

In-Situ Chemical Precipitation of Radioactive Liquid Waste-12492

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ABSTRACT

This paper presented in-situ chemical precipitation for radioactive liquid waste by using chemical agents. Results are reported on large-scale implementation on the removal of ^{137}Cs , ^{134}Cs and ^{60}Co from liquid radioactive waste generating from Nuclear Research and Training Centre. Total amount of liquid radioactive waste was 35 m³ and main radionuclides were Cs-137, Cs-134 and Co-60. Initial radioactivity concentration of the liquid waste was 2264, 17 and 9 Bq/liter for Cs-137, Cs-134 and Co-60 respectively. Potassium ferro cyanide was selected as chemical agent at high pH levels 8-10 according to laboratory tests. After the process, radioactive sludge precipitated 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 60, 9 and 17 for Cs-137, Cs-134 and Co-60 respectively. At the bottom of the tank radioactive sludge amount was 0.98 m³. It was transferred by sludge pumps to cementation unit for solidification. By in situ chemical processing 97% of volume reduction was achieved. Using the optimal concentration of 0.75M potassium ferro cyanide about 98% of the ^{137}Cs can be removed at pH 8. The Potassium ferro cyanide precipitation method could be used successfully in large scale applications with nickel and ferrum agents for removal of Cs-137, Cs-134 and Co-60.

INTRODUCTION

Removal of radioactive contaminants from radioactive liquid waste is one of the basic methods of radioactive waste management. By this method, majority of liquid waste could be reused or discharged to the environment. One of the removal processes is chemical precipitation and separation of radionuclide in the liquid waste. This process is used in hydrothermal reprocessing of liquid radioactive wastes from nuclear power plants [1]. In addition, determination of radiocesium in environmental water samples by using copper ferro(II)cyanide and sodium tetraphenylborate, is other application field 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] and [12]. Removal of radioactive contaminant from the liquid waste is common problem of all these investigations. In this study new removal technique and different chemical agents were applied on radioactive liquid waste at Nuclear Research and Training Centre (NRTC). Underground radioactive liquid waste tanks are used for collection of liquid wastes. These tanks should be emptied before filling up in a short time for further using. Otherwise it causes to interrupt related waste generation operations. Radioactivity concentrations in the liquid waste tank were 2264, 17 and 9 Bq/liter for Cs-137, Cs-134 and Co-60 respectively.

Instead of transportation of all liquid waste to facility for treatment from the tank, in situ chemical precipitation was applied to avoid additional cost and radiological risks. By this way,

transportation would be limited only bottom sludge. Volume of the sludge is extremely smaller than total liquid amount by application of in-situ precipitation process. Most of the radioactivity was precipitated by chemical agents to the bottom sludge and large amount of clean liquid could be removed. Radioactive homogeneity was important for determination of actual specific radioactivity of the liquid waste. Homogeneity was maintained by a portable air jet mixing in the tank. After mixing, liquid waste samples were taken from different parts and levels of the tank. All samples were analyzed by using gamma spectrometry system. Potassium ferro cyanide, nickel nitrate and ferrum nitrate were selected as chemical agents at high pH levels 8-10 according to laboratory tests. Potassium ferrocyanide, also known as yellow prussiate of potash or potassium hexacyanoferrate(II), is a coordination compound of formula $K_4[Fe(CN)_6] \cdot 3H_2O$. According to analyze results, chemical precipitation procedure was determined at laboratory conditions. Experimental studies were used for selection of the best chemical precipitation conditions. Chemical precipitation in the laboratory was scale up to the liquid waste tank. Initially, liquid waste properties were arranged to laboratory conditions in the tank. Then in-situ chemical precipitation procedure was applied.

EXPERIMENTAL METHOD

Initial specific radioactivity of the liquid waste was determined by analyzing of the samples which were taken from the tank. In this study, a spectrometric analysis system was used to determine activity concentrations. The system consisted of a coaxial-type high-purity germanium (HPGe) detector that was linked to a multi-channel buffer (MCB) consisting of an analog-to-digital converter (ADC). For data acquisition, ACCUSPEC was used as the multi-channel analyzer software. The energy resolution (FWHM) observed in the measurements was 1.8 keV at the 1.33 MeV ^{60}Co 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.

In this study, different chemical agents were used as in radioactive waste management. Potassium ferro cyanide and ferrum nitrate were selected as chemical agents on chemical precipitation processes. Potassium ferro cyanide was selected for Cs-137 and Cs-134. Ferrum sulphate was selected for Co-60 and also nickel nitrate was chosen for supporting of precipitation process. Temperature was recorded as 21°C. Chemical agent amounts and pH levels were selected as main parameters with a constant mixing time and temperature. Optimum precipitation conditions were determined at the laboratory according to the main parameters (Fig.1).



Fig 1. Chemical precipitation test for radioactive liquid waste.

Decontamination Factors (DF) for each radionuclide was calculated by the initial and final activity of the radionuclide. Decontamination factor of each sample versus pH levels were shown in Fig 2. Sample S4 parameters were selected for application of in-situ chemical precipitation process.

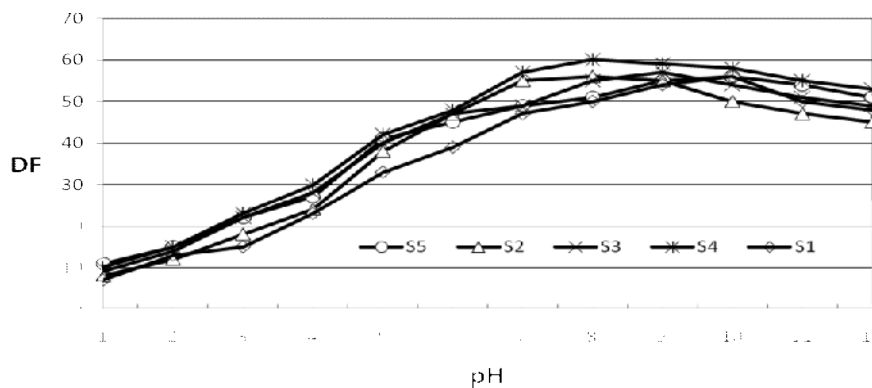


Fig 2. Decontamination factors at different pH levels.

In-Situ Chemical Precipitation

Chemical agents in the solid phase were taken into liquid phase by mixing 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 slightly addition of NaOH solution into the tank pH level was increased to 8. Then chemical agents were poured into the tank. After 3 hours of mixing, tank was 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. Activity levels were increased regularly at transition level between the liquid and the sludge. Upper decontaminated liquid was pumped to outside tank for further control of environmental pollutants. Liquid from transition zone was pumped outside to another tank for further settling and the sludge was taken to drums for solidification process. Clean liquid was evaluated according to EPA limits for discharging to environment and discharged. Transition zone liquid was remained for two weeks for further settling and upper clean liquid was taken for analyze and discharge. Sludge was taken to drums for solidification process. Drums were transported to waste processing facility. Total amounts of the sludge and liquid was shown in Table I.

Table I. In-Situ Chemical Precipitation Process.

In-Situ Chemical Precipitation Process	Volume (liter)	Specific activities (Bq/lit)		
		Cs-134	Cs-137	Co-60
Total liquid waste in the tank	35000	17.2 ± 1	2264 ± 113	9 ± 0.5
Decontaminated liquid after the first process	33550	1 ± 0.2	28 ± 1	0 ± 0.1
Transition zone liquid/sludge mix	600	6 ± 0.5	460 ± 50	2 ± 0.2
Sludge after the first process	850	12 ± 1	1780 ± 75	6 ± 0.3
Clean liquid at secondary settling tank	470	1 ± 0.2	10 ± 1	0 ± 0.1
Sludge at secondary settling tank	130	3 ± 0.3	450 ± 56	1 ± 0.1
Total discharged liquid	34020	2 ± 0.2	38 ± 5	1 ± 0.1
Total Sludge	980	15 ± 1	2210 ± 100	8 ± 0.3

Decontamination factor of each radionuclide was shown in Table II. At the end of this process, 97.2% of the liquid waste amount was decontaminated and discharged.

Table II. Decontamination Factors

Radionuclides	Initial Specific Radioactivity (Bq/lit)	Final Specific Radioactivity (Bq/lit)	Decontamination Factor (DF)
Cs-134	17.2 ± 1	2 ± 0.2	9
Cs-137	2264 ± 113	38 ± 5	60
Co-60	9 ± 0.5	1 ± 0.1	9

Solidification Process

Sludge drums were transferred to waste treatment facility. Liquid/solid ratio was determined as 0.80 lt/kg by using thermo analyzer. Cementation was used for solidification of the sludge. Cement/water ratio was taken as 0.50. Water amount in the sludge (980 liters) was 784 liters. 300 kg cement with 60 kg sand was used for cementation. Cementation was applied in drums by using in-drum mixing machine (Fig 3 and Fig 4).



Fig 3. Radioactive sludge in drum.



Fig 4. In-drum mixer for cementation process.

After cementation process, 5 cm of each drum was filled with pure cement paste. Solidified drums and samples were remained for 21 days in the facility for curing. After 21 days, uni-axial compressive strength tests were applied on the samples. During cementation, samples were taken from the mixture for mechanical tests. Samples for uniaxial compressive strength tests were performed 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 cylindrical shaped grout samples with 50 mm diameter and 120 mm height were prepared. Manual loading compressive test machine was used. 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. In addition, leaching properties is other important parameter for solidified waste form in radioactive waste management [14]. Surface radiation rates of drums were measured between 150-250 $\mu\text{R/h}$. After surface contamination controls of drums, final parameters were evaluated as convenient for transporting them safely to storage facility.

RESULTS AND DISCUSSION

Although DF values of laboratory test were much higher than in-situ implementation, liquid radioactive waste was decontaminated successfully by using potassium ferro cyanide. Majority of liquid waste were discharged as clean liquid. %97.2 volumetric amount of liquid waste was cleaned and discharged at the original site. Reduced amount of sludge transportation in drums is more economical and safer method than liquid transportation. Although DF values could be different for each of applications related to main specifications of original liquid waste, this study shows that in-situ treatment of liquid waste by using potassium ferro cyanide is not only a cost effective method but also reduce radiological risks as well.

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