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Study on volume reduction of cesium contaminated soil by magnetic separation

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***Abstract*— In this study, we developed a new volume reduction method for contaminated soil by magnetic separation. We succeeded in selective separation of paramagnetic 2:1 type clay minerals, which strongly adsorb Cs, from 1:1 type clay minerals. As a result, it was shown that the radiation dose of 1:1 type clay minerals can be reduced.**

We examined magnetic separation conditions for efficient separation of 2:1 type clay minerals. First, the separation rate of each particle size of 2:1 type clay minerals was calculated by particle trajectory simulation, because magnetic separation rate largely depends on the objective size. According to the calculation, 93.8% of 2:1 type of clay minerals could be separated at 7 T. Next, high gradient magnetic separation (HGMS) experiment was conducted using superconducting magnet. 97 % of 2:1 type clay minerals were separated under the condition of 7 T and 3 cm/s of flow rate. The separation experiment of 2:1 type clay minerals from the mixture of 1:1 and 2:1 type clay minerals was performed at 7 T. 97 % of 2:1 type clay minerals were selectively separated from the model soil. It was shown magnetic separation with superconducting magnet would contribute to the volume reduction of contaminated soil.

***Index Terms*— clay minerals, magnetic separation, radioactive Cs, superconducting magnet, volume reduction**

I. Introduction

The accident of Fukushima Daiichi nuclear power plant in 2011 caused the diffusion of a considerable amount of radioactive substances over a wide area. A large amount of soil was contaminated by the radioactive substances, and among them, ^{137}Cs is currently the most serious problem. Because ^{137}Cs were diffused in large quantity from Nuclear Power Plant and has a long half-life (30 years), in comparison with other radioactive nuclides. Accordingly, decreasing the air dose rate in the short period cannot be expected. Ministry of the Environment in Japan has been proceeding decontamination work after the accident. The total quantity of contaminated soil discharged through the work is expected to be 16-22 million m^3 in Fukushima prefecture [1]. The government has been planning to store all the collected soil in the interim storage facilities. However, it must take huge cost and time to construct the interim storage facilities and to transport the large volume of soil. Therefore, the volume reduction technique of massive amount of Cs contaminated soil has been required.

In this study, we developed a new volume reduction method for the contaminated soil. This method divides soils into two portions; one is a large amount of low-dose soil which can be reused for road material, and the other is a small amount of high-dose soil which needs strict management. The flow diagram of the proposed volume reduction process is shown in Fig.1.

The process of this technology consists of two processes; the soil classification and the magnetic separation process. It is known that Cs ions in the soil are accumulated in the clay minerals with relativity small size [2]. Firstly, the soil radiation dose is reduced by removing silt and clay minerals from sand gravels by the soil classification process. Secondly, the high gradient magnetic separation (HGMS) with using superconducting magnet is applied to the classified silt and clay minerals. The magnetic separation process was focused in this work.

Clay minerals contain 1:1 type and 2:1 type clay minerals. It is known that Cs ions are mainly adsorbed on the paramagnetic 2:1 type clay minerals, such as vermiculite. They have the characteristics to adsorb and fix a large amount of Cs ions. On the other hand, 1:1 type clay minerals such as kaolinite show diamagnetism and weakly adsorb a small amount of Cs ions. The clay minerals in Fukushima prefecture mainly consist of smectite, vermiculite and kaolinite [3]. Smectite and vermiculite belong to 2:1 type clay minerals and kaolinite belongs to 1:1 type clay mineral. The silt also shows diamagnetism and weak adsorption of Cs. Thus, we can realize the effective volume reduction methodology by means of the selective separation of high-dose 2:1 type clay minerals utilizing the superconducting magnetic separation system.

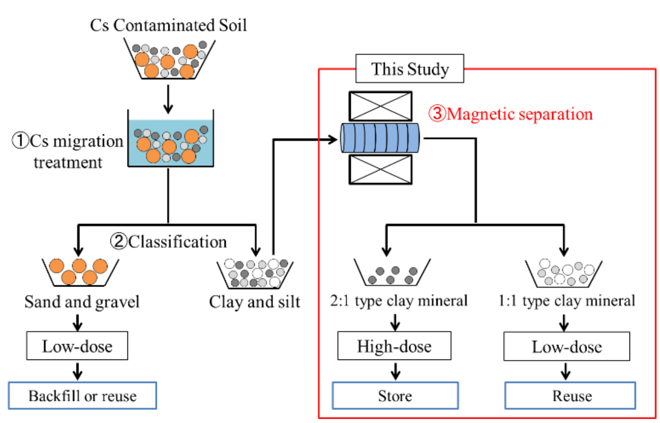

Fig. 1. Flow diagram of volume reduction method with magnetic separation

This study intends to find magnetic separation conditions demanded for efficient separation of paramagnetic 2:1 type clay minerals. Firstly, we investigated the separation rate by particle trajectory simulation in order to examine the influence of particle diameter of the clay minerals on the separation rate.

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This is because magnetic separation system largely depends on the size of the objective particles. Secondly, the separation rate of 2:1 type clay minerals was experimentally evaluated by changing the magnetic field in order to investigate the magnetic field required for the separation. Based on the results, the possibility of separating 2:1 type clay minerals from the mixture of 1:1 and 2:1 type clay minerals was examined.

II. Theory

A. Properties of clay minerals

It is known that Cs ions are adsorbed by clay minerals whose particle diameter is smaller than 5 μm in the contaminated soil. Clay minerals are divided into 1:1 and 2:1 type by their structures. Generally clay and silt consist of silica and alumina. 1:1 type clay minerals are constructed by the combination of one silica tetrahedral sheet and one alumina octahedral sheet. On the other hand, 2:1 type clay minerals are constructed by one alumina octahedral sheets sandwiched by two silica tetrahedral sheets.

These clay minerals are different in Cs adsorption properties due to the difference in structures. 1:1 type clay minerals adsorb Cs ions by the variable charge on the surface. The variable charge depends on the pH, a type of cation and its concentration of solution [4]. Cs ions are adsorbed weakly when the surface of 1:1 type clay minerals have a negative charge, and are desorbed easily by washing with the solution containing potassium or ammonium ions.

On the other hand, 2:1 type clay minerals adsorb Cs ions not only by the variable charges but also by the permanent charges originated from its structure. Permanent charge is negative induced by the imbalance of electrical charges formed by substitution of Si by Al and of Al by Mg or Fe. Moreover, Cs ions are fixed between the layers spatially and electrostatically by the negative charge. Thus, Cs ions adsorbed and fixed to the interlayer of 2:1 type clay minerals are difficult to desorb.

Concerning magnetic susceptibility, 2:1 type clay minerals are different from silt and 1:1 type clay minerals in magnetic susceptibility. Silt and clay minerals essentially show diamagnetism, because they mainly consist of silica and alumina. However, most of 2:1 type clay minerals show paramagnetism by substitution of Al by Fe. Thus, silt and1:1 type clay minerals are diamagnetic, whereas 2:1 type clay minerals are paramagnetic.

1:1 and 2:1 type clay minerals are much different not only in Cs adsorption properties but also in magnetic susceptibilities. Based on this, HGMS using superconducting magnet can significantly contribute to the volume reduction of Cs contaminated soil by separating 2:1 type clay minerals from other components.

B. High gradient magnetic separation (HGMS)

Magnetic separation is a method to separate the objective materials selectively utilizing the difference of magnetic susceptibility. In this method, we consider the magnetic force and the drag force acting on the objective materials. Magnetic force ($\mathbf{F_M}$) and drag force ($\mathbf{F_D}$) are shown in (1) and (2). In (1), r[m] is radius of the particles, $\mathbf{m}$ [A/m] is magnetization of the particles and $\mathbf{B}$ [T] shows magnetic flux density. In (2), η [Pa・s] is a viscosity of the solvent, and $\mathbf{v_f}$ and $\mathbf{v_p}$ are the flow velocity of fluid and particles, respectively.

$$\mathbf{F_M} = \frac{4}{3}\pi r^3 (\mathbf{m}\cdot\nabla)\mathbf{B} \quad (1)$$

$$\mathbf{F_D} = 6\pi\eta r(\mathbf{v_f} - \mathbf{v_p}) \quad (2)$$

The magnetic force is larger than a drag force to separate successfully. High magnetic field and high magnetic gradient is needed to realize the large magnetic force. In order to separate the paramagnetic particle with low magnetic susceptibility, a superconducting magnet must be used to generate enough strong magnetic field in the large space. Ferromagnetic wires are used to generate high magnetic gradient. The magnetic filters were made of 430 stainless steel wire. The system having the magnetic filters are called HGMS.

Focusing on the radius of the particles, magnetic force is proportional to the cubic of the radius, whereas drag force is proportional to the radius. It indicates that separation of smaller particles is difficult because the magnetic separation efficiency largely depends on the volume of objective particles.

III. Separation of 2:1 type clay minerals

A. Particle trajectory simulation

As previously noted, paramagnetic vermiculite is separated from other soil components by using HGMS [5]-[6]. It is expected that the separation rate largely changes with the particle diameter. Therefore, we conducted the particle trajectory simulation to calculate the separation rate of vermiculite. Calculation of magnetic force and drag force are required to conduct the particle trajectory simulation. Magnetic field and fluid analysis were performed by finite element method (FEM) using ANSYS 10.0. The calculation system of magnetic field analysis and fluid analysis are shown in Fig.2.

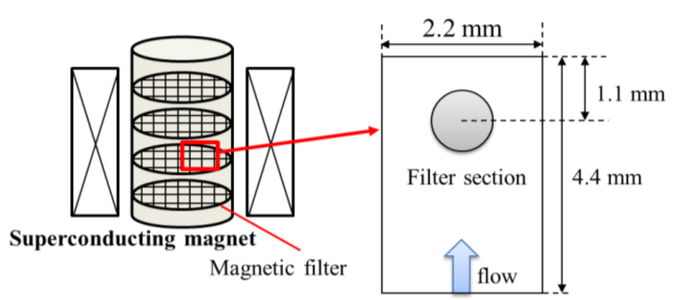

Fig. 2. Analysis model for magnetic field analysis and fluid analysis

Using the results, the particle trajectory calculation was conducted by solving the motion of particle equation under the resultant force of magnetic and drag force with time evolution by Euler's method.

The object particle to be separated is vermiculite. The analysis conditions are shown in Table I. Theoretical separation rate was calculated on each particle diameter. The range of the diameter was decided by the actual measurement with Laser diffraction-scattering type particle size distribution analyzer (LA-920,HORIBA). The results are shown in Fig.3. The particles with diameter larger than 1.3 μm can be captured at 7 T and larger than 3.0 μm at 2 T.

TABLE I ANALYSIS CONDITION OF THE SIMULATION

Analysis condition	Volume
Filter material	SUS430
Wire diameter [mm]	0.34
External magnetic field [T]	2, 5, 7
Viscosity coefficient of the fluid [Pa・s]	1.0×10^{-3}
Flow velocity [cm/s]	3.0
Magnetic susceptibility [-]	7.0×10^{-4}

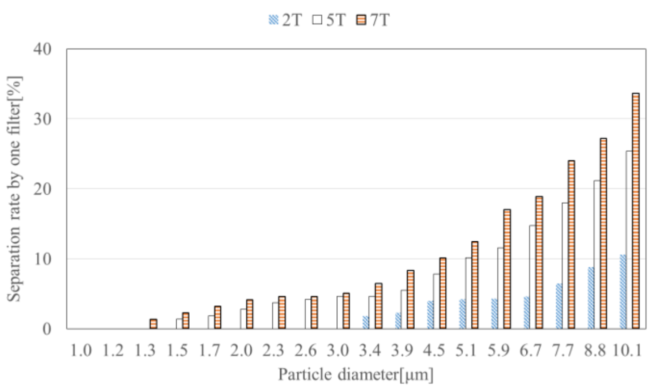

Fig. 3. Separation rate by each particle diameter

Based on the result in Fig.3, the entire separation rate with 30 magnetic filters was estimated considering the size distribution of the 2:1 type clay minerals. The calculated result is shown in Table II. 82 % of vermiculite could be captured at 2 T and 93 % at 7 T.

The volume fraction of the particles considering captured and passed for each particle size was estimated the calculated results at 7 T.

The result is shown in Fig.4. It suggests that 50 % of particles less than 1.5 μm in diameter are not captured even at 7 T. We propose the multiple-step magnetic separation system in order to separate particles smaller than 1.5 μm if needed. For much smaller particles, the higher magnetic field or filters with smaller wire diameter would be used in the second separation.

TABLE II SEPARATION RATE AT EACH MAGNETIC FIELD

Magnetic field	Separation rate [%]
2 T	81.6
5 T	92.0
7 T	93.8

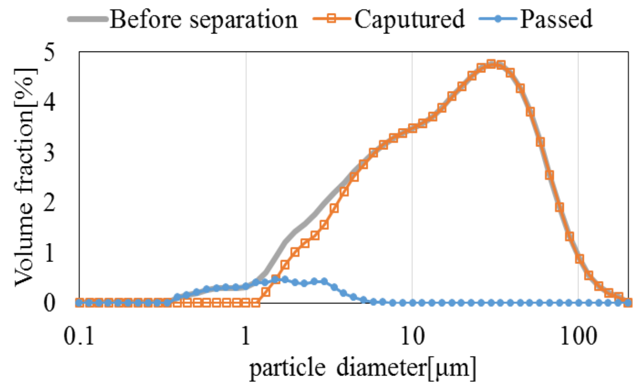

Fig. 4. Calculation of particle size distribution after magnetic separation at 7 T

B. *Experimental method*

We conducted the demonstration experiments of HGMS to confirm the simulation results in Section A.

The soil suspension with solid-liquid ratio of 1:300 was prepared using 1.5 L of deionized water and 5.0 g of vermiculate having less than 75 μm in diameter (Tomoe Engineering CO.,LTD.) . HGMS was conducted at the maximum center magnetic flux density of 2, 5, and 7 T. The solenoidal superconducting magnet (JMTD-10T100ES, Japan Superconductor Technology, Inc.) was used. The flow velocity 3 cm/s was controlled by a roller pump. 30 filters (stainless steel, wire diameter 340 μm, 20 mesh) arrayed at 5 mm spacing were installed in the separation area. The soil suspension was circulated for 3 minutes in the magnetic separation system. The experimental setup is shown in Fig.5. The weight of separated and passed particles were measured after filtration and drying.

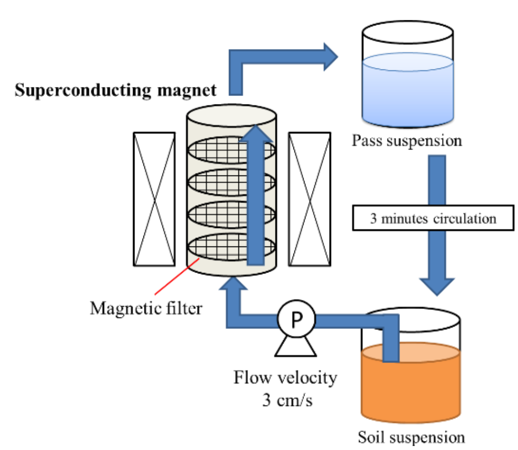

Fig. 5. Experimental system of magnetic separation

C. *Results and discussion*

Separation rates at each magnetic field were calculated by (3). Median sizes of particles and the separation rates at each magnetic field are shown in Table III. The table reveals that high separation rate was achieved under 7 T and 3 cm/s with HGMS.

It was found that the experimental result was consistent with the calculation result shown in Table II.

$$\text{Separation rate}(\%) = \frac{Captured[g]}{Captured[g]+Passed[g]} \times 100 \quad (3)$$

TABLEIII
SEPARATION RATE AND MEDIAN SIZE AFTER MAGNETIC SEPARATION

Magnetic field	Separation rate[%]	Captured[μm]	Passed[μm]
2 T	75	19	4.2
5 T	90	15	3.4
7 T	97	12	2.9

The median size of the particles before separation was 15.6 μm, and that of passed particles becomes smaller with increasing the magnetic field. It indicates that higher magnetic field enables to capture smaller particles. It is also confirmed that the median size of captured particles become smaller at higher magnetic field. The stronger magnetic field is needed to capture smaller sized particles.

Fig. 6 shows the particle size distribution before and after the magnetic separation at 7 T. Comparing the calculated results is shown in Fig. 5, these two figures are almost consistent. It indicates that the change in particle size distribution can be predicted by the particle trajectory simulation. A small disagreement was found in mass balance before and after separation. This might attribute to the experimental error.

Considering the separation efficiency of small sized vermiculite, the marked volume reduction can be expected because the radioactivity of the vermiculite is thought to be proportional to the volume.

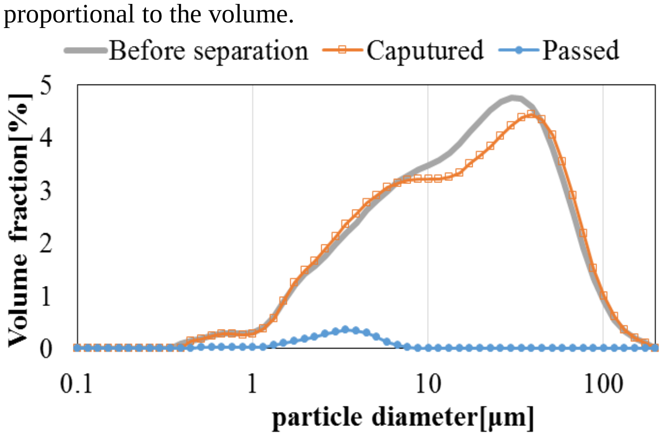

Fig. 6. Particle size distribution after magnetic separation experiment at 7 T

IV. MAGNETIC SEPARATION OF 2:1 AND 1:1 TYPE CLAY MINERALS

A. *Materials and methods*

Finally, selective separation of vermiculite from mixture with kaolinite was conducted. The soil suspension was prepared with 5.0 g of vermiculite, 5.0 g of kaolinite (The Clay Science Society of Japan) and 1.5 L of deionized water. HGMS experiments were conducted just same manner as described "III".

After the separation, the magnetic susceptibility of the captured and passed mixed clay were measured by magnetic balance (Sherwood scientific, Ltd,MSB-AUTO) in order to estimate the ratio of two types of clay minerals.

The calibration curve was prepared with known amount of vermiculite and kaolinite before the experiment. We evaluated the ratio of clay minerals of captured and passed particles with the calibration curve.

B. *Results and discussions*

The mass ratio of vermiculite in passed particles was 2.7 %, whereas that of vermiculite in the captured particles was 93 %. The results are shown in Fig.7. In this experiment, approximately 97 % of vermiculite were captured by the magnetic force. This separation rate agrees with the obtained separation rate in "III" of the paper.

The interaction between vermiculite and kaolinite should not have much influence on magnetic separation rate. The feasibility of selective separation of vermiculite from actual soil using magnetic force was confirmed.

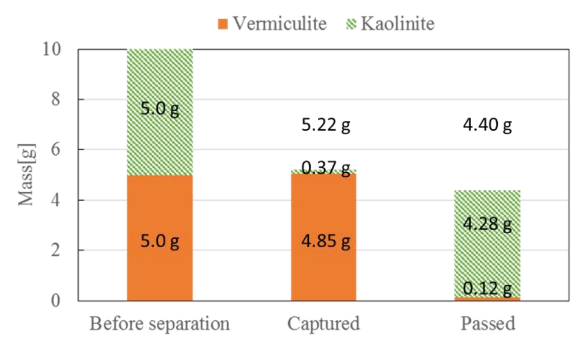

Fig. 7. Ratios of clay minerals before and after separation

V. CONCLUSION

In this study, the magnetic separation was studied for efficient separation of 2:1 type clay minerals for volume reduction of contaminated soil. The separation rate of vermiculite was calculated by the particle trajectory simulation considering the particle size distribution. The simulation reveals that the particle of which diameter larger than 1.3 μm can be separated in the magnetic field of 7 T.

The HGMS experiments were performed and 97 % of vermiculite was confirmed to be separated. The vermiculite separation from the mixture with kaolinite was conducted under 7 T. It was conformed that 97 % of vermiculite was successfully separated from the mixture.

The results strongly suggests that the magnetic separation contributes to the volume reduction of the contaminated soil.

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