

Volume reduction of cesium contaminated soil by magnetic separation – Pretreatment of organic matters –

Hiroki Horie¹, Kazuki Yukumatsu¹, Fumihito Mishima², Yoko Akiyama¹,
Shigehiro Nishijima¹, Tomio Sekiyama³, Seiichiro Mitsui³ and Mitsugu Kato³

¹ Graduate School of Engineering Osaka university, 2-1 Yamadaoka, Suita, Osaka, Japan

² Fukui University of Technology 3-6-1 Gakuen, Fukui, Fukui, Japan

³ Japan Atomic Energy Agency (JAEA) 2-10 Fukasaku, Miharumachi, Tamuragun, Fusima, Japan

E-mail address horie@qb.see.eng.osaka-u.ac.jp

Abstract. By the accident of Fukushima Daiichi Nuclear Power Plant, a large amount of soil was contaminated by radioactive cesium. We developed a new volume reduction method of contaminated soil combining classification and magnetic separation. In magnetic separation, 2:1 type clay minerals, which adsorb cesium strongly and show paramagnetism, are removed from soil suspension of silt and clay, and then the contaminated soil can be separated into two groups that is high and low dose soil. However, there is an issue that the clay aggregates induced by organic matters prevent 2:1 type clay minerals from selective separation magnetically. The purpose of this study is to disperse aggregates by means of the alkaline K_2CO_3 solution treatment for selective separation of 2:1 type clay minerals. Firstly, particle size distribution was measured and the dispersion by K_2CO_3 treatment was investigated. Moreover, the radioactivity of passed soils after magnetic separation was measured to investigate the effect of dispersion treatment before magnetic separation. The result showed the possibility of more selective separation for 2:1 type clay minerals by treatment of organic matters.

1. Introduction

By the accident of Fukushima Daiichi Nuclear Power Plant, many kind of radioactive substances were released and discharged around the plant, which caused increase in air dose rate. Cs^{137} is one of the radioactive substances that has a long half-life (approximately 30 years) and released amount was large. In Fukushima prefecture, the surface of the soil was removed by the decontamination works to reduce air dose rate. According to Ministry of the Environment, the total quantity of contaminated soils discharged through the work is expected to be 16-22 million m^3 [1]. Therefore, volume reduction of removed contaminated soil is needed.

We examined the volume reduction system combining wet classification and magnetic separation with superconducting magnet. The flow diagram of the decontamination process is shown in figure 1. Firstly, in the process of classification, soil is separated depending on their particle size. The soil radioactivity is reduced by removing silt and clay minerals from the soil. Secondly, in the process of magnetic separation with superconducting magnet, silt and clay minerals are separated into low dose soil mainly consists of 1:1 type clay minerals and high dose soil mainly consists of 2:1 type clay minerals. However, there is an issue that clay aggregates by organic matters could prevent 2:1 type



clay minerals from selective separation magnetically [2]. The purpose of this study is to propose a method of disaggregation of 2:1 type clay minerals and other soil components. 2:1 type clay minerals show paramagnetism. Therefore, a superconducting magnet as high magnetic field source is required for this method.

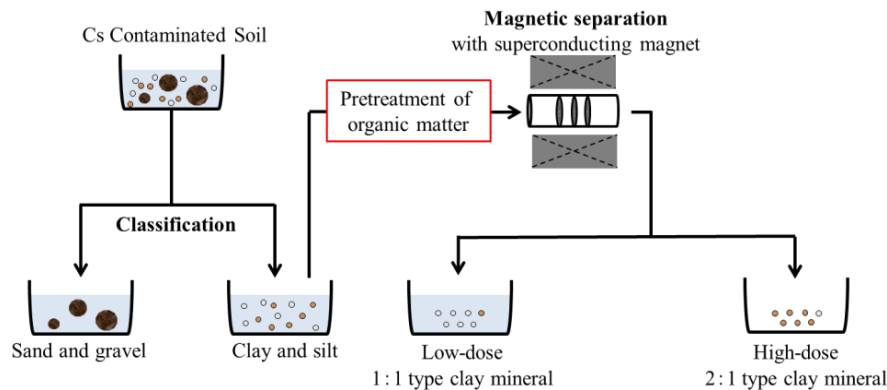


Figure 1. Flow diagram of soil decontamination by magnetic separation.

2. Theory

2.1. Properties of clay minerals

Clay minerals are divided into two groups; 1:1 and 2:1 type clay. They are constructed by the combination of the layers of Al octahedral and Si tetrahedral structure. Two kinds of minerals are much different in Cs ions adsorption ability [3].

1:1 type clay mineral mainly adsorbs Cs ions by variable charge on the surface and its Cs adsorption ability is low. On the other hand, 2:1 type clay mineral adsorbs Cs ions by negative permanent charge and its Cs adsorption ability is high. In addition, 2:1 type clay mineral has cavities called “frayed edge site” which can fix Cs ions strongly in the interlayer space [4].

Moreover, these clay minerals are different in magnetic susceptibility. The magnetic susceptibilities of kaolinite and vermiculite, which are 1:1 and 2:1 type clay minerals respectively are shown in table 1 [5]. Kaolinite and vermiculite show diamagnetic and paramagnetic properties, respectively.

Thus, selective separation of 2:1 type clay mineral can effectively reduce the dose of silt and clay fraction. The separation of these clay minerals can not be realized without solenoidal superconducting magnet for two reasons. One is that the superconducting magnet can generate high magnetic field and magnetic field gradient to capture paramagnetic 2:1 type clay mineral. The other is that the superconducting magnet has wide magnetic field area to separate a large amount of contaminated soil. The magnet makes it possible to reduce the radioactivity of soil passed through the magnet by removing 2:1 type clay minerals.

Table 1. Magnetic susceptibility of clay minerals. [5]

	Volume Susceptibility (-)
Kaolinite (1:1 type clay mineral)	-6.0×10^{-5}
Vermiculite (2:1 type clay mineral)	7.0×10^{-4}

2.2. Reaction between organic matters and clay minerals

Minerals and organic matters such as humic substance are usually aggregated in the soil. Reaction between humic substance and clay minerals is shown in figure 2 and 3. Humic substance in the soil has a large number of hydroxyl groups and carboxyl groups. These functional groups are negatively charged by dissociation in water. Therefore, humic substance is combined with metal ions such as Al^{3+}

to make insoluble substance in neutral solution as figure 2. On the other hand, aggregates of humic substance and clay minerals is disaggregated in alkaline solution and Al^{3+} combined with organic matters changes into $(\text{Al}(\text{OH})_4)^-$. In this way, humic substance is dissolved into the solution as shown in figure 3[6]. For that reason, it can be presumed that dispersion of soils is improved by treatment of soil with alkaline solution. In this study, K_2CO_3 , whose solution shows alkaline, was used as dispersing agent for the soils. K_2CO_3 is used as a food additive and fertilizer that have low environmental burden.

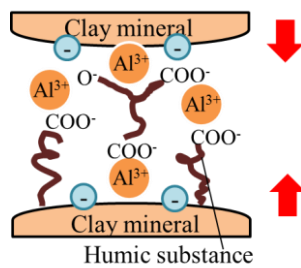


Figure 2. Reaction between organic matters and clay mineral in neutral solution.

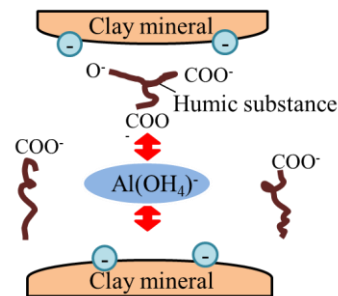


Figure 3. Reaction between organic matters and clay mineral in alkaline solution.

2.3. High gradient magnetic separation (HGMS)

HGMS is the method that enables to separate and capture ferromagnetic or paramagnetic particles on the magnetic filters made of ferromagnetic wires by making sharp magnetic gradient around them. Magnetic force and drag force acting on the particles in the fluid in magnetic separation method is shown in equations (1) and (2).

$$\mathbf{F}_M = \frac{4}{3} \pi r_p^3 (\mathbf{m} \cdot \nabla) \mathbf{B} \quad (1)$$

$$\mathbf{F}_D = 6\pi\eta r_p (\mathbf{v}_f - \mathbf{v}_p) \quad (2)$$

Here, \mathbf{F}_M [N] and \mathbf{F}_D [N] indicates magnetic and drag force, \mathbf{m} [A m^{-1}], \mathbf{B} [T], η [$\text{Pa}\cdot\text{s}$], r_p [m], \mathbf{v}_f [m s^{-1}] and \mathbf{v}_p [m s^{-1}] respectively indicates the magnetization of the particle, the magnetic field strength, the viscosity of the solvent, the radius of the particle, the velocity of the solvent and the particle. However, aggregates of paramagnetic and diamagnetic particles might prevent them from selective separation as shown in figure 4(a). In order to capture only paramagnetic 2:1 clay particles, it is necessary to disaggregation as shown in figure 4(b).

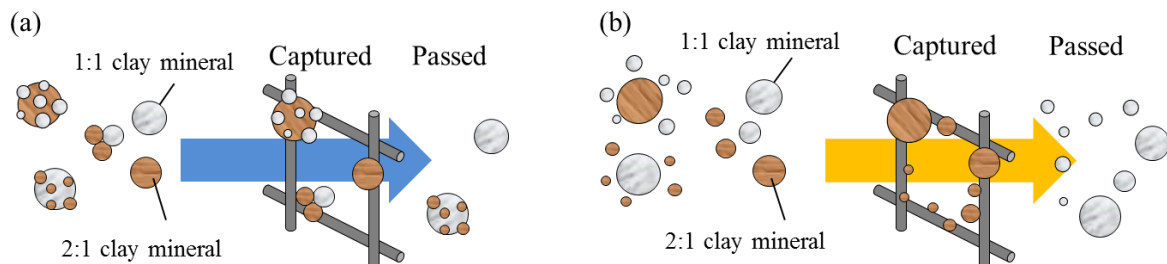


Figure 4. Schematic illustration of effect of disaggregation of clay mineral.

3. Treatment of organic matters

3.1. Materials and method

In order to investigate the dispersion effect of soil by organic matters treatment, non-contaminated soil was used. The soil was rich in organic matters and was collected from Tochigi prefecture. The particles smaller than 75 μm were separated from the soil with a grading sieve. 1 g of the classified soil (under 75 μm) was added into 100 mL of pure water and 0.1 mol L⁻¹ K₂CO₃, respectively. The soil suspensions were shaken at 120 rpm for 1 hour. The particle size distribution for each suspension was measured by particle size analyser (LA-920, HORIBA). As a reference experiment, H₂O₂ treatment used in the sequential extraction of soil, that can resolve the organic matters absolutely, was also conducted. The classified soil was added into 50 mL of 30 wt% H₂O₂ (pH was adjusted to 2 with HNO₃), keeping the temperature stable with a water bath for 2 hours at 85 °C.

3.2. Results and discussions

Figure 5 shows the particle size distribution before and after K₂CO₃ and H₂O₂ treatments. The particle distribution in water had a peak at around 30 μm . In case of organic matters treatment, the height of the particles around 30 μm decreased and smaller particles increased. The result indicates that particle aggregates was dispersed by the treatment. In addition, the distribution in H₂O₂ was almost as same as that in K₂CO₃. The result showed that K₂CO₃ has same dispersion ability as H₂O₂ and that the soil particles can be effectively dispersed by K₂CO₃.

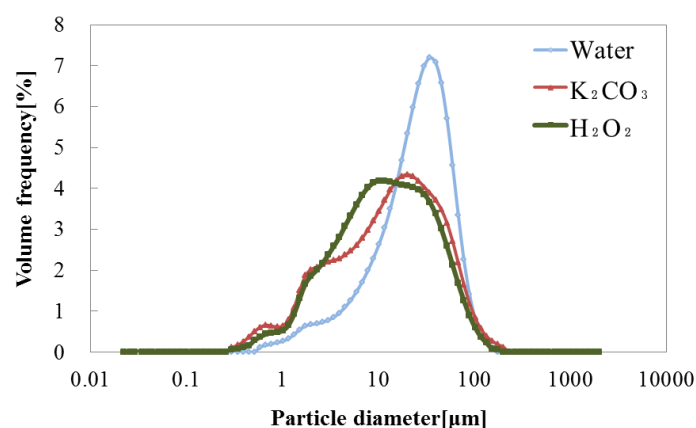


Figure 5. Particle size distribution of soils by treatment of organic matters.

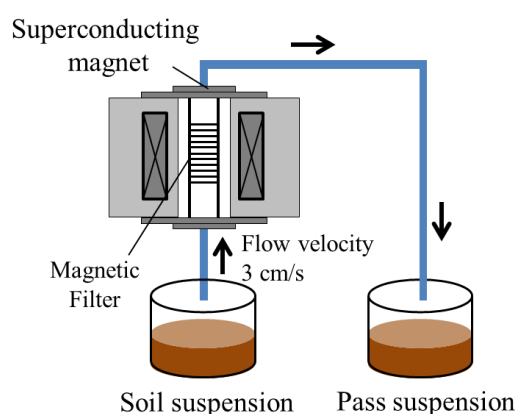
4. Magnetic separation of Cs contaminated soil

4.1. Materials and method

It became clear by the above experiment that clay aggregates by organic matters can be dispersed by K₂CO₃ solution treatment. In this section, the effect of the treatment on the magnetic separation efficiency was examined. The soil was collected in agricultural field in Fukushima prefecture. Here, the particles smaller than 75 μm (silt and clay) were separated from contaminated soil with a grading sieve. After the classification, the suspension was adjusted at solid-liquid ratio of 1:100. In order to disperse aggregates, K₂CO₃ was added into the suspension whose concentration was adjusted to be 0.1 mol L⁻¹. Then, the suspension was shaken for 1 hour at 120 rpm and was subjected to the magnetic separation. The conditions of magnetic separation is shown in table 2. For reference, water suspension without treatment of organic matters was also prepared and the magnetic separation was performed in the same condition. Passed and captured soil after magnetic separation were respectively divided into 4 size fractions (0-2 μm , 2-10 μm , 10-30 μm and 30-75 μm) with grading sieves. Mass and radioactivity for each fraction were measured by NaI scintillation detector (EMF211 EMF Japan Co., Ltd.).

Table 2. Experimental condition of magnetic separation.

Filter material	SUS430
Wire diameter of filter	0.34 mm
Applied magnetic field	6 T
Number of mesh	20 mesh
Number of filter	100

**Figure 6.** Schematic setup of experimental system of magnetic separation.

4.2. Results and discussions

Figure 7 shows change in radioactivity of each fractions of the passed suspension. Without the treatment of organic matters, the radioactivity in the fraction of 30-75 μm and 10-30 μm decreased by 44 % and 34 % compared with that before magnetic separation. After K_2CO_3 treatment, radioactivity decreased by 63 % and 40 % for each fractions. It indicates that the selective separation of 2:1 type clay minerals was enhanced by K_2CO_3 treatment. On the other hand, in the fraction of 2-10 μm and 0-2 μm , the radioactivity was not decreased by the magnetic separation both in water and in K_2CO_3 solution. It indicates that 2:1 type clay minerals having smaller size of 10 μm could not be captured in the magnetic separation. Therefore, it is necessary to improve the magnetic separation efficiency to capture smaller particles than 10 μm .

Moreover, figure 8 shows change of mass ratio of the passed suspension. The mass ratio in the fraction of 0-2 μm increased by particle dispersion treatment. It indicates that it is more important to capture 0-10 μm particles for volume reduction of the soil after particle dispersion treatment. Thus, the treatment of organic matters and the improving magnetic separation efficiency could make it possible to reduce radioactivity.

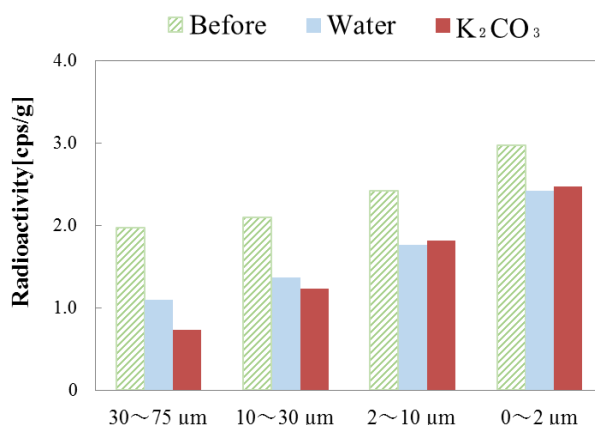


Figure 7. Radioactivity of passed soil.

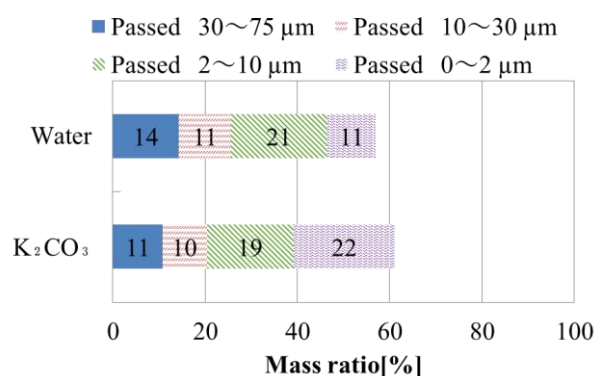


Figure 8. Mass ratio of passed soil.

5. Conclusion

In this study, we aimed to disperse clay aggregates with organic matters for selective separation of 1:1 and 2:1 type clay minerals magnetically. The particle size distribution of the particles of silt and clay in K₂CO₃ indicated that aggregates can be dispersed effectively by treatment of organic matters. In the fraction larger than 10 μm, 1:1 and 2:1 type clay mineral could be separated selectively by magnetic separation after treatment of organic matters. On the other hand, in the fraction smaller than 10 μm, 2:1 type clay might be passed through the magnetic filters even after K₂CO₃ treatment. It is concluded that the pretreatment of organic matters in combination with improvement of magnetic separation will be achieved effective volume reduction of contaminated soil. In the practical application, the solenoidal superconducting magnet which has larger bore diameter could enable to increase the processing amount of soil.

References

- [1] Ministry of the Environment, Japan, 2016. "Progress on Off-site Cleanup and Interim Storage in Japan,"
- [2] H Mukai, T Hatta, H Kitazawa, H Yamada, T Yaita, T Kogure 2014 *Environmental. Science and Technology*. **48** 13053–59
- [3] A Nomura, S Ogasawara, O Sanob, T Ito, J Yanai 2014 *Science of the Total Environment*. **468–9** 523–9
- [4] N Yamaguchi *et al.* 2012 *Bulletin of National Institute for Agro-Environmental Sciences* **31** 75–129

- [5] K Sekiya, H Kuwahara, Y Yoshida, S Igarashi, N Nomura, F Mishima, Y Akiyama, S Nishijia
2014 *IEEE Transactions on Applied Superconductivity* **24** 3700205
- [6] M Kimura *et al.* 1994 Soil biochemistry (Japan: Asakura Publishing Co., Ltd.) p 77