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Using bentonite for NPP liquid waste treatment

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Abstract: During operation, nuclear power plants (NPPs) release a large quantity of water waste containing radionuclides required treatment for protection of the radiation workers and the environment. This paper introduces processes used to treat water waste from Paks NPP in Hungary and it also presents the results of a study on the use of Vietnamese bentonite to remove radioactive Caesium from a simulated water waste containing Cs.

Keywords: *liquid waste, remove Cs, Vietnamese Bentonite, Paks NPP.*

I. INTRODUCTION

Water waste from a NPP includes several sources: waste leaked from the primary cooling loop of a pressurized water reactor, aqueous solution used to decontaminate equipment installed on the primary loop and other sources. Thiswaste usually is collected in storage system located at the NPP.

Radionuclides existed in the liquid waste include fission products like Cs-137, and activation products such as Co-60, Fe-59, Cr-51, Mn-54, etc. [1-4]. In NPP with WWER-400 type – reactor in Paks (Hungary), the aqueous solutions used to decontaminate equipments contain chemicals such as alkaline, $KMnO_4$, EDTA, gluconic acid, etc [4] to form complexes with the radionuclides which easily solubilize into the decontamination solution. The water waste with radionuclides collected has been stored for a certain time to decay. During this time period, the short lived radionuclides like Fe-59, Cr-51, and Mn-54 will decay completely, however the longer lived radionuclides, e.g. Co-60, Cs-137 in the solution still have a concentration well above the allowable discharge limit of 1 kBq/l and are not allowed to discharge into the environment even after several years of storage [4]. Therefore, the waste is required to remove and concentrate Co-60, Cs-137 radionuclides in a small volume before discharging the waste into the environment.

The technology for liquid waste treatment which applied at the Paks NPP comprises four stages as described in fig.1

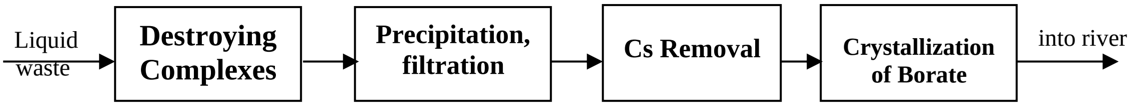

Fig 1. Four stages of the technology of liquid waste treatment used at the Paks NPP

In the first stage, the underwater plasma and H_2O_2 techniques are used to destroy complex of radionuclides. The pH of the liquid waste is adjusted to 13 by NaOH to keep boric acid in the solution. Boric acid will be removed in the last stage.

Plasma in the system will degrade complexes of radionuclides with lagans in the

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decontamination solution. The radionuclides released from the complexes in the form of ions and it is easily to remove by ion exchange and adsorption.

After the destruction of complexes, radionuclides such as Co-60, Fe-59, Cr-51, and Mn-54, etc at high pH condition will precipitate/co precipitate with suspended matters in the solution and it will be removed by filtration. The filtration system includes coarse and fine filter to remove suspended particles with size of 0.1 – 1.0 µm as well as colloidal clusters.

The third stage is the Cs removal. The plant uses a specific ion exchange-resin to remove Cs radionuclide. The name of the resin is Fortum, BME, Termoxid-35 which capable of selective exchange for Cs ion.

The last stage is crystallization of borate. Nitric acid is added to the solution to decrease pH from 13 to 9,2 - 9,3. When the pH of the solution decreases boron in the solution will precipitate as borate sodium ($Na_2B_4O_7$). The borate precipitation is separated by filtration.

Waste water, after removal of radionuclides and boric acid, could be released into the environment (Fig.2).

In this paper, Vietnamese bentonite was tested as an adsorption material to replace the ion exchange resin used in the stage of the Cs removal, i.e. the third stage of the technology applied at the Pak NPP as descibed above.

Commonly, Bentonite is a type of natural clay and the main component is montmorillonite (MMT). Chemical composition of MMT is $Al_2O_3.4SiO_2.nH_2O$, where n ranges from 2 to 8. However, composition of MMT is different from its theoretical composition because Si^{4+} ion could be replaced by ions Al^{3+}, Fe^{3+}, Fe^{3+}, Mg^{2+} in SiO_4 and ion Al^{3+} could be replaced by ions Fe^{3+}, Fe^{3+}, Mg^{2+} in AlO_6. In literatures, it is commonly agreed that MMT consists of two structures: one octahedral Al_2O_3 is in between two tetrahedral SiO_2. Bentonite has a series of outstanding physicochemical properties such as large specific area, high cation exchange capacity, and strong adsorptive affinity for organic and inorganic pollutants, low permeability, low cost, accessibility and ubiquitous presence in most soils. With these advantages, bentonite is considered as one of the most promising candidate as adsorption material for radioactive liquid waste treatment.

II. EXPERIMENTAL SECTION

A. Preparation of Bentonite

Bentonite used in these experiments is supplied from a mine in the Lam Dong Province. The material was refined by dispersing in distillation water with Bentonite-water ratio of 1:10. The mix was stirred for 10 minutes then let settle for 2 hours. The suspended slurry was separated from the sediment in the bottom, and the sediment was discarded. The obtained slurry was centrifuged at the speed of 10000 rounds /min for 15 minutes to separate solid from liquid. The solid fraction was dried at 80^0C and then pulverized for further use.

B. Preparation of solution for the experiment

Solution for the experiment was prepared based on the characteristics of the real solution. The most important characteristics of the real solution are its high concentration of boric and alkaline. The concentration of boric is 120 g/l and NaOH concentration is 90 g/l. Chloride caesium (CsCl, PA grade, Merck) was used to make solution with Cs ion.

C. Experiment for adsorption process

Experiments on the adsorption of Cs on bentonite were performed in batch. An exact amount of bentonite (from 0.1 to 0.5 grams) was put into Erlenmeyer flasks of 250 ml capacity. Then an exact volume of the solution prepared was filled into the flasks (usually with 100 ml). The mixture was shaken at a speed of

100 cycles/minute for a certain period to reach equilibrium. After shaking, the mixture was centrifuged at a speed of 10,000 rounds/min for 15 minutes to separate clear solution for Cs analysis on an atomic absorption spectrometer (AAS) to determine the Cs concentration remaining in the solution. The volume of solution was assumed to be unchanged after the adsorption.

The content of Cs adsorbed on the solid, q_e (mg/g) was calculated from the concentration of the solution as follows:

$$q_e = (C_0 - C).V/G \qquad (1)$$

Where:

C_0 is initial the solution concentration, mg/l;

C is the solution concentration after adsorption, mg/l;

V is the volume of the solution, l;

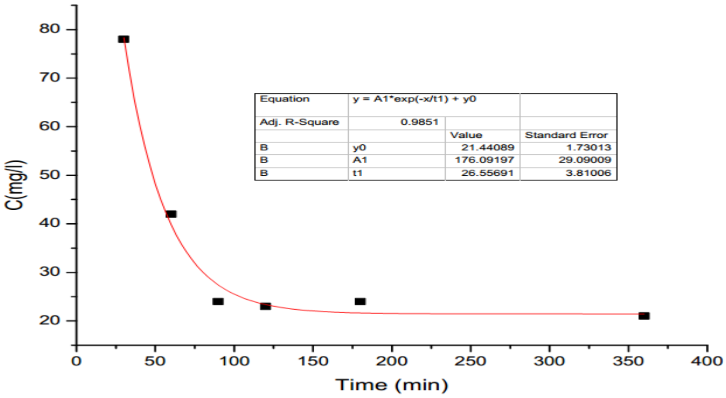
G is the weight of Bentonite, g.

To determine the equilibrium time, the Erlenmeyers containing the mixture of bentonite with solutions were shaken for different interval of time (10 minutes, 30 minutes, 60 minutes, 120 minutes and 180 minutes and 6 hours). After each interval of time the mixture was centrifuged to get solution for AAS analysis to determine the Cs concentration. The sorption was considered to be at the equilibrium if the Cs concentration in solution was unchanged.

III. RESULTS AND DISCUSSIONS

A. The Equilibrium time

Figure 2 depicted the change of Cs concentration in solution with time.



Equation	y = A1*exp(-x/t1) + y0		
Adj. R-Square	0.9851		
		Value	Standard Error
B	y0	21.44089	1.73013
B	A1	176.09197	29.09009
B	t1	26.55691	3.81006

Fig.2. The change of Cs concentration in solution in different periods of time

As seen from figure 2, the period of 120 minutes can be considered as the time to reach the adsorption equilibrium. This interval of time is applied for the experiments of the adsorption of Cs on bentonite.

B. Adsorption isotherms

To evaluate the adsorption ability of Cs on bentonite, Langmuir isotherm model and Freundlich isotherm model were used in the study. Based on experimental data, the typical parameters of adsorption process were determined by using linear regression method.

The Langmuir equation is given by

$$q_e = q_m k_a C_e/(1+k_a C_e) \qquad (2)$$

Linear form is $C_e/q_e = (1/q_m)C_e + 1/(k_a q_m)$ (3)

Where:

q_e is the contentof ion adsorbed (mg/g) corresponding to C_e;

C_e is the equilibrium concentration (mg/l);

q_m is max adsorption capacity (mg/g); k_a is adsorption equilibrium constant.

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/(k_a q_m)$

The Freundlich equation is given by

$$q_e = K_f C_e^{1/n} \quad (4)$$

Linear form is:

$$\ln q_e = (1/n)\ln C_e + \ln K_f \quad (5)$$

Where: K_f and n are constants

Table I presented the equilibrium data of Cs in solution and on the adsorbent- bentonite.

Table I. Equilibrium data of Cs adsorption from in solution containing H3BO3 (120 mg/l) and NaOH (90 mg/l) onto bentonite

V solution (ml)	100	100	100	100	100	100
$M_{Bentonite}$ (g)	0,1	0,1	0,1	0,1	0,1	0,1
C_0 (mgCs/l) (Initial concentration)	10	20	30	40	50	60
$C_{after\ adsorption}$ (C_e, mg/l)	**9,13**	**18,36**	**27,67**	**36,97**	**46,37**	**56,34**
M_{Cs}(mgCs/gBentonite) (q_e, mgCs/g)	**0,87**	**1,64**	**2,33**	**3,03**	**3,63**	**3,66**

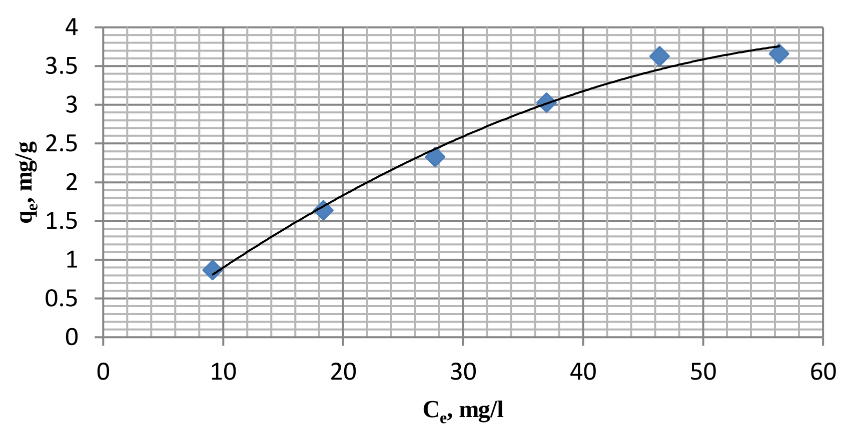


Fig.3. The isotherm of Cs adsorption onto bentonite from a solution of H_3BO_3 (120 mg/L) and NaOH (90 mg/L) in solid phase

Figure 3 depicted the isotherm of the adsorption of Cs from solution of H_3BO_3 (120 mf/L) and NaOH (90 mg/L) onto bentonite.

Table II presented the results of the Table.I but was modified to elucidate whether the Cs adsorption follows the Langmuir or Freundlich models. Figure 3 and 4 showed the relationship of C_e and q_e by the Langmuir (eq.3) and Freundlich (eq.5), respectively.

Table II. The value of C_e/q_e, lnq_e, lnC_e that were derived from the results of table I

$C_{equilibrium}$ (C_e,mg/l)	**9,13**	**18,36**	**27,67**	**36,97**	**46,37**	**56,34**
M_{Cs}(mgCs/gBentonite) (q_e, mgCs/g)	0,87	1,64	2,33	3,03	3,63	3,66
C_e/q_e	10,49	11,19	11,87	12.20	12.77	15,39
Lnqe	-0,14	0,49	0,84	1,10	1,28	1.29
LnCe	2,21	2,91	3,32	3,61	3,84	4,03

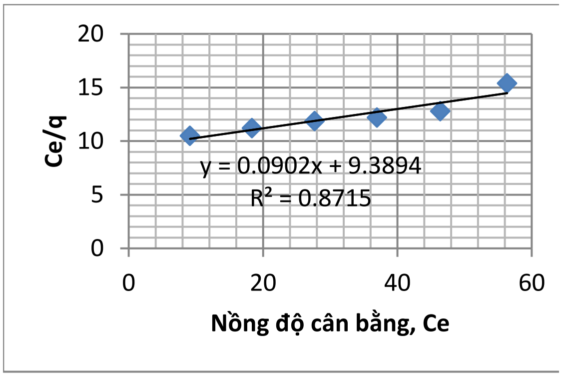


Fig.4. Langmuir isotherm in linear form

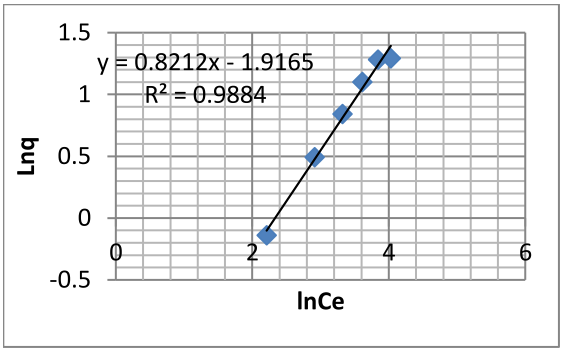


Fig.5. Freudlich isotherm in linear form

As seen from Fig.3 and Fig.4 the correlation coefficients (R^2) for the Freundlich model was higher (R^2=0.988) than that for the Langmuir model (R^2 =0.871) suggesting that adsorption followed the former model. Therefore the equation describing the equilibrium according to Freundlich model is given by:

$$Lnq_e = 0,821lnC_e – 1,916$$

And the constants K_f and n can be calculated as follows:

$$lnK_f = -1,916 \rightarrow K_f = 0,147$$

$$1/n = 0,821 \rightarrow n = 1,218$$

And the adsorption model is

$$q = K_f.C^{1/n} = 0,147C^{0,821}$$

IV. CONCLUSIONS

The equilibrium time for the adsorption of Cs from the solution of boric acid 120g/l and NaOH 90g/l on the Lam Dong bentonite was examined and found to be 120 min. The adsorption follows the Freundlich model with a maximum adsorption capacity of 4 mg/g.

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