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## NEW TECHNOLOGIES FOR DECONTAMINATION OF RADIOACTIVE SUBSTANCES SCATTERED BY NUCLEAR ACCIDENT

### NOWE TECHNOLOGIE DEKONTAMINACJI RADIOAKTYWNYCH SUBSTANCJI ROZPROSZONYCH PRZEZ AWARIĘ NUKLEARNĄ

Our effort for decontamination of radioactive cesium scattered widely by nuclear accident in March 2011 in Fukushima, Japan has been described. Radioactive cesium scattered widely in Japan has been accumulating in arc or plasma molten-solidified ash in waste incinerating facilities up to 90,000 Bq/kg of the radioactive waste. Water rinsing of the ash resulted in dissolution of cesium ions together with high concentrations of potassium and sodium ions. Although potassium inhibits the adsorption of cesium on zeolite, we succeeded to precipitate cesium by in-situ formation of ferric ferrocyanide and iron rust in the radioactive filtrate after rinsing of the radioactive ash with water. Because the regulation of no preservation of any kind of cyanide substances, cesium was separated from the precipitate consisting of cesium-captured ferric ferrocyanide and ferric hydroxide in diluted NaOH solution and subsequent filtration gave rise to the potassium-free radioactive filtrate. Cesium was captured by zeolite from the potassium-free radioactive filtrate. The amount of this final radioactive waste of zeolite was significantly lower than that of the arc-molten-solidified ash.

*Keywords:* nuclear accident, scattered Cs, waste incineration facility, Cs accumulation, Cs decontamination, radioactive waste, Cs-adsorbed clay suspension

Opisano wysiłki podjęte po awarii nuklearnej w marcu 2011 w Fukushima, Japonia. Radioaktywny cez rozproszony na znacznym obszarze Japonii jest akumulowany do poziomu 90,000 Bq/kg w spalarniach śmieci w procesie stapiania w łuku plazmy radioaktywnych śmieci. Przemycanie wodą popiołów powoduje wymywanie radioaktywnego cesu wraz ze znacznymi ilościami potasu i sodu. Ponieważ potas inhibuje adsorpcję cesu na zeolitach, udało się strącić cez w postaci kompleksu z żelazo żelazicyjankiem oraz tlenków żelaza w przesączu po przemywaniu radioaktywnego popiołu. Ustawodawstwo zakazuje przechowywania jakiegokolwiek substancji zawierającej grupę cyjanową, dlatego otrzymany osad rozpuszczono stosując rocznieczony NaOH. Ponowna filtracja doprowadziła do uzyskania radioaktywnego przesączu nie zawierającego jonów potasu. Następnie radioaktywny cez został zaadsorbowany na zeolitach. Końcowa ilość radioaktywnych zeolitów była znacząco mniejsza od popiołów.

#### 1. Introduction

Earthquake and subsequent tsunami on March 11, 2012 seriously damaged Fukushima Nuclear Power Station in Japan. No operation of cooling systems forced to venting of nuclear furnaces and led to explosion and fire of three nuclear furnaces and a cooling pool for used nuclear fuel. The radioactive substances scattered widely in all over Japan, particularly in Northeast and Kanto areas of Honshu Island. The problems of radioactive substances scattered are mostly iodine-131 and 133 and cesium-137 and 134. Iodine contamination was found in tap water in Tokyo and its surrounding area. Because radioactive iodine causes thyroid dysfunction particularly for infants, people could not drink tap water for a few days. The half lives of I-131 and 133 are 8.06 days and 20.8 h, respectively, and the tap water contamination with radioactive iodine had been calmed within about 10 days.

The most serious problem has been widely scattered radioactive cesium. The half lives of Cs-137 and 134 are 30.1671 and 2.0652 years, respectively, and hence their decontamination requires hundreds years. The scattered cesium has been bound mostly with clay [1] in addition to staying on houses, buildings, farms, trees, vegetables, grasses and mountains. In residential area, decontamination has been carried out mostly by pressurized watering of houses, buildings and trees, and by scraping of ground and road surfaces. Scraping has also been carried out in farms and cattle farms. Because of difficulty of decontamination of mountains, contamination of farm, cattle farm and residential area near mountains have been continuing. Scraped soil and surface of pavement have been gathered and kept without further treatment. Water used for decontamination has become clay suspension contaminated with radioactive cesium. Our performance of decontamination of the clay suspension in a hazard area will be written later.

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The widely scattered cesium has been gathering in waste incinerator in various forms of waste. Deep contamination was the result of wind flow and rain just after nuclear accident. Thus, there are deeply contaminated hot spots not only in Fukushima prefecture, but also in some parts of Kanto and Northeast areas. Some waste incinerators in such areas have not been operating because of total occupation by drum cans filling with radioactive ash. For instance, in a waste incinerator with only a combustion system at 850-1000°C, the radioactivities of main (bottom) ash and fly ash that is the residue after filtration of exhaust gas were 2,000-3,500 and 7,000-10,000 Bq/kg, respectively. If a waste incinerating facility equipped with a plasma or arc furnace for reduction of amount of waste by heating at 1,300-1600°C, both main ash and fly ash from the incinerator have been molten in a plasma or arc furnace. The radioactivity of the resultant molten-solidified ash has been in the range of 60,000-90,000 Bq/kg, although that of the molten slag is only less than 500 Bq/kg. Such a highly radioactive ash has been kept in drum cans. It is, therefore, urgent to establish the technology to capture radioactive cesium after its separation from the ash. If we can establish such a technology we can use waste incineration facility as the scavenger and cleaner of radioactive cesium for hundreds years.

The first objective of this work is to establish the technology to capture radioactive cesium after separation of cesium from the ash of waste incineration facility. Table 1 [2] shows an example of average composition of arc molten-solidified ash analyzed 24 times in October 2005- January 2006. Main components are chloride ion, potassium and sodium and hence may be KCl and NaCl. Figure 1 shows our results of X-ray diffraction patterns of arc-molten-solidified ash and the filtration residue after rinsing it by stirring for 24 h in water with the weight ratio of water to ash of 10. As estimated from the composition of ash, major crystalline substances are KCl and NaCl and rinsing of the ash led to dissolution of KCl and NaCl into water. Cesium also seems to be in the form of CsCl and be dissolved in waste by rinsing of the ash. However, the amount of cesium estimated from the radioactivity is of the order of ng/kg and hence the concentration of potassium and sodium will be both more than  $10^{10}$  times as high as that of cesium in the water. In general zeolite has been used to capture cesium in water. However, because preferential adsorption of potassium and some sodium, zeolite will not be effective for direct capture of cesium in the solution containing potassium and sodium.

The good sorbents for the separation of cesium from acidic waste have been listed [3]: crown ether + organic anion exchanger, cobalt dicarbonyl, phosphotungstic acid, nickel-, copper-, iron-ferrocyanides, ammonium molybdophosphate and crystalline silico-titanate. The possibility of ammonium phosphomolybdate has been reported [4]. It has been said [5] that both zirconium monohydrogen phosphate and ammonium molybdophosphate are excellent sorbent. Ammonium molybdophosphate is a very effective sorbent for removing cesium from salt-bearing waste streams for a wide range of pH in the pH range of 2 to 10. There is a report [6] that potassium tetratitanate ( $K_2Ti_4O_9$ ) fibers and potassium dititanate ( $K_2Ti_2O_5$ ) fibers capture cesium in the form of  $Cs_xAl_xTi_{8-x}O_{16}$ ,  $1.5 < x < 2$ . There are many reports [eg.7-10] for the efficiency of

ferrocyanides to capture cesium. Walker Jr, et al. [11] reported about crystalline silicotitanate which has the ability to remove cesium in the presence of high concentrations of potassium.

TABLE 1  
Composition of arc-molten-solidified ash in a waste incinerating facility averaged for 24 measurements in October 2005-January 2006

Component	Weight, mg/kg
Na	139,237
Mg	1,888
Al	5,029
Si	1
P	2
S	5
Cl	266,333
K	196,745
Ca	18,199
Ti	75
Cr	70
Mn	185
Fe	2,374
Ni	31
Cu	6,029
Zn	28,700
Pb	7,010

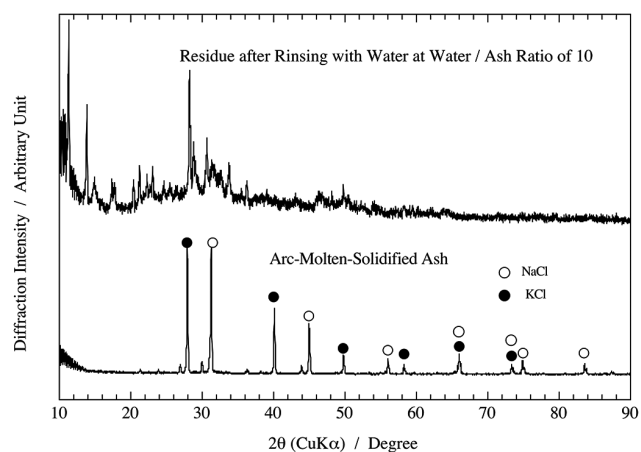


Fig. 1. X ray diffraction patterns of arc-molten-solidified ash of a waste incineration facility and the filtration residue after rinsing of the arc-molten-solidified ash with water

Among various sorbents widely and commonly used sorbents are zeolites and ferrocyanides. Thus, in the present work we established the technology for a significant decrease in the radio active waste by capture of cesium in aqueous solutions with remarkably high concentrations of potassium and sodium using ferric ferrocyanide and zeolite.

## 2. Experimental

### 2.1. Characterization of ash

X ray diffraction patterns before and after rinsing of ash was measured by X-ray diffractometer (SHIMADZU XRD-6100).

### 2.2. Rinsing of ash with water

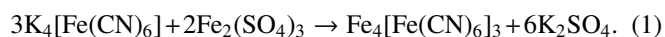
Water containing an arc-molten-solidified ash was stirred for 24 h in which the weight ratio of water to ash were 1.5, 5 and 10. At the weight ratio of water to ash of 10, the pH was adjusted to 8 by HCl addition. After filtration with a 0.8 mm membrane filter the radioactivity of two types of cesium in the filtrate was measured by a LaBr spectrometer of Canberra InSpector 1000. In laboratory experiment the detectable limit of the spectrometer is 300 Bq for 100 mL solution.

### 2.3. Adsorption of cesium on commercial sorbents

After rinsing the ash with water the adsorption of cesium in the filtrate on zeolite powders of Unicellex UR-3103Z of 2-3 mm diameter was carried out stirring 30 min. Adsorption of cesium on granular prussian blue of 11  $\mu\text{m}$  diameter was also carried out stirring 30 min. After filtration with a 0.8  $\mu\text{m}$  membrane filter the radioactivity of the filtrate was measured.

### 2.4. Adsorption of cesium on in-situ synthesized ferric ferrocyanide

For a more effective method to capture cesium, in-situ formation of ferric ferrocyanide in the filtrate after washing the radioactive ash with water was adopted. Ferric ferrocyanide can be formed by the reaction



Stoichiometric composition of reactants cannot lead to complete conversion to ferric ferrocyanide, and the excess addition of ferric sulfate was conducted. Furthermore, fine particle of ferric ferrocyanide does not form filterable precipitate. In this regards, dissolution of ferric sulfate in water generally results in the formation of iron rust,  $\text{Fe}(\text{OH})_3$  which co-precipitates easily with ferric ferrocyanide. Thus, in the experiment of in-situ formation of ferric ferrocyanide in the filtrate after rinsing of radioactive ash, excess amounts of ferric sulfate were added. After addition of potassium ferrocyanide and ferric sulfate the solution was stirred for 30 min. After filtration of precipitate the radioactivity of remaining cesium in the filtrate was measured.

### 2.5. Separation of cesium from ferric ferrocyanide and capture of cesium with zeolite

Even if cesium is captured with ferric ferrocyanide there is a regulation that any kind of cyanide substances should not be preserved. Because the molecular structure of ferric ferrocyanide is destructed by releasing ferric ions by immersion in alkaline solutions, potassium-free cesium-captured ferric ferrocyanide with ferric hydroxide was immersed in 0.009 M

NaOH solution at pH 11.5 stirring for 30 min and kept in the solution for an overnight. After filtration with a 0.8  $\mu\text{m}$  membrane filter the radioactivity of cesium in the filtrate was measured. For the adsorption with zeolite pH was lowered by the addition of HCl and then the adsorption of cesium on zeolite powders of Unicellex UR-3103Z of 2-3 mm diameter was carried out stirring 24 h. Finally the radioactivity of supernatant solution was measured.

## 3. Results and Discussion

Table 2 shows the radioactivity of the arc-molten-solidified ash and the filtration residue after rinsing of the ash with water, at different weight ratios of water to ash. The radioactivity of cesium in the ash was 85,788 Bq/kg but by rinsing with water at the water/ash ratio of 10, 94.4% of radio active cesium was separated into water. In this manner, we can easily wash away the radioactive cesium from the ash and we can send the washed residue to reclamation. Hereafter we take the weight ratio of water to ash of 10 for rinsing of the ash.

TABLE 2  
Radioactivity of arc-molten-solidified ash before and after water rinsing Stirring for 24 h in water, Filtration with 0.8  $\mu\text{m}$  membrane filter

	Weight ratio of water to ash	Radioactivity Bq/kg		Total radioactivity of cesium Bq/kg	Removal ratio %
		Cs-137	Cs-134		
Before rinsing		48,617	37,170	<b>85,788</b>	
After rinsing	1.5	14,243	11,133	25,376	71.4%
	5	6,192	4,508	10,700	87.9%
	10 (pH 8)	2,826	2,120	<b>4,946</b>	<b>94.4%</b>

Table 3 shows the composition of the filtrate after rinsing of the arc-molten-solidified ash. Hereafter the filtrate obtained by filtration of water used for rinsing of the ash will be written as the original filtrate. Because we adjusted pH of rinsing water by adding HCl, we did not analyze the chloride content. In general, a heavy metal immobilizing agent had been added in the ash, and hence amounts of metals detected were low. As has been estimated from Table 1 and Fig. 1, potassium and sodium have been dissolved in the water. It is well known that potassium prevents adsorption of cesium on zeolite.

Figure 2 shows the radioactivity of the filtrate filtered after stirring of the original filtrate with zeolite for 24 h. Initially the radioactivity was 8,184  $\text{BqL}^{-1}$  but the addition of 50  $\text{gL}^{-1}$  of zeolite removed 87% of cesium. This corresponds to 141,800 Bq/kg of zeolite. A comparison of this value with 85,788 Bq/kg of the arc-molten-solidified ash indicates that the radioactive waste in the form of zeolite is 3/5 of that in the form of the ash. This lower efficiency to decrease the radioactive waste is due to preferential adsorption of potassium

and sodium whose concentrations more than  $10^{10}$  times as high as that of cesium.

TABLE 3  
Composition of filtrate after rinsing the arc-molten-solidified ash with water  
The weight ratio of water/ash : 10, pH 8

Species	Concentration/mgL <sup>-1</sup>	Analytical Method
Na <sup>+</sup>	7,500	Frame AAS
K <sup>+</sup>	15,000	Frame AAS
Ca <sup>2+</sup>	175	ICPS
NH <sub>4</sub> <sup>+</sup>	<25	ICPS
Cd and its compounds	<0.2	ICPS
Pb and its compounds	<0.4	ICPS
Cr	<0.8	ICPS
As and its compounds	<0.2	ICPS
Hg, alkylmercuric compounds and other Hg compounds	<0.02	AAS
Zn	1.28	ICPS
Sn	<0.4	Indophenol blue absorptiometry

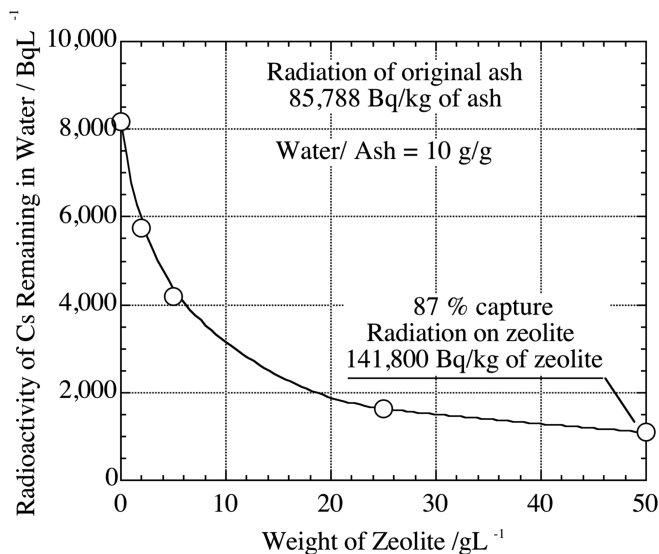


Fig. 2. Radioactivity of cesium remaining in water filtrated after addition of zeolite to the filtrate of water used for rinsing of the arc-molten-solidified ash of a waste incineration facility

Figure 3 shows a better performance of commercial prussian blue than zeolite. The addition of 1 gL<sup>-1</sup> of prussian blue to the original filtrate removed 94% of radioactivity. The radioactivity of 1 g of Prussian blue is 8,350,000 Bq/kg. In comparison with 85,788 Bq/kg of the arc-molten-solidified ash, the radioactive waste in the form of prussian blue is 1/97. If we make in-situ synthesis of ferric ferrocyanide in the original filtrate from the ash, further better performance will be attained.

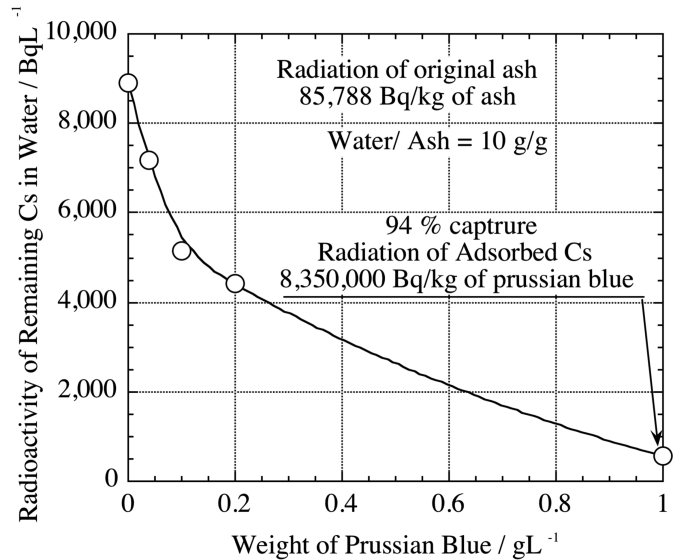


Fig. 3. Radioactivity of cesium remaining in water filtrated after addition of commercial prussian blue to the filtrate of water used for rinsing of the arc-molten-solidified ash of a waste incineration facility

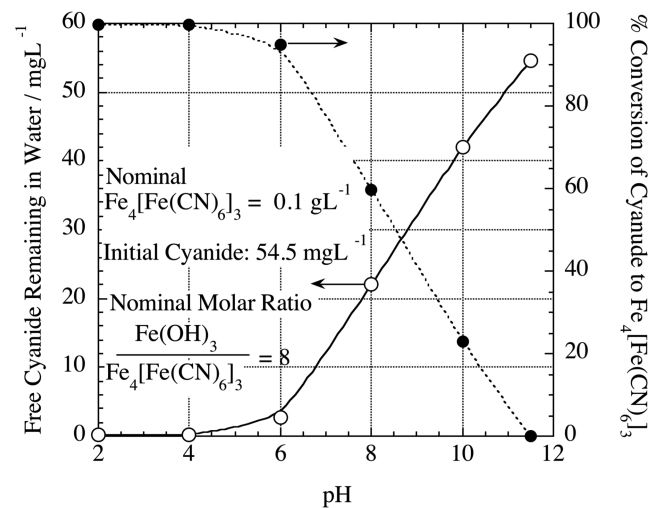


Fig. 4. Amount of free cyanide remaining in water and % conversion to ferric ferrocyanide at the nominal ferric ferrocyanide of 0.1 gL<sup>-1</sup> and nominal molar ratio of ferric ferrocyanide to ferric hydroxide of 8 as a function of pH

Before examination of capture of cesium by in-situ synthesis of ferric ferrocyanide, the formation of ferric ferrocyanide and its precipitation were examined. Figure 4 shows the amount of free cyanide without conversion to ferric ferrocyanide and % conversion to ferric ferrocyanide as a function of pH at the nominal molar ratio of ferric hydroxide to ferric ferrocyanide of 8 and nominal weight of ferric ferrocyanide of 0.1 gL<sup>-1</sup>. At higher pH and lower concentration of ferric hydroxide the conversion to ferric ferrocyanide is not high, and the ratio is just the ratio of ferric hydroxide supposed to be formed to ferric ferrocyanide supposed to be formed. Thus, the ratio is written as the nominal molar ratio of ferric hydroxide to ferric ferrocyanide, and concentrations of ferric ferrocyanide and ferric hydroxide are also nominal. It seems that at the nominal ratio of ferric hydroxide to ferric ferrocyanide of 8, if only ferric ferrocyanide is formed the ferric

ferrocyanide precipitates with ferric hydroxide. The conversion to ferric ferrocyanide increases with decreasing pH, and 95% conversion is attained at pH 6. Although complete precipitation occurs at lower pH such as pH 4 and 2, both precipitation and filtration were very slow because of fine precipitates. Thus, the optimum pH for precipitation was 6, and the experiment was carried out at pH 6 unless otherwise stated.

Figure 5 shows the amount of free cyanide without conversion to ferric ferrocyanide and % conversion to ferric ferrocyanide as a function of nominal molar ratio of ferric hydroxide to ferric ferrocyanide. The conversion to ferric ferrocyanide and precipitation of ferric ferrocyanide together with ferric hydroxide increase with increasing excess amount of ferric hydroxide and at the nominal molar ratio of ferric hydroxide to ferric ferrocyanide of 8, the conversion reaches 95%.

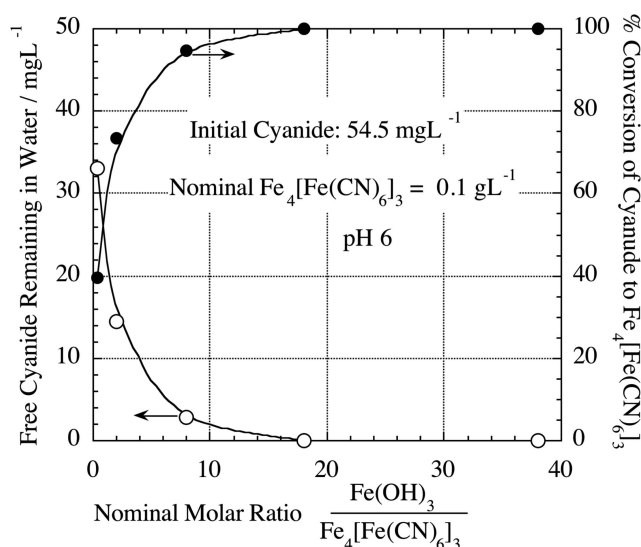


Fig. 5. Amount of free cyanide remaining in water and % conversion to ferric ferrocyanide at the nominal ferric ferrocyanide of  $0.1 \text{ gL}^{-1}$  and pH 6 as a function of the nominal molar ratio of ferric hydroxide to ferric ferrocyanide

Figure 6 shows the performance of in-situ synthesis of ferric ferrocyanide in the original filtrate after rinsing of the arc-molten-solidified ash. For complete conversion of potassium ferrocyanide to ferric ferrocyanide and for co-precipitation of ferric ferrocyanide with ferric hydroxide the excess amount of ferric sulfate was required. In this figure the curves have been distinguished by the nominal molar ratio of ferric hydroxide to ferric ferrocyanide. At the nominal ratio of ferric hydroxide to ferric ferrocyanide of 8, 0.05 g of ferric ferrocyanide captures almost all radioactive cesium. However, when the amount of ferric ferrocyanide is further lower the radioactivity remaining in the water is significantly high and also if the nominal ratio of ferric hydroxide to ferric ferrocyanide is lower such as 2 and 0.4 the radioactive cesium is mostly remaining in the water unless large amount of ferric ferrocyanide is added. This is mostly due to incomplete conversion of potassium ferrocyanide to ferric ferrocyanide at lower amount of addition of ferric sulfate. It is clear that when the nominal ratio of ferric hydroxide to ferric ferrocyanide becomes 18 the complete conversion of potassium ferrocyanide to ferric ferrocyanide occurs at nominal weight

of ferric ferrocyanide of  $0.05 \text{ gL}^{-1}$ . A comparison of Figs. 4 and 6 indicates that if both ferrocyanide and iron rust are not sufficient, precipitation of cesium-captured ferric ferrocyanide with iron rust is difficult and even if the amount of ferric ferrocyanide is not high such as  $0.05 \text{ gL}^{-1}$  for 7,680 Bq/kg of radioactivity, sufficient addition of iron rust results in precipitation of all radioactive cesium. A comparison of Figs. 4 and 6 also shows that precipitation of cesium at the nominal ferric ferrocyanide of  $0.1 \text{ gL}^{-1}$  and at the nominal molar ratios of ferric hydroxide to ferric ferrocyanide of 0.4, 2 and 8 occurs depending on the amount of ferric ferrocyanide formed.

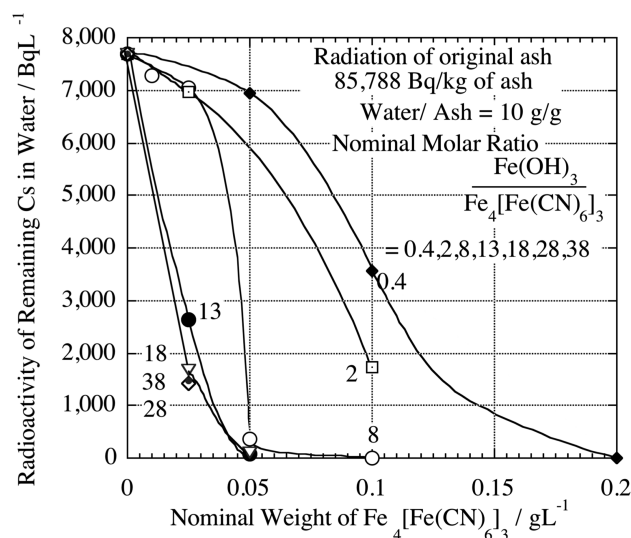


Fig. 6. Radioactivity of cesium remaining in water filtrated after in-situ formation of ferric ferrocyanide in the filtrate of water used for rinsing of the arc-molten-solidified ash of a waste incineration facility as a function of the nominal weight of ferric ferrocyanide

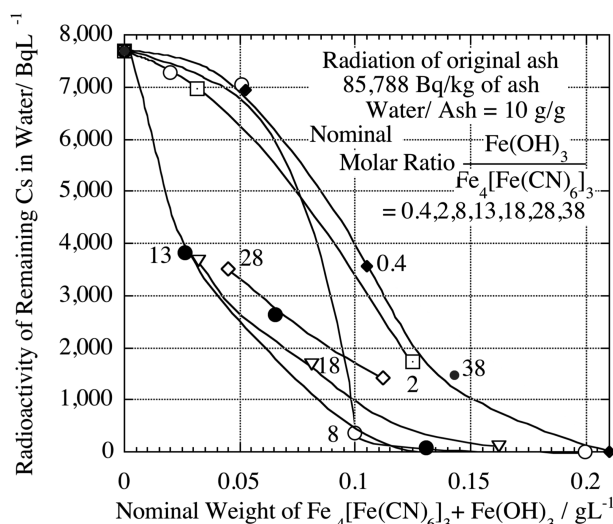


Fig. 7. Radioactivity of cesium remaining in water filtrated after in-situ formation of ferric ferrocyanide in the filtrate of water used for rinsing of the arc-molten-solidified ash of a waste incineration facility as a function of sum of nominal weights of ferric ferrocyanide and ferric hydroxide

Figure 7 shows the radioactivity of cesium remaining in water as a function of total nominal weight of radioactive waste, that is the sum of ferric ferrocyanide and ferric hy-

droxide. At a given constant sum of ferric ferrocyanide and ferric hydroxide, the higher ratio of ferric hydroxide to ferric ferrocyanide corresponds to lower amount of heavy ferric ferrocyanide. Thus, the increase in the ratio of ferric hydroxide to ferric ferrocyanide is more effective than increase in heavy ferric ferrocyanide.

Figure 8 shows the radioactivity on the radioactive waste as a function of the weight of radioactive waste. When the ratio of ferric hydroxide to ferric ferrocyanide is 8 and when the sum of ferric hydroxide and ferric ferrocyanide is 0.1, 94% of cesium has been captured as shown in Fig. 7, and the radioactivity is 73,243,000 Bq/kg of the waste which corresponds to that the radioactive waste become only 1/854 of 85,788 Bq/kg of the arc-molten-solidified ash.

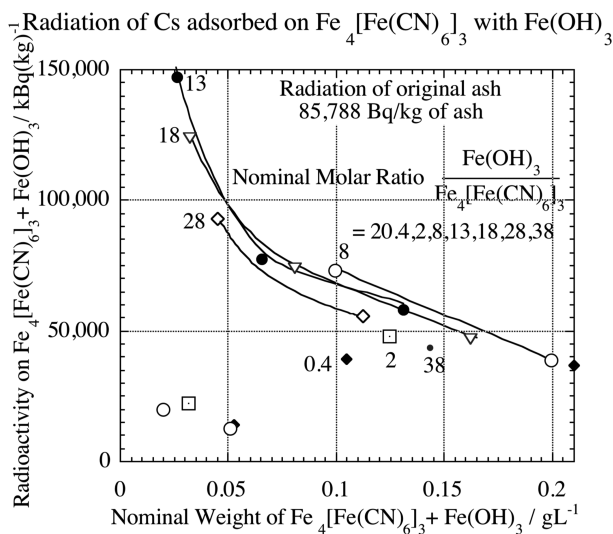


Fig. 8. Radioactivity of cesium on the precipitate consisting of cesium-captured ferric ferrocyanide and ferric hydroxide after in-situ formation of ferric ferrocyanide in the filtrate of water used for rinsing of the arc-molten-solidified ash of a waste incineration facility as a function of sum of nominal weights of ferric ferrocyanide and ferric hydroxide

Now we can get the radioactive waste consisting of ferric ferrocyanide and ferric hydroxide on which cesium is highly concentrated such as 854 times as high as the arc-molten-solidified ash. There is, however, the regulation in Japan that any kind of cyanide substances should not be preserved. Our radioactive waste now does not contain potassium which inhibits the adsorption of cesium on zeolite. Thus, if we can separate cesium in water from the radioactive waste consisting of ferric ferrocyanide and ferric hydroxide we can capture cesium by zeolite.

Starting from the original filtrate containing 1.5 wt.% potassium and 0.75 wt.% sodium ions with 9,010 BqL<sup>-1</sup> of radioactivity of cesium after rinsing of the arc-molten-solidified ash, we captured cesium by ferric ferrocyanide with ferric hydroxide at nominal weight of ferric ferrocyanide of 0.1 gL<sup>-1</sup>, nominal molar ratio of ferric hydroxide to ferric ferrocyanide of 8 and pH 6. After filtration of the mixture of cesium-captured ferric ferrocyanide and ferric hydroxide, the mixture of cesium-captured ferric ferrocyanide and ferric hydroxide was immersed in 0.009 M NaOH solution at pH 11.5 stirring for 30 min and under stagnant condition for an overnight. In the alkaline solution the molecular structure of

ferric ferrocyanide was destructed by releasing ferric ions from the molecule and cesium ions were separated from ferric ferrocyanide. After filtration of cesium dissolving solution with a 0.8 μm membrane filter, the radioactivity of the filtrate was 8,600 BqL<sup>-1</sup>. Thus, this filtrate solution consisting of 0.036 wt.% Na<sup>+</sup> and ferrocyanide anion contains 95% of radioactive cesium in the original filtrate with 9,010 BqL<sup>-1</sup> after rinsing of the arc-molten-solidified ash. After lowering pH by the addition of HCl, zeolite was added to the filtrate solutions of pH 7, 10 and 11.5 which were stirred for 24 h, and the radioactivity of supernatant was measured.

Figure 9 shows the radioactivity of the supernatant solutions. At higher pH such as 10 and 11.5 some cesium ions were remaining in the solution but at pH 7 all cesium ions were captured by zeolite. On 2.5 gL<sup>-1</sup> zeolite the radioactivity is 3,440,000 Bq/kg of zeolite and hence the radioactive waste became 1/40 of 85,788 Bq/kg of the arc-molten-solidified ash. According to cold experiment, the adsorption capacity of cesium on zeolite is more than an order of magnitude as high as this value. Thus, we can expect that the radioactive waste of zeolite formed by this procedure will be almost 1/500 of the arc-molten-solidified ash in waste incineration facility.

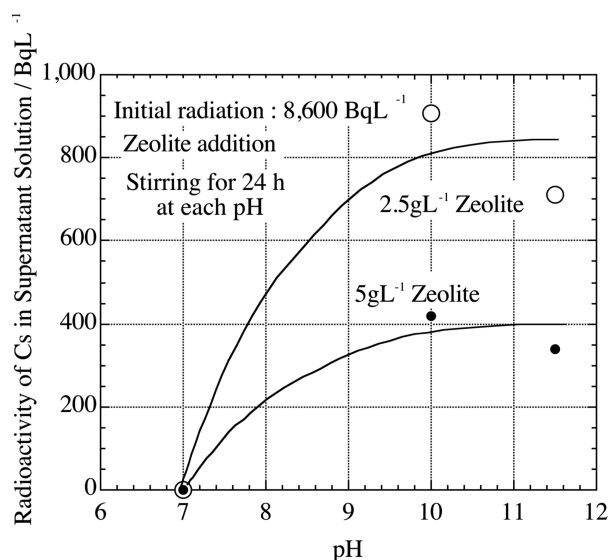
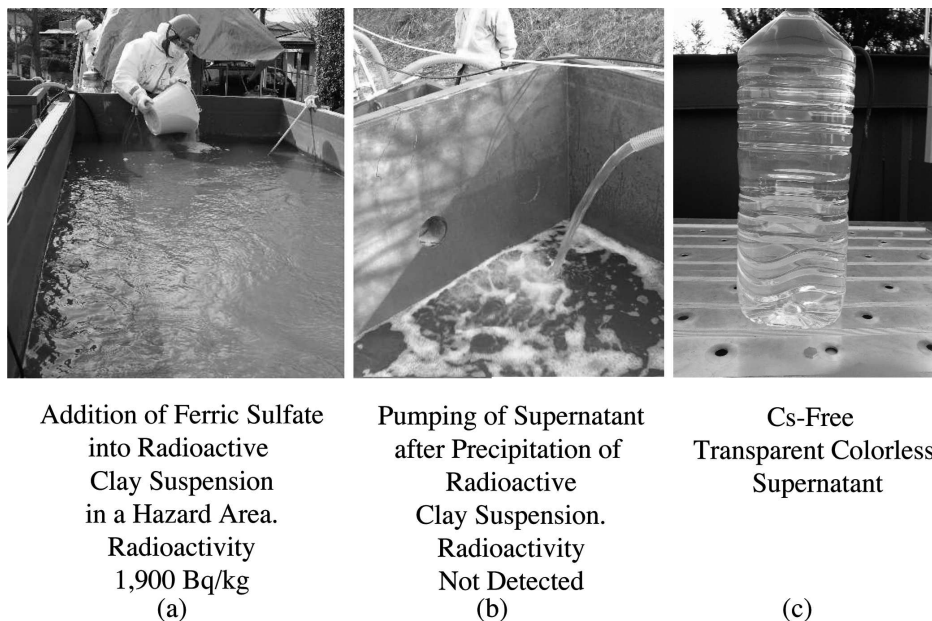


Fig. 9. Radioactivity of cesium in supernatant of the zeolite-added water filtrated after separating cesium from cesium-captured ferric ferrocyanide with ferric hydroxide in 0.009 M NaOH solution

In this manner, widely scattered radioactive cesium has been gathering in waste incineration facility and we can use waste incineration facility as the scavenger and cleaner of radioactive cesium for hundreds years.

#### 4. Field Examination of Decontamination

We utilized the beneficial effect of iron rust for purification of water containing clay suspension contaminated with radioactive cesium. When we use water for decontamination of houses and farming field, cesium is mostly combining with clay and forming clay suspension contaminated heavily with radioactive cesium. We performed purification of water gathering in the gutter after washing of housing in a radioactive hazard area.



Addition of Ferric Sulfate into Radioactive Clay Suspension in a Hazard Area. Radioactivity 1,900 Bq/kg (a)

Pumping of Supernatant after Precipitation of Radioactive Clay Suspension. Radioactivity Not Detected (b)

Cs-Free Transparent Colorless Supernatant (c)

Fig. 10. Decontamination of water used for rising of houses in a hazard area: a) Precipitation treatment of Cs-contaminated clay suspension; b) Pumping of decontaminated water; c) Decontaminated transparent colorless water

We added ferric sulfate and anionic coagulant for condensation precipitation of cesium-contaminated clay suspension. About 90% of cesium had been adsorbing on clay, but about 10% of cesium had been dissolving in water. Thus, after precipitation of clay suspension we added zeolite to capture dissolving cesium ions.

Figure 10 shows the pictures in a hazard area. By these procedures the supernatant was changed from muddy water to transparent and colorless water. We measured radioactivity of the supernatant water by Gamma spectrometry with Ge crystal of Canberra Model GC2520, whose detectable limit was more than 20 Bq/kg. The radioactivity of the muddy water was 1,900 Bq/kg but after the above-mentioned treatment the radioactivity was not detectable. We could use colorless and transparent cesium-free supernatant water again for pressurized water washing of contaminated houses. Because of no water supply due to cut of life-line by earthquake, repeated use of water has been essential in hazard areas.

## 5. Conclusions

Our effort for decontamination of radioactive cesium scattered widely by nuclear accident in March 2011 in Fukushima, Japan has been described.

1. Radioactive cesium scattered widely in Japan has been accumulating in arc or plasma molten-solidified ash in waste incinerating facilities up to 90,000 Bq/kg of the radioactive waste. The radioactivity of cesium of the arc-molten-solidified ash in the present work was 85,788 Bq/kg.
2. Cesium can be dissolved from the ash into water together with potassium and sodium ions by rinsing of the ash with water. The concentrations of potassium and sodium ions in filtrate after rinsing of the ash with water in the present work were 1.5 and 0.75 wt.%, respectively.

3. The decrease in the radioactive waste by adsorption on commercial granular zeolite and prussian blue from the filtrate was not sufficient.
4. In-situ simultaneous formation of ferric ferrocyanide and ferric hydroxide by addition of potassium ferrocyanide and excessive ferric sulfate in the solution containing cesium ions with high concentrations of potassium and sodium ions was effective for complete removal of radioactive cesium in the form of very low amounts of highly radioactive waste of cesium-captured ferric ferrocyanide with ferric hydroxide.
5. Because of regulation of no preservation of any kind of cyanide substances, cesium was separated from potassium-free cesium-captured ferric ferrocyanide with ferric hydroxide in a diluted NaOH solution and then captured by zeolite. Final radioactive waste, cesium-captured zeolite, was significantly lower than the radioactive waste from waste incinerating facility.
6. In situ formation of ferric hydroxide was effective in leading to no detectable radioactivity by condensation precipitation of cesium-adsorbed clay suspension formed by water washing of contaminated houses in a radioactive hazard area.

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