

## **Preliminary Evaluation of Cesium Distribution for Wet Sieving Process Planned for Soil Decontamination in Japan – 13104**

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### **ABSTRACT**

For the purpose of decontaminating radioactive cesium from a huge amount of soil, which has been estimated to be  $1.2 \times 10^8 \text{ m}^3$  by excavating to a 5-cm depth from the surface of Fukushima Prefecture where a severe nuclear accident occurred at TEPCO's power generating site and has emitted a significant amount of radioactive materials, mainly radioactive cesium, a wet sieving process was selected as one of effective methods available in Japan. Some private companies have demonstrated this process for soil treatment in the Fukushima area by testing at their plants. The results were very promising, and a full-fledged application is expected to follow. In the present study, we spiked several aqueous samples containing soil collected from an industrial wet sieving plant located near our university for the recycling of construction wastes with non-radioactive cesium hydroxide. The present study provides scientific data concerning the effectiveness in volume reduction of the contaminated soil by a wet sieving process as well as the cesium distribution between the liquid phase and clay minerals for each sub-process of the full-scale one, but a simulating plant equipped with a process of coagulating sedimentation and operational safety fundamentals for the plant. Especially for the latter aspect, the study showed that clay minerals of submicron size strongly bind a high content of cesium, which was only slightly removed by coagulation with natural sedimentation (1G) nor centrifugal sedimentation (3,700G) and some of the cesium may be transferred to the effluent or recycled water. By applying ultracentrifugation (257,000G), most of submicron clay minerals containing cesium was removed, and the cesium amount which might be transferred to the effluent or recycled water, could be reduced to less than 2.3 % of the original design by the addition of a cesium barrier consisting of ultracentrifugation or a hollow fiber membrane.

### **INTRODUCTION**

In order to decontaminate radioactive cesium from a huge amount of soil, which has been estimated to be  $1.2 \times 10^8 \text{ m}^3$  by excavating to a 5-cm depth from the land surface having a dose rate of over  $1 \mu\text{Sv/h}$  in Fukushima Prefecture, Japan, where a severe nuclear accident occurred at TEPCO's power generating site, and a significant amount of radioactive materials, mainly radioactive cesium, has been emitted, a wet sieving process was selected as one of the effective methods by the Radioactive Waste Management and Facility Decommissioning Technology Center and the Ministry of the Environment, Japan [1-2]. The dose rate of  $1 \mu\text{Sv/h}$  is equivalent

to the addition of 5 mSv/y to the background radiation dose in Japan, and evaluated as the radioactive cesium content of 8000 Bq/kg [2]. IAEA's handbook suggests that the vertical radioactive cesium transfer in land is limited to within 1cm during the initial year and 5 cm within 5 years [3]. Therefore, the evaluation of the soil amount, which should be processed, seems reasonable, but the total amount shall reach the residual capacity of the final disposal site for non-radioactive wastes in Japan; we actually need a volume reduction in the contaminated soil. The wet sieving process has been successfully utilized in Japan for the decontamination of chemical contaminants from land soils on an industrial scale throughout the country in this past decade. Five private companies in Japan, most of them being large construction companies, have already demonstrated the process for the soil treatment in the Fukushima area shortly using their testing plants [2]. The results were promising, and a full-fledged application is expected to follow.

In the present study, we spiked non-radioactive cesium hydroxide in several aqueous samples containing soil collected from a real and industrial wet sieving plant located near our university for the recycling of construction wastes, and investigated the physicochemical behaviors of cesium with clay minerals in the process in order to obtain fundamental data for the safe environmental remediation in Fukushima prefecture. This study has been independently and solely performed by Nagoya University, Japan, as a third party independent from the stake holders. As a result, we have obtained scientific data in order to understand the cesium behavior in the process, and provided an important suggestion to prevent secondary environmental proliferation of radioactive cesium into the hydrosphere near the plant.

## EXPERIMENTAL

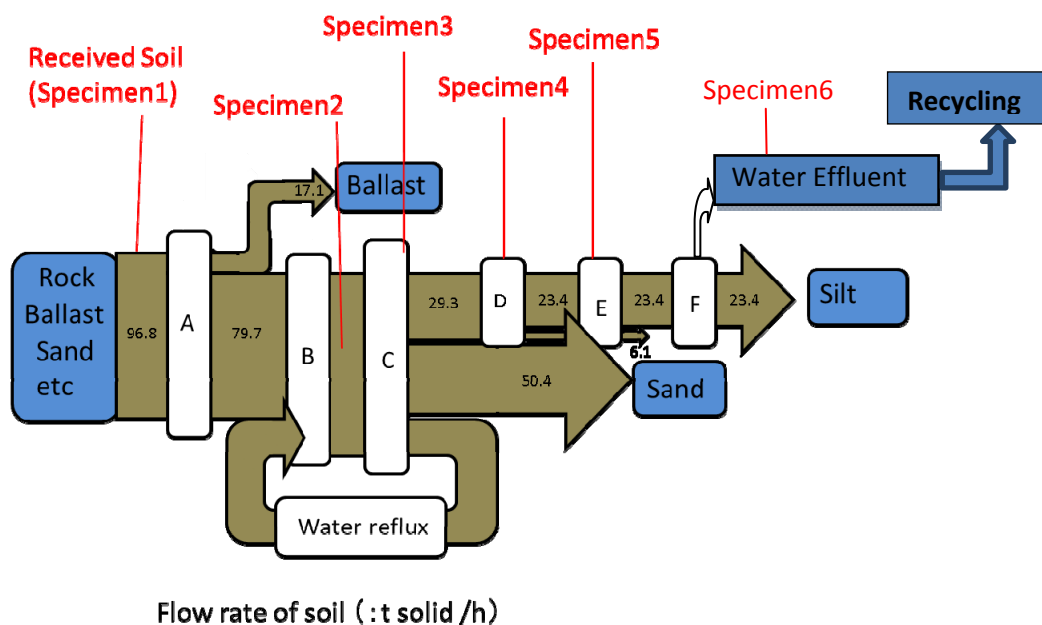
### Collection of Soil Specimens from a Wet Sieving Plant and Spiking Non-radioactive Cs on a Laboratory Scale

A wet sieving plant operated by Shin-ei Heavy Industry is located in Komaki city, Aichi Prefecture, Japan, near Nagoya University. The plant has been utilized for the recycling of waste soils from construction activities around Aichi prefecture and surrounding areas [4]. The plant capacity is 720 m<sup>3</sup>/day for the sieving of soils with water. The soil to be processed is always delivered from the construction sites for condominiums or commercial buildings for general purposes. The soils are not contaminated with radioactive materials or chemicals. The waste soil delivered to the plant is a typical Japanese soil consisting of ballasts of 5 to 39 mm in effective diameter, sands of less than 5 mm, and silts and clay minerals, which are formed over long periods of time by the gradual chemical weathering of rocks usually silicate-bearing on Japan's main island. Fukushima Prefecture is also located on Japan's main island; the characteristics of the soils in both areas are similar in mineral components [5]. **Table 1** shows the weight fractions of the soil treated at the plant. **Fig. 1** illustrates a block-flow diagram for the

plant where we obtained six specimens of soil and water slurries. The points in the process for collecting specimens are also illustrated in Fig. 1. Following the wet sieving, the clay minerals were treated by coagulating with a commercial coagulant, poly-aluminum chloride, followed by natural sedimentation and filter pressing and part of the processed water effluent is internally recycled in the plant as shown in Fig. 1. Twenty-four percent of the total water stream finally turns into the effluent. Some of it is used again with the feed stream. The samplings were performed during a commercial operation in 2011. Each slurry specimen was always stored and shaken in a 200 cm<sup>3</sup> glass container with a screw cap on a mechanical shaker (SA-300, Yamato Science, Japan) in order to avoid any unexpected sedimentation in the laboratory.

**Table 1. Typical Weight Fractions of the Treated Soil in the Shin-ei Heavy Industry’s Plant at Komaki-city, Aichi Prefecture.**

Ballast	Sand	Silts and clay	Total
18%	57%	25%	100%



**Fig. 1. A block-flow diagram for a wet sieving plant where specimens of the slurry-containing soil and water were collected.**

Note: A; trommel sieve, B; wet cyclone, C; overflow decanting tank, D; thickener, E; slurry tank, F; filter press, numbers in the diagram show flow rates in mass of soil as dry solid without water evaluated based on a design document. Water effluent is partially recycled in the plant.

A chemical reagent of cesium hydroxide monohydrate (>99.9% in purity), commercially

obtained from Wako Pure Chemical Industries, Ltd., Japan, was spiked in each specimen to investigate the distribution of cesium in the soil components in the process. Twenty mg of cesium as metallic cesium was spiked in each specimen of 100 g following the first partial partitioning of the specimens for physical characterization in order to measure the viscosity, bulk density, water content, pH of the liquid phase as well as size distribution of the clay minerals using sedimentation and dynamic laser scattering. Each spiked specimen in a glass vial was screw-capped and shaken at 50 rpm for 7 weeks in this study.

The viscosity, bulk density, water fraction and pH of the liquid phase of each specimen were measured using a viscometer (HBDV-1, As One Corp., Japan), weighing bottle (40 mm in diameter ×40 mm in height, 371-65-53-06, Shibata Scientific Technology, Ltd., Japan), Karl Fischer coulometric titrator (AQ-2200, Hiranuma Sangyo Co., Ltd., Japan), and pH meter (C-73, As One Corp., Japan), respectively.

The particle size distribution measurement of the specimens was performed using a dynamic laser scattering system (DLS-6500, Otsuka Electronics Co., Ltd., Japan) combined with centrifugation using a normal table-top centrifuge (Model 4000, Kubota Corporation, Japan) or an ultracentrifuge (CP70MX, Hitachi Koki Co., Ltd., Japan).

The cesium content in each fraction of the liquid filtrate and filtered solid was determined using an inductively coupled plasma mass spectrometer (SPQ 9700, SII Nanotechnology, Inc., Japan) following alkali fused treatment with solid sodium hydroxide in platinum crucibles, which has been performed even for the liquid filtrate in order to confirm the cesium contribution from a tiny portion of a solid particle. The detection limit was approximately 0.1 ppt for cesium.

The liquid filtrate was collected from the liquid phase of each specimen following centrifugation at 6000 rpm (3,700G) for one hour by a normal table-top centrifuge (Model 4000, Kubota Corporation, Japan). The filtered solid was collected from the centrifuged one after mixing with ultrapure water and centrifugation. This washing procedure was repeated three times before the solid collection.

### **Wet Sieving of the Actual Soil from Fukushima Prefecture on a Laboratory Scale and Radiological Measurement**

The actual soil in Fukushima city, Fukushima prefecture, was collected 6 months after the nuclear accident, and the collected specimens were wet sieved in a chemical laboratory on a very small scale by manually operated sedimentation and centrifugation using an ultracentrifuge (CP70MX, Hitachi Koki Co., Ltd., Japan).

The radioactivities of the original actual soil and fractionated parts of the soil based upon the mineral sizes by centrifugation were measured using a well-shaped germanium detector

equipped with a multi-channel analyzer (GEMHPGe Coax, GWL-300-15-S, Perkin-Elmer Instruments) for the cesium-137 and 134 isotopes. The detection efficiencies for the gamma-rays of 662 keV of Cs-137 and 605 keV of Cs-134 were 0.190 and 0.081 on average from 0 through 35mm from the bottom of the well, respectively.

## RESULTS AND DISCUSSION

### Collection of Soil Specimens from a Wet Sieving Plant and Spiking of Non-radioactive Cs on a Laboratory Scale

The results of the viscosity, bulk density, water fraction and pH of the liquid phase measurements of six specimens are summarized in **Table 2**.

**Table 2. Summary of simple characterization of six specimens collected from the wet sieving plant.**

Specimen number	Viscosity, mPa s	Bulk density, kg dm <sup>-3</sup>	Water content, %	pH
1	$2.2 \times 10^2$	1.44	57.7	12.0
2	4.6	1.11	84.8	9.7
3	5.5	1.14	81.7	10.7
4	2.7	1.12	90.0	10.9
5	$1.0 \times 10^3$	1.39	64.7	11.4
6	1.5	1.05	99.0	11.0

Generally, the measured pH values in the liquid phase were relatively high because the streams in the process contains cement or concrete materials generated from the construction sites.

**Table 3** shows the distribution ratios of the spiked cesium for each specimen. The distribution ratio varied and that of the number 5 specimen was the highest. Generally speaking, the distribution ratios observed downstream in the plant would increase. We could discussed this fact compared to the results of the particle size distribution measurement of the specimens which are illustrated in **Table 4** and **Fig. 2**.

If smaller size clay minerals in abnormally bind cesium rather than the larger size particles, the obtained results in **Table 3** can be justified. The detail measurement results for the three size classes in **Table 4** are summarized in **Fig. 3**. This result suggests silt and colloidal particles will bind cesium more strongly than would sand; up to 1.4 to 1.7 times greater, and the colloidal particles of the clay minerals play a significant role in the cesium binding. The cesium content increased as the size mean decreased and approached the value of 0.77 mg-Cs/g-solid for

the reagent bentonite that is commercially obtained from Wako Pure Chemical Industries, Ltd., Japan. This sample was separately tested as a reference experiment.

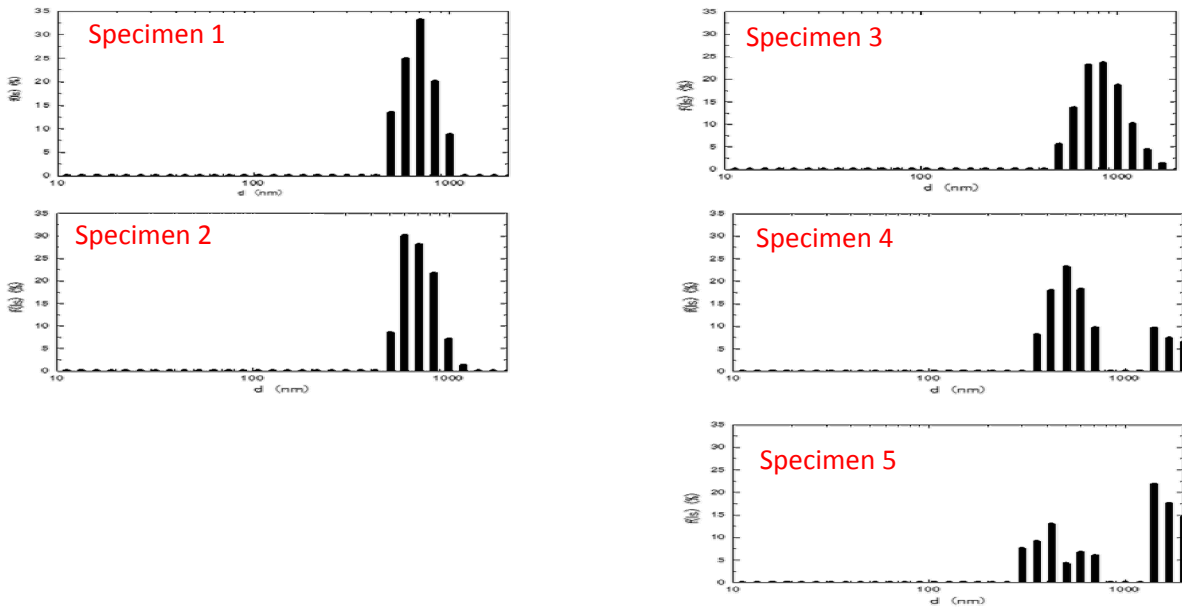
**Table 3. Summary of spiked cesium distribution ratios for specimens collected from the wet sieving plant.**

Specimen number	Solid fraction, weight %	Water fraction, weigh %	Cesium content, 10 <sup>-4</sup> weight %	Cesium content, 10 <sup>-4</sup> weight %	Distribution ratio
1	30.1	69.9	0.05	0.02	2.0
2	13.2	86.8	0.08	0.01	9.0
3	15.4	84.6	0.11	0.02	5.6
4	9.1	90.9	0.17	0.02	8.6
5	26.1	73.9	0.16	0.01	11.9
6	No data were available because a sufficient amount of the solid phase for the measurement could not be recovered in the experiment.				

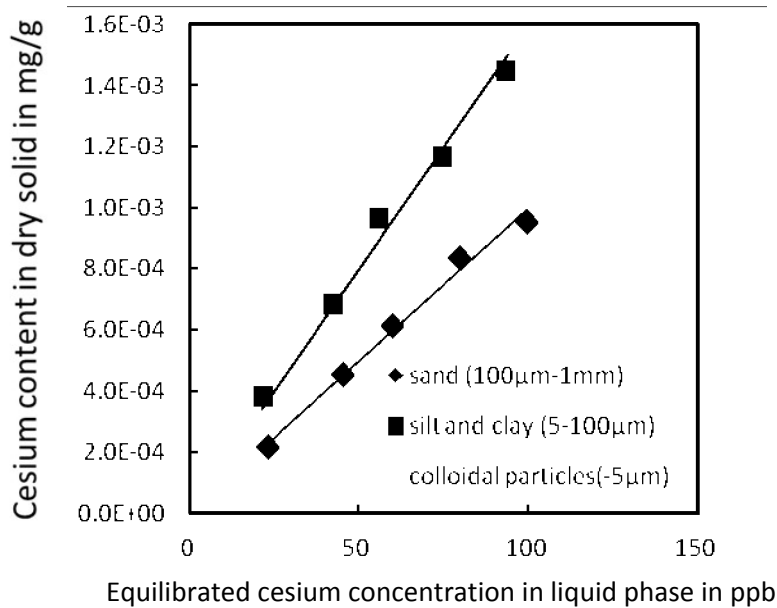
**Table 4. Compositions of effective size of solid components in each specimen.**

Specimen number	1	2	3	4	5
Colloidal particles of under 10 μm in effective diameter	3.9	6.3	5.2	8.2	0.9
Silt and clay of 10 to 100 μm in effective diameter	71.1	85.3	67.3	77.1	87.9
Sand of 1 mm to 100 μm in effective diameter	25.0	8.4	27.5	14.7	11.2

Note: No data were available for specimen 6 because not enough of the solid phase for the measurement could be recovered.



**Fig. 2. Measurement results of solid size distribution in each specimen.**



**Fig. 3. Dependence of distribution ratio of cesium upon the soil components.**

On the other hand, we found based on an estimation using the data from a material balance design flow sheet and our measurement of the size distribution of the solids in the samples that the total recovery of the large size components, except for the clay minerals was 83%. A reduction factor of approximately six can then be achieved. This value is slightly

higher than that reported for the demonstration test by the large construction companies in Fukushima prefecture. The value of six is an ideal one when we remove all the clay minerals from the process streams, and then the small discrepancy seems reasonable. A higher reduction may be achieved if we optimize the process, and in order to obtain basic information to tune the process, we can perform a tracer experiment using a stable cesium chemical reagent for actual plants planned in Fukushima prefecture.

In the effluent process stream of the wet sieving plant, 84% of the spiked cesium was found to exist in the aqueous phase because the tiny fragments of clay minerals were contained in the aqueous phase even after coagulating the sedimentation promoted by the coagulating chemicals, which is shown as a bimodal size distribution for specimen 5 in **Fig. 2**. The size distribution measurement of the fragment shows the presence of the solids of less than 100 nm in diameter. These fragments were difficult to remove by the addition of a coagulating reagent and natural sedimentation (1G) or conventional centrifugal sedimentation (3,700G). By applying ultracentrifugation (257,000G), we successfully removed most of submicron clay minerals binding cesium. The cesium content in the supernatant was reduced from 8.82 mgCs/dm<sup>3</sup> for natural sedimentation to 0.20mgCs/ dm<sup>3</sup> for the ultracentrifugation. Therefore, the fraction of cesium that may leak into the effluent or recycled water could be reduced to less than 2.3% of the original design by the addition of a cesium barrier consisting of ultracentrifugation or a hollow fiber membrane. For the latter method, however, we need further experimental work to confirm its effectiveness as a future study.

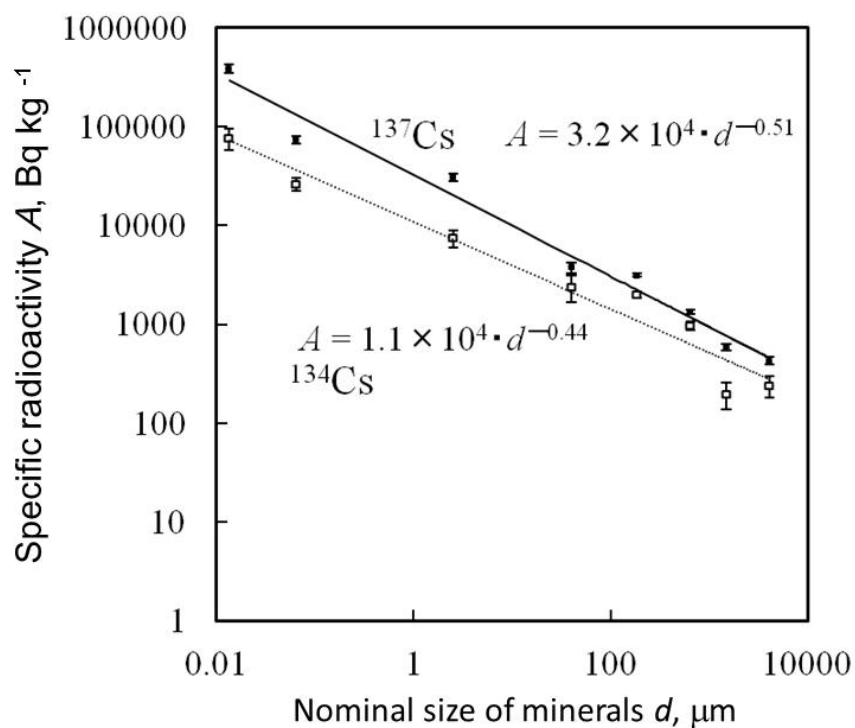
### **Wet Sieving of the Soil from Fukushima Prefecture and Radiological Measurement**

The actual soil collected from Fukushima prefecture was fractionated into eight samples by filtration and ultracentrifugation. The nominal size of the minerals fractionated widely ranged from (i) 2.0-6.2 mm to (viii) less than 25 nm as shown in **Table 5**. Since it is well known that the fraction of soil with the smaller mineral size contains a larger content of clay minerals, the observed fact that radioactive concentration increases as the mineral size decreases is reasonably understandable due to the clay mineral of a smaller size strongly binding the cesium ion in the bulk or on its surface. A logarithmic correlation between the specific radioactivity and mineral size is illustrated in **Fig. 4** for Cs-134 and 137. The slopes shown in **Fig. 4** lie between -1, which is proportional to the specific surface area, and 0, which indicates bulk binding; this fact may indicate that cesium ions are bound by the ion exchange phenomena on the complicated geometry of the surface formed by the weathering and/or in the layer structure of the clay minerals, and seems identical to previous results [6-7].



**Table 5. Size distribution of soil components for the soil specimen from Fukushima city, and fractional radioactivity.**

Fraction number	Size range in each fraction	Fractional weight, %	Fractional radioactivity, %
(i)	2.0-6.2 mm	12.8	1.0
(ii)	1.0 -2.0 mm	20.1	1.9
(iii)	0.3 - 1.0 mm	19.4	5.3
(iv)	75 -300 $\mu\text{m}$	16.9	10.3
(v)	5 - 75 $\mu\text{m}$	23.2	16.9
(vi)	105 - 5000 nm	5.2	23.6
(vii)	25 - 105 nm	2.1	24.6
(viii)	<25 nm	0.3	16.4
total		100.0	100.0



**Fig. 4. Logarithmic relationship between specific activity and size of minerals in the soil obtained from Fukushima area.**

## CONCLUSION

The present study provides scientific data concerning the effectiveness of volume reduction in contaminated soil by a wet sieving process as well as the cesium distribution between the liquid phase and clay minerals for each sub-process on a full-scale, but for a simulating plant equipped with a process of coagulating sedimentation and operational safety fundamentals for the plant. Especially for the latter aspect, the study clearly showed that the clay minerals of submicron size strongly bind cesium with a higher content, and they are only slightly removed by coagulating with natural sedimentation (1G) or centrifugal sedimentation (3,700G). By applying ultracentrifugation (257,000G) most of the submicron clay minerals binding cesium were removed, and the remaining fraction of cesium that may leak into the effluent or recycled water could be reduced to less than 2.3% of the original design by the addition of a cesium barrier consisting of ultracentrifugation or a hollow fiber membrane.

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