Practical Approach to Decontamination of Radioactive Cesium-Contaminated Matter in Agricultural Region by Improved Wet Classification and Use of Geomaterials

Kenichi ITO^{1,*}, Hidetaka MIYAHARA², Toru UJIIE³, Toshikatsu TAKESHIMA⁴, Shingo YOKOYAMA⁵, Kotaro NAKATA⁵, Tetsushi NAGANO⁶, Tsutomu SATO⁷, Tamao HATTA⁸ and Hirohisa YAMADA²

¹ Department of Geo Environmental Preservation, Center for International Relations, University of Miyazaki, 1-1 Gakuenkibanadai-nishi, Miyazaki-shi, Miyazaki 889-2192, Japan

² Environmental Remediation Materials Unit, Environment and Energy Materials Division, National Institute for Materials Science, 1-1 Namiki, Tsukuba-shi, Ibaraki 305-0044, Japan

³ Japan Conservation Engineers & Co., Ltd., 1-12-11 Kitaurawa, Urawa-ku, Saitama 330-0074, Japan

⁴ Astec Tokyo Co., Ltd., 5-21-3 Hirai, Edogawa-ku, Tokyo 132-0035, Japan

⁵ Nuclear Fuel Cycle Backend Research Center, Civil Engineering Research Laboratory, Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko-shi, Chiba 270-1194, Japan

⁶ Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency, 2-4 Shirakatashirane, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan

⁷ Division of Sustainable Resources Engineering, Department of Socio-Environmental Engineering, Faculty and Graduate School of Engineering, Hokkaido University, Kita-13, Nishi-8, Kita-ku, Sapporo 060-8628, Japan ⁸ Environmental Resources Division, Japan International Research Center for Agricultural Sciences,

1-1 Ohwashi, Tsukuba-shi, Ibaraki 305-8686, Japan

In the radiation dosimetry of radiocesium in Iitate, Fukushima, the level of radiocesium around the environment did not exceed the criteria in liquid phases such as puddle water, but was distributed in solid phases such as some soil types and organic matter. On the other hand, retting of the cut bamboo grass and hemlock fir in water allowed the release of radiocesium, about 230 Bq/kg exceeding the criteria for a bathing area. The flow-thru test using zeolite showed the removal of radiocesium-contaminated soil. According to the results of wet classification, radiocesium was detected and its level exceeded the cropping restriction level in almost all classified particle fractions. The decontamination effect of wet classification on radiocesium contamination was smaller than that on heavy metal contamination. Specifically, the wet classification process were devised and examined as improved processing techniques. As a result, the effectual volume reduction of the radiocesium-contaminated soil was confirmed by adding an intermediate process such as the surface attrition in the vibrator.

KEYWORDS: radiocesium, released radiocesium from organic matter, radiocesium-contaminated soil, wet classification, volume reduction

© 2021 Atomic Energy Society of Japan. All rights reserved.

^{*} Corresponding author, E-mail: itoken@cc.miyazaki-u.ac.jp

DOI: 10.15669/fukushimainsights.Vol.4.100

Originally published in Transactions of the Atomic Energy Society of Japan (ISSN 1347–2879), Vol. 11, No. 4, p.255–271 (2012) in Japanese. (Japanese version accepted: July 23, 2012)

I. Introduction

Due to the large quantity of radioactive material released during the Fukushima Daiichi Nuclear Power Plant Accident, caused by the Great East Japan Earthquake Disaster, the areas contaminated with comparatively high radiation are not only those surrounding the Fukushima Daiichi Nuclear Power Plant, but are distributed throughout various regions of South Tohoku and Kanto. The predominant radioactive materials in the contaminated areas, excluding the evacuation zone, are ¹³¹I. ¹³⁴Cs and ¹³⁷Cs¹). Among these, almost no ¹³¹I, which has a short halflife of eight days, was detected by the surveys after May 2011. The radioactive cesium isotopes ¹³⁴Cs and ¹³⁷Cs were reported by environmental monitoring surveys to be residual materials that persist in the land surface due to forming cations with a low translocation tendency¹). Based on this, it is explained that reducing the influence of radiation on residential areas on the land surface and minimizing health risks is possible by actions such as inversion tillage, which digs or peels off the surface soil with high radioactivity (due to residual radioactive cesium) and replaces it with soil from a deeper zone²⁾. However, because of the wide area of contamination, the variety in geographical features such as ground water levels, land forms, and land use types, the necessity was felt for control over each piece of land for an extended period of time after any such action. Obstacles to land digging, land use, and land trading, and difficulty with gaining agreement and providing adequate comfort for nearby residents were anticipated. However, removing the surface soil layer by peeling, etc. and storing it in a controlled place (temporary storage yard, etc.) that satisfies certain requirements until the radioactivity doses go under a certain level, is regarded as a safety measure. Technologies such as safe peeling using polymers, etc. are already being studied as ways to prevent the surface layer from becoming airborne^{3,4}).

On the other hand, according to the Ministry of the Environment, if the areal decontamination of regions including forests emitting 5 mSv/y and over and of spots of 1 mSv/y and over is conducted, the area of regions requiring decontamination adds up to 2,419 km^{2,5)}. Furthermore, the quantity of generated debris is estimated at 28,785 \times 10³ m³, considering the 40% of land under buildings, peeling 100% of a 5 cm thick surface layer from agricultural lands, cutting 10% of branches and 10–100% recovery of fallen leaves, and mowing⁵⁾. For handling such an enormous amount of contaminated debris, an efficient removal method and volume reduction technology is expected to be easily possible at the relocation site. The extraction technology for radioactive cesium in the contaminated peripheral soils was studied after the Chernobyl Nuclear Power Plant Accident^{6,7)}. After the Great East Japan Earthquake, a method for extracting the radioactive cesium using acids was studied in Japan as well⁸⁾. However, because the chemical processing will change the nature of the soil, its reuse after decontamination would be difficult. The use of this method in outdoor sites is problematic, and it may generate secondary wastes in the process of treating the soils with acid. Also, its operation at numerous and varied sites over a wide area is difficult. Consequently simpler and safer methods are expected.

In the field of soil contamination, **Figure 1** shows how the soil purification technology termed "soil wet-classification" separates and classifies fine grains such as heavy metals and clays that are distributed throughout the soil by separation, classification, etc. and compresses and reduces the volume of contaminated soil that exceeds specified standards^{9,10}. The cesium in the contaminated soils is radioactive, but is also a non-organic harmful metal similar to heavy metals such as arsenic, lead and cadmium. Therefore, like heavy metals, cesium is also considered to be present in the finer grains in relatively large quantities. Consequently, volume reduction is expected by wet-classification of soils contaminated by radioactive cesium as well.

On the other hand, many agricultural lands and mountain forests are included in the contaminated regions, mainly in Fukushima Prefecture. According to a document of the Ministry of INSIGHTS CONCERNING THE FUKUSHIMA DAIICHI NUCLEAR ACCIDENT Vol. 4



Figure 1 Conceptual scheme of wet-classification and washing for decontamination of heavy-metal contaminated soil⁹⁾

the Environment, of the total area of 2,373 km² of lands emitting radiation exceeding 1 μ Sv/h, 26.5% is agricultural land and 62.6% forest ⁵). However, in the Soil Contamination Countermeasures Act enforced in 2003, agricultural lands and mountain forests are outside of the scope of the law, whose major object is old factory sites that treated hazardous substances, or soil contamination in urban areas¹¹). Due to this, the available examples and data for soil wet-classification on agricultural lands, etc. are inadequate. Furthermore, because the soils of agricultural land, etc. contain finer grains such as clay, and soil enrichment agents such as fertilizer retainers, their physical and chemical properties presumably differ from urban area soils. For example, the ion exchange capacity (anion and cation exchange capacity, AEC and CEC) and water retaining capabilities are higher in agricultural soil.

Hence, a hot test was conducted in an agricultural village in a mountain area included in the planned evacuation area, Iitate-mura, Soma-gun, Fukushima-Prefecture It aimed at the validation of the volume reduction effect by soil wet-classification on the contaminated agricultural soils, etc. by tracking radioactive cesium.

An in-situ hot test was conducted twice, first from Aug. 23 to 25, and then from Oct. 16 to 21, 2011. All procedures, including the sampling of specimens, tests, measurements, etc. were conducted in Iitate-mura. Additionally, because no storage place had been selected, after the test the specimens were returned to the specimen sampling location, after confirmation from the village office of Iitate-mura.

II. Measuring Method and Specimens

1. Workplace

The specimens were sampled in Iitate-mura, mainly from the agricultural land around the Iitate-mura village office, and with the cooperation of the office, were contained in the indoor parking place on the premises of the office. The testing of the specimen was conducted in the building of Iitate-mura village office to avoid the radiation in the environment and to suppress the background during measurement.

2. Measuring Methods

For measuring the radioactivity of the radioactive cesium in the test specimens, an NaI (TI)

scintillation type γ -ray spectrometer (EMF-211, 3 × 3 in./AMPTEK) was used. To suppress the background, measurements were conducted with equipment that was contained in a lead shielding system, covered with 5-cm-thick lead blocks together with the specimen being measured (Figure 2). For measuring, 100 to 300 g soil specimens and approximately 100 g fluid specimens were used. The measurements were converted to Bq (becquerel) equivalents of ¹³⁴Cs and ¹³⁷Cs and the sum was divided by the weight of the specimens used, to provide the radioactive cesium concentration as Bq/kg. The determined lower sensitivity limit was 33 Bq/kg, and the measurement error was approximately $\pm 10\%$. For details please refer to the reports by Uiiie et al. (2012) and the documents from the device supplier^{12, 13}. When sampling a specimen in the field, a β/γ -ray GM Survey meter was used (TGS-121/Hitachi Aloka Medical) to provide a rough standard for locating and identifying contaminated specimens. Also, some of the fluid specimens were measured by the Japan Atomic Energy Agency after the recovery of cesium using an Empore TM Rad Disk (Sumitomo 3M)¹⁴⁾. The Empore TM Rad Disk is a disk-type solid phase extraction material that collects the specific elements, ions, etc. dissolved in the liquid phase. In this study, a cesium Rad Disk was used that incorporates a type of ferrocyanide, cobalt-modified hexacvanoferrate as the cesium capturing material that selectively adsorbs the dissolved cesium without being obstructively influenced by the major ions contained in the water present in the general environment, including potable water, river water, and ground water (Figure 3)¹⁴). The measuring methods are as follows: A 100 mL water specimen was vacuum-filtered, and the cesium in the liquid phase was collected in the Rad Disk. Next, the



Figure 2 Gamma ray spectrometer detector enclosed by radioprotective lead blocks (left) and appearance of field assay (right)



Figure 3 EmporeTM RAD disk for cesium

	γ -ray spectrometer	GM survey meter with rad disk	
-	γ-ray spectrometer EMF-211 (Amptek inc.)	selective SPE disk Empore TM RAD disk (3M)	
Instrument & specification	3×3 inch,	pore: 0.1~0.2 μm	
	NaI(TI) scintillation counter	β-ray and $γ$ -ray GM survey meter	
		TGS-136 (Hitachi Aloka Medical,	
		Ltd.)	
Measurement time	10min.	10 min.	
Objective sample	Liquid and solid	Liquid	
Form in measuring	In vinyl bag.	RAD disk filtrated sample	
Sample amount in measuring	Liquid: 100 g Solid: 300 g	100 mL	
Measurable form of radiocesium	All phase in sample	Soluble ion phase, fine particulate	
Unmeasurable form	-	Colloidal phase under 0.1~0.2 µm	

 Table 1
 Two radiocesium measurement methods used on samples

Rad Disk was assessed in the detection zone of a β/γ -ray GM Survey Meter (TGS-136/Hitachi Aloka Medical). The acquired β -ray dose count rate (cpm) of the Rad Disk was multiplied by a conservative conversion coefficient (0.0644 Bq/cpm) for the radioactive cesium acquired, using a standard source. The value was then divided by the filtered water quantity and considered to be the water's radioactive cesium concentration (Bq/L)^{15, 16)}. The general detection limit of this method is 400 mBq/L and lower. This method is considered capable of collecting radioactive cesium with a high capture rate ¹⁴.

Additionally, the physical hole diameter of a Rad Disk is $0.1-0.2 \ \mu m^{17}$. Hereinafter this measuring method is referred to as the "Rad Disk method." The specific weights of liquid phase specimens such as water were regarded as 1 kg/L and recorded as Bq/kg in the measurement results. The above two types of measuring methods are shown in **Table 1**.

3. Contamination Survey and Specimen Sampling of Agricultural Soils, etc.

Specimens were sampled from substances such as the soils in the periphery of the litate-mura village office, agricultural land, branches and leaves, water, etc., and evaluated (Figure 4).

Because the fallout radioactive cesium or the fine grains that contain it might remain in the liquid phase in a closed system of water fields, water in a fireproof concrete water tank was sampled, since this water was presumably stored outdoors in the liquid phase for an extended period. For comparison purposes, water in a pool formed on a covering sheet near a forest was sampled as land surface water, reflecting the rainfall water after the accident. Also, in the paddy field in Iitate-mura, on Aug. 24, 2011 during this hot test period, sampling was conducted on the muddy water discharged during the 'soil pudding forced water falling' test, in which the paddy field soil with farming water was stirred and discharged together with surface soil. This sampling was conducted by the National Institute for Rural Engineering, and the National Agriculture and Food Research Organization as one of the potential physical methods for removing the radioactive material from the paddy field soil¹⁸). This sample was a specimen containing the surface soil of a paddy field. Because the draining of water after a flood generally only involves the supernatant, two types of supernatant were prepared; the water after natural settling-out of soil pudding muddy water and the water treated by filtration through a sieve of 75 μ m, stirring with 200 μ L/L of added poly aluminum chloride (PAC), and concentrated sedimentation. These procedures were used on the liquid phase specimens representing flooding in the paddy field.

Solid specimens were the sampled plants and soils. Branches of bamboo and hemlock, and the grass around the office were cut for the purpose of decreasing the air doses, and these were sampled as plants on which the adhesion of fallout radioactive cesium was presumed.



Figure 4 Field research and sampling in litate, Fukushima (top left: rotary on paddy-field, top center: forced overfall, top right: topsoil sampling, middle left: handy sampler, middle center: soil sampling, middle right: borehole sampling, bottom left: dose measurement of pruned hemlock fir, bottom center: pruned bamboo grass, bottom right: pruned blanches being sampled for immersion test)

Because the plants in the grass, forest, etc., are exposed to rainfall outdoors, the cut branches and leaves of bamboo grass and hemlock were immersed in the ion-exchange water overnight (approximately 16 hours) and a solid/liquid separation was conducted through a 3 μ m porosity approximately 5 mm thick non-woven bag filter and the possibility of translocation of radioactive cesium to water was validated. The surface soils were sampled from the dry lands, ridge soils, grass lands, drained paddy lands, and sandy ground. Among these, in three places (paddy field, dry land and sandy ground), soil as deep as 30 cm was sampled, and the distribution of radioactive cesium was confirmed to the maximum sampling depth. The radioactive cesium concentration per dry weight of solid phase specimens was calculated after drying to a constant mass in a constant-temperature chamber at 110°C after measuring the as-is specimen and acquiring the water content ratio.

The specimens were selected from the survey results above, and a study was conducted mainly on the soil wet-classification and the processing of radioactive cesium by the minerals.

III. Results and Discussion of Measurements

1. Land Surface Specimens

The concentration of radioactive cesium in the samples and the various adjusted specimens

are shown in **Table 2**. The concentration of radioactive cesium in the fireproof water tank was equal to or lower than the guideline of 50 Bq/L of radioactive material in the bathing area, as specified by the Ministry of the Environment. When the specific weight of water was regarded as 1 kg/L¹⁹, the concentration was lower than the determination limit in a pool. The soil pudding muddy water showed 2,100 Bq/kg and was not allowed to drain, but its supernatant water showed values lower than the determination limit for both natural settling and flocculent settling processing. This indicates that the radioactive fallout cesium in the hydrosphere from March was removed comparatively more quickly from the liquid phase after being distributed onto the soil grains and concrete surfaces. Additionally, the naturally generated water pool also showed values equal to or lower than the determination limit. This indicates that the radioactive cesium was distributed on the solid surfaces as explained above or was not contained in the rainwater.

All the soil samples showed a concentration of radioactive cesium, per dry weight, exceeding the standard restriction limit of 5,000 Bq/kg for rice²⁰⁾ but fell within the specified standard of 8,000–100,000 Bq/kg set by the Ordinance for Enforcement of the Act on Special Measures concerning the Handling of Contamination from Radioactive Materials (Special Measures Act), a standard for safe processing of wastes except for dry lands and grass field surface soils in August^{21, 22)}. However, this exceeded the range of the standard specified by the Special Measures Act for grass-surfaced soils. Furthermore, the radioactive cesium concentration of cut branches and leaves showed high values of 53,000 Bq/kg for bamboo grasses, and 65,000 Bq/kg for hemlock in a wet condition.

Because the moisture content is presumed to be more than 50% in undried plants, the possibility of exceeding the upper limit specified in the Special Measures Act was pointed out for these as well. The water seeping from cut branches and leaves immersed in the water overnight showed a concentration of 230 Bq/kg, which exceeded the guideline of 50 Bq/L for bathing areas, as set by the Ministry of the Environment (Table 2, **Figure 5**).

The results of the above survey implied that the objects that caused contamination were the soils and the vegetation, i.e. the solid phases in the muddy water. This further implied the possibility of translocation of radioactive cesium adhering to vegetation, or in water by eluviation due to rainfall. The radioactive cesium concentration on cut branches and leaves of bamboo

				Cs (B	Cs (Bq/kg)		
Time		Sample	Aspect and sampling site	Per wet weight	Per dry weight		
		Soil: croft	Near Iitate village office	3,640	5,620		
		Soil: line soil	Same as above	24,800	35,900		
	0.111	Soil: grass topsoil	Same as above, twined soil round grasses	93,900	208,700		
	Solid	Organic matter: bamboo grass	Near Iitate village office	53,000	_		
		Organic matter: hemlock fir	Same as above	65,000	_		
2012.		Muddy water: Paddy-field	From rotary and forced overfall test	2,100	_		
mug.		Rotary muddy water	Supernatent after spontaneous precipitation	<33	_		
			Supernatent after sieve and precipitation with PAC	< 33	_		
	Liquid	Fire-fighting water tank	Near Iitate village office	39	_		
		Puddle water	On the coating sheet near Iitate village office	< 33	_		
		Seeping water	With organic matter	230	_		
		Soil: Paddy-field	Kusano area	12,000	18,500		
Oct.	Solid	Soil: Croft	Akaishizawamaeda area	13,000	18,255		
		Soil: Ground	In front of Iitate village office	34,000	37,810		
Ministry of Agriculture, Forestry and Fisheries of Japan: Cropping restriction level about paddy-field				5,0	000		
Enviror	nment M	inistry: Criterion of designation (storage direction)	$8,000 \sim$	8,000~100,000		
Enviro	nment M	inistry: Criterion of bathing area		5	0		

Table 2 Radioactive cesium concentrations of substances around litate village office

% The error range of all data in this table is $\pm 10\%$.

Kenichi ITO et al.



Figure 5 Radioactive cesium concentrations on substances around the litate village office

grass and hemlock used in the test showed 53,000 Bq/kg for bamboo grass and 65,000 Bq/kg for hemlock. The bulk volume of those was approximately 10 L. Where the quantity ratio of tested bamboo grass and hemlock is assumed to be approximately the same and the bulk specific weight of branches and leaves of woody plants is 0.1 kg/L, the quantity of cut branches and leaves used in the test was estimated to be approximately 1 kg and the radioactive cesium concentration at 59,000 Bq/kg. Because the radioactive cesium concentration in seeping water acquired by immersing 1 kg of these cut branches and leaves in approximately 10 L of ion-exchange water was 230 Bq/kg, the quantity of radioactive cesium translocated from the immersed cut branches and leaves to the liquid phase was 2,300 Bq by rough calculation, and approximately 4% of the cesium contained in the branches and leaves leached into the liquid phase when immersed in the water.

2. Depth Distribution of Radioactive Cesium

Soils were sampled at three locations using a hand sampler (HS-25S/Fujiwara) in a paddy field, on dry land and in the ground as deep as 30 cm. The radioactive cesium concentration was measured after sampling at 2 cm depth intervals.

The results are shown in **Figure 6**. The distribution of radioactive cesium was limited to less than the top 10 cm at all three locations, and was below detection limit in soils deeper than 10 cm. Based on this, as seen in the surveillance research report by the Ministry of Agriculture, Forestry and Fisheries²), it was confirmed that the radioactive cesium that fell out on the land surface did not penetrate deep into the soil but became fixed at a comparatively shallow depth. On the other hand, penetration as deep as approximately 20 cm was reported in the paddy fields, etc. in the surveillance research report of the Ministry of Agriculture, Forestry and Fisheries. The difference in the penetration of radioactive cesium with soil quality was presumably influenced by the soil's water permeability or the presence of clay minerals that easily adsorb and retain the radioactive cesium. Furthermore, in the agricultural lands, it is assumed that some regions were disturbed by plowing or cultivation during farming work after the accident. So although the penetration of radioactive cesium was 10 cm or less in this survey, but deeper



Figure 6 Radioactive cesium distribution in 3 types of soil

than that in other locations, it can be said that it is necessary to remove at least enough surface soil to provide a sufficient check of the local air dose and radioactive cesium concentration in soil during real decontamination work.

IV. Removal of Eluviated Cesium

1. Adsorption Test Method

During the survey, the eluviation of radioactive cesium from plants to water was recognized. This implies the possibility of secondary contamination of the peripheral environment due to leaching of radioactive cesium by rainfall and runoff from the plants and forest plants, etc. cut/ stored to decrease the air dose. So the reduction of leaching water volume during storage and the volume reduction of stored plants were studied as possible methods to remove radioactive cesium by using a mineral to treat the water used for its active eluviation from plants. For this purpose, a contact adsorption test with a mineral was conducted by both batch and column methods on the leaching water (water in which cut branches and leaves were immersed) during the survey.

The batch adsorption test was as follows: For 1 L of plant leachate water, 100 mg of powders of each mineral were added and stirred using a spoon, for dispersion. Then 200 μ L of PAC was immediately added for flocculent settling, and was stirred again. After leaving this for 30 minutes, the liquid phase was collected using a 0.45 μ m membrane filter, as used for solid/liquid separation in the official test for soil contamination. Thus, the solid phase and liquid phases were separated and used as measurement specimens²³⁾. Because the specimen was a liquid, the Rad Disk method was used to measure the radioactive cesium concentration. As a mineral powder, the Hokkaido Niki zeolite (clinoptilolite) of under 100 mesh, phlogopite, South African vermiculite powder and the mesoporous silica for cesium synthesized by the Natl. Inst. for Materials Science (NIMS) were used. PAC was not added to the mesoporous silica because a

flocculant is not usually used.

Two types of Niki grain zeolite, Size-M(grain size 2–5 mm) and Size-L(grain size 5–10 mm) were used (**Figure 7**). Almost equal volumes of Size-M(27 g) and Size-L(25 g) were placed in a polypropylene resin column (ID 15 mm × H 175 mm) and four test sections were set up with one each of Size-M and Size-L and two sets in which the same sizes were connected (**Figure 8** and **Figure 9**). Through each of the columns, the plant leachate water was passed upward using a tubing pump. The water that came though was collected as two samples, during 0–30 min (first 30 min) from the start and during 30–90 min (next 60 min), and the as-found measurement of radioactive cesium concentration was conducted. The flow rate was SV6.6–7.6 h⁻¹. SV (Space Velocity) is the space flow rate indicated by the water quantity per unit time divided by the volume of filtered material.

2. Results and Discussion: Cesium Adsorption Test

The results of batch adsorption tests are shown in **Table 3**. While the radioactive cesium concentration of plant leachate water measured by γ -ray spectrometer was 230 ± 23 Bq/kg, the



Figure 7 Granular Niki-zeolite (left : M size, right : L size).



Figure 8 Appearance of the columns for flow-thru test



Figure 9 Scheme of the flow-thru test using columns

Table 3 Results of batch adsorption test for cesium eluted from organic matter using geomaterials

Sample	Cs (Bq/kg)	$\underset{(\%)}{\operatorname{Removal efficiency}}$	$\begin{array}{c} Adsorbed \ amount \\ (Bq/kg) \end{array}$	$\begin{array}{c} Partition \ coefficient \\ (mL/g) \end{array}$	Comment
Seeping water from organic matter	$\begin{array}{c}(230\pm23)\\133.8\pm4.9\end{array}$	(y-ray spec Measured us	ctrometer) ing rad disk		
Zeolite	93.9 ± 4.1	29.8	399,000	$4.2 imes 10^3$	At Niki, Hokkaido, <100 mesh
Phlogopite	65.4 ± 6.6	51.1	684,000	$1.0 imes10^4$	
Vermiculite	87.5 ± 4.0	34.6	463,000	$5.3 imes10^3$	In South Africa
Meso-porous silica	110.9 ± 8.0	17.1	229,000	$2.1 imes10^3$	Cs target type

radioactive cesium concentration of plant leachate water measured with the Rad Disk method was 133.8 ± 4.9 Bq/kg. The difference of 68.3-124.1 Bq/kg between the two measuring methods was recognized as being due to the error range of each measurement. The γ -ray spectrometer is a method to measure the γ -radiation emitted from a whole object in the lead shielded space, and the value reflects the concentration of total radioactive cesium contained in the object specimen.

The Rad Disk is a filter with an effective hole diameter of $0.1-0.2 \mu m$ that selectively adsorbs the dissolved cesium ion with ferrocyanide ^{14, 17)}. Consequently, the radioactive cesium measured by the Rad Disk method is considered to be the sum of the dissolved cesium ion adsorbed by the ferrocyanide and the radioactive cesium physically adhering to the fine grains larger than $0.1-0.2 \mu m$ in the plant leachate water. Also, the difference between the two measuring methods (68.3–124.1 Bq/kg) is assumed to be due to the radioactive cesium adsorbed by the colloid that passed through the holes of Rad Disk or that formed a complex with an organic acid, etc. Based on these test conditions and measurement techniques, the results of the batch test by the Rad Disk method are considered to reflect the removal effect of various minerals that target the radioactive cesium in dissolved form and in the adsorbed form on the fine grains exceeding $0.1-0.2 \mu m$ in size.

Considerations have been made based on the results of the adsorption test of various minerals. The concentration of radioactive cesium after the batch adsorption test using minerals was 65.4–110.9 Bq/kg, the removal rate 17.1–51.1%, and the distribution coefficient 2.1×10^3 – 1.0×10^4 mL/g by the Rad Disk method; higher effects were observed, in the order of phlogopite, vermiculite, zeolite, and mesoporous silicate. For comparison of the cesium adsorption tests using identical minerals, the data for the cold state dissolved cesium adsorption test are shown in **Table 4** and **Figure 10**. The test was conducted using a cesium solution on Niki zeolite and

Sample	Initial Cs (mg/L)	pH	Removal efficiency $(\%)$	$\begin{array}{c} Partition \ coefficient \\ (mL/g) \end{array}$	Condition
	0.01	8.27	93.45	$1.4 imes10^3$	
	0.1	8.11	96.60	$2.8 imes 10^3$	
Zeolite at Niki, Hokkaido	1	8.43	98.99	$9.8 imes10^3$	L/S = 100 Shaking: 24 h
	2	8.25	99.26	$1.3 imes10^4$	
	10	7.75	99.56	$2.2 imes 10^4$	
	0.04	6.0	84.0	$5.2 imes 10^2$	
	0.1	6.8	97.9	$4.8 imes 10^{3}$	
	2	6.1	98.9	$8.6 imes10^3$	
Vermiculite in South Africa	10	5.8	99.5	$1.9 imes10^4$	L/S=100 Shaking: 24 h
	20	5.9	99.4	$1.7 imes10^4$	
	100	5.9	99.8	$5.3 imes10^4$	
	200	5.6	99.9	$7.1 imes 10^4$	

Table 4 Cesium removal efficiency of 2 geomaterials according to READS 24)



Figure 10 Relationship between the equilibrium concentration of cesium in the liquid phase and in the solid phase of 2 geomaterials according to READS²⁴)

South African vermiculite from the same sampling batch as used for the radioactive material removal/collection technology by NIMS²⁴. The cesium removal rate of zeolite and vermiculite in Table 4 was 84.0–99.9% whereas the removal rates of this batch test in Table 3 were low.

However, because the test results from this batch test fell within the range of the distribution coefficients $5.2 \times 10^2 - 7.1 \times 10^4$ mL/g of the cold test, the results of zeolite and vermiculite in this batch test are considered to have shown its effectiveness. This is because the data fell within the cesium removal performance of each mineral indicated by the cold tests although the removal behavior from the liquid phase is uncertain because the form of cesium in the plant leachate water was not identified. Furthermore, the minerals showed a trend of lower values on both removal rate and distribution coefficient with the lower initial cesium concentration in the cold test, while vermiculite showed a trend of slightly increased concentration in the solid phase at low concentration (Figure 10). Zeolite showed a slightly high value of 4.2×10^3 mL/g in this batch test against the distribution coefficient 1.4×10^3 mL/g when the cesium concentration was 0.01 mg/L in the cold test, and vermiculite showed a one digit higher value of 5.3×10^3 mL/g in this batch test against the distribution coefficient 5.2×10^2 mL/g when the cesium concentration was 0.04 mg/L in the cold test.

The concentration of radioactive cesium, 133.8 ± 4.9 Bq/kg in the plant leachate water in this batch test, shown in Table 3, is the sum of multiple cesium isotopes because it was calculated

from the β -ray count of a Rad Disk, as measured by a β/γ -ray GM survey meter. However, if the contained radioactive cesium is assumed to be ¹³⁷Cs, the concentration is approximately 4.16×10^{-8} mg/kg, with a decay constant of ¹³⁷Cs, $\lambda = 7.32 \times 10^{-10}$ s⁻¹ and an atomic mass of approximately 137, which is regarded as an extremely low concentration compared to the initial cesium in the test condition of READS in Table 4.

The removal of dissolved cesium ions by various minerals indicates that a lower initial cesium concentration resulted in a lower distribution coefficient. However, in this batch test with an extremely low cesium concentration compared with the cold test, the minerals showed a higher distribution coefficient than in the cold test with the lowest cesium concentration. Furthermore, as mentioned earlier, the radioactive cesium detected by the Rad Disk method is supposed to be from dissolution and adsorption on fine grains larger than $0.1-0.2 \mu m$. Due to this, it is considered that the cesium removal effect of minerals from the plant leachate water shown by this batch test may not be solely the adsorption effect of the minerals on the dissolved cesium ion. As for the other actions, the influence of added PAC as a flocculant and the filtering through the membrane filter during solid/liquid separation needs to be considered. If all these factors are considered, then apart from the adsorption of cesium ions by the minerals, it is supposed that the fine grains and colloids that adsorbed the radioactive cesium may have caused a flocculent settling of minerals due to the addition of PAC and their physical removal by filtering through the 0.45 µm membrane filter.

The water passing test results on the column filled with granular zeolite are shown in **Table 5**. The measurements were taken mainly using a γ -ray spectrometer and parts of columns 3 and 4 that could not be measured at the site were measured using the Rad Disk method. The plant leachate water that passed through showed lower values than the bathing area guideline of the Ministry of Environment of 50 Bq/L for both the first 30 min (0–30 min) and the next, after 60 min (60–90 min). The specimens in columns 3 and 4 for 60–90 min measured with the Rad Disk method also showed a decreased radioactive cesium concentration that was lower than the lower determination limit of the γ -ray spectrometer. Furthermore, the Size-M columns 1 and 3 with smaller grain size showed a lower concentration of radioactive cesium after passing than

					•		
Sa	ample	Cooning	Column 1	Column 2	Column 3	Column 4	Critorion of
& condition		water		$\begin{array}{c} L \text{ size} \\ imes 1 \text{ stem} \end{array}$		$\begin{array}{c} L \text{ size} \\ imes 2 \text{ stems} \end{array}$	bathing area
Amount o	f mineral (g)		27	25	54	50	
Column v	volume (mL)		30	30	60	60	
1st time:	Cs (Bq/L)	230 ± 4.6	< 33	46 ± 4.6	< 33	32 ± 3.2	50
$(0 \sim 30 \text{ min})$	Treated water (mL)		—	194.79	223.38	214.6	
	Removal Cs (Bq)		11.6	9.3	52.5	46.3	
2nd time:	Cs (Bq/L)	230 ± 4.6	—	<33	$8.3\pm2.7^{\text{a})}$	$27.2\pm2.9^{a)}$	50
$60 \min_{(30 \sim 90 \min)}$	Treated water (mL)		—	101.11	456.09	468	
	Removal Cs (Bq)		—	23.3	101.1	94.9	
Total: 90 min	Treated water (mL)		—	296	679	682.6	
	Ave. SV (h^{-1})		—	6.6	7.5	7.6	
	Removal Cs (Bq)		11.6	32.6	153.6	141.2	
	L/S		—	11.8	12.6	13.7	
	Ave. Reaction time (min.)		—	9.1	7.9	7.9	
	Partition coefficient		—	$7.8 imes 10^1$	$5.1 imes 10^2$	$9.6 imes 10^1$	

 Table 5
 Results of flow-thru test using columns filled with granular zeolite

a) Measured using rad disk. Others are measured by γ -ray spectrometer. The values are indicated as Bq/L on the assumption that water density is 1.

the Size-L columns 2 and 4. It is considered that the processing efficiency was enhanced simply because the smaller grain size meant that a larger quantity of mineral, with a larger surface area, occupied the a same volume. The distribution coefficient in zeolite under the conditions in each column, measured in terms of the radioactive cesium removed and the quantity of water passed through was $7.8 \times 10^1 - 5.1 \times 10^2$ mL/g and lower than the distribution coefficient in zeolite by the batch test, 4.2×10^3 as shown in Table 3. This is because: (1) The adsorption efficiency per unit weight of mineral decreased because the total water quantity that passed through with regard to the mineral quantity in each column, i.e., the solid/liquid ratio, was 11.8 to 13.7, which was extremely low compared to the solid/liquid ratio of 10,000 in the batch test, (2) The reaction time for a column test (7.9-9.1 min) was less than 1/3 of the 30 min reaction time of a batch test, but the ion-exchange reaction of zeolite seems to be relatively slow in spite of the long reaction time of SV of 6.6–7.6 h^{-1} compared to the SV 10–100, etc. when tap water is treated using the ion-exchange resin. As a result, the effect of zeolite was not fully used for the radioactive cesium in the plant leachate water within the reaction time available during water passage, (3) The physical removal effect on the adsorbed cesium by the fine grains and colloids due to the addition of PAC and filtering that was suggested for the batch testing was not part of the column water-through test. However, the concentration of radioactive cesium that passed through the column was lower than in the batch test, and lower than the guideline of treatment 50 Bq/L.

From all the above results, it can be concluded that the reduction in the distribution coefficient of minerals means the reduction of utilization efficiency of a material under those conditions, but it was shown that even if this value is lower, the concentration of radioactive cesium in the liquid phase could be sufficiently decreased by a treatment with a low liquid/solid ratio, such as having the water pass through a column.

V. Wet-classification of Agricultural Soils

1. Soil Wet-classification Test Method

A soil wet-classification test was conducted with the aim of decreasing the volume of surface layer soils containing radioactive cesium. For the test, surface soils such as ridge soil, paddy field, dry land and the ground were used, in which a high level of radioactive cesium was detected from bulk measurement. The survey showed that the concentration of radioactive cesium was the highest in the grass field surface soils, but these were excluded because there were local specimens of soil adhering to the grass roots, and a sufficient quantity of specimens for testing was not secured.

The soil wet-classification test was conducted as follows. The soils were separately sampled as-is in raw weights of 1.5 kg (equivalent to dry weight of approximately 1 kg.) and wet-classification was conducted while water-washing using an electromagnetic experimental screening shaking apparatus (A-3/FRITSCH) (**Figure 11**). The tap water of the Itate-mura village office, in which radioactive cesium was not detected, was used as the cleaning water and the quantity used was approximately 7 times as much as the raw weight of specime soil.

Seven stages of sieve mesh were set up as grain size fractions: < 0.075 mm, 0.075-0.125 mm, 0.125-0.25 mm, 0.25-0.5 mm, 0.5-2 mm, 2-4.75 mm, and > 4.75 mm. The < 0.075 mm specimen was collected as muddy water and processed with a 3 µm bag filter similar to that used for filtering plant leachate water to remove the suspended component.

Since the radioactive cesium adsorbed due to ion-exchange in the clay minerals may be replaced by other cations, a study was also conducted on using an ammonium ion solution that





is considered to have less influence on farming if added to the agricultural soil for the ridge soils in place of cleaning water. A 0.1 mol/L ammonium nitrate solution was prepared and an ammonium nitrate solution of approximately 1.5 L, an amount equal to the volume of the soil, was added to the specimen soil, which was left immersed for 1 h. Then a soil wet-classification test was conducted.

2. Soil Wet-classification Test Results and Discussion

The results of the wet-classification of ridge soils conducted using water and ammonium nitrate are shown in **Table 6**. As all the desired equipment was not ready for in-situ measurement of soil moisture content after classification in August, when the ridge soils were tested, the concentration of radioactive cesium was measured using a γ -ray spectrometer on each 1 kg of agricultural field soil, from which water was removed by sieving. The original soil was dried in the wind and the dry weight was acquired.

The concentration of radioactive cesium was reduced as the grain size used became coarser compared to the original soil in both water cleaning and ammonium nitrate solution cleaning. However, the effect of the ammonium nitrate solution was not recognizable. Although not precise enough because the value was based on wet weight, it was presumed for the case of general wet soil of moisture content 30–50%, that the radioactive cesium would be reduced to half of that in the original soil by wet-classification for under 6,000 Bq/kg in wet weight and in the grain size larger greater than 0.5 mm. However, because the concentration of radioactive cesium exceeded the acreage limit of 5,000 Bq/kg for rice in the grain size fraction 0.075–4.75 mm, the expected volume reduction effect on the processed soil by wet-classification was not achieved for the ridge soils.

The muddy water with grains under 0.075 mm was processed through a bag filter. However, the suspended substances in the muddy water managed to pass through the non-woven bag filter, which expanded due to the hydraulic pressure, so that the liquid still contained

	Cs (Bq/kg)					
Line soil	$25,794^{a)}$	Per natural wet weight				
	38,731	Per dry weight				
Washing solvent	Water	$1 \ \mathrm{mol}/\mathrm{L}$ ammonium nitrate				
>4.75 mm	$2,200^{a)}$	$5,500^{a)}$				
$2{\sim}4.75~\mathrm{mm}$	5,100 ^{a)}	4,700 ^{a)}				
$0.5{\sim}2~\mathrm{mm}$	5,300 ^{a)}	5,600 ^{a)}				
$0.25{\sim}0.5\mathrm{mm}$	9,500 ^{a)}	8,700 ^{a)}				
$0.125{\sim}0.25\mathrm{mm}$	10,000 ^{a)}	9,800 ^{a)}				
$0.075{\sim}0.25\mathrm{mm}$	10,000 ^{a)}	12,000 ^{a)}				
$< 0.075 \text{ mm}^{\mathrm{b})}$	320					
$< 0.075 \ mm^{c)}$	< 33	—				

Table 6 Radioactive cesium in each particle fraction from each soil after wet-classification

^{a)} Per natural wet weight.

^{b)} Muddy water.

 $^{\rm c)}\,$ Filtrated b water using 10 $\mu{\rm m}$ membrane filter.

 $\%\,$ The error range of all data in this table is $\pm 10\%.$

suspended solids after filtration, and showed a radioactive cesium concentration of 320 Bq/kg. Because the forced filtration of muddy water is not possible using a non-woven bag filter, it is considered that filtration using a strong filtration cloth such as filter press is appropriate for in-situ dewatering of suspended solids and solid/liquid separation. Hence, a single sheet of 10 μ m membrane filter having an equivalent mesh opening to filtration cloth was used for filtering the water that passed through the bag filter. The fine soil grains, etc. were removed, the filtered liquid obtained was clear, and the radioactive cesium concentration was lower than the determination limit of 33 Bq/kg.

This implied that the radioactive cesium content may be reduced to half by removing soil particles under 0.5 mm with soil wet-classification on ridge soils. The presence of radioactive cesium in soil in the liquid phase was decreased by soil wet-classification.

Next, after the results of the soil classification test on ridge soils, tests were also conducted on three types of soils: from paddy fields, dry land, and the ground, to compare the effect of wet-classification on the agricultural soils under different conditions. The results are shown in **Table 7** and **Figure 12**.

Of the radioactive cesium contained in these soils, 63–85% was present in grain sizes under 0.075 mm. However, it was also present in the coarse grain size fractions, so the considered grain size fractions and weight percentage of soils under 5,000 Bq/kg were 12.2% for paddy fields over 2 mm, 29.5% for dry lands over 0.25 mm and 0% for the ground. Furthermore, it may be considered that after removing the highly contaminated fine grains by wet-classification, an equivalent quantity of healthy soil can be mixed with the original ground soil and water to recover the physical properties of soil. When lower than 5,000 Bq/kg is achieved by dilution, the paddy fields and dry lands of lower than 0.075 mm and the ground lower than 0.25 mm are removal object, and the collection rates are expected to be 39%, 44% and 75%. To enhance the efficiency of volume reduction by the soil wet-classification method, it is necessary (1) to conduct further classification in the soils containing significant quantities of fine grains such as paddy fields and dry lands using a highly precise wet-classification apparatus such as cyclone for the soil grains smaller than 0.075 mm not separable by a simple mesh sieve, and (2) to conduct an additional treatment such as chemical treatment depending on the cost and effect for the sludges of high

Sample	Water content ratio (%)	Dry weight ratio of particle fraction (%)	Cs per dry weight (Bq/kg)	Cs per 1 kg dry weight sample (Bq)	Cs distribution
Paddy-field	35.1%		18,500		
$> 4.75 \text{ mm}^{a)}$	_	_	_	_	_
$2{\sim}4.75~\mathrm{mm}$	5.3	2.8	4.011	111.3	0.8
$0.5{\sim}2~\mathrm{mm}$	33.9	9.4 } 12.2	3,782	356.5	2.5
$0.25{\sim}0.5~{\rm mm}$	35.9	12.4	8,733	1,084.4	7.5
$0.125{\sim}0.25~{ m mm}$	43.0	7.4	13,674	1,008.9	7.0
$0.075{\sim}0.125~{ m mm}$	47.6	7.1	16,418	1,160.6	8.0
$< 0.075 \mathrm{~mm}$	77.9	60.9	17,618	10,736.1	74.3
Croft	28.8		18,255		
>4.75 mm	23.9	3.1	1,445	45.1	0.3
$2{\sim}4.75~{\rm mm}$	24.6	7.2	2,918	210.5	1.6
$0.5{\sim}2 \text{ mm}$	39.6	11.0	2,981	327.0	2.4
$0.25{\sim}0.5{ m mm}$	39.6	8.2	4,805	396.0	2.9
$0.125{\sim}0.25~{ m mm}$	45.2	8.5	7,301	618.2	4.6
$0.075{\sim}0.125~{ m mm}$	41.6	6.2	7,363	459.4	3.4
$<\!0.075\;\mathrm{mm}$	79.0	55.7	20,525	11,440.9	84.8
Ground	10.1		37,810		
>4.75 mm	22.5	1.1	30,968	325.9	1.1
$2{\sim}4.75{ m mm}$	4.4	9.5	16,732	1,584.0	5.3
$0.5{\sim}2~\mathrm{mm}$	15.5	33.0	9,946	3,286.9	11.1
$0.25 \sim 0.5 \text{ mm}$	15.0	31.4	10,701	3,364.5	11.3
$0.125{\sim}0.25~{ m mm}$	8.8	9.6	19,733	1,892.4	6.4
$0.075{\sim}0.125~{ m mm}$	0.9	2.4	26,228	617.9	2.1
$<\!0.075\;\mathrm{mm}$	73.3	13.0	142,500	18,589.8	62.7
Cropping restriction 1	evel about paddy-fi	eld	8,000~100,000		
Criterion of designati	on (storage directio	on)	5.000		

 Table 7
 Particle size and radioactive cesium distribution in 3 types of soil in wet-classification

Criterion of designation (storage direction)

a) preclusion for less amount to measure.

% The error range of all data in this table is $\pm 10\%$.



Figure 12 Radioactive cesium concentration and amount recovered from 3 types of soil

concentration that are finally discharged. Importantly, the concentration of radioactive cesium exceeded 8,000 Bq/kg in all grain fractions including the coarse grain sizes in the sandy ground.

This indicates the possibility of residual radioactive cesium due to the adsorption by the coarse soil grain surfaces or due to the adhesion of clay minerals, etc. that adsorbed the radioactive cesium. The grain size fractions showing high and coarse values should be treated by the soil wet-classification process, not by an additional treatment from the viewpoint of volume reduction. For this case, it is necessary to reduce the radioactive cesium concentration in the coarse grain fractions by devising a sieving or pre-treatment process.

VI. Study of Pre-Treatment for Wet-classification

1. Study Method

A pre-treatment was studied to improve the efficiency of wet-classification for the ground soils in which high radioactive cesium concentration was observed in the coarse grain fraction, also after wet-classification. The methods studied are listed in **Table 8**. Assuming in-situ operation, the methods applicable using general purpose instruments were used. Furthermore, either direct adsorption to coarse grains or the adhesion of fine grains such as clay that adsorb cesium are considered to be the causes of residual radioactive cesium, but the range of its presence is assumed to include at least the surface of coarse soil grains. So a study was conducted using four types of pre-treatment methods acting on the grain surfaces: an ultrasonic apparatus and a vibrator for fresh concrete whose functions are mainly dispersion and vibration, a pot mixer + weight and, a mortar + vibrator whose main function is grinding.

These methods, excluding mortar + vibrator, were used as a pre-treatment for wet-classification, and the mortar + vibrator was used for intermediate processing in wet-classification. However, the ultrasonic apparatus is not a general purpose in-situ instrument but is used to compare typical dispersion methods. The details of study methods are as follows (**Figure 13**):

(1) Pre-Treatment 1: Ultrasonic Device

A vinyl bag containing 1 kg of soil and 1 kg water was set in a laboratory compact ultrasonic shaker (As One) and a dispersion of 10 min \times 3 times (total 30 min) was conducted for wet-classification.

(2) Pre-Treatment 2: Vibrator for Fresh Concrete

Added 1 kg of soil and 1 kg of water to a 5 L stainless steel container and attached an iron vibrator (Iron type 50 W formwork vibrator, owned by AKTIO) and wet-classification was conducted after vibrating for 5 mins.

(3) Pre-Treatment 3: Pot Mixer + Weight

A 20.5 cm diameter basketball was filled with 8.5 kg of sand and 1.5 kg of soil, put in a 70 L pot mixer (owned by AKTIO) and rotated (at 24 rpm) for 3 min with a tilt of approximately 45 degrees. Then 1.5 kg of water was added and the pot rotated for another 2 mins because the soil

 Table 8
 Efficiency improvement methods for removal of radioactive cesium from coarse-grained particle fractions

Method	Effect
Target and equipment	
Preprocessing 1: Ultrasonic vibration	Dispersion
Dispersing soil particles by about 20 kHz Ultrasonic vibration.	
Preprocessing 2: Vibration using degasser for fresh concrete	Dispersion, shaking
Dispersing and shaking soil particles using with about 120 Hz vibration using degasser for fresh concrete.	
Preprocessing 3: Pot-mixing with rubber weight	Weighted attrition
Mixing soil in rotary pot with rubber weight ball frictionally.	
Intermediate processing: Attrition by vibrator and mortar	Surface attrition
Rubbing soil with rubber coating 6,500 Hz vibrator in deep mortar.	



Figure 13 Efficiency improvement methods for the removal of residual radioactive cesium from coarse-grained particle fractions (Preprocessing 1: Ultrasonic vibration, Preprocessing 2: Vibration using degasser for fresh concrete, Preprocessing 3: pot-mixing with rubber weight, Intermediate processing: Attrition by vibrator and mortar)

slipped in the mixer and no loss in weight occurred. Then the pot was tilted to approximately 10 degrees and was rotated for 30 min, but again no loss in weight was observed as the abrasion was insignificant. After treatment, wet-classification was conducted.

(4) Intermediate Treatment: Mortar + Vibrator

This treatment aimed at the removal of residual radioactive cesium in the coarse soil grains after wet-classification. The grain fraction of 0.125–4.75 mm was separated as a coarse grain soil from the sample soil. Coarse grain soil 200 g and water 100 g were fed into the steel deep mortar. Treatment was applied using a bar-type vibrator with a rubber ball fitted on the contact zone, which was pressed lightly on the coarse grain soil with vibration (of 6,500 rpm) for 10 mins, sieving with a 0.125 mm filter. Concentration measurement was performed for both the remaining portion and the passed portion. Also, a study was conducted on the mixture of coarse soil (100 g) and water (100 g) for 20 min using the same procedure for increased water percentage and duration of treatment.

2. Results and Discussion on Three Types of Pre-Treatment

The results of three pre-treatments for wet-classification are shown in **Table 9**. 1: Ultrasonic Device; 2: Vibrator pretreatment for Fresh Concrete; 3: Treatment in Pot Mixer + Weight. The study showed that the radioactive cesium concentration was slightly decreased by the dispersion treatment with an ultrasonic apparatus in Pre-Treatment 1 for grain size fractions 0.075-0.125 mm, 0.125-0.25 mm and 2-4.75 mm, but on the other hand, an increase was observed in the grain size fractions 0.25-0.5 mm and 0.5-2 mm. Pre-Treatment 2 and Pre-Treatment 3 reduced the concentration of radioactive cesium to half of the concentration left by Pre-Treatment 1 or less at 2-4.75 mm, while the radioactive cesium concentration in other grain size fractions showed a similar trend as Pre-Treatment 1.

Soil wet-classification is a method aimed at separation by concentrating the harmful substances on finer grains. To assess the effect, the distribution of radioactive cesium onto each grain size fraction relative to the radioactive cesium concentration in whole soil was calculated using the radioactive cesium concentration of each grain size fraction and its weight percent. The radioactive cesium distribution onto each grain size fraction was compared to an untreated sample of all the grain size fractions of 0.25 mm and above. A significant reduction, especially by Pre-Treatment 3, was seen in 0.125–0.25 mm as well, and the effect was verified (Table. 9). The changes in weight percentage and the distribution ratio of radioactive cesium on the grain size fractions of 0.075 mm and below are shown in **Figure 14**. From Table 9 and Figure 13, after each Pre-Treatment (1, 2 and 3) an increase was seen in the percentage of radioactive cesium distributed in grain size fractions 0.075 mm and smaller.

These results implied that part of the radioactive cesium present in the coarser grain size

		Cs (B	q/kg)		Particle size distribution (%) Cs distribut					tion (%)		
Sample	Preprocessing			Preprocessing			Control	Preprocessing				
	Control	1	2	3	Control	1	2	3	Control	1	2	3
>4.75 mm	30,968	_	_	_	1.1	_	_	_	1.1	_	_	_
$2{\sim}4.75~\mathrm{mm}$	16,732	15,535	6,249	6,239	9.5	13.8	12.1	18.2	5.3	5.3	1.7	2.0
$0.5{\sim}2~\rm{mm}$	9,946	10,252	10,449	9,555	33.0	16.7	26.3	19.5	11.1	4.2	6.3	3.3
$0.25{\sim}0.5~\mathrm{mm}$	10,701	14,175	12,234	12,857	31.4	20.7	11.1	10.1	11.3	7.2	3.1	2.3
$0.125{\sim}0.25~{\rm mm}$	19,733	15,206	12,879	12,762	9.6	17.0	19.6	12.0	6.4	6.4	5.8	2.7
$0.075{\sim}0.125~{\rm mm}$	26,228	15,697	18,095	23,385	2.4	8.6	5.6	7.7	2.1	3.3	2.3	3.3
$< 0.075 \mathrm{~mm}$	142,500	128,531	139,832	147,705	13.0	23.2	25.3	32.5	62.7	73.5	80.8	86.3

Table 9 Results of wet-classification after 3 types of preprocessing

% The error range of all data in this table is ±10%.



Figure 14 Results of wet-classification after 3 types of preprocessing

fractions translocated to the grain size fractions of 0.075 mm and smaller, together with fine particles such as clay minerals that adsorb them in the pre-treatment.

Furthermore, the fine grain portion of 0.075 mm and lower increases from 13.0% to 32.5% by wet-classification following Pre-Treatment 3, that is Pot Mixer + Weight. As a result, it is considered that the removal rate of radioactive cesium when the above fine grain portion was separated from the contaminated soil can be enhanced from 62.7% to 86.3%.

We also observed that the increase in the weight percentage and the distribution rate of radioactive cesium in the particle size fractions less than 0.075 mm were higher in order of the ultrasonic apparatus of Pre-Treatment 1, the vibrator for fresh concrete of Pre-Treatment 2 and the pot mixer + weight of Pre-Treatment 3. This is thought to mean that a higher wet-classification effect may be achieved by methods that have the effect of grinding the soil grain surfaces, such as vibration and grinding as a pre-treatment of soil, rather than by applying a dispersion treatment, e.g. using a high frequency for the dispersion of powder in liquid.

3. Results and Discussion on Intermediate Treatment

When the soil is pre-treated in bulk, the fine grain portion of 0.075 mm and smaller that is separated by the wet-classification of original soil is obtained. This fine grain portion may inhibit the functioning, e.g., by damping the physical shocks by cushioning the coarse soil grains during the dispersion or grinding in the pre-treatment stage. Hence, a wet-classification was conducted on the original soil, only the grain size of 0.125-4.75 mm was collected, and water was added. The surface grinding was conducted using a rubber-coated vibrator, using a deep steel mortar as a capturing tray, and was sieved with a 0.125 mm sieve while washing with water. The grinding with soil:water = 2:1 for 10 mins was defined as Condition 1 and soil: water = 1:1, for 20 min as Condition 2.

The results are shown in **Table 10**. As a result of grinding, a weight percentage of 6–10% was classified as the fine grain portion of 0.125 mm and smaller. The radioactive cesium concentration did not go below 5,000 Bq/kg but was at least less than the standard of 8,000 Bq/kg subjected to storage, and the reduction of the Cs residual rate to as low as 53–55% was achieved.

From these results of the experiment, it was demonstrated that by applying grinding and wet-classification after removing the fine grains by classification in pretreatment greatly enhances the separation efficiency for radioactive cesium by wet-classification.

Sample	$\underset{\left(Bq/kg\right)}{Cs}$	Soil residual rate $(\%)$	Cs residual rate $(\%)$
Coarse-grained soil 0.125~4.75 mm	11,706	100.0	100.0
Condition 1	6,490	93.6	55.4
Condition 2	6,217	89.5	53.1

 Table 10
 Efficiency of intermediate processing on wet-classification

% The error range of all data in this table is $\pm 10\%$.

VII. Summary of the Implemented Research

Through the sampling of specimens and the survey conducted in Iitate-mura, it was confirmed that the radioactive cesium is distributed mainly on solids such as soils and plants on the land surface. Soil will hold it securely, while plants release it when exposed to water. There is thus a concern that the release of radioactive cesium distributed on plants by rainfall, etc., can cause secondary contamination in the peripheral environment.

On the other hand, it was confirmed that the radioactive cesium released from plants can be removed from the liquid phase by treatment with minerals such as zeolite, as was proved through the batch adsorption test and the column water passing test.

The possibility of reducing the concentration in the soil with grain sizes of 0.075–0.125 mm and above while in storage was confirmed by collecting the radioactive cesium in the fine grain portion of contaminated soil using the soil wet-classification test. The classification efficiency depended on the type of soil. Especially in sandy-ground soils, the radioactive cesium remained in the coarse-grain fractions when only the wet-classification of soils was conducted. It was confirmed that by using dispersion, vibration and grinding in the pre-treatment, and also using grinding in the intermediate treatment, and an additional wet-classification is conducted, that more effectively translocating the radioactive cesium to the fine grain portion was possible.

Some possible measures for the decontamination of agricultural soils, etc., are presented as follows. These are based on the results of work in litate-mura and studies of radioactive cesium removal methods in this research: First, when storing plants with a high concentration of radioactive cesium, use a waterproof sheet, foil, etc. as a cover to avoid exposure to rainfall, etc. and prevent any secondary damage due to leaching of the radioactive cesium from the plants. Also, as a countermeasure to the leaching of cesium during storage, it is considered effective to arrange natural minerals such as zeolite or vermiculite under or around the contaminated substances as adsorbents. Because the minerals can exert the desired effect not only in powder form but also in grains, it is worth noting that the grain form is easy to use in water-passing types of treatment, easy to handle, and does not disperse easily, making it better for use than powder. For contaminated soils, the wet-classification treatment of soil is suggested. The treatment flow chart is shown in Figure 15. First, collect the highly contaminated surface layer soil using a polymer, etc. and immerse it in water to avoid dispersion. In surface layer soils, organic substances such as the roots and leaves of plants and humus are present in relatively large amounts. Because organic substances such as plants may be highly contaminated, there is the possibility of effective volume reduction by drying or incineration separately from soils. Thus, they are separated from soil grains by floatation.

Separated organic substances such as plants, etc. are dehydrated, measured and stored. Storage procedures for the plants are explained above. Also, it is best to apply this volume reduction separately, through decomposition or by incineration, or to apply a treatment to prevent the release of radioactive cesium. For soils from which the organic substances have been removed, the soil mass is smashed and rough sorting of stones and gravel is conducted using a drum washer, a rougher or a sieve. The sieved soils are cleaned and separated using a trommel, sieving shaker, high-mesh separator, cyclone, etc. in the order of grain size from rough soil to fine, with the soil grains of 0.02-0.75 mm and above collected in stages. The fine grains smaller than that are sent as muddy water containing radioactive cesium to the solid/liquid separation process. Because the radioactive cesium tends to remain in the coarse grain size fractions, as seen in the classification result of ground soil in this study, the status of residual radioactive cesium is checked for the soil grains in each collected grain size fraction using a sieve shaker, etc. Those lower than the standard specified in the guidelines of government, etc. are regenerated as soil. For those higher than the standard, a surface grinding process is applied such as an attrition mixer, vibrator, or loaded grinding, and a wet-classification is conducted to remove the fine grains peeled from the coarse soil grains containing radioactive cesium. After the second wet-classification, each collected grain size fraction is re-measured to confirm its safety. The



Figure 15 Conceptual schema for improved wet-classification decreasing the amount of radioactive cesium contaminated soil

muddy water is transferred to the solid/liquid separation process and separated into solid and liquid by flocculant settling. As shown in this study, almost no radioactive cesium in the soil is released into the water, the supernatant solution is used and recirculated as cleaning water. The fine grains in the muddy water collected in the solid/liquid separation process are dehydrated. The soil grains that exceeded the standard in the second wet-classification are stored as specified after evaluating their contamination level as a concentrated contaminated soil.

As explained above, it is expected that the efficient in-situ volume reduction treatment of agricultural land soils, etc. generated in the contaminated area becomes possible by implementing the storage procedures according to the results of this study. i.e. classification, grinding, etc.

VIII. Future Subjects

It was confirmed that the separation and volume reduction of contaminated soils was possible by the soil wet-classification method. However, in this study, the status or the presence of radioactive cesium in the soils sorted by the wet-classification could not be evaluated or discussed. However several different statuses of cesium have been reported, including its adsorption by ion-exchange between layers of micro lamellar clay minerals such as smectite, etc. having exchangeable cations²⁵, and the adsorption/retention of illite on the frayed edge sites^{26,27)}.

Among the clay minerals universally present in the surface layer soils in Japan, mica and illite are the non-swellable lamellar silicate minerals in which the hydrated cations do not enter in between layers, and their cation exchange ability is regarded as inferior to that of swellable clays. However, the frayed gap on the edge of this mineral grain is called the "frayed edgesite" and it is known to be steadily restored if the potassium and cesium in between the layers are exchanged ^{26, 27)}. However, because agricultural lands contain artificial materials such as those for soil enrichment, etc., and radioactive cesium is inevitably present in the coarse grain fractions that apparently contain pebbles with almost no clay mineral, the immediate cesium environment or chemical associations may not be limited to those suggested in the existing bibliography. Accordingly, for soils, the essential subjects for future decontamination and volume reduction treatment are to conduct the validation of mineral composition and surface observations with respect to grain size fraction after wet-classification of various soils and soil qualities. Also, on the fine grain portion containing the radioactive cesium removed from the coarse grain fraction by grinding, etc., clarification of the present form is required, especially in the coarse grain size fractions in the real soil contaminated with radioactive cesium. Further, the adsorption and desorption properties should be evaluated.

For conducting this test and summarizing the above report, we received a considerable amount of cooperation and advice from concerned persons. First, we express our gratitude to the people of the Iitate-mura village office, including Mr. Ryuji Honda/Industrial Promotion Section, and the residents in Iitate-mura who kindly permitted the sampling of specimens. When conducting the tests, Mr. Mitsuru Yamamura of JCE Co., Ltd. conducted in-situ measurement using a γ -ray spectrometer. During the in-situ testing, Mr. Takuya Echigo of NIMS, Dr. Hirochika Naganawa, Dr. Nobuyuki Yanase and Dr. Hisayoshi Mitamura of JAEA, Dr. Yujiro Watanabe of the Kanazawa Institute of Technology cooperated. Mr. Takashi Kobayashi of NIMS recorded images of the whole process. We are grateful to them, and to all those who supported and cooperated us.

Additionally, the contents of this research were acquired from the FY2011 Commissioned Project on Science and Technology Strategic Promotion "Development of Radioactive Materials Decontamination Technology for Agricultural Land Soils."

References

- Survey and Research Report on Radioactive Material Concentration Distribution Mapping on Farmland Soils, MAFF, The Office of Agriculture, Forestry and Fisheries Research Council, Edition 3, p58 (2012). [in Japanese] http://radioactivity.mext.go.jp/ja/distribution_map_around_FukushimaNPP / 5600_201203131000_report3.pdf
- On the Farmland Radioactive Material Removal Technologies (Decontamination Technology) Attachment 4, 4. Reversal Tillage, MAFF, Press Release on Sep.14, 2011, 11-12 (2011). [in Japanese] http://www.s.affrc.go.jp/docs/press/110914.htm
- H. Naganawa, N. Kumazawa, H. Saitoh et al., "Removal of radioactive cesium from surface soils solidified using polyion complex rapid communication for decontamination test at litate-mura in Fukushima prefecture," *Trans. At. Energy Soc. Jpn.*, 10[4], 227-234 (2011). [in Japanese]
- 4) H. Naganawa, "Removal of radioactive cesium from contaminated soil by using poly-ion complex with clay," *Nendo Kagaku*, 50[2], 52-57 (2011). [in Japanese]
- No.2 Environmental Restoration Commission, Distributed Material 7, No.2 Environmental Restoration Commission, MOE, Sep.27, 2011(2011). [in Japanese] http://www.env.go.jp/jishin/rmp/conf/02-mat4. pdf
- S. V. Krouglov, A. D. Kurinov, R. M. Alexakhin, "Chemical fractionation of ⁹⁰Sr, ¹⁰⁶Ru, ¹³⁷Cs, and ¹⁴⁴Ce in Chernobyl-contaminated soils: An evolution in the course of time," *J. Environ. Radioact.*, 38, 59-76 (1998).

- K. Bunzl, W. Kracke, W. Schimmack, L. Zelles, "Forms of fallout ¹³⁷Cs and ²³⁹⁺²⁴⁰Pu in successive horizons of a forest soil," *J. Environ. Radioact.*, 39, 55-68 (1998).
- Succeeded in Extracting Cesium from Soil Using Low-Level Acid, National Institute of Advanced Industrial Science and Technology, Press Release, Aug.31, 2011. [in Japanese] http://www.aist.go.jp/aist_j/ press_release/pr2011/pr20110831/pr20110831.html
- 9) Guidebook for Improved Measures in the District, MOE, Soil Environment Management Division, Water-Air Environment Management Bureau, 43-46 (2011). [in Japanese] http://www.env.go.jp/water/ dojo/gb_me/
- T. Futami, "Practical approach to remediating heavy metal-contaminated soil by grain sorting, gravity separation, and grain-surface attrition," *Chigaku-zasshi (J. Geography)*, 116[6], 932-940 (2007). [in Japanese]
- 11) FY2010 The Statuses of Enforcement of Soil Contamination Countermeasures Act and the Survey Results on Soil Contamination Survey/Case Examples of Countermeasures, MOE, MOE Water-Air Environment Management Bureau, Mar.2012(2012). [in Japanese] http://www.env.go.jp/water/report/ h23-02/index.html
- T. Ujiie, M. Yamamura, N. Narisawa, "Investigation of onsite analysis method for the concentrations of Radiocesium," *Proc. 21st Symp. Geo-Environ. and Geo-Techn.*, Tsukuba, Japan, Jun. 24-25, 2012, 17-22 (2012). [in Japanese]
- EMF211 γ-Ray Spectrometer, EMF Japan Co., Ltd., p5 (2012). [in Japanese] http://www.emf-japan. com/emf/img/PDF/EMF211.pdf
- 3MTM EmporeTM Rad Disk Cesium Catalog, Sumitomo 3M Ltd., p2 (2011). [in Japanese] http://www. mmm.co.jp/filter/empore/rad/pdf/sced11-014.pdf
- 15) T. Nagano, H. Mitamura, N. Yanase, H. Naganawa, K. Yasuda, Z. Yoshida, H. Yamaguchi, "On-site monitoring method of radioactive cesium in water sample using cesium adsorption disk and GM survey metereter," *Nihon- Genshiryoku-Gakkai Shi (J. At. Energy Soc. Jpn.*), in preparation (2012). [in Japanese]
- D. M. Beals, W. G. Britt, J. P. Bibler, D. A. Brooks, "Radionuclide analysis using solid phase extraction disks," J. Radioanal. Nucl. Chem., 236[1-2], 187-191 (1998).
- D. M. Beals, K. J. Hofstetter, V. G. Johnson, G. W. Patton, D. C. Seely, "Development of field portable sampling and analysis systems," *J. Radioanal. Nucl. Chem.*, 248[2], 315-319 (2001).
- 18) On the Farmland Radioactive Material Removal Technologies (Decontamination Technology), 3. Stirring and Removal of Soil with Water, Press Release, MAFF, Sep.14, 2011, Attachment 4, 9-10 (2011). [in Japanese] http://www.s.affrc.go.jp/docs/press/110914.htm
- 19) Guidelines on Radioactive Substances in Bathing Areas, MOE, Water-Air Environment Management Bureau, EWAWR No. 110624001, Jun.24, 2011 (2011). [in Japanese] http://www.env.go.jp/jishin/attach/no110624001.pdf
- 20) Guidelines for Rice Acreage, Cabinet Office, Nuclear Emergency Headquarters, Apr.08, 2011 (2011). [in Japanese] http://www.maff.go.jp/j/kanbo/joho/saigai/ine_sakutuke.html
- 21) Policies on disposal methods for incineration ash exceeding 8,000 Bq/kg and less than or equal to 100,000 Bq/kg, *EDCR* No.110831001, *EDCR* No.110831001, MOE, Minister's Secretariat/Waste Management and Recycling Department, Aug. 31, 2011. [in Japanese] http://www.env.go.jp/jishin/attach/no110831001.pdf
- 22) On the difference of duplicated standards 100 Bq/kg and 8,000 Bq/kg, MOE, Waste Management and Recycling Department (2011). [in Japanese] http://www.env.go.jp/jishin/attach/waste_100-8000.pdf
- 23) On the environmental standards relevant to soil contamination, *MOE Notification* No.46, Aug.23, 1993(1993), *Last Amendment: MOE Notification* No. 37, Jun. 16, 2010). [in Japanese]
- 24) READS Database for radioactive material removal and collection technology, Natl. Inst. for Materials Science (2012). [in Japanese] http://reads.nims.go.jp/
- H. Shirozu, Nendokobutsugaku Nendokagaku-no-kiso, Asakurashoten, Tokyo, 38-42, ISBN4-254-16231-6 C 344 (1988). [in Japanese]
- A. Cremers, A. Elsen, P. D. Preter, A. Maes, "Quantitative analysis of radiocaesium retention in soils," *Nature*, 335, 247-249 (1988).
- N. Ishikawa, S. Uchida, K. Tagami, "Effects of clay minerals on radiocesium sorption behavior onto paddy field soils," *Radioisotopes*, 56[9], 519-528 (2007). [in Japanese]