Contents lists available at ScienceDirect

Nuclear Engineering and Technology

journal homepage: www.elsevier.com/locate/net

Original Article

Decontamination of radioactive wastewater by two-staged chemical precipitation

Ahmet E. Osmanlioglu

Department of Mining Engineering, Istanbul University, Avcilar 34320, Istanbul, Turkey

A B S T R A C T

This article presented two-staged chemical precipitation for radioactive wastewater decontamination by using chemical agents. The total amount of radioactive wastewater was 35 m^3, and main radionuclides were Cs-137, Cs-134, and Co-60. Initial radioactivity concentration of the liquid waste was 2264, 17, and 9 Bq/L for Cs-137, Cs-134 and Co-60, respectively. Potassium ferrocyanide, nickel nitrate, and ferrum nitrate were selected as chemical agents at high pH levels 8–10 according to the laboratory jar tests. After the process, radioactivity was precipitated as sludge at the bottom of the tank and decontaminated clean liquid was evaluated depending on discharge limits. By this precipitation method decontamination factors were determined as 66.5, 8.6, and 9 for Cs-137, Cs-134, and Co-60, respectively. By using the potassium ferrocyanide, about 98% of the Cs-137 was removed at pH 9. At the bottom of the tank, radioactive sludge amount from both stages was totally 0.98 m^3. It was transferred by sludge pumps to cementation unit for solidification. By chemical processing, 97.2% of volume reduction was achieved. The potassium ferrocyanide in two-staged precipitation method could be used successfully in large-scale applications for removal of Cs-137, Cs-134, and Co-60.

© 2018 Korean Nuclear Society, Published by Elsevier Korea LLC. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Removal of radioactive contaminants from radioactive liquid waste is one of the basic methods of radioactive waste management. By this method, a majority of liquid waste could be reused or safely discharged to the environment. One of the removal processes is chemical precipitation and separation of the radionuclide from the wastewater. This process is used in hydrothermal reprocessing of liquid radioactive wastes from nuclear power plants [1]. In addition, determination of radio cesium in environmental water samples by using copper ferro(II)cyanide and sodium tetraphenylborate is another application of this method [2]. Many organic and inorganic materials are used for removal of radioactive cesium from liquid waste [3]. Selectivity [4] and [5] ion exchange mechanisms are determined [6]. By using a calix crown ether, removal efficiency of cesium ions from aqueous solution are investigated [7]. Potassium iron(III) hexacyanoferrate(II) supported on polymethylmethacrylate [8], adsorption–microfiltration process with potassium zinc hexacyanoferrate [9], and solution using nano-zirconium vanadate ion exchanger [10] are other research studies for cesium removal from

liquid waste. Large-scale implementations were carried out for radioactive liquid wastes by using oxalic acid and titanium tungstate ion exchanger [11,12]. Removal of a radioactive contaminant from the liquid waste is a common problem of all these investigations. Removal of radioactive contaminants from the wastewater is important to avoid additional cost and radiological risks. By application of this method, transportation would be limited to only reduced volume of the radioactive bottom sludge. By application of the precipitation process, the volume of the sludge is extremely smaller than the total liquid amount. Most of the radioactivity was precipitated by chemical agents to the bottom sludge, and a large amount of clean liquid could be discharged. In this study, a two-staged chemical precipitation technique using potassium ferrocyanide, nickel nitrate, and ferrum nitrate were applied to radioactive wastewater. Soluble nickel and ferrocyanide salt solutions were added simultaneously to precipitate $Ni_2Fe(CN)_6$ which ion exchanges some of the Ni for Cs. Ferrum nitrate was used as a coagulant carrier in precipitations and as soluble salts of both Fe(II) and Fe(III) in the initial precipitation reaction.

2. Material and methods

In this study, a spectrometric analysis system was used to determine activity concentrations. The system consisted of a

E-mail address: ahmet.osmanlioglu@istanbul.edu.tr.

coaxial-type high-purity germanium detector that was linked to a multichannel buffer consisting of an analog-to-digital converter. For data acquisition, ACCUSPEC was used as the multichannel analyzer software. The energy resolution full width at half maximum (FWHM) observed in the measurements was 1.8 keV at the 1.33 MeV Co-60 reference transition. Counting times were arranged up to 20,000 s to provide sufficient counting statistics. The detector was surrounded by lead and copper that provide an efficient suppression of background γ radiation present at the laboratory.

Radioactive homogeneity was important for the determination of actual specific radioactivity of the wastewater. Homogeneity was maintained by a portable air jet mixing in the tank during sampling. After mixing, wastewater samples were taken from different parts and levels of the tank. Three samples from different layers of the tank were taken. Initial specific radioactivity of the wastewater was determined as 2,264, 17, and 9 Bq/L for Cs-137, Cs-134, and Co-60, respectively, by analyzing of the samples which were taken from the tank. Experimental studies were used for selection of the best chemical precipitation conditions by using jar test. The jar test was applied to all samples, and precipitation sludge of each sample was analyzed by using gamma spectrometry system. Potassium ferrocyanide, nickel nitrate, and ferrum nitrate were selected as chemical agents at high pH levels 8−10 according to laboratory jar test results. In this study, potassium ferrocyanide, nickel nitrate, and ferrum nitrate were used as chemical agents during chemical precipitation. Potassium ferrocyanide and ferrum nitrate were selected as chemical agents on chemical precipitation processes. Potassium ferrocyanide was selected for Cs-137 and Cs-134. Ferrum nitrate was selected for Co-60, and also nickel nitrate was chosen for supporting of precipitation process. Potassium ferrocyanide, also known as yellow prussiate of potash or potassium hexacyanoferrate(II), is a coordination compound of formula $K_4 [Fe(CN)_6]$ $3H_2O$. Optimum precipitation conditions were determined at the laboratory according to the different pH and a constant temperature (21°C). Decontamination factors (DFs) of each radionuclide versus pH levels were shown in Fig. 1.

According to the test results, pH levels between 8 and 10 were selected for application of chemical precipitation process.

2.1. Two-staged precipitation

According to jar test analysis results, chemical precipitation procedure was determined under facility conditions. Radioactive wastewater was decontaminated by two-staged chemical precipitation process (Fig. 2). Initially, wastewater properties (pH, temperature, and mixing time) were arranged according to jar test conditions in the tank. Then chemical precipitation procedure was applied in the tank. Chemical agents in the solid phase were converted to the liquid phase by mixi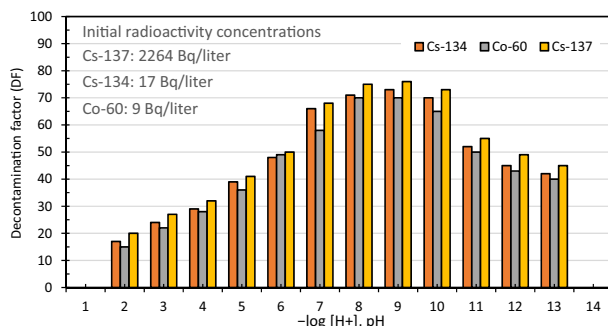ng with pure water before adding into the tank. During the mixing operation by air jet, initial pH level was determined by using portable pH meter. By slight addition of NaOH solution into the tank, the pH level was increased to 9. Then chemical agents were poured into the tank.

Chemical precipitation test in the laboratory was scaled up to the liquid wastewater tank as shown in Fig. 3. Wastewater pH level was stabilized at 9 by adding chemical agents. A constant mixing time (3 hour) and temperature (21°C) were recorded as main parameters during precipitation process. After 3 hour of mixing, the tank remained for settling. After 7 days, samples were taken from different levels of the tank. Radioactivity of the liquid at upper levels was almost zero.

Majority (33,550 L) of the wastewater was decontaminated at the first stage (Fig. 4). Radioactivity levels were increased regularly at starting from the upper clean liquid to the sludge. This transition zone (600 L) was sucked up from the tank for the secondary precipitation. The upper decontaminated liquid was pumped to outside tank for further control of environmental polluters.

Liquid from transition zone (600 L) was pumped outside to another tank for the secondary precipitation and settling. Transition zone liquid remained for further settling. After 7 days, decontaminated water was collected from the upper levels of the tank. Most (470 L) of the wastewater was decontaminated at the secondary stage (Fig. 5). The clean liquid was removed for further control of environmental polluters. The bottom sludge was again collected in drums for solidification process.

After precipitation process, samples were taken from the bottom sludge and analyzed by using gamma spectrometry system.

Decontaminated wastewater amount was calculated by using the following equation;

$$\text{Decontamination amount} = [(\text{Wastewater} - \text{Sludge})/ \text{Wastewater}] \times 100$$

$$\text{Decontamination amount} = [(35000 - 980)/35000] \times 100$$
$$= 97.2\%$$

At the end of this process, 97.2% of the wastewater was decontaminated and discharged.

Volumes and activities of the two-staged precipitation process were shown in Table 1.

According to the initial and final radioactivity of each radionuclide in wastewater DF values were determined as:

DF = Initial radioactivity/final radioactivity.
$DF_{Cs-137} = 2,264/34 = 66.5$.
$DF_{Cs-134} = 17.2/2 = 8.6$.
$DF_{Co-60} = 9/1 = 9$.

Decontamination factors (DFs) for each radionuclide was determined and presented in Table 2.

2.2. Solidification process

Liquid/solid ratio was determined as 0.80 L/kg by using a thermo analyzer. Cementation was used for solidification of the sludge. Cement/water ratio was taken as 0.50. Water amount in the sludge (980 L) was 784 L. For cementation, 300 kg cement with 60 kg sand was used. Cementation was carried out in drums by using in-drum mixing machine (Fig. 6).

During cementation, samples were taken from the concrete mixture for quality control. After cementation process, 5 cm of each drum was filled with pure cement paste to avoid contamination. Solidified drums and samples remained for 21 days in the facility
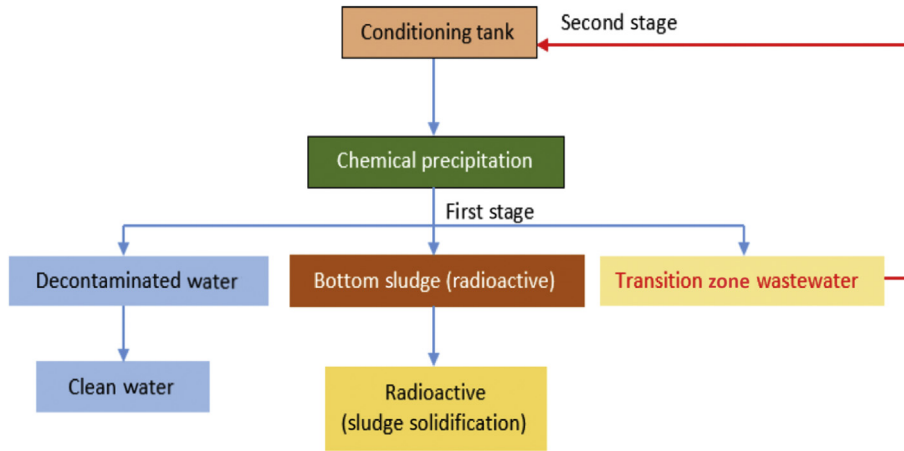

Fig. 1. Decontamination factors at different pH levels.

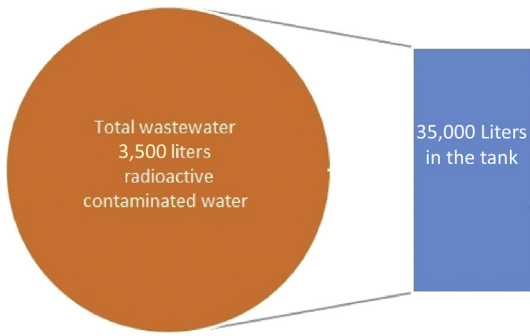**Fig. 2.** Two-staged chemical precipitation.

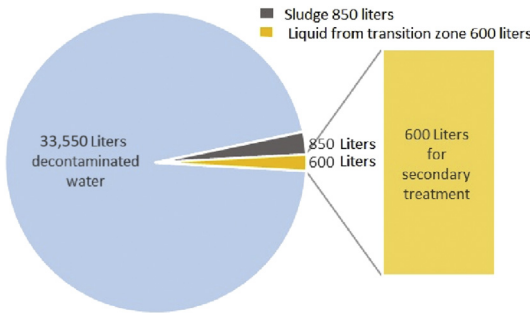**Fig. 3.** Chemical precipitation tank for radioactive wastewater.
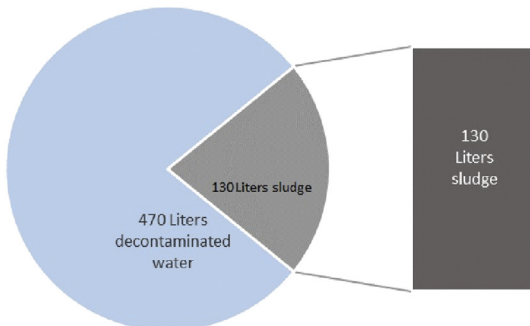

Fig. 4. First stage of chemical precipitation.

Fig. 5. Secondary chemical precipitation stage.

Table 1
Chemical precipitation process.

	Chemical precipitation process	Volume (L)	Specific activities (Bq/L)		
			Cs-134	Cs-137	Co-60
1	Total wastewater in the tank	35,000	17.2 ± 1	2264 ± 113	9 ± 0.5
2	Decontaminated water after the first process	33,550	7 ± 0.2	87 ± 1	3 ± 0.1
3	Transition zone liquid/sludge mix	600	10 ± 0.5	460 ± 50	5 ± 0.2
4	Sludge after the first process	850	12 ± 1	1780 ± 75	7 ± 0.3
5	Clean water at secondary settling tank	470	1 ± 0.2	10 ± 1	1 ± 0.1
6	Sludge at secondary settling tank	130	3 ± 0.3	450 ± 56	1 ± 0.1
7	Total discharged water	34,020	2 ± 0.2	34 ± 5	1 ± 0.1
8	Total Sludge	980	15 ± 1	2210 ± 100	8 ± 0.3

for curing. After 21 days, uniaxial compressive strength tests were applied to the samples. Samples for uniaxial compressive strength tests were obtained by preparation of mixtures and by using 50 mm diameter cylindrical molds with a height of 120 mm. For uniaxial compressive strength tests, procedures were followed according to American Society for Testing and Materials (ASTM C39-86) standard [13]. Preliminary testing of grout compressive strength is used as a classical method, which is practiced in civil engineering. NX type of cylindrically shaped grout samples with 50 mm diameter and 120 mm height were prepared. The uniaxial compressive strength of the samples was calculated as MPa, and mechanical test results were determined as in the range of 15–25 MPa. Mechanical stability level of cemented waste form has vital importance in long-term storage. In addition, leaching is another important parameter for solidified waste form in radioactive waste management [14]. Surface radiation rates of drums were measured between 150–250 μR/hour. After surface contamination controls of drums,

Table 2
Decontamination factors.

Radionuclides	Initial specific radioactivity (Bq/L)	Final specific radioactivity (Bq/L)	Decontamination factor
Cs-134	17.2 ± 1	2 ± 0.2	8.6
Cs-137	2264 ± 113	34 ± 5	66.5
Co-60	9 ± 0.5	1 ± 0.1	9

Fig. 6. Radioactive sludge in a drum.

final parameters were evaluated as convenient for transporting them safely to the storage facility.

3. Discussion

Although DF results of the laboratory test of Cs-137, Cs-134, and Co-60 have been found higher (70–76) than the DF values of the large-scale chemical precipitation, radioactive wastewater was decontaminated successfully by using potassium ferrocyanide, nickel nitrate, and ferrum nitrate. DF value of Cs-137 was determined as 66.5. Radioactivity levels of Cs-134 and Co-60 were significantly lower than Cs-137. For this reason, DF values of Cs-134 and Co-60 contaminants have not reached to test values because of their low radioactivity. Radioactivity level is significant parameter to determine reliable DF values. In this study, Most of wastewater (97.2%) was decontaminated, and it could be discharged as clean water. Radioactive sludge volume became extremely small when compared to the initial amount of wastewater. By this method, transportation of sludge in drums is more economical and safer method than initial transportation of wastewater. Although DF

values could be different for each of applications related to main specifications of original liquid waste, this study confirms that removal of radioactive contaminants from wastewater by using potassium ferrocyanide, nickel nitrate, and ferrum nitrate is not only a cost-effective method but also reduces radiological risks as well.

Conflict of interest

All authors have no conflicts of interest to declare.

Acknowledgment

References

[1] V. Avramenko, A. Voit, A. Golub, V. Dobzhansky, A. Egorin, V. Maiorov, V. Sergienko, S. Shmatko, Y. Korchagin, Hydrothermal reprocessing of liquid radwastes from nuclear power plants, At. Energy 105 (2008) 150–154.

[2] L. Popov, I. Kuleff, R. Djingova, Determination of radiocesium in environmental water samples using copper Ferro(II)cyanide and sodium tetraphenylborate, J. Radioanal. Nuclear Chem. 269 (2006) 203–207.

[3] A. Mollah, A. Begum, M. Rahman, Removal of radionuclides from low-level radioactive liquid waste by precipitation, J. Radioanal. Nuclear Chem. 229 (1998) 187–189.

[4] E. Lee, J. Lim, D. Chung, H. Yang, K. Kim, Selective removal of Cs and Re by precipitation in a Na_2CO_3-H_2O_2 solution, J. Radioanal. Nuclear Chem. 284 (2010) 387–395.

[5] J. Mertz, E. Manos, M. Kanatzidis, Selective radionuclide (Cs^+, Sr^{2+}, and Ni^{2+}) ion-exchange by $K_{2x}Mg_xSn_{3-x}S_6$ (x=0.5-0.95) (KMS-2), Mater. Res. Soc. Symp. Proc. 1265 (2010) 53–58.

[6] G. Ibrahim, Removal of ^{60}Co and ^{134}Cs radionuclides from aqueous solution using titanium tungstate ion exchanger, Desalin. Water Treat. 13 (2010) 418–426.

[7] C. Xu, L. Yuan, X. Shen, M. Zhai, Efficient removal of cesium ions from aqueous solution using a calix crown ether in ionic liquids: mechanism and radiation effect, Dalton Trans. 39 (2010) 3897–3902.

[8] S. Taj, D. Muhammad, M. Chaudhry, M. Mazhar, Lithium, rubidium and cesium ion removal using potassium iron(III) hexacyanoferrate(II) supported on polymethylmethacrylate, J. Radioanal. Nuclear Chem. 288 (2011) 79–88.

[9] C. Zhang, P. Gu, J. Zhao, D. Zhang, Y. Deng, Research on the treatment of liquid waste containing cesium by an adsorption-microfiltration process with potassium zinc hexacyanoferrate, J. Hazard. Mater. 167 (2009) 1057–1062.

[10] M. Abd El-Latif, M. Elkady, Kinetics study and thermodynamic behavior for removing cesium, cobalt and nickel ions from aqueous solution using nano-zirconium vanadate ion exchanger, Desalination 271 (2011) 41–54.

[11] M. Poirier, M. Hay, D. Herman, K. Crapse, G. Thaxton, S. Fink, Removal of sludge heels in Savannah river site waste tanks with oxalic acid, Sep. Sci. Technol. 45 (2010) 1858–1875.

[12] M. Duignan, C. Nash, Removal of cesium from Savannah river site waste with spherical resorcinol formaldehyde ion exchange resin: experimental tests, Sep. Sci. Technol. 45 (2010) 1828–1840.

[13] ASTM, Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, The American Society for Testing and Materials, 1986. ASTM C39-C86.

[14] M. Ojovan, G. Varlackova, Z. Golubeva, O. Burlaka, Long-term field and laboratory leaching tests of cemented radioactive wastes, J. Hazard. Mater. 187 (2011) 296–302.