable for practical applications such as operation in ion exchange column. In order to improve their mechanical properties, ferrocyanide exchangers have been prepared by

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precipitation on solid supports such as silica gel, bentonite [1]. Zeolite X with a relatively large pore volume and specific surface area is available as a carrier for the loading of microcrystalline ferrocyanide. This zeolite also has high resistance to acid and irradiation.

II. EXPERIMENTAL

A. Procedure for preparation of composites

The insoluble ferrocyanide (FC)-loaded zeolite were prepared by successive impregnation of $Ni(NO_3)_2$ and $K_4Fe(CN)_6$ on the macropores of zeolite X carrier (synthetic zeolite of Ha Noi Bach Khoa University). FC-zeolite were prepared as follows: 5.0g of zeolite X carrier dried at 90^{o}C was contacted with a 50 cm^3 solution 1 M $Ni(NO_3)_2$ under shaking at 25^{o}C for 3hours and then washed with distilled water and air-dried at 90^{o}C for 3h. In a similar manner, the zeolite X impregnated with $Ni(NO_3)_2$ was reacted with a 50 cm^3 solution of 0.5 M $K_4Fe(CN)_6$ for 2h under slight shaking to form KNiFC precipitates in pore and surface of zeolite X. The FC-zeolite was washed with distilled water and air-dried at 90^{o}C for 3h and finally stored in a sealed vessel.

B. Characterization of FC-zeolite composites

Surface morphologies of FC-zeolite X were examined by scanning electron microscopy (SEM), Nova Nano. The structure of FC-zeolite was determined by powder X-ray diffractometry (XRD), SIEMEN D5005.

C. Determination of uptake (R%) and ion exchange capacity (mg/g) of FC-zeolite (A & X) for ion Cs^+

Two kinds of FC-zeolite (A &X) and two kinds of aqueous solution were used for the batch adsorption experiments. FC-zeolite (100 mg) were contacted in a centrifugation tube with aqueous solutions (10 cm^3, pure water and sea water (Sam Son,Thanh Hoa prefecture) containing 100 ppm Cs^+ at 25±0.1°C for 1 day. The tubes were horizontally shaken at 100-150r/min. After the supernatant solution was separated, the concentration of Cs^+ ions was measured by atomic absorption spectrometry (AAS). The uptake (*R*, %) and ion exchange capacity (Q) of FC-zeolite for Cs^+ ions removed from the solution are defined as:

$$R = (C_i - C_f)/C_i \times 100, (\%) \qquad (1)$$

$$Q = (Ci - C_f)\ V/m \quad (mg/g) \qquad (2)$$

where C_i and C_f are the concentrations (ppm) of Cs^+ ions initially and at equilibrium respectively. V is volume of solution (cm^3), m is the amount of FC-zeolite (g)

D. Determination of decontamination factor of ^{134}Cs

Two kinds of FC-zeolite (A & X) and two kinds of aqueous solutions were used for the batch adsorption experiments. FC-zeolite (100 mg) were contacted in a centrifugation tube with 10 ml solutions of radioisotope ^{134}Cs: 20.066 Bq/l; 12.001Bq/l and 6137Bq/l (in pure water and seawater) at 25±0.1°C for 1 day. The tubes were horizontally shaken at 100-150r/min. After the supernatant solution was separated, the Activity of ^{134}Cs was measured by gamma spectrometry (GEM30P), Ge detector. Decontamination efficiency (K%) of FC-zeolite for ^{134}Cs or decontamination factor (DF) was calculated by following formula:

$$K\ (\%) = [(A_j – A_f)/A_i]*100 \qquad (2)$$

$$DF = A_i\ /A_f \qquad (3)$$

Where: A_i and A_f are ^{134}Cs activity in solution before and after decontamination

E. Procedure for solidification of spent KNiFC-zeolite composites

The FC-zeolite composites saturated with Cs^+ ions were prepared as follows**.** The composites were treated with 0.5 M $CsNO_3$ solution. The Cs^+ saturated composites were mixed with 5% $Na_2B_4O_7$. The mixtures were then pulverized and molded as a disc by cold-pressing (Fig.1).The molded discs were calcined at temperatures 900°C for 2h in the air.

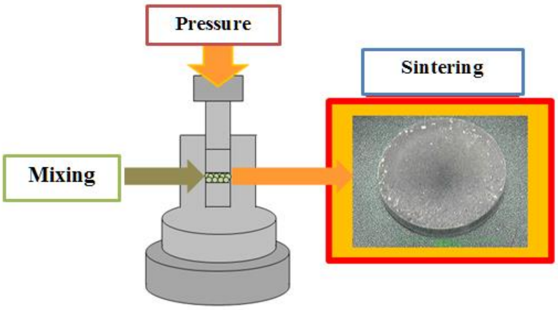

Fig.1. Solidification procedure

F. Characterization of Cs KNiFC-zeolite solid form

The KNiFC-zeolite X were treated with 0.5 M $CsNO_3$ solution. The Cs content (wt%) was measured by Energy-dispersive X-ray spectroscopy (EDX). The Cs immobilization ratio (%) was estimated from the difference of the Cs content before and after calcination. Compressive strength of solid form after calcination was determined by compression test. The solid form calcined products of the mixture of CsKNiFC-zeolite-$Na_2B_4O_7$ (5%) were used for leaching test in deionized water (DW) for period: 1;7; 14; 21; 28 days, temperature: 25°C, solid-leachant ratio: 1/10. After leaching, the Cs^+ concentration of the supernatant solution was measured by Atomic absorption spectrometric (AAS).

III. RESULTS AND DISCUSSION

A. Characterization of FC-zeolite composites

Surface morphology of FC- zeolite X: Photographs (2.a) shows the SEM images of zeolite X with typical crystals in fairly regular hexagon shape. Photographs (2.b) revealed the SEM images of FC-zeolite X to be rather homogeneous crystals and identically spherical shape.

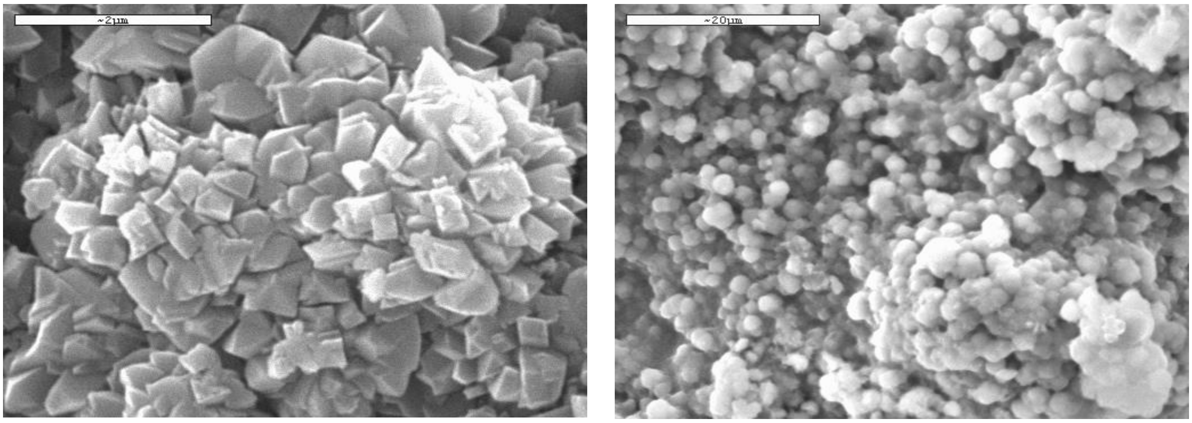

Fig.2. SEM images zeolite X (a) and FC-zeolite X (b)

*The structure of FC- zeolite X***:** Figure 3.a shows a typical XRD patterm of zeolite X (JPCDS 38-0237) with typical pick at 2θ =6,2, zeolite K-F (JPCDS 39-0217), some other minerals such as quartz, kaolin remnained in X zeolite synthesis from kaolin. Both zeolite X và zeolite K-F are crystals . XRD patterm of FC-zeolite X (3.b) is similar of zeolite X. Thus can see that $K_{2-x}Ni_{x/2}[NiFe(CN)_6]$ precipitated on to the zeolite does not alter the structure of the zeolite which only makes the larger crystal size.

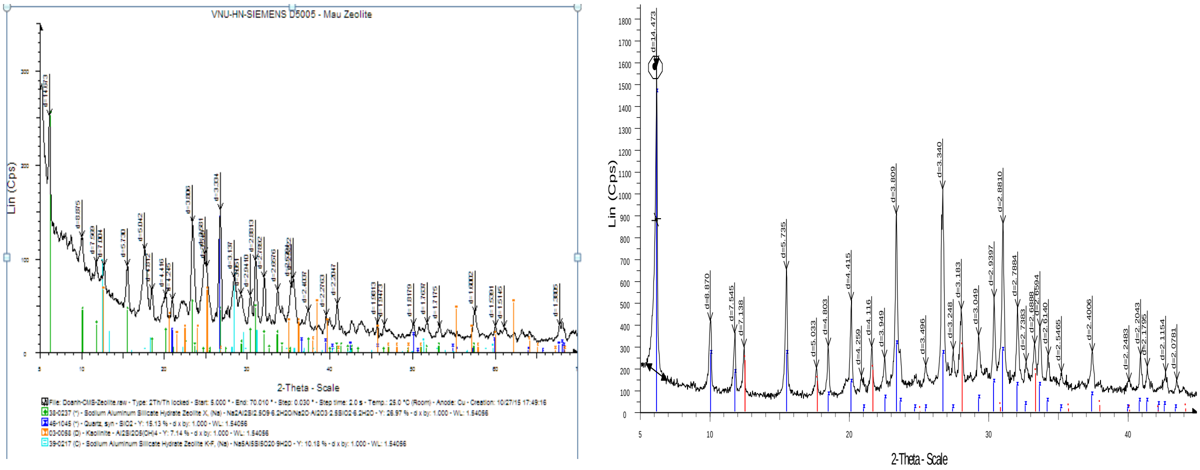

Fig. 3. XRD pattern of zeolite X (a) and FC-zeolite X(b)

B. Uptake behavior (%) of Cs^+ ion for FC-zeolite composites

The uptake rates of Cs^+ for FC-zeolite composites (FC-zeolite X and FC-zeolite A) in pure water (PW) and seawater (SW) were showed in Fig. 4 at different shaking times up to 24 h. In either case, the uptake rate was very large in the initial stage and attained equilibrium within 5 h. Uptake (%) was obtained >97.5% for composites in PW and >65% in SW. Uptake (%) of FC-zeolite X was slightly larger than that for FC-zeolite A and Uptake (%) of composites in PW was larger than that in SW due to the competition with Na^+ in sea water.

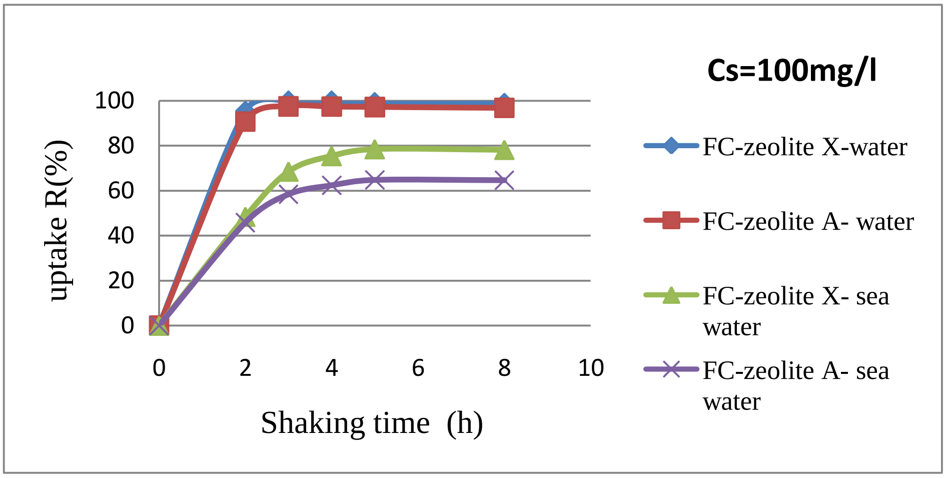

Fig.4. Uptake (%) of Cs^+ ions for FC-zeolite in at different shaking times. [Cs^+]: 100 ppm

C. Effect of pH to uptake behavior (%) of Cs^+ ions for FC-zeolite composites

The results showed that uptake (%) of both FC- zeolite (A and X) were highest at pH: 6-8 and reached 99% in solution of 100mg/l Cs^+ In a wider pH range from 4-10, the uptake (%) also reached more than 97%. Thus H^+ and OH^- ions do not significantly influence on the absorption Cs ions of FC-zeolite (A and X) products, that can used to remove almost Cs ions from the solution with different pH.

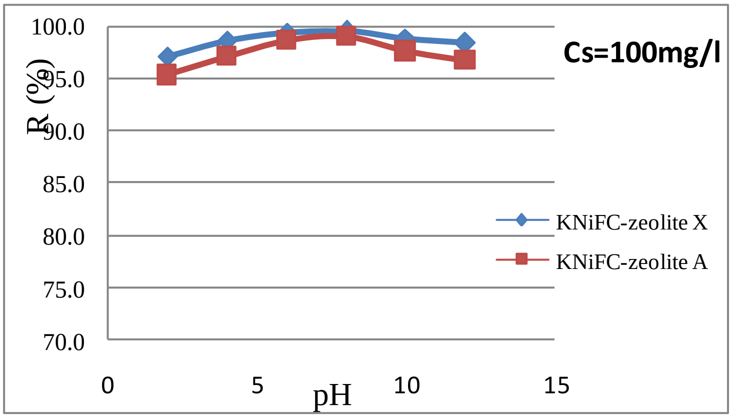

Fig.5. Effect of pH to uptake behavior (%) of Cs^+ ions

D. Absorption capacity of Cs^+ ion for FC-zeolite composites

The ion exchange isotherm was obtained in a wide range of initial Cs+ concentration from 1000 to 2500ppm in both PW and SW. The equilibrium amount of Cs+ adsorbed on FC-zeolite approached a constant value at Cs+ concentration above about 2100mg/l in PW and 1400mg/l in SW, suggesting that the uptake of Cs+ follows a Langmuir-type adsorption equations:

$$Q_{eq}=KQ_{max}C_{eq}/(1+KC_{eq})\ \ (mol/g) \qquad (4)$$

Where: C_{eq} and Q_{eq} are concentration of Cs^+ in the aqueous and solid phases, respectively; Q_{max}(mol/g) is the maximum amount of Cs^+ taken up and K(dm^3/mol) is the Langmuir constant.

The equation (4) can be rewritten as follows:

$$C_{eq}/Q_{eq}= 1/KQ_{max} + (1/Q_{max})C_{eq} \qquad (5)$$

As seen in Fig.5, fairly linear relations between C_{eq}/Q_{eq} and C_{eq} for FC-zeolite in PW and SW were obtained from Langmuir plots, with correlation coefficients above 0.97. The Q_{max} value for FC-zeolite X and FC-zeolite A in PW were calculated to be 112.5 mg/g and 85.6 mg/g. Q_{max} values were to be 67.8 mg/g and 42.7 mg/g respectively in SW.

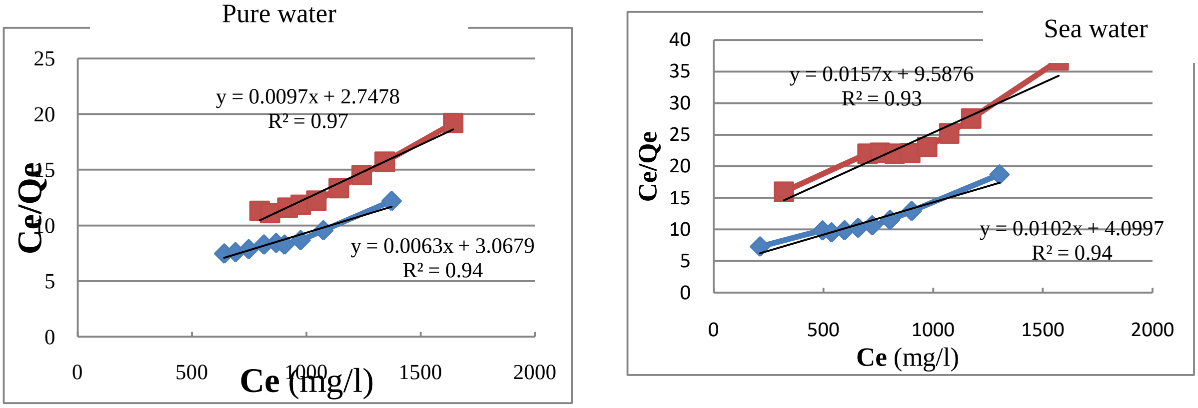

Fig.6. Langmuir - plot of Cs^+ uptake for FC-zeolite in PW and SW

Q_{max} values of FC-zeolite A were rather low compared with those of FC-zeolite X in both PW and SW suggesting that larger specific surface area and capillary size of zeolite X carrier seem to successive loading FC crystals better than zeolite A carrier. Q_{max}

values for FC-zeolite in PW were considerably higher than those in SW due to competition of Cs^+ with Na^+ in sea water.

E. Decontamination factor of FC-zeolite X for ^{134}Cs

The decontamination factor (DF) of FC-zeolite X composite and zeolite X carrier for ^{134}Cs in pure water and sea water were showed in table I. The results indicated that DF of FC-zeolite X were considerably higher than those of zeolite X carrier in both PW and SW. Similar to the uptake of Cs^+ ion, DF of ^{134}Cs for FC-zeolite X and zeolite X in SW were rather lower compared with those in PW because of the influence of Na ion. Experiments also showed that in the range of studied activities of ^{134}Cs, the higher activity causes the lower decontamination factor because at high activity, the densities of ions are very high and they will compete with each other in the interaction with absorbents or they possible need more absorbents to complete this removal process, thus decontamination factor depends on much of activity.

Table I. Decontamination factor (DF) of FC-zeolite X and zeolite X for ^{134}Cs

Absorbents	**Activity A_i (Bq/l)**	**Activity A_f (Bq/l)**	**DF**	**(K%)**
KNiFC-zeoliteX (Pure water)	20066	214	93.8	98.93
	12001	88	136.4	99.27
	6137	41	149.7	99.33
Zeolite X (Pure water)	20066	288	69.7	98.56
	12001	162	74.1	98.65
	6137	79	77.7	98.71
KNiFC-zeoliteX (Sea water)	21278	243	87.6	98.86
	12009	122	98.4	98.98
	5591	52	107.5	99.07
Zeolite X (Sear water)	21278	387	55.0	98.18
	12009	180	64.2	98.50
	5591	82	68.2	98.53

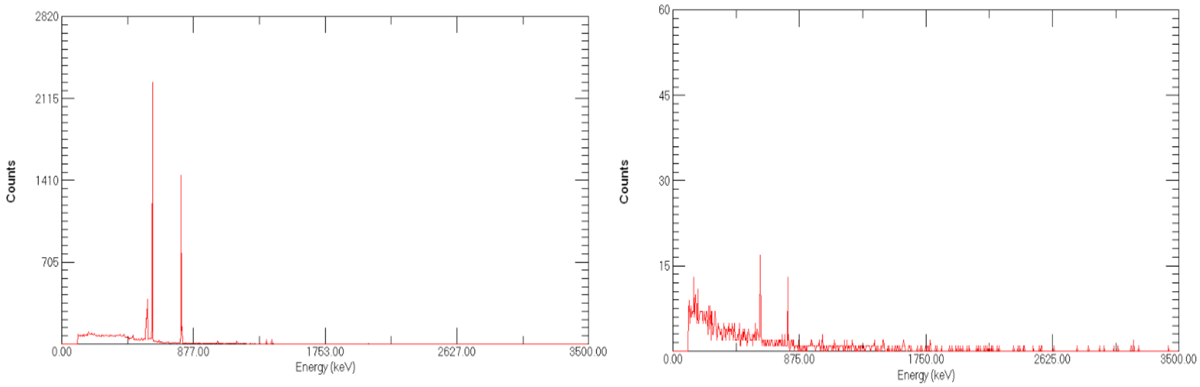

Fig 7. Gamma spectra of ^{134}Cs in liquid samples before and after decontamination

F. Solidification and Cs immobilization ability (%)

The Cs content (wt%) in the calcined products at 900°C was almost the same as that in the original mixture, indicating no loss of Cs (due to the volatilization of Cs_2O at higher temperature above 700°C) [5]. Cs immobilization ability (%) was above 97% compared with 50% in the case of the silica gel carrier [5]. This suggests that the zeolite X carrier can Cs trapping and self-sintering abilities (Fig.7). The decomposition and immobilization mechanism can be follows: First, the insoluble ferrocyanide loaded in zeolite was thermally decomposed to metal oxides and CO_2; NO_x gases around 300-350°C. Secondly, the volatilized Cs_2O gas was trapped in the zeolite structure. At higher temperature above 800°C, zeolite structure begins to collapse gradually and above 1,000°C, zeolite is converted to crystal phase (nepheline) and amorphous phase (melting), respectively [6]. Thus mixing of FC-zeolite X- was effective for immobilization ability of Cs when solidification of CsFC-zeolite X to environmental remediation.

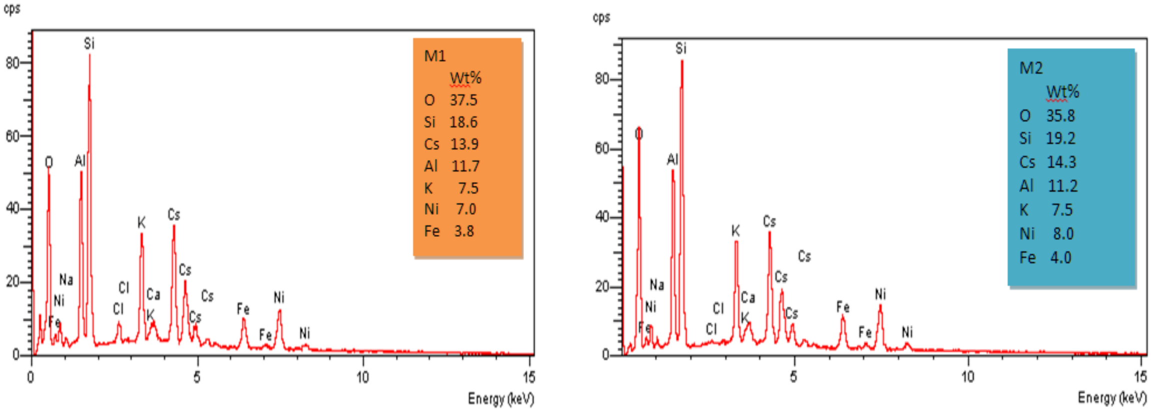

Fig. 8. EDS spectra of solid product before and after calcination

G. Effect of calcination time to compressive strength and volume reduction of solid form:

Volume reduction degree and compressive strength for the calcined products of the mixture of CsFC-zeolite X and $Na_2B_4O_7$(5%) at 900^0C in different times in table 2 showed that compressive strength and volume reduction of solid disc increased as calcination time increasing (in the range of studied times). However, the calcination time is too long will be uneconomical.

The selection of the optimum calcination time is necessary and must be incorporated a number of factors such as compressive strength, volume reduction, the leaching rate and economic.

Table II. Effect of calcination time to compressive strength and volume reduction

Calcined time (h)	Volume of dics before calcination (cm^3)	Volume of dics after calcination (cm^3)	Volume reduction (%)	Compressive strength (MPa)
0.5	2.21	1.40	36.66	7.84
1.0	2.30	1.37	40.58	10.45
1.5	2.21	1.20	45.40	11.76
2.0	2.01	0.98	51.08	12.10

G. Leachability of Cs from calcined products

The leachability is an important factor for the evaluation of long-term chemical durability of solid forms. The leachability of Cs for the solid forms in different solidification condition (M1-M5) was examined under the same leaching conditions is shown in Fig.9:

M1: CsFC-zeolite X without $Na_2B_4O_7$ calcined at 900^0C for 2h

M2: CsFC-zeolite X with $Na_2B_4O_7$(5%); at 900^0C; 0.5h

M3: CsFC-zeolite X with $Na_2B_4O_7$(5%); at 900^0C for 1.5h

M4: CsFC-zeolite X with $Na_2B_4O_7$(5%) at 900^0C for 2.0h

M5. CsFC-zeolite X without $Na_2B_4O_7$ calcined at 1.200^0C for 2.0h

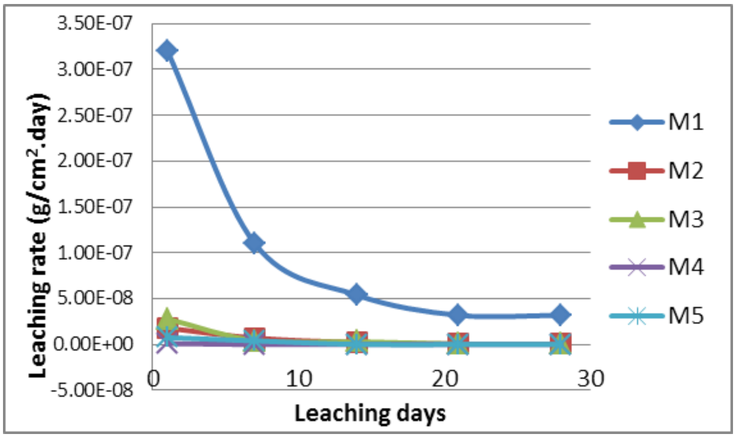

Fig. 9. Leachability of Cs from calcined products

As the leaching period, the leachability of Cs^+ ions from M1 - M5 calcined products were in the order: 1 day > 7 days >14 days > 21 days > 28 days due to small amount of free Cs^+ ion can dissolve in demineralized water easily when contacting and leachability will decrease over the next time periods

The mixing CsFC-zeolite X with additive of $Na_2B_4O_7$ (5%) calcined at 900^0C for 2.0h has leachability of Cs ion as almost low as the mixing without $Na_2B_4O_7$ calcined at 1.200^0C for 2.0h, that were 1.2E-09 and 7.6E-09 (g/cm^2.day) for 1 day period, respectively. Those values were 4.1E-11 and 1.2E-10 (g/cm^2.day) for 28 days period, respectively. The low leachability is essential for the long-term disposal of the solid forms, and hence finding the optimization conditions such as mixing ratio, calcination temperature, and additives, etc are very important for solidification method of spent CsFC-zeolite composites.

IV. CONCLUSIONS

Potassium nickel hexacyanoferrate II(KNiFC) were loaded on porrous zeolite X (FC-zeolite) by successive impregnation of $Ni(NO_3)$ and $K_4Fe(CN)_6$. The loading of KNiFC on zeolite X led to improvements in both mechanical stability and absorption capacity of Cs^+ ions in the large range of pH (4-10) and reached at more 97% in Cs 100mg/l solution. Absorption capacity of FC-zeolite for Cs^+ ions in pure water was 112.5 mg/g, that considerably higher than those in sea water (85.5mg/l) due to competition with Na^+.

Decontamination factor of FC-zeolite X for ^{134}Cs was significantly higher than the zeolite X carrier, those values decontamination factor depends on initial activity of ^{134}Cs.

The optimization of solidification method for spent FC-zeolite was: Additives $Na_2B_4O_7$ 5%; calcination temperature 900^0C for 2h in air. Cs immobilization ability about 97%; compressive strength was 12Mpa; volume reduction: 50%; leaching rate of Cs^+ ions in deionization water: 4.1E-11g/cm^2.day for 28days period. The immobilization of Cs^+ ions and solidification of the spent FC-zeolite composites was effective for the safety treatment and disposal of secondary of solid waste.

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