
ARTICLE

Study on evaluation of applying flocculating agents for efficient decontamination of radioactively contaminated soil

Jong-Soon Song and Sun-Il Kim*

Chosun University, 309 Pilmun-Daero, Dong-Gu, Gwangju, 501-759, Republic of Korea

The cases where the soil is widely contaminated by radioactive material include nuclear power plant accidents, such as Chernobyl and Fukushima, and repair of NPPs. The key nuclide involved in soil contamination is Cs, and Cs is emitted in gaseous form during an NPP accident and contaminates a wide area. The methods of recovering soil contaminated by radioactive materials include soil washing and electro-kinetic. In this paper, the authors selected the soil washing process, used flocculating agents, and measured the removal rate of the fine soil and Cs ions which are strongly combined with Cs. When the flocculating agent was put into the aqueous solution containing the fine soil and cesium, the maximum removal rate was 88%, and the minimum removal rate was about 67%.

Keywords: Soil-washing; Visual MINTEQ; decontamination; cesium; flocculating agent

1. Introduction

The representative cases in which radioactive materials are emitted in the soil are NPP accidents and maintenance of NPPs. The nuclides, which get the most interest in such cases, are Cs-137 and I-131, and these nuclides are emitted in gaseous form and causes contamination of a wide area. In particular, as the radioactive cesium ion (Cs⁺) emitted in the soil is strongly combined with clay and organic and inorganic materials, they are difficult to decontaminate. In this paper, the soil washing method was selected among soil decontamination methods. Flocculating agents were injected during the soil washing process, and the cesium strongly combined with the fine soil was removed for the purpose of reducing the soil decontamination time [1, 2].

2. Soil decontamination methods and selections

2.1. Soil decontamination methods

Soil decontamination methods are divided into physico-chemical methods, such as soil washing, soil vapor extraction and electro-kinetic, and biological methods, such as phytoremediation, bioventing and land-farming [3].

2.2. Soil decontamination method selections

2.2.1 Application case of soil washing (Korea)

The representative process, used to decontaminate

soil contaminated with Cs is the soil washing method. This method was applied to decontamination of the soil TRIGA-Mark II&III, the research reactors of the Korea Atomic Energy Research Institute as shown in **Table 1** [4].

2.2.2 Application case of soil washing (U.S.)

Additionally, the international case was the decontamination of soil containing cesium-137 at the Oak Ridge National Lab. The US cases of soil washing are shown in **Table 2** [5].

Table 1. Application case of soil washing (Korea).

Soil Washing process(0.05mR/h)	Cs-137 (Removal rate)
Citric Acid 0.05M, 3 times repeated decontamination (0.063~1.0mm)	13.8 %
Citric 0.05M+Ammonium sulfate 0.2M, 3 times repeated decontamination (0.063~1.0mm)	40.6 %
Citric 0.05M+Ammonium Nitrate 0.2M, 3 times repeated decontamination (0.063~1.0mm)	38.8 %
Citric 0.05M+Ammonium Potassium Oxalate 0.2M, 3 times repeated decontamination (0.063~1.0mm)	3.1 %

*Corresponding author. Email: kingdom17c@naver.com

Table 2. Application case of soil washing (U.S.).

Site	Radio-nuclide	Pre-Treatment activity	Post-Treatment activity	Amount of Soil Treatment	Volume Reduction
Montclair-West Orange, New Jersey, 1996	Ra-226 U-235 U-238 Th-230	40 pCi/g	11 pCi/g	323,000 yd ³	54%
Oak Ridge National Lab.	Cs-137	Not available	Not available	25.5 tons	70%
Brunei Site, Texas	U, Ra	70 ppm (U)	20.7(U)	22,800 tons	99%
Maywood, Superfund Site, New Jersey	Th-232 Ra-226 U-238	34 pCi/g (Th) 8 pCi/g (Ra) 7 pCi/g (U)	1 pCi/g (Th) 1 pCi/g (Ra) 1 pCi/g (U)	8,000 tons	Not Available
Newpark Environment, Texas	Ra-226	100-700 pCi/g	< 5 pCi/g	2,700 drums	95%

3. Soil washing process and flocculating agent application experiment

3.1. Soil washing process

If cesium is exposed and combined with the soil, it is combined with silt and clay, making it difficult to separate them. Accordingly, in this experiment, flocculating agents were injected into the fine soil in the Waste Water Equalization Tank for particle separation during the soil washing process in order to remove cesium. The soil washing process is illustrated in **Figure 1**.

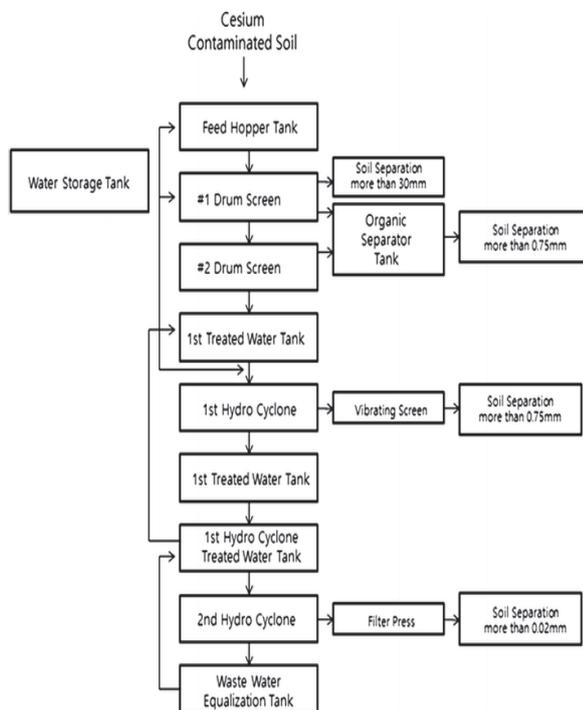


Figure 1. Soil washing process.

3.2. Flocculating agent

The Phyllite-based flocculating agent (J-AF) was selected for the cesium removal experiment. J-AF is a flocculating agent developed by Jeon Tech Co., Ltd. as part of the government project for wide-area soil decontamination. To examine the components of this flocculating agent, MSDS (Material Safety Data Sheets) analysis was conducted, and the components are listed in **Table 3**.

Table 3. Components of J-AF.

Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO
21.74	0.12	18.75	18.01	8.13
K ₂ O	Na ₂ O	SO ₃	Cl	OH
2.12	11.62	6.29	0.13	13.08

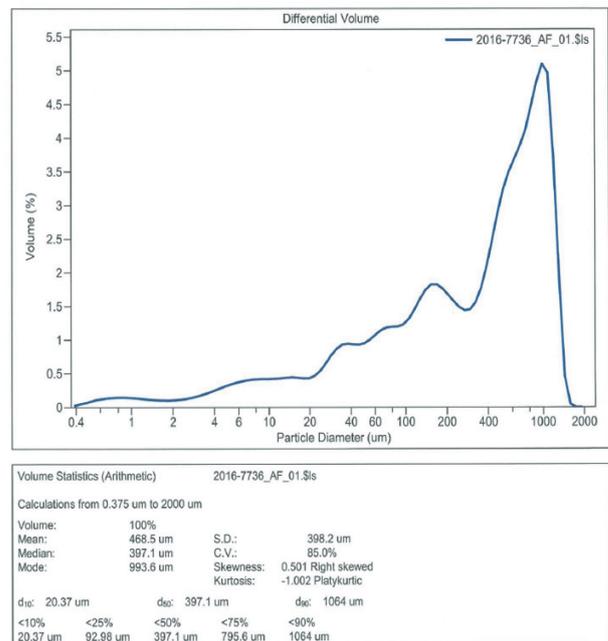


Figure 2. Particle size analysis of flocculating agent (J-AF).

3.3. Flocculating agent application experiment

Before the experiment, soil was collected from the site of Chosun University, and was separated with a 38µm sift. The sifted soil was dried for 20 minutes in a vacuum dryer. The 1g of dried soil was put in the 100mL of 10 mmol/L cesium solution made of CsNO₃ (99%, Sigma-Aldrich, USA). It was mixed for 24 hours under the conditions of pH6.5, 25°C and 250rpm.

In the first experiment, after the injection of the flocculating agent (J-AF), the degree to which the fine soil, combined with cesium, was removed over time was analyzed. 0.1g of the flocculating agent was injected into the conical tubes, containing 50mL of simulated cesium aqueous solution, with the initial concentration being 0.1, 1, 2, 5 and 10 mmol/L. The supernatant of the aqueous solution was extracted using the 0.2µm (Cellulose Nitrate Membrane Filter) filter. The extracted supernatant was used to analyze the concentration of the

residual cesium by means of ICP-OES (Optima 2100DV, PerkinElmer Co., USA). The cesium removal rate of the flocculating agent over time is shown in **Figure 2**.

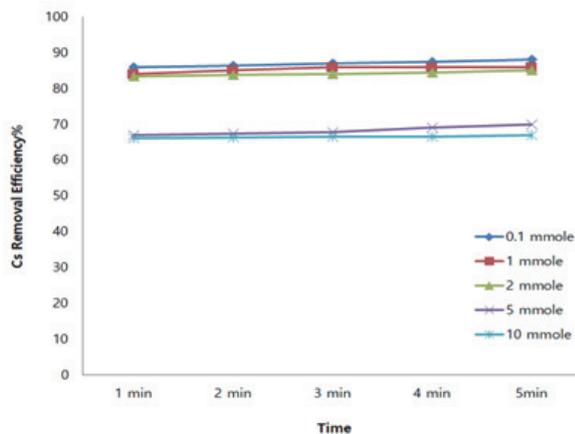


Figure 3. Flocculating agent removal rate performance over time.

In the second experiment, the cesium removal rate of the flocculating agent by cesium concentration was measured. The experiment was conducted in the same conditions as the first experiment, and the supernatant was extracted every minute a total of 5 times using the 0.2 μ m (Cellulose Nitrate Membrane Filter) filter, and the concentration of the residual cesium was measured with ICP-OES. The removal rate by cesium concentration is shown in **Figure 3**.

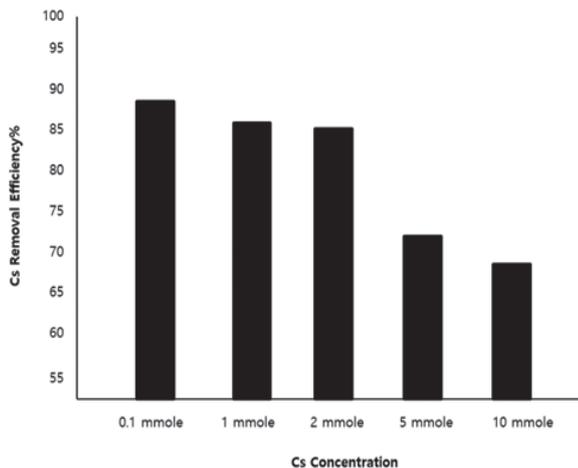


Figure 4. Flocculating agent removal rate performance for each Cs concentration.

3.4. Prediction of species bond by Visual MINTEQ

In this experiment, the flocculating agent was injected into the wash water during the soil washing process, and the fine soil, combined with cesium, was sedimented to reduce the decontamination and improve the efficiency of decontamination. The Visual MINTEQ Code, an adsorption isotherm code, was used to predict the degree of combination between the fine soil and Cs. Also, the degree to which the flocculating agent sedimented the fine soil in the wash water was analyzed through

measurement of turbidity.

The Visual MINTEQ Code is made using the MINTEQA2 software of U.S.EPA, and makes it possible to calculate equilibrium, sorption and adsorption in the aqueous solution. The components of the soil, collected from the school site, were applied to the Visual MINTEQ Code [6]. As the authors failed to obtain the component analysis data of the soil from Chosun University, however, the cation and anion CEC (Cation Exchange Capacity) of the soil, collected from the date farm in Boeun, Chungcheongbuk-do, were converted into ppm, and applied, and the cation and anion concentration of the soil is shown in **Table 4** [7]. The temperature as 25°C, pH was 6.5, the concentration unit was mg/kg, and the L/S ratio was 0.01, and the default values of the Code were used for the remaining values. Table 5 shows the result values of the Code. Cs+1 ion was applied to the Code by concentration, i.e. 0.1, 1, 2, 5 and 10mmol, and species bond, i.e. the degree to which it is combined with the components of the soil, was predicted. It can be said that % of the Cs+1 ion in the species name is not combined with the components of the soil, and the Cs+ ion remains as is [8,9].

Table 4. Soil CEC of Gochang-gun, Jeollabuk-do.

Soluble Cation and Anion(Cmolc/kg)			
K	Ca	Mg	
0.3	2.4	1.2	
Concentration of Anion(mg/kg)			
Cl	NO ₃	PO ₄	SO ₄
536	374	18.4	1,068

Table 5. Cs and Soil Species combination predict of by Visual MINTEQ.

Component	% of total Concentration	Species name
Cs+1 (0.1 mmol)	8.433	Cs+1
	47.877	CsCl
	15.417	CsSO ₄
	28.272	CsNO ₃
Cs+1 (1 mmol)	8.605	Cs+1
	47.946	CsCl
	15.230	CsSO ₄
	28.219	CsNO ₃
Cs+1 (2 mmol)	8.801	Cs+1
	48.014	CsCl
	15.028	CsSO ₄
	28.157	CsNO ₃
Cs+1 (5 mmol)	9.431	Cs+1
	48.172	CsCl
	14.455	CsSO ₄
	27.943	CsNO ₃
Cs+1 (10 mmol)	10.633	Cs+1
	48.271	CsCl
	13.595	CsSO ₄
	27.502	CsNO ₃

3.5. Measurement of turbidity

Turbidity was measured before and after the flocculating agent was injected into the aqueous solution in which the soil and Cs were mixed to check (1) flocculating agent whether the wash water could be reused, (2) how much fine soil was removed from the aqueous solution, and (3) how much soil was removed by the flocculating agent. Turbidity, as measured by a LaMotte 2020 turbidity meter, was recorded to be 47.2 NTU (Nephelometric Turbidity Units) before the flocculating agent was administered, and it was found that the wash water became clear at 4.39 NTU after the flocculating agent was administered [10].

3.6. Result of assessment

In the experiment, ICP-OPS was used to measure the removal rate when 0.1g of flocculating agent was applied. It was found that when the concentration of Cs is 0.1mmol, the maximum Cs removal rate is about 88%, when it is 1mmol, it is 85.8%, when it is 2mmol, it is about 85%, when it is 5mmol, it is about 71%, and when it is 10mmol, it is about 67%.

Also, if the turbidity values before and after injections of flocculating agent are compared, turbidity is 4.39 NTU after the injection. This is below the 10-NTU approved for domestic water quality criterion for reuse as industrial water. Additionally, pH is 5.8~8.5 and BOD (Biochemical Oxygen Demand) is 6mg/L or less. When turbidity and pH are taken into consideration, it is believed that the wash water can be reused [10].

Cs and soil are mixed in the Cs removal experiment to create an environment similar to a situation in which Cs and soil are combined in the natural environment. Accordingly, the prediction of the combination between soil and Cs using Visual MINTEQ indicates how much Cs and soil are combined and adsorbed.

Turbidity measurements indicate how much the flocculating agent can remove soil adsorbed with Cs from the mock Cs waste. To compare actual measurements and predicted values, the value obtained by multiplying the value of species bond predicted using Visual MINTEQ according to turbidity, and the actual ICP-OES measurements were compared. The graph comparing the actual measurements and predicted values is shown in **Figure 4**.

The graph comparing the actual measurements and predicted values show that the values are similar in the 0.1~2mmol area, but if the concentration becomes 2mmol or higher, it was confirmed that the difference between the two values was obvious. If more time is given for mixing soil and Cs than in this experiment, it is believed that the differences in the graph can be reduced. Also, if the CEC of the soil of nuclear power plants and related facilities using nuclear power is measured, and the species bond predicted, it is believed that the efficiency of the soil washing process can be predicted.

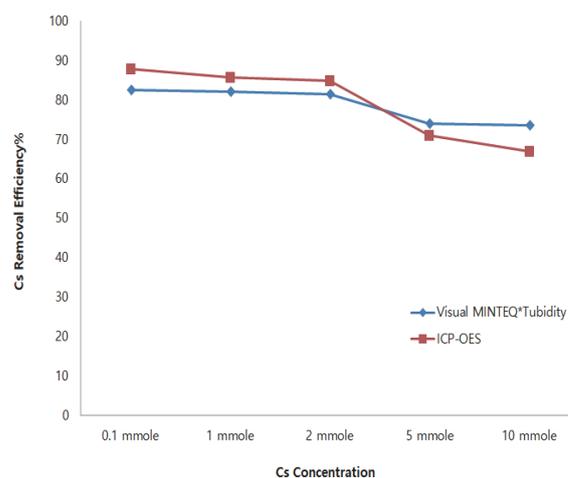


Figure 5. Comparison of ICP-OES and Visual MINTEQ*turbidity.

4. Conclusion

To The most suitable method of removing radionuclides from soil contaminated as a result of unexpected accidents during dismantling and maintenance of nuclear power plants is the soil washing method, which is commonly used domestically as well as internationally. The soil washing process takes less time than other processes but offers relatively high decontamination efficiency. The most important factors of the soil washing process are the particle separation of the soil, wash water selection, and the application of the adsorbent and flocculating agent to improve efficiency. In consideration of this, if a small area is contaminated with radioactive materials, simultaneous soil decontamination is not necessary. So the soil washing process, which has high decontamination efficiency as it applies the acid wash water and selective adsorbent, is appropriate. If a wide area is contaminated with radioactive materials, however, decontamination activities must be carried out simultaneously in a short period time. For these reasons, the soil washing process, which uses water together with flocculating agent injected into the soil in order to render the wash water reusable and improve the Cs removal rate, is more suitable. Also, as the flocculating agent, which was applied to the experiment for this study, takes very little time to form flocs it can further reduce the soil washing time. It is believed that this method can be used to more quickly process soil contaminated by radioactive materials as a result of a nuclear power plant accident or decommissioning.

The concentration of soil contamination due to nuclear power plant accidents and leakage of radioactive materials is very low being at the level of ppb. Accordingly, the authors are planning to supplement the experiment conducted for this study by conducting a low-concentration experiment at the ppb level. Also, as a follow-up, the authors will analyze the flocculating agent mechanism of the flocculating agent to improve the overall efficiency of the soil washing process.

Acknowledgements

This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20164030201290, 20141510300310).

References

- [1] J.S. Song and S.I. Kim, A study on the assessment of treatment technologies for efficient remediation of radioactively-contaminated soil, *JNFCWT*, Vol.14(3) (2016), pp.245-251.
 - [2] W.S Kim, S.S Kim, G.N Kim, U.R Park and J.K Moon, Improved treatment technique for the reuse of waste solution generated from a electrokinetic decontamination system, *Journal of Nuclear Fuel Cycle and Waste Technology* 12 (1) (2014), pp.1-6.
 - [3] G.N. Kim, W.K. Choi, C.H. Jung and J.K. Moon, Development of a washing system for soil contaminated with radionuclides around TRIGA reactors, *JKSIEC*, 1(3) (2007), pp.406-413.
 - [4] W.J. Oh, H.J. Won, C.H. Jung, W.K. Choi, G.N. Kim and G.W. Lee, Decontamination technology development for nuclear research facilities, *KAERI Technical Report*, RR-2416 (2003).
 - [5] Technology Reference Guide for Radioactively Contaminated Media, U.S.EPA, EPA 402-R-07-004 (2007).
 - [6] J.P Gustafsson, *Visual MINTEQ Ver3.1 Manual*, Royal Institute of Technology, Sweden (2000).
 - [7] B.Y. Jung, K.S. Lee, M.G. Kim, Y.H. Choi, M.K. Kim and J.Y. Cho Physico-chemical properties of rainfall interception culture and open field culture soil of of rubus sp. in Gochang-gun, Jeollabuk-do, *Korean J. Soil Sci. Fert*, 41(5) (2008), pp.303-309.
 - [8] J.S Yoon, Absorption characteristics of heavy metals in soils and their removal efficiency of soil washing technique using EDTA and NTA, *Thesis of Master's Degree*, Seoul National University (1999).
 - [9] H.S Lee, Y.H Choi, H.J Choi and H.S Kang Development of periodic safety review technology for nuclear power plant, *KAERI*, KAERI/RR-2245/2011 (2001).
 - [10] K.H Park, Based on guidelines for water reuse facility design and maintenance, Korea Water and Wastewater Works Association, Ministry of Environment, GSDS Press, Seoul (2007).
-