

CHEMICAL DECONTAMINATION OF SOIL CONTAMINATED WITH Cs-137

H. J. Won, G. N. Kim, C. H. Jung, W. K. Choi, M. G. Kim, W. Z. Oh and J. H. Park

Korea Atomic Energy Research Institute

P. O. Box 105, Yuseong, Taejon 305-600, Korea

nhjwon@kaeri.re.kr

ABSTRACT

The removal efficiency of several washing agents on the Cs⁺ ion was investigated. Leaching of Cs⁺ ion from the soil surface by washing agents is affected by the exchange capability of the washing solution. Reuse tests of the effective soil washing agents such as BaCl₂, NaOH, citric acid + HNO₃ and oxalic acid were performed. NaOH, citric acid + HNO₃ and oxalic acid solutions can be reused after passing through the ion exchange column. Among the tested solutions, both of citric acid + HNO₃ and oxalic acid were effective for the decontamination of TRIGA research reactor soil. The radioactivity of soils can be reduced to a release level by the successive application.

INTRODUCTION

Radioactively contaminated soil is one of the most common problems constraining cleanup at hazardous waste sites. There are many sites that contain soils contaminated with

heavy metals and low levels of radionuclides all over the world. In 1988, the radioactively contaminated soil was found around the research reactor site in Seoul. The soils were excavated, packed and moved to the temporary storage facility located in Korea Atomic Energy Research Institute. The excavated soils were stored in approximately 4,000 radioactive waste drums.

Many U. S. Department of Energy(DOE) sites are contaminated with radionuclides and heavy metals. Contamination exists in mixed wastes (any media containing hazardous and radioactive components), groundwater, surface soils, and subsurface soils. The volume of soil contaminated with radionuclides and/or heavy metals within the DOE complex is estimated to exceed 200 million m³ [1].

There are two main types of remediation for metal contaminated soils: (1) technologies that leave the radionuclides in the soil, and (2) technologies that remove the radionuclides from the soil[2]. Technologies such as solidification/stabilization and vitrification immobilize contaminants, thereby minimizing their migration. Techniques such as soil washing and in situ soil flushing transfer the contaminants to a liquid phase by desorption and solubilization. Soil washing can be a physical and/or chemical process that results in the separation and volume reduction of hazardous materials and the chemical transformation of contaminants to nonhazardous materials. In general, in situ technologies are more economical and are safer than ex situ technologies because excavation is not required.

Soil washing involves the separation of contaminants from soil solids by solubilizing them in a washing solution. The technology is generally an ex situ method. Soil washing usually employs washing solutions that contains acids, bases, chelating agents, or other additives. A chelant is a ligand that contains two or more electron-donor groups so that more than one bond is formed between the metal ion and the ligand. Citric acid forms 1:1 molar ratio

complexes with several metal ions. Acids and chelating agents are generally used to remove the radionuclides from soils, but the particular reagent needed can depend not only on the radionuclides involved but also on the specific radionuclide compound or species involved. The soil washing efficiency may be augmented by the addition of a surfactant, pH control agent and a chelating agent. A number of reagents have been used in decontamination efforts. The chelating agents are generally preferred since they form stable, soluble complexes with a variety of metal and radioactive nuclide ions. The most commonly used chelating agents in the nuclear industry are EDTA, NTA, DTPA, oxalic acid and citric acid.

In this study, leaching of Cs⁺ ion from soils gathered from the research reactor site using various soil washing agents. The feasibility study of reuse of various soil washing agents were discussed. The decontamination performances of citric acid and oxalic acid solutions on soils stored in the radioactive waste drums were also investigated.

EXPERIMENTAL

A. Removal efficiency of washing agents on the Cs⁺ ion

Soil was taken at a depth of 40 cm from an open grass field around the TRIGA MARK III in Seoul. The soil was air dried and passed through a 10 mesh (2mm) sieve for this study. It was treated with 1 M sodium acetate at pH 5 to remove surface carbonates, then treated with 20 % hydrogen peroxide to oxidize organic material[3]. The chemical composition of the soil was analyzed by X-ray fluorescence (Model; SIEMENS SRS 303). It was mainly composed of Si, Al, K, Na and oxygen. The X-ray diffraction analysis(Rigaku Denki Co., model; Reigerflex, with CuK radiation) of the soil was also carried out. As shown in Figure 1, the crystal structure of iron oxide in soil was found to be Fe₂O₃, FeO(OH) and Fe₃O₄.

The soil(100g) was contaminated with 250 ml of 0.01M Cs⁺ ion solution for 48 hrs at pH 5.4(25 oC). The soil (10 g) was used in a leaching test using 250 ml of various candidate solutions. The tested solutions are water, HCl, oxalic acid, citric acid, CaCl₂, BaCl₂, NH₄NO₃, NaOH and citric acid + HNO₃ solutions. The samples were shaken for about 3 hrs at 25 oC, centrifuged at 4000 rpm for 10 min, and then filtered (by injection) through a 0.2- m Whatman filter. Cesium ion concentration was determined by flame AAS (PERKIN ELMER, model; AAnalyst 300).

B. Reuse test of washing agent

Tests of reuse the soil washing agent were performed in an ion exchange column. Washing agents tested were BaCl₂, NaOH, oxalic acid and citric acid.

C. Decontamination of radioactive waste soil

Radioactive waste soil was taken from a radioactive waste drum. The two different size soils were used in the study. The bigger one is in the range from 1 to 2 mm, and the small one is in the range from 0.063 to 1 mm. 50 g of soil was immersed in 500 ml of decontamination solution. 0.05 M citric acid + 0.03 M HNO₃ solution and 0.5 M oxalic acid solution were used respectively as a decontamination solution. Decontamination of soil was conducted three times for each soil sample. The radioactivity of soils before and after decontamination was determined by gamma spectroscopy[Multichannel Analyzer(Canberra, Model 2024) with a high purity Ge-detector (Canberra, Model GC 3019)] and listed in Table 1. Counting time was 100,000 seconds. The predominant radioactive nuclides are Cs- 137 and Co-60.

Figure 1. XRD pattern of soil .

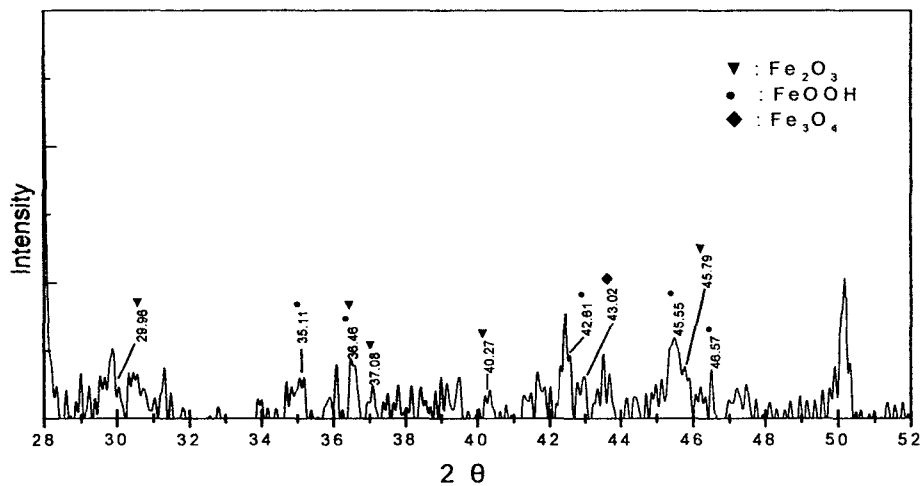


Table 1. Radioactivity of soil in a radioactive waste storage drum..

Soil Particle Diameter	Radionuclide	Radioactivity (Bq/kg)
0.063 – 1 mm	Cs-134,137	3069.1 ±2.7
	Co-60	920.6 ±5.5
	Cr-51	<7.3
	Fe-59	<6.2
	I-131	<2.3
	Mn-54	<1.5
	K-40	1623.1 ±77.6
1 – 2 mm	Cs-134, 137	1321.4 ±3.9
	Co-60	631.7 ±7.1
	Cr-51	<4.3
	Fe-59	< 5.5
	I-131	<1.7
	Mn-54	<3.6
	K-40	1363.5 ±75.5

RESULTS AND DISCUSSION

A. Removal efficiency of washing agents on the Cs⁺ ion

The TRIGA research reactor site soils artificially contaminated with Cs⁺ ion were subject to a series of batch shaker flask experiments to identify the candidate washing agents that showed good efficiency in removing Cs⁺ ion from the soils. The washing agents investigated included water, HCl, oxalic acid, citric acid, CaCl₂, BaCl₂, NH₄NO₃, NaOH and Citric acid + HNO₃. The removal efficiency of the washing agents on Cs⁺ ion is shown in Figure 2. The order of performance for Cs removal is HCl > BaCl₂ > NH₄NO₃ > Citric acid + HNO₃ > oxalic acid > CaCl₂ > NaOH > citric acid > water. The total molar concentration of Citric acid + HNO₃ solution is 0.08 M. It was reported that pH is the most important factor controlling adsorption and solubility of radionuclide metals in soil[4]. From the previous study, it was found that metal ions such as Fe, Ca, Mg and Al were dissolved out from soil in acidic solution[5]. Metal ions in neutral and alkaline solution, however, were hardly dissolved out. Figure 3-A and 3-B show the plot of pH change against time.

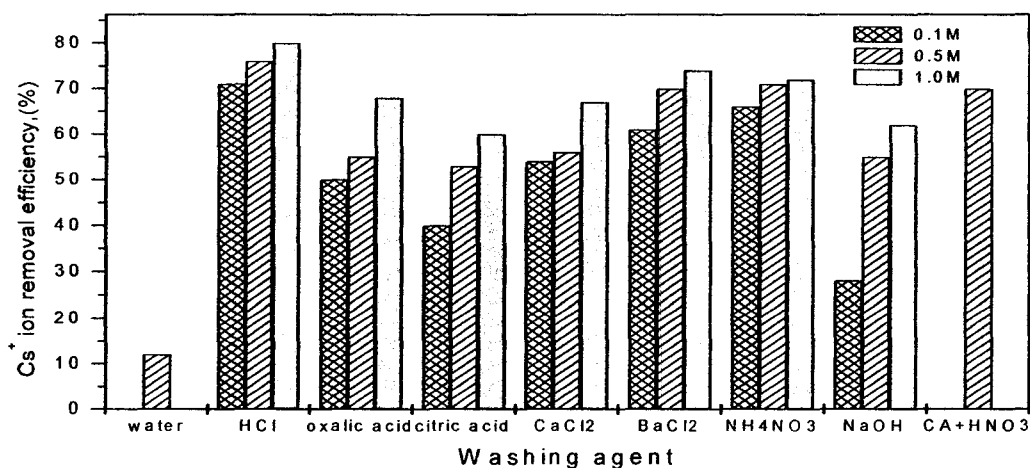


Figure 2. Cs Removal from soil.

As shown in Figure 3-a, the solution pH maintained around 4. The chemical species such as Ba, Ca and ammonium ion affect the Cs removal efficiency. Especially, the ionic radii of barium ion(13.5 nm) is almost same that of the cesium ion(16.9 nm). The main factor that affects the efficiency is supposed to be the ion exchange between positive ion and Cs ion on the soil surface. Figure 3-b also shows the similar results. In this case, the metal ion dissolved out from the soil surface is supposed to promote the Cs removal.

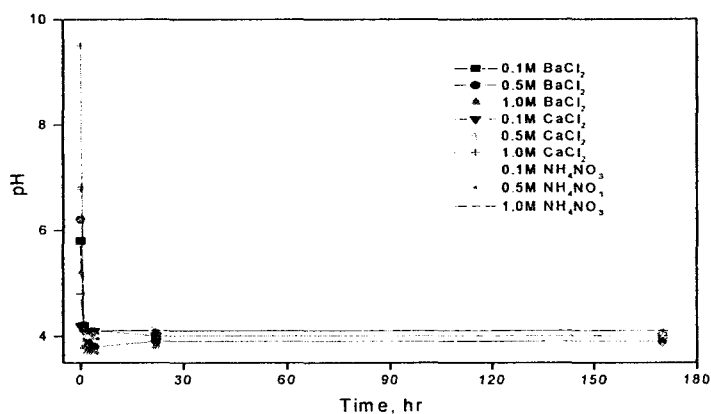


Figure 3-a. Change of solution pH against time.

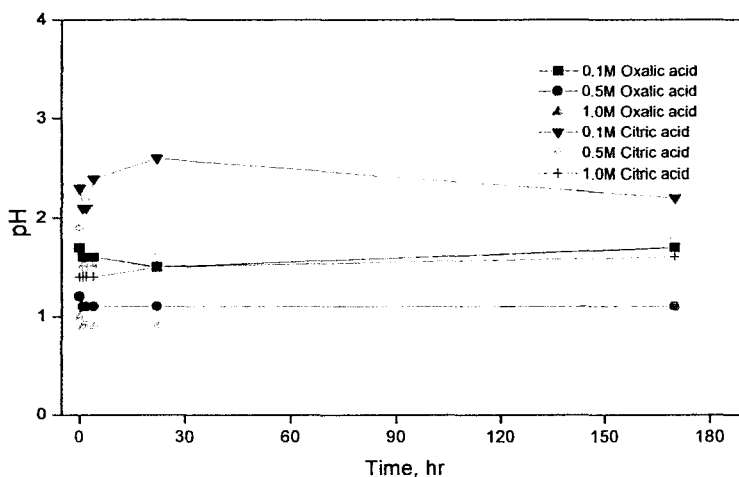


Figure 3-b. Change of solution pH against time.

B. Reuse of washing agents

Reuse tests were performed for the most probable washing agents

1) Reuse of BaCl₂

Figure 4 is the plot of the Cs ion concentration ratio against the bed volumes. The initial concentration of Cs⁺ ion was 0.0008 M and Ba²⁺ ion concentration was 0.1 M. Before the column test, H⁺ ion type cation exchange resin was changed to Ba²⁺ ion type. As shown in Figure 4, Cs⁺ ion is not removed effectively in an exchange column. Break through appears before the passage of 15 bed volumes. This means that Ba²⁺ ion washing agent cannot be reused.

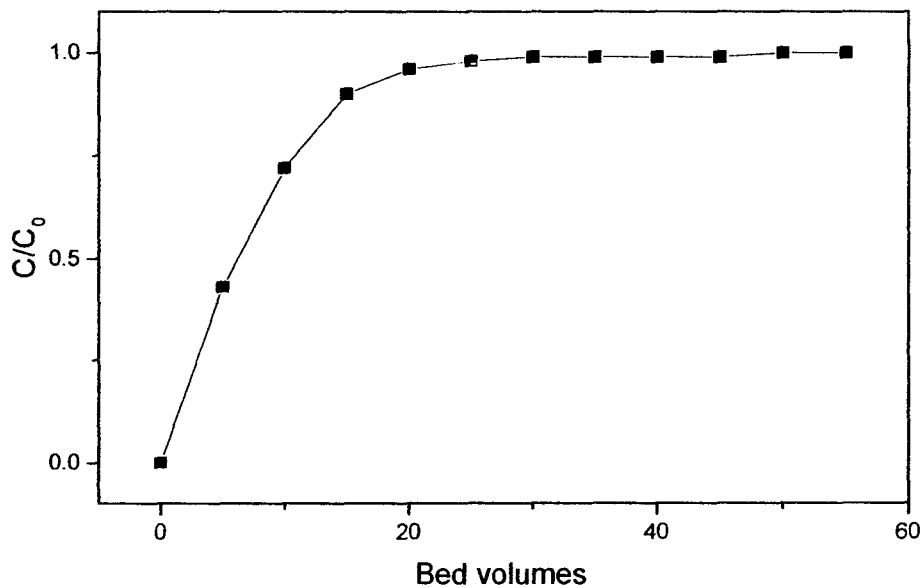


Figure 4. Breakthrough curve of Cs ion(bed volume: 4.2 ml, flow rate: 1ml/min, BaCl₂).

2) Reuse of NaOH

Figure 5 is the plot of the Cs ion concentration ratio against the bed volumes. The initial concentration of Cs⁺ ion was 0.0004 M and the concentration of NaOH was 0.5 M. Before

the column test, H⁺ ion type cation exchange resin was changed to Na⁺ ion type. As shown in Figure 5, Cs⁺ ion is removed effectively in an exchange column. Break through does not appear after the passage of 100 bed volumes. This means that Na⁺ ion washing agent can be reused on soil contaminated with Cs. But, this washing agent has a problem to participate Co-60 as Co(OH)₂.

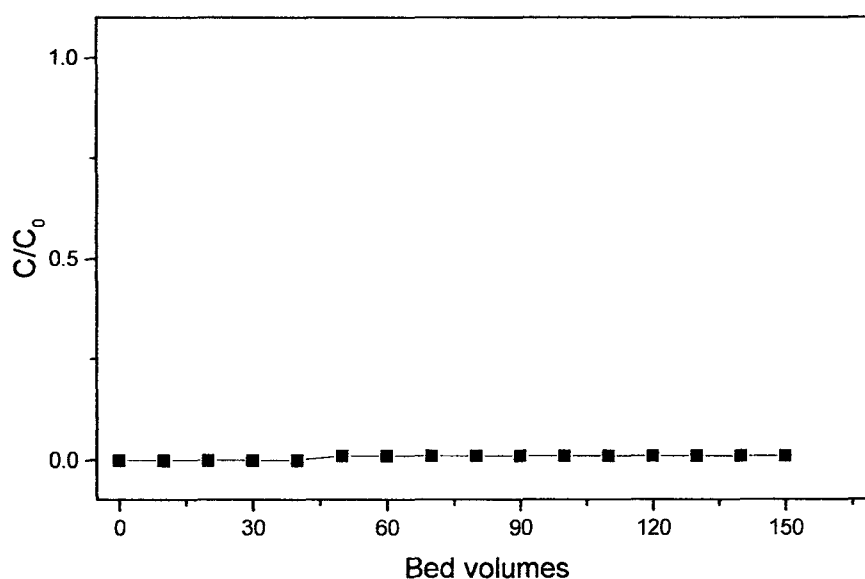


Figure 5. Breakthrough curve of Cs ion
(bed volume: 4.2 ml,flow rate: 1ml/min, NaOH).

3) Reuse of oxalic acid

Figure 6 is the plot of the metal ion concentration ratio against the bed volumes. The initial concentration of Ca²⁺, Mg²⁺, Fe³⁺ and Cs⁺ ion were 0.002, 0.002, 0.001 and 0.004 M, respectively. And the concentration of oxalic acid was 0.5 M. As shown in Figure 6, break through of Cs⁺ ion appeared after the passage of 55 bed volumes. Iron ion is not removed in a cation exchange column. In a separate test, it was found that iron ion was removed effectively

in an anion exchange column. As oxalic acid is an organic ligand, it can be reused for Cs and Co decontamination.

4) Reuse of citric acid

Figure 7 is the plot of the metal ion concentration ratio against the bed volumes. The initial concentration of Ca^{2+} , Mg^{2+} , Co^{2+} , Cs^+ and Fe^{3+} ion were 0.002, 0.002, 0.002, 0.004 and 0.001 M, respectively. The total concentration of citric acid + HNO_3 solution was 0.08 M. As shown in Figure 7, break through of Cs^+ ion appeared after the passage of 76 bed volumes. Contrary to the oxalic acid solution, iron ion is removed in a cation exchange column. As a result, citric acid can be reused for Cs and Co decontamination.

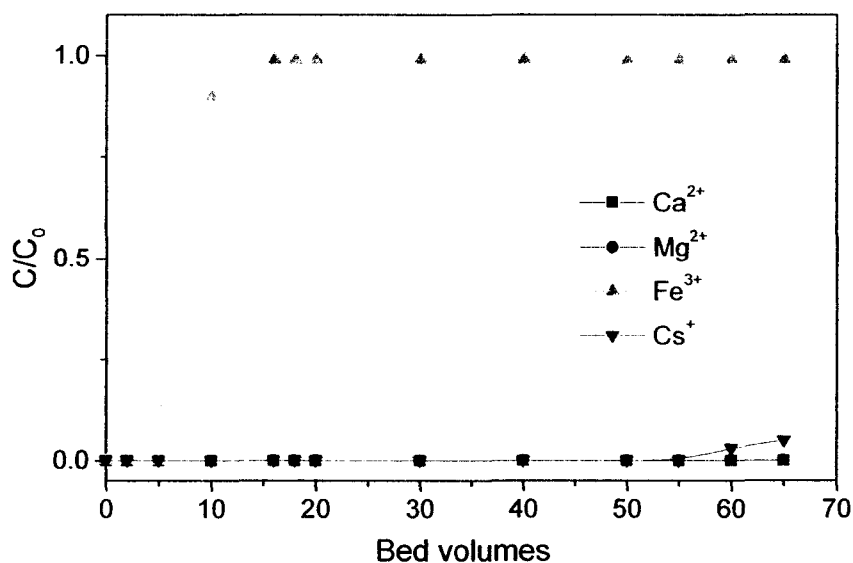


Figure 6. Breakthrough curve of various ions (bed volume:4.2 ml, flow rate: 1ml/min, oxalic acid).

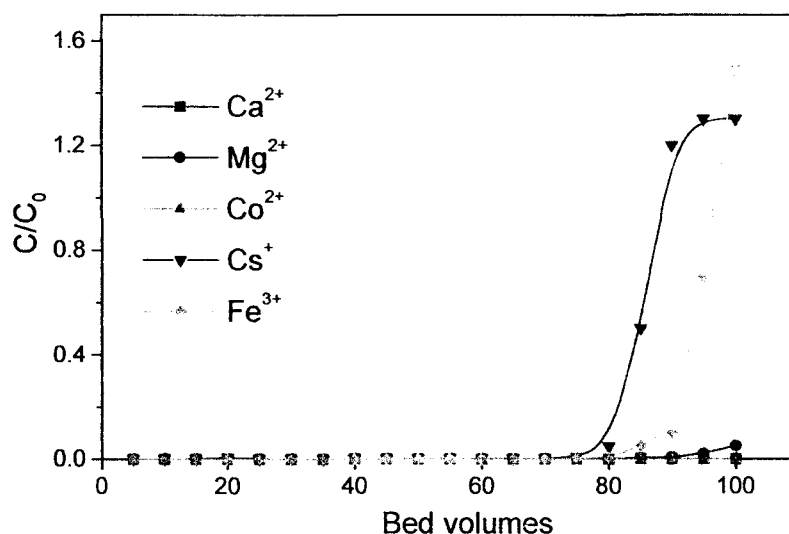


Figure 7. Breakthrough curve of various metal ions (bedvolume: 4.2 ml, flow rate: 1ml/min, citric acid).

C. Decontamination of radioactive waste soil

A plot of activity ratio of residual to initial Cs-134, 137 and Co-60 against the sequential extractions is shown in Figure. 8. As the number of extractions increases, the residual activity gradually decreases. Contrary to the former study[6], decontamination efficiency (the ratio of residual to initial radioactivity) on Co-60 ion is similar to that on Cs-134, 137. The complexing capability of citric acid and oxalic acid influences the decontamination efficiency on Co-60. Hydrogen ion of organic acid influences the decontamination efficiency on Cs-134, 137. The removed portion of Co and Cs of the real soil is less than the simulated the decontamination. This may be attributed to the aging effect.

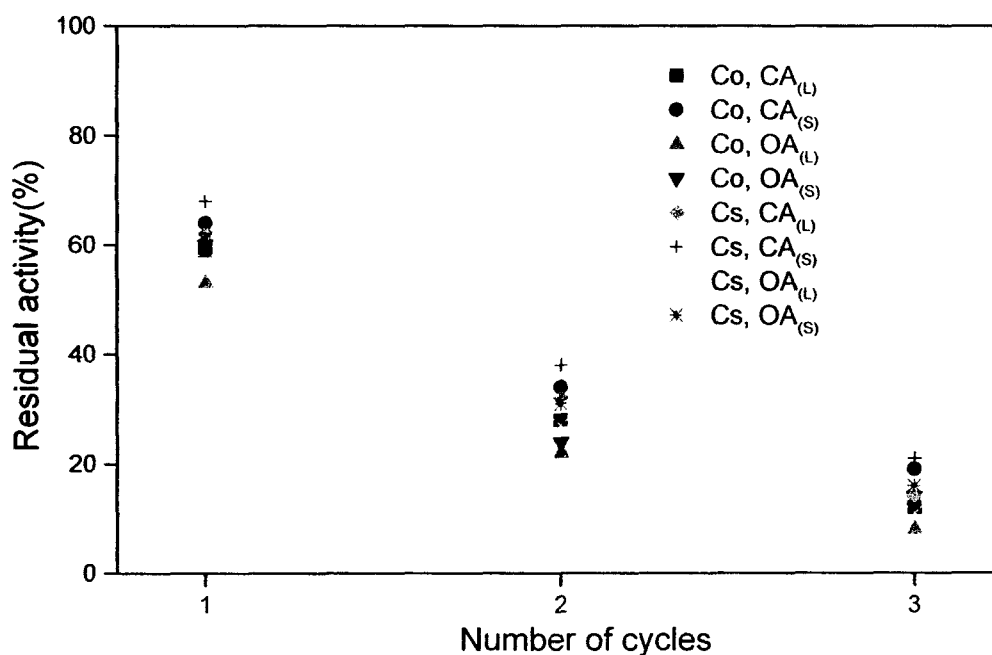


Figure 8. Residual activity remained in soil after 3 sequential extractions ([CA+ HNO₃] = 0.08M, [OA]= 0.5 M. pH = 1 at 25 °C).

CONCLUSION

Leaching of Cs⁺ ion from soil surface by the candidate washing agents is predominantly caused by the ion exchange capability of the agents. NaOH, citric acid + HNO₃ and oxalic acid are regenerated in an ion exchange column among the tested solutions. Although BaCl₂ and NaOH were effective for Cs removal, they can not be applied to the cobalt removal. The radioactive soils contaminated with Cs-37 and Co-60 were effectively decontaminated by the successive application of the decontamination agents such as citric acid + HNO₃ or oxalic acid. From the test results, we found that most of radioactive soils (> 80 %) stored in a temporary storage facility in KAERI can be decontaminated to a release level.

ACKNOWLEDGEMENTS

This work has been carried out under the Nuclear R & D Program funded by the Ministry of Science and Technology.

REFERENCES

1. U. S. Department of Energy, Office of Science and technology, Subsurface contaminants focus area: technology summary, DOE/EM-2096, August, 1996.
2. G. Rampley, K. L. Ogden, Preliminary studies for removal of lead from surrogate and real soils using a water soluble chelator: adsorption and batch extraction, *Environ. Sci. Technol.* 32(7), 1998.
3. T. J. Esters, R. V. Shah and V. L. Vilker, Adsorption of Low Molecular Weight Halocarbons by Montmorillonite, *J. Environ. Sci. Technol. Inc.*, 22(4), 1988.
4. Welp and G. W. Brummer, Adsorption and solubility of ten metals in soil samples of different composition, *J. Plant Nutr. Soil Sci.*, 162, 1999.
5. J. Won, W. K. Choi, G. N. Kim, C. H. Jung and W.Z Oh, Dissolution reaction of magnetite in citric acid solution, *J. Korean Ind. Eng. Chem.*, 14(5), 2003.
6. J. Won, G. N. Kim and W. Z. Oh, Chemical decontamination of soil contaminated with Co-60, *Proceedings of the 3rd Korea-China Radioactive Waste Workshop*, Shanghai, 2002.