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Decontamination of radioactive soil wastes using an agglomeration-leaching process

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Abstract−An agglomeration-leaching process was evaluated to decontaminate Co-60 and Cs-137 from radioactive soils. Radioactive soils were screened based on the particle size of 0.075 mm. The soils with particle size of less than 0.075 mm were agglomerated by using a 2 wt% Na_2SiO_3 which had been predetermined to be an optimum reagent for an agglomeration. The agglomerated soils were mixed with the other soils with particle size bigger than 0.075 mm for leaching tests. Several leaching solutions were evaluated for their leaching performances for Co-60 and Cs-137 from simulated soil wastes, and the 0.1 M HCl solution was shown to be the most effective one. Leaching tests for radioactive soils in a column showed that the radioactive soils contaminated with Co-60 and Cs-137 radionuclides could be decontaminated down to the potential release criteria (~100 Bq/kg) by using the appropriate conditions of an agglomeration-leaching process.

Key words: Agglomeration, Leaching, Radioactive Soil, Decontamination, Co, Cs

INTRODUCTION

Several hundred tons of radioactive soil wastes have been generated from the decommissioned site of TRIGA research reactor in Korea. The contamination is mainly due to the leak of waste solution from the storage tank during operation for more than 20 years and the main contaminants are reportedly Co-60 and Cs-137 [1-3]. The soil wastes have been stored in the temporary storage facility of KAERI (Korea Atomic Energy Research Institute). Since the final disposal cost of radioactive wastes is very expensive in Korea, the soil wastes are considered to be released unlimitedly after decontamination.

A soil washing process that uses low molecular organic acids, such as citric acid and acetic acid together with EDTA (Ethylenediaminetetraacetic Acid), has been investigated to decontaminate Co-60 and Cs-137 from soils [2-4]. However, the soil washing process showed limited applicability, due to a filtering problem for soils with fine particles and a large amount of secondary waste generation. An electrokinetic-flushing soil decontamination process has also been developed as an alternative process for improving decontamination efficiency and reducing secondary waste generation [4,5]. Despite the fact that the electrokinetic process showed the characteristic features, such as a low secondary waste generation and high decontamination efficiency, it also showed a scale-up problem which would limit the large scale operation. Thus, every soil remediation process has some advantages and also some disadvantages.

On the other hand, an agglomeration-leaching process would be an alternative option for the remediation of radioactive soils. It has some advantages, such as a relatively low secondary waste generation and a large scale operation compared with a batchwise soil washing process. The leaching process has been used for a remediation of soil contaminated by heavy metals [6-11] and uranium [12,13]. Leaching includes sieving, agglomeration and chemical leaching steps. In the sieving step, fine particles such as silt and clay can cause a filtering problem when they are used in a column are screened for agglomeration. Also, large particles such as gravel and coarse sand can be also screened if they are contaminated below the free release level.

In this study an agglomeration-leaching process was evaluated to decontaminate soil wastes contaminated with Co-60 and Cs-137. The particle size required for agglomeration and an optimum agglomeration reagent condition were determined. The leaching tests were performed in a batchwise reactor and in a column by using the simulated soils contaminated by surrogates and radioactive isotopes.

MATERIALS AND METHODS

1. Soil Sample Preparation

The simulated soil samples were prepared by using the non-radioactive soils taken from around the TRIGA research reactor in Seoul. The soils with particle size smaller than 2 mm were sieved for test samples. The dried soils were mixed with the solution of 0.01 M Co and Cs, respectively, to make 0.4 of L/S (liquid to solid) ratio. The mixture was dried at room temperature under periodical stirring. The initial contamination levels of the soil samples for Co and Cs measured by AAS (Atomic Absorption Spectrophotometer, Analyst 300, Perkin-Elmer Co) after dissolving the samples with a con-

Table 1. Concentrations of Co and Cs calculated by mg/kg soil samples

Soil size (mm)	Size distribution (wt%)	Concentrations in soil samples (mg/kg)	
		Co	Cs
0.075-2.0	89.4	201	388
<0.075	10.6	1346	1540
Total	100	235	532

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Table 2. Concentrations of Co-60 and Cs-137 calculated by Bq/kg in soil samples with radioactivities

Soil size (mm)	Size distribution (wt%)	Concentrations in soil samples (Bq/kg)					
		Sample 1			Sample 2		
		Co-60	Cs-137	Sum	Co-60	Cs-137	Sum
0.075-2.0	10.6	277	364	641	1180	1560	2740
<0.075	89.4	273	362	635	1090	1450	2540
Total	100	277	364	640	1170	1550	2720

centrated nitric acid were 235 and 532 mg/kg, respectively. The initial concentrations of Co and Cs ions in the soil samples with particle sizes are shown in Table 1.

The two kinds of radioactive soil samples were prepared by the same procedures as the surrogate samples. A given amount of Co-60 and Cs-137 radio isotopes, referencing the contamination levels of the real radioactive soils in the TRIGA research reactor site, were mixed with the dried soil samples to be about 600 and 2,500 Bq/kg in the initial contamination levels, respectively. The radioactivities of the samples depending on the particle sizes are shown in Table 2. The contamination level was measured by using a MCA (Multi-Channel Analyzer, Ortec Co.).

2. Size Sieving and the Determination of the Agglomeration Reagent

In a column-leaching process, water permeability, which is closely related with the particle size of a packing material, is a very important factor for successful operation of the process. In this study, considering the water permeability, the soil particles of smaller than 0.075 mm such as silt (0.002-0.05 mm) and clay (<0.002 mm), which can be the impediments for the flow of leaching solution in the column, were separated for agglomeration. Starch (Duksan), vinyl acetate (Alpha, GR grade), vinyl amide (Aldrich, GR grade), acryl amide (Aldrich, GR grade), sodium carboxy-methyl-cellulose (Aldrich, GR grade) and a sodium silicate solution (Alpha) were evaluated as the candidate agglomeration reagents. The concentration of agglomeration reagents was varied in the range between 0.5 and 20 wt%. The agglomerated particles were dried at room temperature for 48 h, and then dissolution stability tests were performed using H_2O and 0.1 M HCl solution for 10 days.

Hydrochloric acid (Aldrich, HCl), acetic acid (Aldrich, CH_3COOH), oxalic acid (Aldrich, $(COOH)_2$) and citric acid (Aldrich, 2-hydroxypropane-1,2,3-tricarboxylic acid, $C_6H_8O_7$) were used as leaching reagents.

3. Batch Scale Leaching Test

An optimum leaching reagent and its concentration for decontamination of Co and Cs were investigated by batchwise leaching tests. A 10 gram simulated soil sample was immersed into the can- didate leaching reagents, such as hydrochloric acid, oxalic acid, acetic acid and citric acid. The concentrations of leaching solutions were varied in the range of 0.001 and 0.5 M and the L/S ratio was fixed at 10. The mixture was stirred for 1 h and then filtered to assess the leaching performance. The leaching efficiency was defined as the concentration difference in the leaching solution before and after the tests.

4. Column Leaching Tests

After determining the optimum leaching solution conditions, the leaching tests were carried out using a column of 20 mm in diameter and 150 mm in height. To confirm the effect of agglomeration on the leaching, the tests were performed with the agglomerated soils separately with the remaining coarse soils bigger than 0.075 mm, which were not agglomerated. A given amount of soil samples were packed in the column and the leaching solution was fed from the top of the column with the flow rate of 3.0 mL/min. The amounts of leaching solution were varied in the range of 10 and 60 mL per gram of soil samples. To prevent channeling in the column, the solution level was kept at the top position of the bed. The concentrations of Co and Cs in the effluent solution together with the soils were analyzed periodically to assess the decontamination efficiencies.

RESULTS AND DISCUSSION

1. Determination of an Optimum Binder

Various candidate binders were evaluated as the agglomeration reagents as shown in Table 3. Only sodium silicate solution with the concentrations more than 2 wt% shows the dissolution stability against H_2O and 0.1 M HCl solution for 10 days. However, since the soil samples have different organic content which affects the agglomeration process, even if they have the similar particle size distributions, it would be desirable for the binder concentration to be varied from 2 to 5 wt%.

2. Particle Size Change After an Agglomeration

Since the soils with fine particles can cause a filtration problem in a column operation, they should be agglomerated for successful column operation. In this study, the soils with the particle size smaller than 0.075 mm, most of them are clay and silt, were agglomerated and the average particle size increased to about 3.0 mm. Fig. 1 shows the increasing shift of the particle size distribution after an agglomeration, which implies possibly improvement for a column leaching process.

There are reportedly some examples of agglomerations of fine soils for decontamination. Tampouris et al. [7], in their study on the

Table 3. Applicability of binders for the agglomeration of soils as a function of binder addition ratio

Binders	Addition ratio (wt%)					
	0.5	1	2	5	10	20
Starch	×	×	×	×	×	×
Vinyl acetate	×	×	×	×	×	×
Vinyl amide	×	×	×	×	×	×
Acryl amide	×	×	×	×	×	×
Sodium carboxymethylcellulose	×	×	×	×	×	×
Sodium silicate	×	△	○	○	○	○

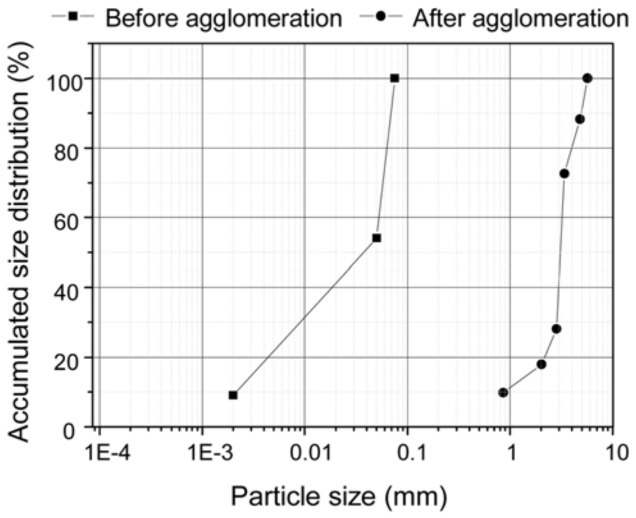


Fig. 1. The comparison of particle size distribution before an agglomeration and after an agglomeration of soils with particle sizes smaller than 0.075 mm.

decontamination of soils contaminated with heavy metals, reportedly carried out the agglomeration of the soils with particle size smaller than 0.06 mm, and the final average particle size was 1.5 mm, which is about 25 times bigger than the original one. Majid et al. [6] also suggested that the soils with smaller than 0.15 mm in diameter should be agglomerated to make them bigger than 0.5 mm, and reported a successful operation of column leaching process for the uranium bearing soil wastes. Thus, the size limits for an agglomeration are reportedly somewhat different from case by case depending on the kinds of soils.

3. Determination of a Leaching Reagent

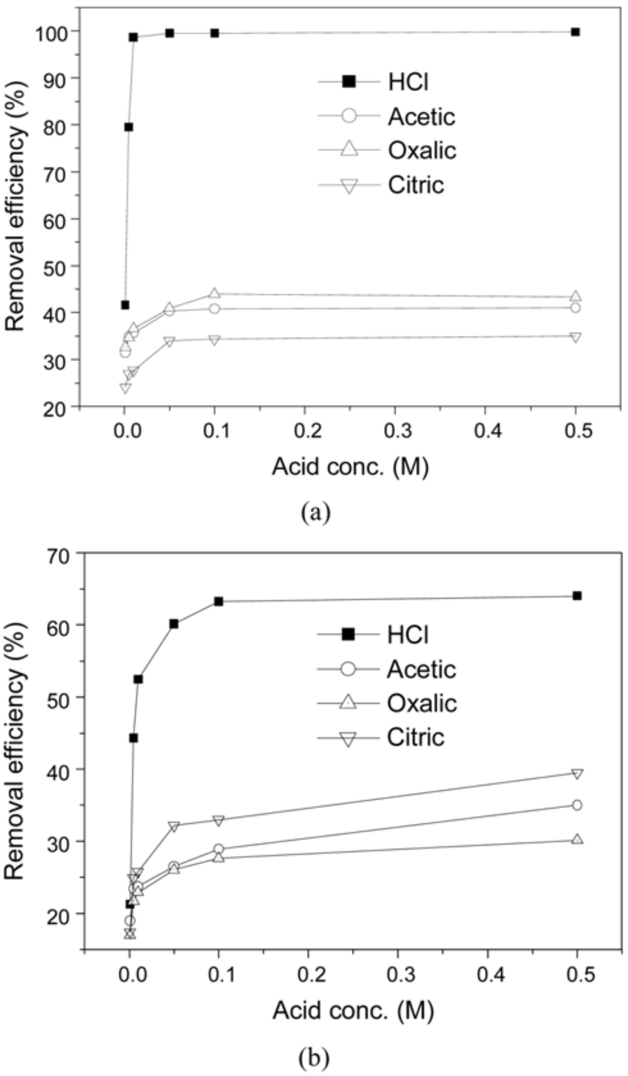
Hydrochloric acid, acetic acid, oxalic acid and citric acid were evaluated on the leaching performance for determination of a proper leaching reagent, and the results are shown in Fig. 2. The HCl solution shows the best leaching performance among the tested solutions. Considering that the leaching reaction is related closely with an active cation to exchange the radio nuclides in the soil matrix, it is due to high ionization characteristics of HCl to produce H^+ ion, compared with the other tested reagents. The effect of the concentration of HCl solution on the removal of Co and Cs is also given in Fig. 2.

In the case of Co, the removal efficiency reaches its plateau with about 99% when the concentration is 0.01 M. However, in the case of Cs, the removal efficiency increases more or less slowly up to about 63% for 0.1 M of HCl solution. Therefore, 0.1 M of HCl solution was determined to be a proper concentration of the HCl solution. The spent HCl solution can be easily treated by simple methods such as precipitation, evaporation and ion exchange [14,15]. Furthermore, it has a characteristic advantage that it does not contain any chelating reagents such as EDTA and therefore does not cause any problem when disposed at a final repository.

4. Column Leaching Tests

4-1. Leaching Behavior of Inactive Co and Cs in a Column

The soil samples of particle sizes in the range between 0.075-2.0 mm, which are not agglomerated, were contacted with a 0.1 M HCl solution for about 14 days in a column and about 99.9% of Co and 96.5% Cs were removed as given in Fig. 3. On the other hand, in the case of the agglomerated soils, 97.7% of Co and 81.1% of Cs were removed for 29 days. This is obviously due to the mass transfer resistance of Co and Cs ions in the macropores of the agglomerated particles.



(a)

(b)

Fig. 2. The effect of the solution concentrations of the various leaching reagents on the removal of Co (a) and Cs (b) from simulated soils.

Even though the decontamination time increases when the fine soil particle is agglomerated, however, taking into account the filtration problem of the fine soils when operated continuously in a column, it would be desirable to agglomerate fine particles using a sodium silicate solution. One more characterizing feature is that the leaching of Cs is much slower than Co. It might be related with a higher mobility of Cs ion compared with Co ion. Cs ion reportedly moves more or less easily through the pores of the soil matrix, and some of them exist deeply in the micropores of the soil particles. In order for the Cs ion to be desorbed, the counterion H^+ should diffuse into the site where the Cs ion is adsorbed. When we consider that the effective micropore diffusivity of Cs ion is less than 10^{-10} cm^2/sec and the particle size is 0.1 cm, the diffusion time con-

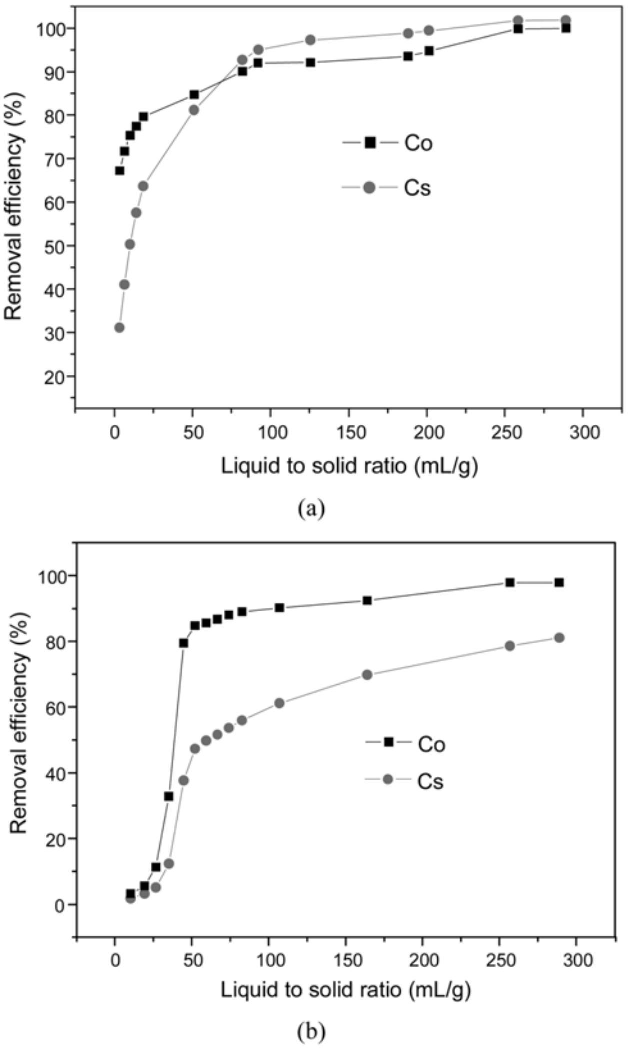


Fig. 3. The effect of liquid to solid ratio on the removal of Co and Cs from the soils; not-agglomerated soils (a) and agglomerated soils (b).

stant, D/R^2 is less than 10^{-7}/sec. Therefore, it takes more than 100 days for Cs ion to come out to the particle surface by diffusion.

4-2. Hot Tests Using Radioactive Soil Wastes

Column leaching tests were performed by using the two kinds of radioactive soil wastes contaminated with Co-60 and Cs-137. The total initial contamination levels of them are 600 and 2,500 Bq/kg, respectively. The soil samples, not-agglomerated soil which has the particle sizes of 0.075-2.0 mm and the agglomerated soils with the particle sizes of smaller than 0.075 mm, were packed together in a column. One example of the leaching test results is shown in Fig. 4.

In the case of Co-60, an application of 10 mL of leaching solution to 1 g of soil waste is enough to meet potential free release criteria of 100 Bq/kg [1]. However, in the case of Cs-137, a 30 mL leaching solution is required to reduce the contamination down to the release criteria. Another example of column leaching test results for more or less highly contaminated soils is also shown in Fig. 5.

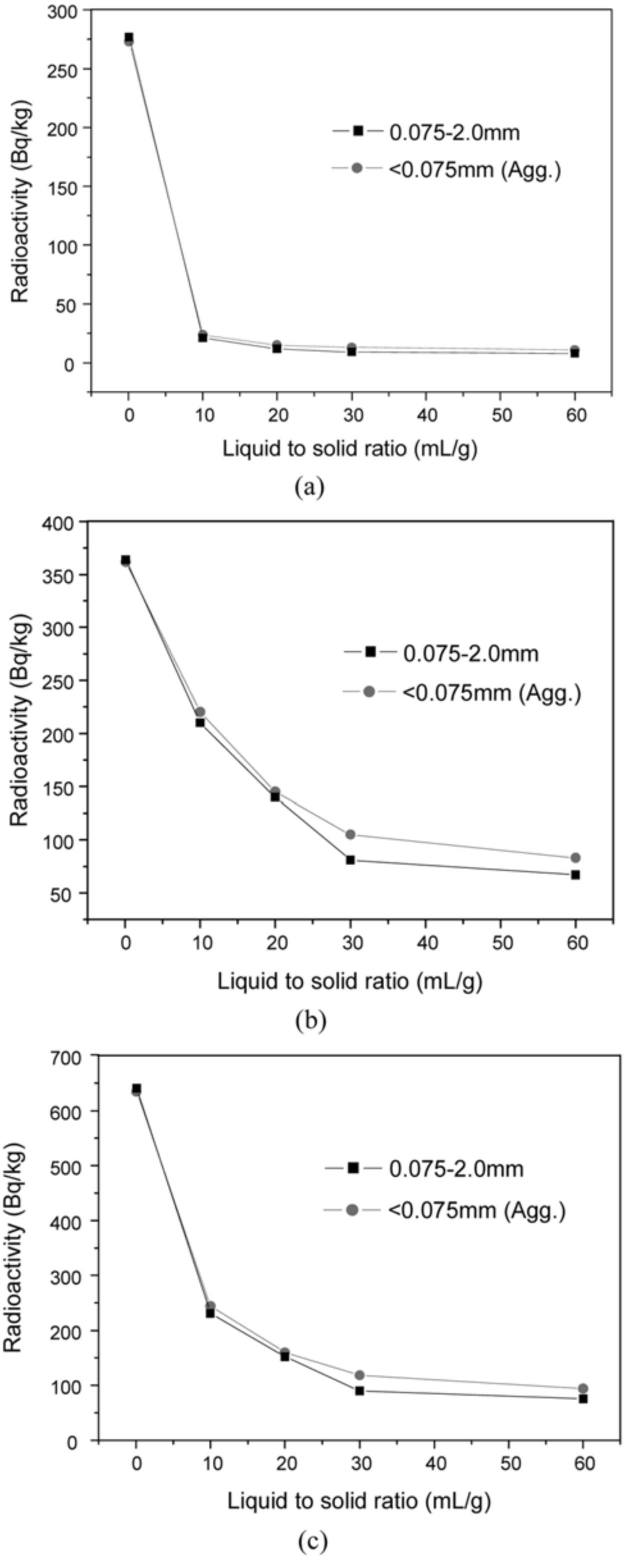


Fig. 4. The effect of liquid to solid ratio on the removal of Co-60 (a), Cs-137 (b) and Sum (c) in the leaching tests using a column packed with not-agglomerated soils and agglomerated soils (initial total radioactivities: about 600 Bq/kg).

The leaching solutions of 30 and 60 mL are shown to be required to reduce the contamination levels down to the potential release criteria for Co-60 and Cs-137, respectively.

As in the leaching tests with simulated soils, two or three times

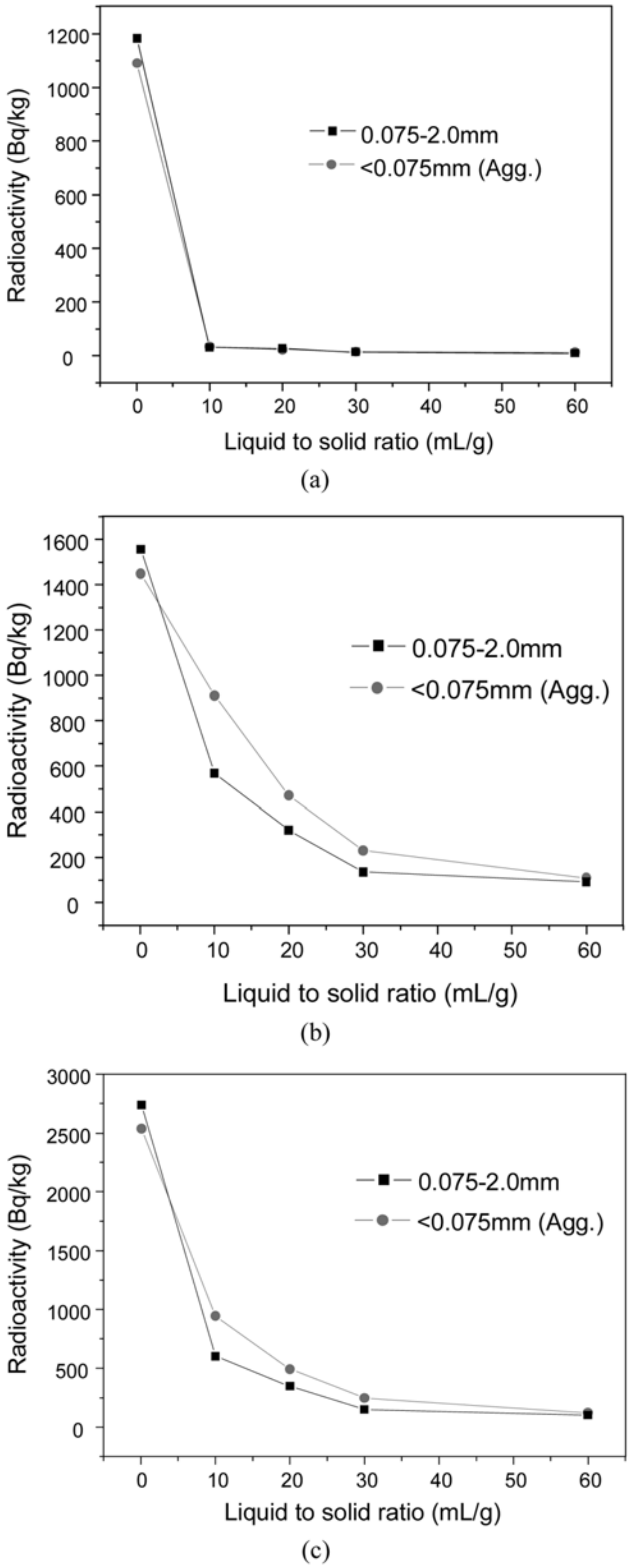


Fig. 5. The effect of liquid to solid ratio on the removal of Co-60 (a), Cs-137 (b) and Sum (c) in the leaching tests using a column packed with not-agglomerated soils and agglomerated soils (initial total radioactivities: about 2,500 Bq/kg).

more amounts of leaching solutions were required for agglomerated soils than for not-agglomerated soils. For this reason, in the treatment of soil wastes contaminated with heavy metals, it has been questioned about the effectiveness of an agglomeration-leaching process in comparison with a soil washing method. In fact, a soil washing process seems promising because of its operation time and the residual fine particles have less limitation for disposal. However, in the case of radioactive soils, when we consider that the radioactive soil wastes contain a variety of fine particles where the most contaminants are adsorbed, and it is very important to reduce the volume to be disposed, an agglomeration process would be indispensable for a successful treatment of radioactive soil wastes. Even though an agglomeration-leaching process in this study showed more or less successful results for radioactive soils contaminated by radio isotopes of Co-60 and Cs-137, further investigation on the effect of weathering and organic contents in soils would be supplemented.

CONCLUSIONS

A column type leaching process was evaluated to decontaminate radioactive soil wastes contaminated with Co-60 and Cs-137. The soil particles smaller than 0.075 mm could be agglomerated successfully by using a sodium silicate solution, and the optimum concentrations were found to be in the range between 2 and 5 wt%. It was also confirmed that HCl solution is the most effective leaching reagent among the tested solutions and an optimum concentration of HCl was 0.1 M. Leaching tests were performed in a column with a simulated soil waste and a radioactive soil waste. In the leaching tests using a surrogate, 99.9% of Co and 96.5% of Cs from a not agglomerated soil were removed by applying 0.1 M HCl solution for 14 days. However, the leaching efficiency for an agglomerated soil decreased a little bit to 97.7% of Co and 81.1% of Cs for 29 days, due to the mass transfer resistance in the macropores of the particle. In the leaching tests using radioactive soils, it showed that the removal efficiencies were different depending on the initial contamination level. However, it was found that the radioactive soils contaminated with Co-60 and Cs-137 could be decontaminated down to the potential release criteria (~100 Bq/kg) by using an appropriate amount of leaching solution.

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