

Radioactive cesium decontamination technology for ash

— Utilization and application of nanoparticles as an adsorbent —

Tohru KAWAMOTO^{1*}, Hisashi TANAKA¹, Yukiya HAKUTA¹, Akira TAKAHASHI¹, Durga PARAJULI¹,
Kimitaka MINAMI¹, Tetsuo YASUTAKA² and Tatsuya UCHIDA¹

[Translation from *Synthesiology*, Vol.9, No.3, p.139–153 (2016)]

The accident at the Fukushima Daiichi Nuclear Power Station in 2011 spurred rapid research and development at AIST for radioactive cesium decontamination systems. In this paper, we introduce the development of an ash-decontamination technology that uses Prussian blue (PB) nanoparticles. We developed all aspects of the system using a combination of fundamental technologies, which included optimization of the PB nanoparticle structure for use as a cesium adsorbent, composite fabrication as granules for use as an adsorbent, and extraction of radioactive cesium from contaminated ash. All aspects of development were achieved rapidly through close collaboration among materials science, computational science, and geology researchers. Collaboration with private companies was also effective.

Keywords : Prussian blue, nanoparticle, radioactive cesium, decontamination, ash

1 Background: Radiation leakage accident and AIST efforts

As a consequence of the great earthquake which occurred on March 11, 2011, a giant tsunami struck the Fukushima Daiichi Nuclear Power Plant operated by Tokyo Electric Power Company. In the aftermath, the nuclear reactors, which could not be cooled, leaked radioactive materials. Most of those leaked materials had a low boiling point, which exacerbated their release: an estimated 1.6×10^{17} Bq of iodine-131 and 1.5×10^{17} Bq of cesium-137 were ejected into the environment.^[1] Because iodine and cesium exist as salt compounds at room temperature, they fell on the ground to contaminate the soil, or dissolved in river and sea waters. The respective half-lives of cesium-134 and cesium-137 are approximately two years and 30 years. Therefore, their effects are expected to persist for a long time. The Japanese government has held the decontamination of radioactive cesium from the environment as an urgent task, and has concentrated on research and development to achieve that objective.

Great efforts for decontamination have been undertaken at AIST for various developments, such as those of decontamination technology for contaminated water, soil, and incinerated ash using Prussian blue (PB) nanoparticles,^{[2]–[6]} of a concentrator for analyzing ultra-trace radioactive materials in environmental water,^{[7]–[8]} of reference materials to evaluate brown rice contamination,^[9] of dynamic evaluation methods for radioactive cesium in the environment,^{[10]–[11]} and of decontamination cost estimation.^[12] We specifically examined the development of

decontamination and measurement technologies using PB nanoparticles having high adsorption capacities for radioactive cesium.

Decontamination technology is an extremely urgent topic. Therefore, R&D has been conducted more rapidly than a regular schedule might allow. Our core material is PB nanoparticles. Although R&D activities are mainly conducted from the standpoint of materials science, for the practical application of decontamination technology, it has also been necessary to combine diverse specialties such as chemical engineering, geo-engineering, and agriculture. Because AIST is a research institute, it cannot engage in final commercial projects. Therefore, the developed technologies must be transferred to a company to carry out commercial tasks. It is also necessary to pursue coordination with the national government and local governments, particularly with efforts of coordination with the local area in which the pilot plant tests would be done.

As described in this paper, we address the example of the decontamination technology of incinerated ash using PB nanoparticles. Details of the R&D are presented in Chapter 2. The strategy and management for conducting this technological development are presented in Chapter 3.

2 Development of incinerated ash decontamination technology

2.1 Technological background

The radioactive cesium adsorbent, our core technology,

1. Nanomaterials Research Institute, AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565, Japan * E-mail: tohru.kawamoto@aist.go.jp, 2. Research Institute for Geo-Resources and Environment, AIST Tsukuba Central 7, 1-1-1 Higashi, Tsukuba 305-8567, Japan

Original manuscript received March 29, 2016, Revisions received May 16, 2016, Accepted June 6, 2016

consists of metal hexacyanoferrate (MHCF or Prussian blue type complex) nanoparticles. Actually, MHCF is a porous coordination polymer with chemical composition of $A_xM[Fe(CN)_6]_{1-x} \cdot zH_2O$, where A stands for a cation such as an alkali metal, and M denotes a transition metal cation. When $M = Fe$, it is Prussian blue (PB), an artificial pigment synthesized in the early 18th century, used by van Gogh and Hokusai in their paintings, and even used in present days. The metal species (A, M) and composition (x, y, z) can be controlled over a wide range. The crystal structure, presented in Fig. 1, has a jungle-gym structure in which the cyano group crosslinks the metal atoms. The crystal includes a hollow network in which cation A adsorbs and desorbs. It is known for its highly selective adsorption of cesium ions.^[13]

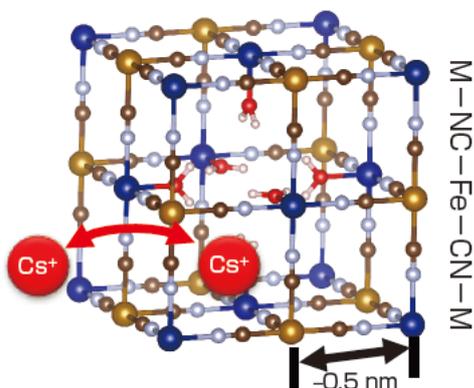


Fig. 1 The crystal structure of hexacyanoferrate $A_xM[Fe(CN)_6]_{1-x} \cdot zH_2O$, where A and M indicate the cations and the transition metal ions of Fe, Cu, Co, or others. The red atoms around the vacancy show the oxygen in the H_2O molecule.

The first report of the radioactive cesium adsorption capacity of PB was published around 1950.^[14] Since then, radioactive cesium adsorption by various MHCFs, not only PB, has been investigated and used.^{[13][15]-[17]} For example, various MHCFs were used for removing radioactive cesium from contaminated water at Hanford, where nuclear development was conducted in the United States in the 1960s.^[18] Recently, nickel hexacyanoferrate (NiHCF) was used in the Areva device for decontamination of contaminated water from the nuclear plant accident in 2011.^{[19][20]}

An outline of PB research at AIST is presented in Fig. 2. At AIST, the development of a PB type complex has been conducted jointly with Yamagata University from 2005,^{[21][22]} with particular emphasis on the development of electrochromic devices.^{[23]-[26]} Before the accident at Fukushima, we had been involved in R&D of a system for electrochemically adsorbing/desorbing and concentrating radioactive cesium.^{[27]-[29]} The accident at Fukushima occurred as we were accumulating related technological knowledge. In its aftermath, we immediately shifted the main focus of our R&D to decontamination. We conducted R&D of two main areas: the development of an adsorbent based on PB nanoparticles,^{[30]-[34]} and the development of decontamination technology using this adsorbent.^{[35]-[38]}

2.2 Outline of incinerated ash decontamination technology

One specifically examined technological development topic is the volume reduction of vegetal contaminants.^{[3][5][6]} Actually, incinerated ash decontamination includes this technology. An

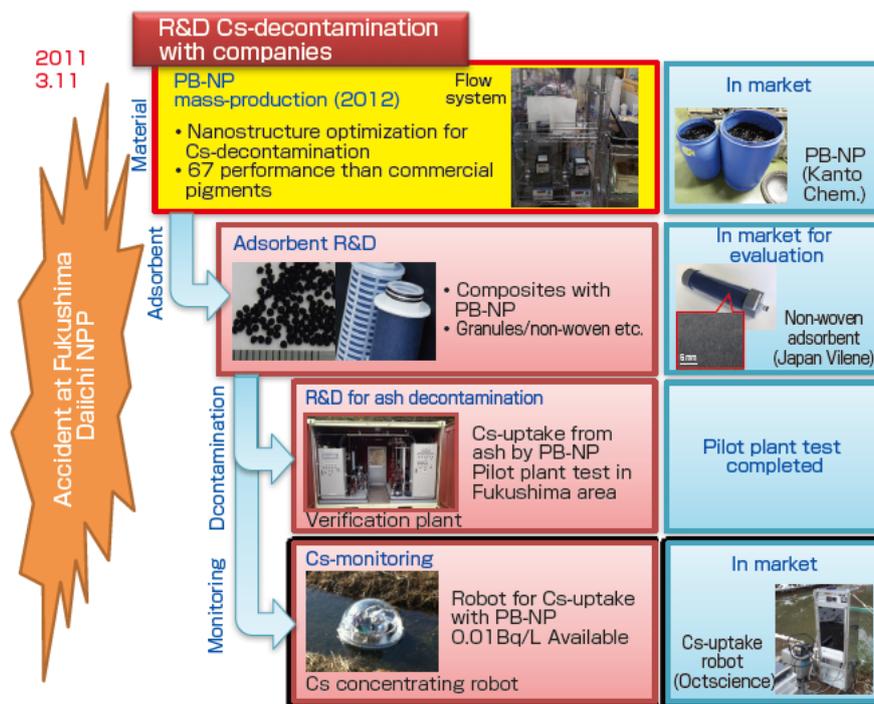


Fig. 2 History of the development of radioactive cesium decontamination technology using PB nanoparticles at AIST, where PB and PB-NP represent Prussian blue and PB nanoparticles, respectively

outline of the technology is depicted in Fig. 3. The vegetal materials contaminated by radioactive cesium would be produced in large amounts because of forest contamination. If such combustible contaminants are not treated appropriately, then they might be heated by fermentation or other processes and then ignite. Therefore, appropriate incineration is necessary. However, because radioactive cesium elutes from the incinerated ash through contact with water,^{[39][40]} such ash cannot be processed as regular industrial waste. Our approach is washing after incineration of the contaminants, followed by radioactive uptake by the adsorbent, resulting in volume reduction to 1/500–1/3,000 of the ash, or 1/25,000–1/300,000 of the material before incineration.

Although similar decontamination technology has been investigated by many organizations,^{[41]–[44]} the advantage of our technology is the high radioactive cesium adsorption

capacity of the PB nanoparticles. Nevertheless, it is unrealistic to apply powder or dispersion liquid of the nanoparticles to the decontamination site. R&D is required for various stages of fabrication of the adsorbent and design of the plant facility. The technology flow is portrayed in Fig. 4 for materials, development of the adsorbent, plant design, and demonstration. By developing the whole process from materials to the plant facility based on the PB nanoparticles, we aimed at making the most of the nanomaterial function for contribution to cesium decontamination. During progress from this material to the plant facility, our development involves different scales from atomic size, nanometer, micrometer to meter scales. For example, control of the chemical composition is necessary in materials development, whereas plant design is development of a metric scale. Such integrated development from materials to plant facilities necessitates the development of technologies on various scales.

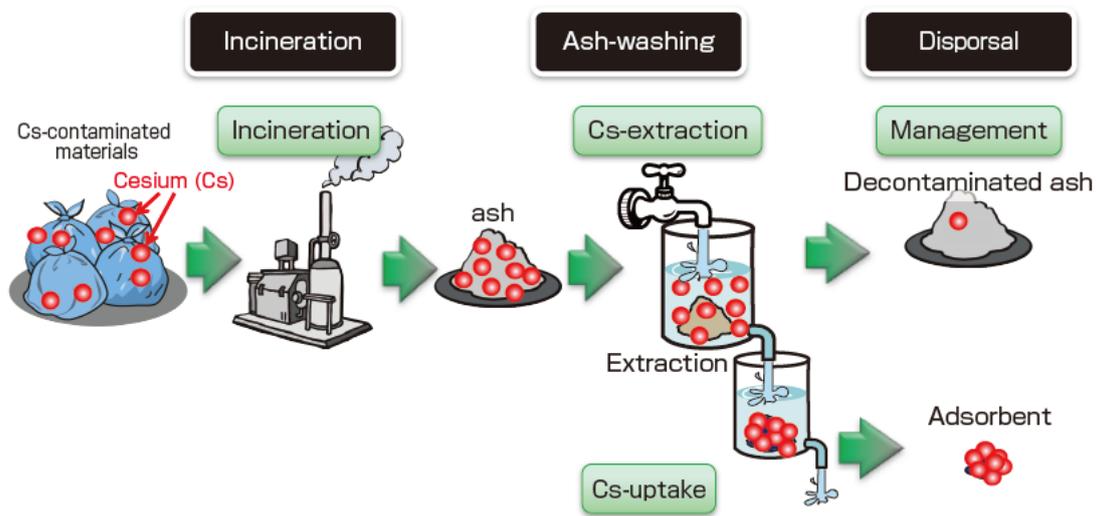


Fig. 3 Outline of volume reduction of vegetal contaminants and incinerated ash using PB nanoparticles^[6]

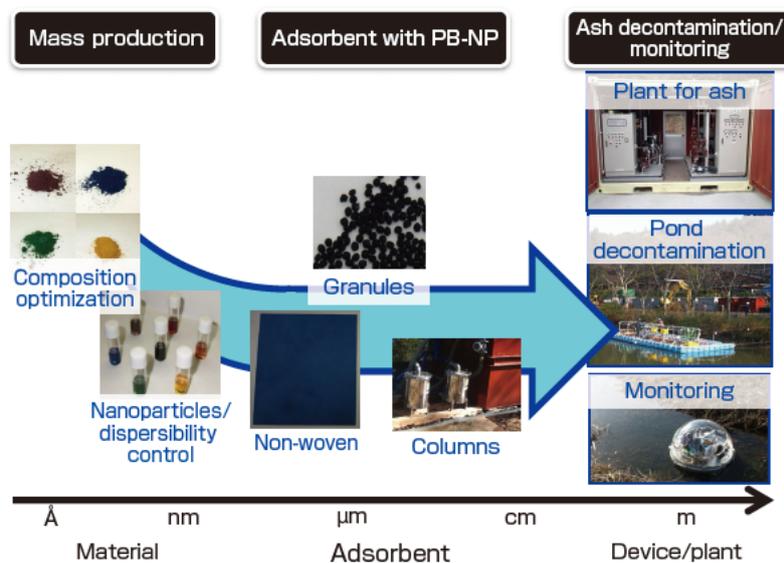


Fig. 4 Technology development for each scale of the decontamination technology development using PB nanoparticles at AIST

Table 1. Outline of Prussian blue nanoparticle^[30]

Name	Nanoparticle (11 μm)	Nanoparticle (60 μm)	Commercially available PB
Composition	Fe [Fe(CN) ₆] _{0.75}		(NH ₄) _{0.64} Fe[Fe(CN) ₆] _{0.91}
Primary particle diameter	8.8 nm		36 nm
Secondary particle diameter	11 μm	60 μm	9 μm

2.2.1 Development of PB nanoparticles for use as radioactive cesium adsorbents

The benefits of the PB nanoparticles, the material of our technology for use with radioactive cesium, is its high selectivity and efficient adsorption. Although PB tends to form fine particles, the cesium adsorption performance can be increased through optimization of the chemical composition as well as its particle size.^{[30][32]} The particle size and composition of the PB nanoparticles is shown in Table 1 in comparison with “konjo” (905; Dainichiseika Color & Chemicals Manufacturing Co., Ltd.), a commercially available form of Prussian blue.^[30] The points are the optimization of the composition and the control of the particle size. In general, the Prussian blue composition is expressed as A_yFe[Fe(CN)₆]_{1-x}, implying the vacancies of [Fe(CN)₆]^s or alkali cations insertion in its structure. The *x* and *y* in the chemical composition respectively represent the amount of the [Fe(CN)₆]^s vacancies, and the amount of cation introduced. Prussian blue is obtainable by mixing the Fe²⁺ ion water solution and [Fe(CN)₆]³⁻ ion solution. It is possible to control the composition by appropriate choice of the mixing ratio, types of counter ion, and valence numbers of the ions. Results show that the adsorption capacity changed greatly according to the composition.^[45]

To increase the adsorption performance, we reduced the material to nanoparticles. The size of our nanoparticles was about 8–20 nm (Fig. 5(a)). The primary particle size of nanoparticles is dependent on the synthesis method. For

example, it is possible to reduce the particle size by rapid mixing. In the case of copper hexacyanoferrate, a Prussian blue analog, we achieved improvement of 7.7 times in adsorption speed compared with the case of conventional synthesis by the reduction of the particle size by micro-mixer synthesis.^[33] The particle size can also be controlled to a certain degree by controlling the ionic valence number or temperature during mixing.

Powder size, the secondary particle size, also affects the adsorption performance. The diffusion coefficient of radioactive cesium in a powder is low compared to that in liquid, implying that a higher adsorption rate is possible by reducing the secondary particle diameter. For example, for powder synthesis by drying of the PB nanoparticle suspension, an appropriate choice of the drying method is necessary to achieve the small secondary particle size.

Figure 5(b) presents the dependence of the cesium adsorption rate on the liquid–solid ratio when various adsorbent powders were added to water for washing the incinerated ash. When our PB nanoparticles were used, almost 100 % adsorption was observed with a liquid–solid ratio of 5,000 or 200 ppm contents. However, the adsorption rate of commercial PB was approximately 80 %, and for zeolite, it was used frequently as a cesium adsorbent: it was 20 % or less. The reasons for the difference of the adsorption rate against the commercial PB are its different particle size and different chemical composition. The poor adsorption of zeolite derives from its

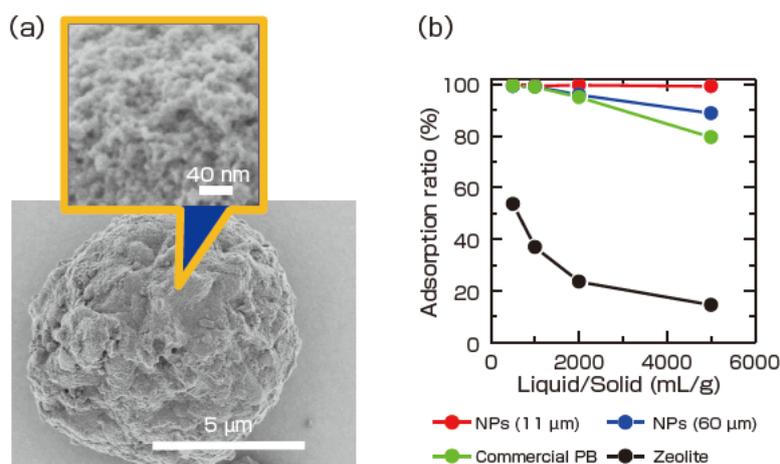


Fig. 5 (a) Electron microscope image of PB nanoparticle powder. (b) Liquid–solid ratio dependency of adsorption performance when various cesium adsorbents are added to the water after washing the incinerated ash^{[3][30]}

poor selectivity for cesium uptake and the high concentration of other ions in the ash washing water.

2.2.2 Mass production of the PB nanoparticles and adsorbent development

Mass production of the PB nanoparticles was conducted through joint research with Kanto Chemical Co., Inc. Our fundamental strategy was the following: AIST determined the appropriate composition and crystal structure for the radioactive adsorbent. The manufacturing method was also investigated among the methods available for mass-production. Finally, this technology was transferred to the company, and Kanto Chemical improved the manufacturing method for mass production.

We were successful at developing the PB nanoparticles exhibiting high cesium adsorption capacity, but this material was normally obtained in the form of powder or slurry. For radioactive cesium removal from ash washing water, solid-liquid separation with powder or slurry must be done after adding the powder to washing water.^[46] However, safety concerns were often raised for the powder addition method for the concentration of radioactive materials. Especially, the risk of system trouble exists because an engineer must handle the adsorbent powder with high concentrations of radioactive cesium. To avoid such a risk, with cooperation from companies, we started the development of another system with the adsorbent sealed in a container such as a column. If the adsorbent is enclosed in a column, even if clogging occurs, it would only be necessary to exchange the column. There would be no need to handle the adsorbent directly.

First, we originally developed the adsorbent supported by cotton cloth, and confirmed its sufficient adsorbent properties.^[47] Next, through collaboration with Kanto Chemical and Japan Vilene Co., Ltd., we developed adsorbents of two types: a granular one^{[34][36]} and an adsorbent-immobilized nonwoven one^{[38][48]} (Fig. 6). The granules contain 80 % PB nanoparticles with high adsorption capacity. The nonwoven adsorbent has a large surface area that supports high-speed adsorption. These adsorbents are used for another purpose: concentration of radioactive material in environmental water for pretreatment of the trace analysis and pond water decontamination. For this development, computational approaches such as a simulation of adsorption performance were also used.^[49]

2.2.3 System development of volume reduction of incinerated ash

We sought to create an ash washing system using the adsorbents. Our goal was to reduce the volume of contaminants generated in environmental decontamination work by the government. The government planned that the contaminated materials would be collected and incinerated in a newly built temporary incinerator.^[50] Therefore, all facilities including the

washing device and the storage will be newly constructed. Considering this situation, we designed the most efficient method for volume reduction of waste. We integrated the components from incineration, ash washing, recovery of radioactive cesium by adsorbents, and a storage of used adsorbents.

For the pilot plant for demonstration at a realistic scale, we designed each component as follows: as an incinerator, a biomass boiler was used. To remove radioactive cesium completely from the exhaust gas and to study the contaminant behavior, a three-step treatment device was installed for the exhaust gas, a cyclone, a bag filter, and a HEPA filter. We also confirmed that the addition of calcium chloride during incineration improves the extraction rate of radioactive cesium by washing at a later stage. Particularly, the “main ash” recovered from the bottom of the incinerator presents difficulties for extraction of radioactive cesium by washing. Those difficulties are different from those related to the “fly ash” recovered from the chimney. Nevertheless, we were able to achieve a high extraction rate of 60 % by adding calcium chloride.^[6]

Regarding the washing process, we tried to reduce the water demand. For decontamination activities, great concern has arisen in relation to contaminated water processing because the handling of contaminated water storage at the Fukushima Daiichi Nuclear Power Plant is a serious matter, and because drinking water and agricultural water might be directly affected if environmental water is contaminated. Therefore, it is important to reduce the amount of water used to the greatest degree possible. For cases in which water discharge is not permitted even if it is properly treated, water treatment without discharge is necessary. By reduction of the water amount, it is possible to avoid discharge, e.g. by evaporation. A schematic diagram of the plant for ash washing and recovery by adsorbents is portrayed in Fig. 7. Our design has three important points: (1) use of a vibrating granulator to mix the ash with as little water as possible, (2) avoiding clogging by increasing the

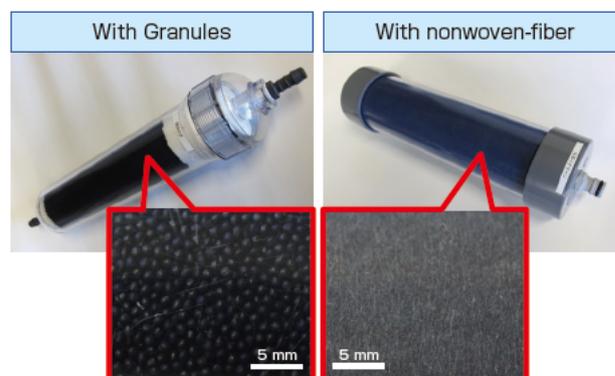


Fig. 6 Radioactive cesium adsorbents that contain PB nanoparticles

Left: Granular adsorbent made by Kanto Chemical. Right: Nonwoven fabric supported adsorbent made by Japan Vilene.

solid-liquid ratio at the dehydration of ash, and (3) reuse of water used for washing. Because ash often exhibits extreme hydrophobicity, water and ash cannot be mixed by simple stirring. The cesium extraction is difficult. Point (1) is effective to resolve the problem. A vibrating granulator is normally used at incineration plants as a device to create granules when transporting incinerated ash to the final disposal site. Water and ash are mixed to form granules by adding only a small amount of water. Using this device, it was possible to mix water and ash effectively. In addition, because block-like ash can be ground by the device, the washing was done smoothly. With point (2), the filter press method was used as an inexpensive solid-liquid separation device. By setting up a circulating route, the solid-liquid ratio in the dehydration area was increased to avoid clogging. For point (3), water reuse became possible by installing a coagulation-sedimentation basin to remove harmful substances other than radioactive cesium.

For the recovery of radioactive cesium that is dissolved in water, the granular adsorbent or the nonwoven type with the PB nanoparticles was used. Results verified that the expected adsorption was generally achieved. Results clarified that the adsorption behavior was estimated by the dosage monitor set on the column.

Figure 8 presents the effect on volume reduction of waste using this technology. For example, when one ton of combustible waste contaminated by 1,800 Bq/kg of radioactive cesium was processed, the waste materials that can be treated as regular waste, those that must be disposed in managed disposal sites, and those that must be stored at interim storage facilities were 7.8 kg, 6.0 kg, and 4.4 g, respectively. Thereby, extremely high volume reduction was achieved.^[6]

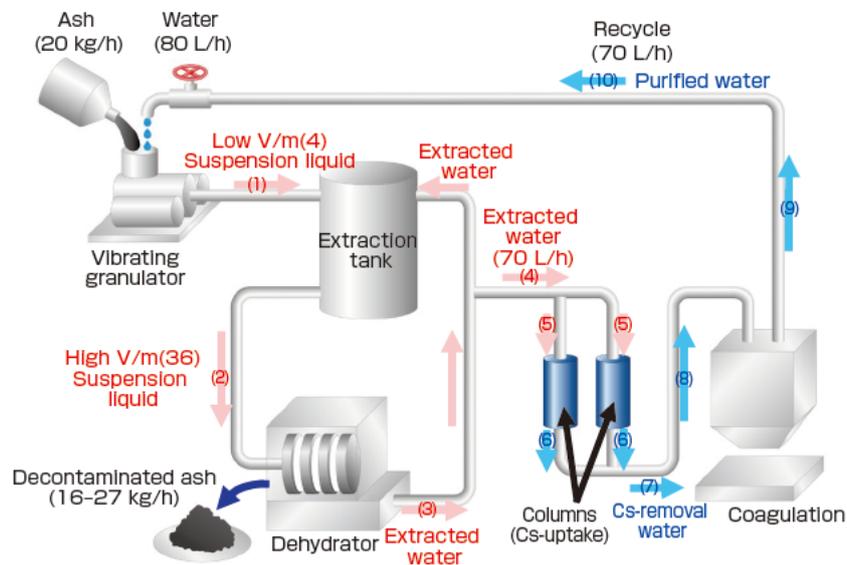


Fig. 7 Schematic view of the ash washing and recovery plant^[6]

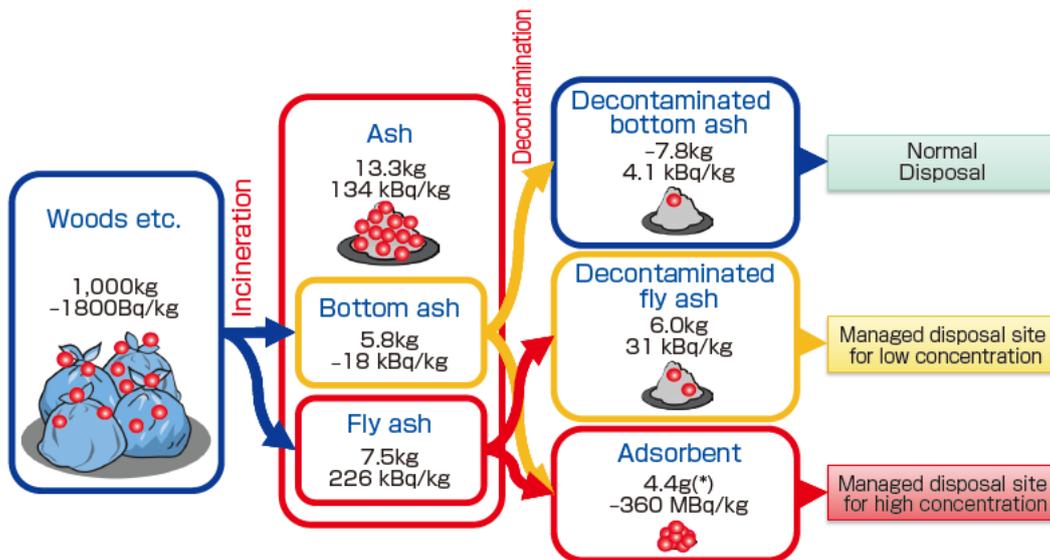


Fig. 8 Example of volume reduction when the incinerated ash processing technology is used^[6]

Table 2. Research for the development of ash decontamination technology and the policies for technological development

The transferring strategies are: (1) patent + technological transfer, (2) technology disclosure, (3) research by companies, and (4) utilization of conventional technology

Components of technology		R&D method				Experiments		
		Method for R&D	Technology transfer				Laboratory	Pilot plant
			(1)	(2)	(3)	(4)		
Incineration		Purchase		○		○	Convectional technology 20kg/h biomass boiler	
Cs-extraction		Internal collaboration + Invited researchers		○		○	Conventional/condition optimization Ash crushing/decrease of water amount	
Cs-uptake	Material	Original + universities	○				Optimization of PB-NP composition Mass-production	
	Granulation /immobilization	With companies			○		Granule/non-woven Mass production	
	Adsorbent management	Original + with companies		○			Elution management Scale up	
Plant-site management		With companies + support by AIST			○		– Local agreement/on-site management	
Waste management	Ash/liquid	Conventional technology		○		○	– Law-compliance	
	Adsorbent	Original+ With companies	○	○			Method development	

2.2.4 Storage and disposal of post-treatment waste

Regarding the practical application of our technology, the remaining issue is storage of the waste materials generated by the treatment. The main waste materials are washed incinerated ash, wastewater used for washing, and the adsorbents after adsorption. With regard to washed ash, waste standards are 8,000 Bq/kg and 100,000 Bq/kg of radioactive cesium concentration, the criteria for the storage level by regulation of the Japanese government. The washed ash could be stored or disposed of to maintain the standards. Regarding wastewater, because radioactive cesium can be removed sufficiently by the adsorbent, the water can be released after conducting regular wastewater processing. Even in cases where release is difficult because of the concerns of local governments, treatment is possible by minimization of the amount of water use by reuse, followed by evaporation.

The used adsorbent would pose no problem for regular storage because it is sufficiently stable. However, in this case, extremely long-term storage might be necessary because it includes radioactive materials. In this case, safer storage methods will be requested. To convert the used adsorbents into oxides is an approach for storage in a stable condition. However, oxidation reaction of PB entails large amounts of oxidative heat, implying the evaporation of the adsorbed radioactive cesium at temperatures higher than 600 °C. For stable oxidation at temperatures lower than 500 °C, we established an oxidation method under mild conditions using superheated steam. Using this method, we converted the adsorbents into oxides while maintaining evaporation of cesium at an extremely low level.^[51]

3 Team formation for the ash decontamination technology development

As described above, we proceeded with the integration of technologies using the incineration method, the extraction of radioactive cesium from ash, recovery by adsorbents, and the safe storage of waste products. We also conducted tests at a pilot plant on site after laboratory tests. Using these approaches, it was possible to establish technologies for practical use in a short period. At the initial stage of this research, the researchers in materials science played a central role, followed by participation of chemical engineering and geo-engineering researchers at AIST. However, it was impossible for the AIST researchers to construct everything. For example, incineration technology, plant design, operation, and the design of adsorbents that could be set for mass production in a short time could not be accomplished by AIST, a research institute, alone. For these missions, corporate collaboration is necessary.

We first produced a ground design for commercialization, extracted elemental technologies to achieve such commercialization from the design, and formulated a strategy for the realization of the elemental technologies. What is important is that the strategy must include “who” will conduct the process, “when” the R&D for each technology will be done, “who” will do it, and “when” the commercialization will be done. As described above, because AIST is a research institute that cannot engage in commercial projects, commercialization is conducted by companies. Therefore, it is necessary to produce an R&D plan with consideration of the technology transfer to companies at a certain time. For the specific R&D contents, the theme in the pilot plant must be determined with tests to realize the technology transfer strategy. Moreover, the theme at the laboratory must be determined to find a means of deciding the parameters used in the pilot plant test. The strategy established in this manner is presented in Table 2, which shows the experiment contents and the R&D method, which are presented in a bottom-up fashion from the initial stage or a small-scale stage. It

is noteworthy that the actual thinking process functions in reverse. In the following section, the procedures for setting the strategy will be described according to the order in which they were formulated.

3.1 Strategy for technology transfer

As a strategy for transferring technology to companies, we decided to use four methods so that the appropriate person might work for each mission. These are (1) retaining the intellectual property by AIST + technology transfer, (2) publication of our technology with appropriate retention of intellectual property, (3) research by companies, and (4) utilization of conventional technology. In a usual case of technology transfer by a research institute, it is considered that the institute obtains intellectual property rights. Then this technology is transferred to a company, as in case (1). However, when conducting R&D for the total integration of issues as in this case, the development rate will be slowed if all the intellectual property is retained, which is unrealistic for companies to derive some benefits. Therefore, the R&D strategy should be determined through comparison of technology maps of AIST and those of the companies.

A requirement for pursuing our strategy is to enable collaboration simultaneously with various companies. For this R&D, coherent development is necessary for materials, plant design, and waste storage, as described earlier. It is unrealistic to address such a wide scope of issues through collaboration with only one company. Even if there were a company that could accommodate all the technologies, much time would be necessary to find such a partner company: the plan might become deadlocked. Therefore, we chose to conduct simultaneous collaborations with various companies to increase the R&D speed and raise the technology to a practical level. This was the main reason to choose a method for each issue in our technology transfer from (1)–(4), as shown below.

The following is a description of the outline of methods of technology transfer.

(1) Retaining intellectual property + technology transfer

This is the main method of technology transfer by R&D institutes. The invention is patented or transformed into know-how. Then the technology is transferred to a company under an appropriate contract. The contract includes joint research agreements, information disclosure agreements, licensing, and other matters. We use this scheme for a technology in which the core technology is held by AIST, and for which AIST would have an advantage in competition against other companies. The technology of PB nanoparticles fits the scheme. The PB nanoparticles have been studied by AIST for a long time, giving AIST advantages in potential R&D development over other companies. Additionally, we also have

unreleased technologies. Under such circumstances, if the technology is disclosed without patenting, then some companies might monopolize the technology by patenting the peripheral technology. If such a limitation of access occurs, then it will be difficult to conduct simultaneous collaboration with multiple companies.

Given such circumstances, we chose to patent the intellectual property for PB nanoparticles to manage through licensing by AIST. We also chose to preserve intellectual property for basic methods for ash decontamination and post-treatment processes for adsorbents after use.

(2) Technology disclosure

Although it is ideal for AIST to manage all related intellectual properties, it is unrealistic because AIST has no superior standing against companies in all technological fields and because time and different costs must be incurred to retain and maintain intellectual property rights. If there is a low risk of exclusion by a company through patenting peripheral technologies, then we were willing to disclose the technology to accelerate the technology transfer.

For example, we distributed knowledge related to the properties of ash obtained from each part of the incineration furnace, the washing method to extract radioactive cesium from the ash, and the technology for the treatment of clumped ash, through press releases or other means.^[6] A wastewater management method for cyanide was also distributed through publication of papers because PB nanoparticles contain the cyano group in their structures. Therefore, the elution of cyanide should be a concern.^{[34][52]}

(3) Research by companies

Any technology must be passed to companies for commercialization. Therefore, it is preferred that the companies engage in R&D for technologies if they have some advantage for the technologies. As examples, the method of fabricating adsorbents, methods of preparing compounds with the adsorbent into a usable form, obtaining local agreement to pilot plant construction, on-site plant construction, and plant operation and management have proceeded with this scheme.

For the compound preparation, granulation and immobilization onto nonwoven fabric were considered. In fact, AIST conducted joint research with about 10 companies, including Kanto Chemical, Japan Vilene, and Unitika Trading Co., Ltd. In many cases, the preparation technology was established by the companies, although AIST was in charge of evaluating the performance of the developed adsorbents.

The important point is intellectual property management. In simultaneous collaboration with multiple companies to achieve a mutual goal, it is difficult to manage information while dividing the results into collaboration with each company. To do so, we chose the following policy to manage the knowledge and included it in the joint research agreement: (1) results disclosed to AIST can be disclosed to other joint researchers as necessary; (2) profit of a company that produces an invention will be ensured through patent licensing; and (3) for patents generated through joint research, the percentage of rights will be determined by the degree of contribution to the invention by the parties involved. In addition, even if an invention is patented by a single company, the patent generated via joint research will be licensed to other joint researchers as necessary. The policy means the following.

- Contents that a company wishes to use as know-how should not be discussed with AIST.
- Contents discussed with AIST will be disclosed to other collaborating companies: a company will be able to use other companies' technologies to accelerate development.

This scheme is effective if one needs to share basic technologies among the companies. In the case of the evaluation method of the adsorbents, it is better to follow this scheme. Many companies collaborating for the adsorbent fabrication had no specialization in radioactive materials evaluation. Although the companies have their own core technology for adsorbent fabrication, the performance evaluation should be done with established and unified methods for appropriate comparison, and should be highly rated. Many companies started the joint research with AIST with the agreement of this scheme.

This scheme is expected to be quite effective when development for commercial applications is based on the core technology of public institutes. If a public institute owns the core technology, then a company aiming at practical application must collaborate with the institute. Collaboration with the institute would support future standardization of the technology. It is also important to collaborate with other companies having different core technologies. In this case, our collaboration network included various companies such as an adsorbent manufacturer and plant engineering companies using the adsorbent in their plants, indicating that construction of a supply chain from the material to the plant comes easily. To maintain the scheme, the research institute must have the capacity to manage the supply chain and standardization. This capacity is requested of the research institute in the near future.

(4) Utilization of conventional technology

Using conventional technology to the greatest extent possible is desirable to accelerate research and development. The conventional technology can be expected to provide operational stability, thereby reducing the risks. For this research, we actively used conventional technologies especially those related to incineration technology, ash washing technology, wastewater treatment, and on-site management. For conventional technologies, the companies would have vast knowledge of their business field. Even if they have insufficient knowledge, knowledge acquisition can be done rather easily from public documents.

The most important aspect of technology transfer is how to promote (3) corporate research. The technology should be transferred to companies because an R&D institute cannot accomplish commercialization, and has no knowledge related to commercialization. Construction of the collaboration network is also effective for the company to produce a business plan with a concrete supply chain. The intellectual property should be managed appropriately with appropriate agreement of joint research to encourage understanding of the companies.

3.2 Technology management for R&D

When the strategy for technology transfer is fixed, partners and the approach of the technological development are decided mechanically. In the case of "(3) corporate research," AIST need not introduce the entire technology. For example, for adsorbent fabrication, a company developed the adsorbent fabrication, whereas AIST mainly concentrated on the improvement of the method for evaluating the adsorbent. However, for on-site management of plant engineering, AIST had to provide major support; even though the technology transfer would be done under "(3) corporate research." This was because our theme was the decontamination of radioactive cesium. Even the national government had not investigated cesium decontamination before the accident. Therefore, the technological development was conducted simultaneously with the organization of various legislation. To adjust to the unusual conditions, we were requested to understand the legal policies appropriately, and were asked for requests from the technology side to the government organizations. Especially, AIST participated in the Fly Ash Washing Technology Workshop, conducted by the National Institute of Environmental Studies, to contribute to the publication of "Technical material on fly ash washing technology (Guidelines for performance and design of plants)."^[53] The pilot plant tests were conducted in accordance with guidelines to reduce the risk that our technology would not be able to meet legal requests.

In the case of (1) patent + technological transfer and (2) technological disclosure, the R&D must be conducted by AIST. To achieve this, AIST set research teams for the project with a Vice-President as the leader, and with various

specialists, e.g. a researcher for chemical engineering who participated in the plant and column designs, and a computational scientist devoted to the establishment of radioactive Cs amount estimation methods in the column from the dosage of the column surface. When designing the plant close to commercialization, an engineer with experience at chemical manufacturers was invited to design the pilot plant.

Related to scheme (4) utilization of conventional technology, the outside partner mainly worked on the problem with researchers of the collaborating companies and invited researchers from external organizations. The required equipment was purchased without our own development. We devoted particular attention to usability as a general method in commercialization to avoid company specialization only in implementing the technology. Our objective was the development of ash decontamination technologies using the PB nanoparticles. The strategy was that the companies would use the PB nanoparticles without trouble using conventional technologies for other tasks.

3.3 Determination of R&D contents

After the strategy was fixed, the remaining issue was exact determination of who would do it and what would be done. The appropriate R&D content and the schedule were determined mechanically from available resources, budgets, human resources, time, and existing equipment.

We especially devoted attention to choosing the adsorbent for the pilot plant test so that it could be applicable for mass production, i.e. only adsorbents manufactured by companies were used for the pilot plant test. We did not use adsorbents for which technology transfer was not completed. Regarding plant design, the plant would be constructed only by clarifying the technology using the commercially available components. Regarding the adsorbents, manufacturing equipment necessary for laboratory tests and for mass production are completely different. It is important that even if mass production was not achieved at the time, mass production was possible for the company; and at least cost calculation for mass production had been achieved. To achieve the requirement, technologies for which the technology transfer was not completed were avoided.

Collaboration with universities and other research institutes was fundamentally important. Optimization of the materials for PB nanoparticles was conducted with the cooperation of universities and research institutes. At the materials development level, they have powerful foundations. The research institutes for agriculture and environment held abundant knowledge for various applications. An issue related to collaboration with the universities and the institutes is the management of intellectual property. In our research, collaboration with universities and research institutes was

kept to a fundamental level of materials development.

3.4 Flow of corporate collaboration and collaboration with the government and local governments

For commercialization, a time schedule and a strategy for each stage was fundamentally important. An unusual point of the research is that the demand rose suddenly because of the accident at the nuclear power plant. Consequently, many projects were led by the national government and the local government. This situation led researchers to follow the direction of the national government. The local governments frequently speculated on future markets. We participated in the project funded by the Strategic Funds for the Promotion of Science and Technology, led by the Ministry of Agriculture, Forestry and Fisheries from June 2011, where we engaged in R&D for farmland decontamination. In this project, to develop the contamination technology using adsorbents, we organized a research team including AIST, a university, another research institute, and two companies. Therefore, AIST played a leading role in coordination of efforts by the national government, a research institute, and companies.

The R&D of ash decontamination started in autumn 2011. Initially, efforts emphasized the plant design, with some work on the development of adsorbents with the materials manufacturer. The most pressing problem at this stage was to find a place for pilot plant tests. Conventionally, radioactive materials could only be handled in a strictly managed environment according to Japanese law. After the accident, for similar reasons, it was difficult to manage radioactive materials that had been released into the environment. To resolve this difficulty, the technological development was conducted along with legal adjustments, simultaneously. In finding a place for the pilot plant tests, we were requested to watch the action of the Ministry of Environment, to consider appropriate management to maintain safety, and to present it to the local government and area residents to obtain permission. A reliable relation between the project operator and the local governments and residents is especially important. We conducted pilot plant tests for incinerated ash treatment in two places in Fukushima Prefecture: Koriyama city and Kawauchi village. For the former, we provided technological support for the tests conducted at the plant location of the Koriyama Chip Industry Co., Ltd. Because Koriyama Chip Industry had been operating their business at this location since long before the accident, agreement of the surrounding residents to conduct tests was obtained. The latter was done by AIST in collaboration with the Tokyo Electric Power Environmental Engineering Co., Inc. (TEPCO Environmental Engineering; currently, Tokyo Power Technology Ltd.). TEPCO Environmental Engineering had already been working on the decontamination of Kawauchi village when the pilot plant tests started. At Kawauchi village, the union of the local company conducted

decontamination work, and TEPCO Environmental Engineering provided technical support to the union. They gained the confidence of the local government through this activity. Therefore, the local governments also agreed to pilot plant tests.

Although it was a special case because of this unexpected accident, there are many cases in which the laws would not be adjusted, even in regular R&D. It is necessary to set the direction while understanding the laws appropriately, checking the discussions of the committees and other authorities before the enforcement of laws, and setting the R&D strategy based on them.

We shall discuss the stage of corporate collaboration. R&D is often handled as “step by step,” starting from “upstream” activities such as raw materials development, and assumed to go “downstream,” with development of adsorbents or decontamination methods. However, two problems can hinder such an approach. One is that R&D is time-consuming. Another is that the supply chain is not clear at the start of research: for that reason, one cannot establish a business model. To resolve those difficulties, the R&D of each stage should be conducted “concurrently”. This is generally called “concurrent engineering.” For the approach, it is necessary to clarify the whole picture of the R&D from the research level to elucidate the picture for all people involved, and to elicit frequent feedback.

3.5 Current status of commercialization

The achievement of the development of ash washing technology is presented in Fig. 2. For example, Kanto Chemical and Japan Vilene conducted the development of the adsorbents. Some of them have become commercially available. Kanto Chemical sells PB nanoparticle materials to other companies. It has developed and sells granular adsorbents.

These technologies are used for various purposes other than ash decontamination. For example, the nonwoven adsorbent of Japan Vilene is also used in the pilot plant tests for preventing radioactive cesium leakage from ponds, and is described in the MAFF manual.^[54] Similar nonwoven material is used as a measurement technology for radioactive cesium in environmental waters.^{[8][55]}

4 Conclusion

We developed the technology to remove radioactive cesium from the environment after the leakage of radioactive materials from the Fukushima Daiichi Nuclear Power Plant of the Tokyo Electric Power Company using the PB nanoparticles. As presented in this paper, we described our ash decontamination technology to reduce the volume of combustible contaminants. Because this issue is related to

an urgent matter for Japanese national security, rapid R&D efforts were pursued in preference to those used for regular R&D. Therefore, it was important to clarify the final goal and to build collaboration to reach the goal as quickly as possible. Especially important was the concurrent promotion of both the expansion of collaboration and the management of intellectual property. To achieve such a requirement, we chose the following policy: we retained the intellectual property for the core technology to ourselves to the greatest extent possible, and left R&D for peripheral technology to the companies. We also decided that the know-how disclosed by the companies to AIST would be disclosed to other collaborating companies as necessary, and we decided that licensing to other collaborating companies would be possible even if the technology was patented by a single company.

Through these policies, it was possible to conduct R&D swiftly. This method is expected to be an effective mode of conducting other R&D. However, it is necessary that the research institute possesses the core technology and holds superiority in knowledge and intellectual property. It is also necessary to estimate the supply chain and cost structure in anticipation of commercialization. These are generally not regarded as important for research institutes. However, if a research institute aims to become the nucleus of open innovation in Japan, then these capabilities become necessary. We hope this will be a model of R&D with one research institute at the core. We sincerely wish to contribute to decontamination efforts that are underway in Japan.

Acknowledgements

We acknowledge the government organizations, local governments, and private companies which helped us in the R&D. We particularly thank Kawauchi village for giving a chance to us to use their site for our pilot plant tests. We also thank the people of the companies with which we collaborated through joint research: Tokyo Power Technology Ltd., Kanto Chemical Co. Inc., Japan Vilene Co., Ltd., and Koriyama Chip Industry Co., Ltd. In starting and operating the Fly Ash Washing Technology Workshop, we received valuable help from Director Masahiro Osako, Center for Material Cycles and Waste Management Research, the researchers in National Institute of Environmental Studies and also in participating organizations.

At AIST, we were able to conduct this research with the support of the following people: former Senior Vice-President Shingo Ichimura and Vice-President Masahiro Seto, who acted as the leaders of the Cesium Decontamination Project; Chief Senior Researcher Hiroshi Ogawa, Research Center for Computational Design of Advanced Functional Materials, who contributed generously to the development of simulation technology; former Supervisory Innovation Coordinator Akira Kageyama, Technology Licensing Manager Yuki

Miyamoto, and Patent Officer Hideki Kobayashi, who were involved in the promotion of this project; former Director Akira Kamioka, Acting Director Koichi Yoshinari of the Radiation Safety Management Office, the Safety Management Division, former Superintendent Katsumoto Nakaiwa of Tsukuba Central 5, Research Promotion Director Shuji Watanabe of Tsukuba Central 5, Mr. Masao Kunioka, and Mr. Kenji Ito, who helped us to treat the environmental radioisotopes at AIST; and many, many others. We extend our sincere gratitude to all people involved.

Some results of this research were obtained through grants of FY 2011 Strategic Funds for the Promotion of Science and Technology (Cabinet Office), FY 2011 Decontamination Technology Verification Test Project (Ministry of Environment), and FY 2011 Decontamination Technology Demonstration Project (Ministry of Environment).

References

- [1] Ministry of Economy, Trade and Industry: Genshiryoku anzen ni kansuru IAEA kakuryo kaigi ni taisuru nihon koku seifu no hokokusho ni tsuite (On the report of the Japanese Government for the IAEA Ministerial Conference on Nuclear Safety), <http://www.meti.go.jp/earthquake/nuclear/backdrop/20110607001.html>, accessed 2016-01-17 (in Japanese).
- [2] National Institute of Advanced Industrial Science and Technology: Prussian blue o riyo shite tayona keitai no cesium kyuchakuzai o kaihatsu (Cesium adsorbent of various forms developed using Prussian blue), http://www.aist.go.jp/aist_j/press_release/pr2011/pr20110824/pr20110824.html, accessed 2015-12-19 (in Japanese).
- [3] National Institute of Advanced Industrial Science and Technology: Nano ryushika shita Prussian blue de cesium kyuchakuno ga kojo (Cesium adsorption capacity improved by nanoparticulization of Prussian blue), http://www.aist.go.jp/aist_j/press_release/pr2012/pr20120208/pr20120208.html, accessed 2015-12-19 (in Japanese).
- [4] National Institute of Advanced Industrial Science and Technology: Dojochu no cesium o teinodo no san de chushutsu suru koto ni seiko (Succeeded in extracting cesium in soil using low-concentration acid), http://www.aist.go.jp/aist_j/press_release/pr2011/pr20110831/pr20110831.html, accessed 2015-12-19 (in Japanese).
- [5] National Institute of Advanced Industrial Science and Technology: Shokubutsukei hoshasei cesium osenbutsu o josen gen'yo suru tame no jissho shiken plant (Verification test plant for decontamination and volume reduction of vegetal radioactive cesium contaminants), http://www.aist.go.jp/aist_j/press_release/pr2012/pr20121112/pr20121112.html, accessed 2015-12-19 (in Japanese).
- [6] T. Kawamoto, Y. Hakuta, H. Tanaka, H. Ogawa, K. Minami, A. Kitajima and D. Parajuli: Shokubutsukei hoshasei cesium osenbutsu no shokyakubai o josen suru gijutsu o jissho (Technology for decontaminating incinerated ash of vegetal radioactive cesium contaminants verified), http://www.aist.go.jp/aist_j/press_release/pr2013/pr20131120/pr20131120.html, accessed 2016-06-06 (in Japanese).
- [7] National Institute of Advanced Industrial Science and Technology: Suichu no teinodo no yozontai hoshasei cesium o kan'i jinsoku ni sokutei (Quick and simple measurement of low-concentration radioactive cesium dissolved in water), http://www.aist.go.jp/aist_j/new_research/2012/nr20120905/nr20120905.html, accessed 2015-12-19 (in Japanese).
- [8] National Institute of Advanced Industrial Science and Technology: Suichu no hoshasei cesium wo subayaku monitoring (Quick monitoring of radioactive cesium in water), http://www.aist.go.jp/aist_j/press_release/pr2014/pr20140407/pr20140407.html, accessed 2015-12-19 (in Japanese).
- [9] National Institute of Advanced Industrial Science and Technology: Hoshasei cesium wo fukumu genmai no ninsho hyojun busshitsu o kaihatsu (Certified reference material for brown rice containing radioactive cesium developed), http://www.aist.go.jp/aist_j/press_release/pr2012/pr20120830/pr20120830.html, accessed 2015-12-19 (in Japanese).
- [10] National Institute of Advanced Industrial Science and Technology: Abukuma-gawa no suichu hoshasei cesium nodo wa hikui level de aru koto o kakunin (Confirmed that aquatic radioactive cesium concentration in Abukuma River is low), http://www.aist.go.jp/aist_j/new_research/2013/nr20130204/nr20130204.html, accessed 2015-12-19 (in Japanese).
- [11] National Institute of Advanced Industrial Science and Technology: Kaze ni notte nagai kyori o hakobareru hoshasei cesium no sonzai keitai (Form of radioactive cesium that is carried over long distance by wind), http://www.aist.go.jp/aist_j/new_research/2012/nr20120731/nr20120731.html, accessed 2015-12-19 (in Japanese).
- [12] National Institute of Advanced Industrial Science and Technology: Hoshasen busshitsu josen no koka to hiyo o hyoka (Cost and effect of decontamination of radioactive materials evaluated), http://www.aist.go.jp/aist_j/new_research/2013/nr20130604/nr20130604.html, accessed 2015-12-19 (in Japanese).
- [13] P. A. Haas: A review of information on ferrocyanide solids for removal of cesium from solutions, *Sep. Sci. Technol.*, 28 (17/18), 2479–2506 (1993).
- [14] Oak Ridge National Laboratory: Quarterly report for liquid waste disposal research (1950).
- [15] G. B. Barton, J. L. Hepworth, E. D. McClanahan, R. L. Moore and H. H. Van Tuyl: Chemical processing wastes—Recovering fission products, *Ind. Eng. Chem.*, 50 (2), 212–216 (1958).
- [16] H. H. Van Tuyl and R. L. Moore: Recovery of fission product cesium from acidic wastes, *Ind. Eng. Chem.*, 51 (6), 741–744 (1959).
- [17] R. Harjula, J. Lehto, A. Paajanen, E. Tusa and P. Yarnell: Use inorganic ion exchange materials as precoat filters for nuclear waste effluent treatment, *React. Funct. Polym.*, 60 (1), 85–95 (2004).
- [18] L. L. Burger, D. M. Strachan, D. A. Reynolds and W. W. Schulz: *A Summary of Available Information on Ferrocyanide Tank Wastes*, INIS, (1991).
- [19] T. Prevost, M. Blase, H. Paillard and H. Mizuno: Areva's Actriflo-rad water treatment system for the Fukushima Nuclear Power Plant, *Int. J. Nucl. Power*, 308 (2012).
- [20] A. Gay, P. Gillet, B. Ytournal, T. Varet, L. David, T. Prevost, C. Redonnet, G. Piot, S. Jouaville and G. Pagis: Multi-phased, post-accident support of the Fukushima Dai-Ichi Nuclear Power Plant, *WM2012*, 12246 (2012).
- [21] A. Gotoh, H. Uchida, M. Ishizaki, T. Satoh, S. Kaga, S. Okamoto, M. Ohta, M. Sakamoto, T. Kawamoto, H. Tanaka, M. Tokumoto, S. Hara, H. Shiozaki, M. Yamada, M. Miyake and M. Kurihara: Simple synthesis of three primary colour

- nanoparticle inks of Prussian blue and its analogues, *Nanotechnology*, 18 (34), 345609 (2007).
- [22] M. Ishizaki, K. Kanaizuka, M. Abe, Y. Hoshi, M. Sakamoto, T. Kawamoto, H. Tanaka, and M. Kurihara: Preparation of electrochromic Prussian blue nanoparticles dispersible into various solvents for realisation of printed electronics, *Green Chem.*, 14 (5), 1537–1544 (2012).
- [23] S. Hara, H. Shiozaki, A. Omura, H. Tanaka, T. Kawamoto, M. Tokumoto, M. Yamada, A. Gotoh, M. Kurihara and M. Sakamoto: Color-switchable glass and display devices fabricated by liquid processes with electrochromic nanoparticle “ink”, *Appl. Phys. Express*, 1 (10), 1040021–1040023 (2008).
- [24] S. Hara, H. Tanaka, T. Kawamoto, M. Tokumoto, M. Yamada, A. Gotoh, H. Uchida, M. Kurihara and M. Sakamoto: Electrochromic thin film of Prussian blue nanoparticles fabricated using wet process, *Jpn. J. Appl. Physics*, 46, 945–947 (2007).
- [25] H. Shiozaki, T. Kawamoto, H. Tanaka, S. Hara, M. Tokumoto, A. Gotoh, T. Satoh, M. Ishizaki, M. Kurihara and M. Sakamoto: Electrochromic thin film fabricated using a water-dispersible ink of Prussian blue nanoparticles, *Jpn. J. Appl. Phys.*, 47 (2), 1242–1244 (2008).
- [26] K.M. Lee, H. Tanaka, A. Takahashi, K. H. Kim, M. Kawamura, Y. Abe and T. Kawamoto: Accelerated coloration of electrochromic device with the counter electrode of nanoparticulate Prussian blue-type complexes, *Electrochim. Acta*, 163, 288–295 (2015).
- [27] R. Chen, H. Tanaka, T. Kawamoto, M. Asai, C. Fukushima, M. Kurihara, M. Watanabe, M. Arisaka, and T. Nankawa: Preparation of a film of copper hexacyanoferrate nanoparticles for electrochemical removal of cesium from radioactive wastewater, *Electrochem. Commun.*, 25 (1), 23–25 (2012).
- [28] R. Chen, H. Tanaka, T. Kawamoto, M. Asai, C. Fukushima, H. Na, M. Kurihara, M. Watanabe, M. Arisaka and T. Nankawa: Selective removal of cesium ions from wastewater using copper hexacyanoferrate nanofilms in an electrochemical system, *Electrochim. Acta*, 87, 119–125 (2013).
- [29] R. Chen, M. Asai, C. Fukushima, M. Ishizaki, M. Kurihara, M. Arisaka, T. Nankawa, M. Watanabe, T. Kawamoto and H. Tanaka: Column study on electrochemical separation of cesium ions from wastewater using copper hexacyanoferrate film, *J. Radioanal. Nucl. Chem.*, 303 (2), 1491–1495 (2015).
- [30] D. Parajuli, A. Kitajima, A. Takahashi, H. Tanaka, H. Ogawa, Y. Hakuta, K. Yoshino, T. Funahashi, M. Yamaguchi, M. Osada and T. Kawamoto: Application of Prussian blue nanoparticles for the radioactive Cs decontamination in Fukushima region, *J. Environ. Radioact.*, 151 (P1), 233–237 (2016).
- [31] A. Takahashi, H. Tanaka, N. Minami, M. Kurihara and T. Kawamoto: Simultaneous enhancement of Cs-adsorption and magnetic properties of Prussian blue by thermal partial oxidation, *Bull. Chem. Soc. Jpn.*, 88 (1), 69–73 (2015).
- [32] M. Ishizaki, S. Akiba, A. Ohtani, Y. Hoshi, K. Ono, M. Matsuba, T. Togashi, K. Kananizuka, M. Sakamoto, A. Takahashi, T. Kawamoto, H. Tanaka, M. Watanabe, M. Arisaka, T. Nankawa and M. Kurihara: Proton-exchange mechanism of specific Cs⁺ adsorption via lattice defect sites of Prussian blue filled with coordination and crystallization water molecules, *Dalton Trans.*, 42 (45), 16049–16055 (2013).
- [33] A. Takahashi, N. Minami, H. Tanaka, K. Sue, K. Minami, D. Parajuli, K.M. Lee, S. Ohkoshi, M. Kurihara and T. Kawamoto: Efficient synthesis of size-controlled open-framework nanoparticles fabricated with a micro-mixer - Route to the improvement of Cs adsorption performance, *Green Chem.*, 17 (8), 4228–4233 (2015).
- [34] D. Parajuli, A. Takahashi, H. Noguchi, A. Kitajima, H. Tanaka, M. Takasaki, K. Yoshino and T. Kawamoto: Comparative study of the factors associated with the application of metal hexacyanoferrates for environmental Cs decontamination, *Chem. Eng. J.*, 283, 1322–1328 (2016).
- [35] D. Parajuli, A. Takahashi, H. Tanaka, M. Sato, S. Fukuda, R. Kamimura and T. Kawamoto: Variation in available cesium concentration with parameters during temperature induced extraction of cesium from soil, *J. Environ. Radioact.*, 140, 78–83 (2015).
- [36] G.R. Chen, Y.R. Chang, X. Liu, T. Kawamoto, H. Tanaka, A. Kitajima, D. Parajuli, M. Takasaki, K. Yoshino, M.L. Chen, Y.K. Lo, Z. Lei and D.J. Lee: Prussian blue (PB) granules for cesium (Cs) removal from drinking water, *Sep. Purif. Technol.*, 143, 146–151 (2015).
- [37] D. Parajuli, Y. Suzuki, M. Sato, A. Takahashi, H. Tanaka and T. Kawamoto: Assessment of the measures for the extraction or fixation of radiocesium in soil, *Geoderma*, 267, 169–173 (2016).
- [38] G.R. Chen, Y.R. Chang, X. Liu, T. Kawamoto, H. Tanaka, D. Parajuli, M.L. Chen, Y.K. Lo, Z. Lei and D.J. Lee: Prussian blue non-woven filter for cesium removal from drinking water, *Sep. Purif. Technol.*, 153, 37–42 (2015).
- [39] D. Parajuli, H. Tanaka, Y. Hakuta, K. Minami, S. Fukuda, K. Umeoka, R. Kamimura, Y. Hayashi, M. Ouchi and T. Kawamoto: Dealing with the aftermath of Fukushima Daiichi nuclear accident: Decontamination of radioactive cesium enriched ash, *Environ. Sci. Technol.*, 47 (8), 3800–3806 (2013).
- [40] [40] Ministry of Environment: Isezaki-shi Seiso Recycle Center 21—Ippan haikibutsu saishu shobunjo (dai sanki) shinshutsusui shori shisetsu horyusui ni okeru hoshasei cesium ryushutsu taisaku ni tsuite [Isezaki City Cleaning Recycling Center 21—On the measures against leachate of radioactive cesium in the effluent of the water processing plant of the general final disposal site (phase III)], https://www.env.go.jp/jishin/attach/haikihyouka_kentokai/08-ext_1.pdf, accessed 2015-12-20 (in Japanese).
- [41] National Institute for Environmental Studies: Shokyaku hibai no mizusenjo ni yoru hoshasei cesium no jokyo (Removal of radioactive cesium by washing incinerated fly ash with water), http://www.nies.go.jp/shinsai/techrepo_r4_140414_8-10.pdf, accessed 2015-05-18 (in Japanese).
- [42] Y. Namiki, T. Ueyama, T. Yoshida, R. Watanabe, S. Koido and T. Namiki: Hybrid micro-particles as a magnetically-guidable decontaminant for cesium-eluted ash slurry, *Sci. Rep.*, 4, 6294 (2014).
- [43] Y. Nishizaki, H. Miyamae, S. Ichikawa, K. Izumiya, K. Takano, N. Kumagai and K. Hashimoto: New technologies for decontamination of radioactive substances scattered by nuclear accident, *Metall. Mater.*, 58 (1), 283–290 (2013).
- [44] Mitsubishi Paper Mills Ltd.: Jisei kyuchakuzai o mochiita hoshasei cesium josen system ni tsuite (On the radioactive cesium decontamination system using magnetic adsorbents), <http://www.mpm.co.jp/company/news/pdf/2012/20120517.pdf>, accessed 2016-05-15 (in Japanese).
- [45] M. Ishizaki, S. Akiba, A. Ohtani, Y. Hoshi, K. Ono, M. Matsuba, T. Togashi, K. Kananizuka, M. Sakamoto, A. Takahashi, T. Kawamoto, H. Tanaka, M. Watanabe, M. Arisaka, T. Nankawa and M. Kurihara: Proton-exchange mechanism of specific Cs⁺ adsorption via lattice defect sites of Prussian blue filled with coordination and crystallization

- water molecules, *Dalton Trans.*, 42 (45), 16049–16055 (2013).
- [46] J. Munezawa and K. Nishi: Development of the radioactive cesium recovery system for effective safekeeping at the final disposal site “Adsorption separation-combustion oxidation-concentration”, *Journal of the Society for Remediation of Radioactive Contamination in the Environment*, 2 (2), 101–110 (2014) (in Japanese).
- [47] A. Kitajima, H. Tanaka, N. Minami, K. Yoshino and T. Kawamoto: Efficient cesium adsorbent using Prussian blue nanoparticles immobilized on cotton matrices, *Chem. Lett.*, 41 (11), 1473–1474 (2012).
- [48] A. Kitajima, H. Ogawa, T. Kobayashi, T. Kawasaki, Y. Kawatsu, T. Kawamoto and H. Tanaka: Monitoring low-radioactivity caesium in Fukushima waters, *Environ. Sci. Process. Impacts*, 16 (1), 28–32 (2014).
- [49] H. Ogawa, A. Kitajima, H. Tanaka and T. Kawamoto: Numerical evaluation of Cs adsorption in PB column by extended Langmuir formula and one-dimensional adsorption model, *J. Radioanal. Nucl. Chem.*, 303 (2), 1287–1290 (2014).
- [50] Ministry of Health, Labour and Welfare: *Jiko Yurai Haikibutsu To Shobun Gyomu Tokubetsu Kyoiku Text* (Textbook on special instruction for disposal of waste material arising from the accident), (2013) (in Japanese).
- [51] KM. Lee, M. Asai, T. Uchida, T. Kawamoto, K. Minami, A. Takahashi, D. Parajuli, G. Kido, M. Takasaki, K. Yoshino and H. Tanaka: Decomposition of iron hexacyanoferrate microcapsule beads using superheated steam, *Chem. Lett.*, (2016) (in press).
- [52] D. Parajuli, H. Noguchi, H. Tanaka, T. Kawasaki, Y. Kawatsu, T. Kobayashi and T. Kawamoto: Effective removal of hexacyanoferrate anions using quaternary amine type ion exchange resin, *J. Environ. Chem. Eng.*, 3 (4), 2448–2452 (2015).
- [53] National Institute for Environmental Studies: Hibai senjo gijutsu ni kansuru gijutsu shiryō (Shisetsu seino sekkei ni kakaru shishin) [Technical reference material on fly ash washing technology (Guidelines for performance and design of plants)], (2014) (in Japanese).
- [54] Ministry of Agriculture, Forestry and Fisheries: Tameike no hoshasei busshitsu taisaku gijutsu manual (Manual for measures against radioactive materials in small reservoirs), <http://www.maff.go.jp/j/press/nousin/saigai/150327.html>, accessed 2016-02-28 (in Japanese).
- [55] National Institute of Advanced Industrial Science and Technology: Kaisuichu no teinodo hoshasei cesium o jinsoku ni monitoring (Quick monitoring of low-concentration radioactive cesium in seawater), http://www.aist.go.jp/aist_j/press_release/pr2016/pr20160205/pr20160205.html, accessed 2016-02-28 (in Japanese).

Authors

Tohru KAWAMOTO

Graduated from the Department of Material Physics, School of Engineering Science, Osaka University in 1992. Completed the doctor's program at the Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University in 1997. Joined the Electrotechnical Laboratory, Agency of Industrial Science and Technology,



Ministry of International Trade and Industry in 1997. Engaged in the theoretical research of external responsive materials. Researcher, Nanotechnology Research Institute, AIST in 2001; Senior Researcher in 2006; Group Leader, Molecular Nanophysics Group, Nanosystem Research Institute in 2010; Group Leader, Green Technology Research Group; and Group Leader, Nanoparticle Functional Design Group, Nanomaterials Research Institute in 2015. Visiting Researcher, Graduate School of Science and Engineering, Yamagata University from 2016. In this paper, was in charge of the supervision of the R&D.

Hisashi TANAKA

Graduated from the Department of Chemistry, School of Science, the University of Tokyo in 1994. Completed the doctor's course at the Department of Chemistry, Graduate School of Science, the University of Tokyo in 1999. Doctor (Science). Engaged in the research of molecular superconductor at the Institute for Molecular Science, as Postdoctoral Fellow, Japan Society for the Promotion of Science in 1999. Joined AIST in 2002. Researcher, Nanotechnology Research Institute; Senior Researcher in 2007; Senior Researcher, Nanosystem Research Institute in 2010; and Senior Researcher, Nanomaterials Research Institute in 2015. In this paper, was in charge of the development and evaluation of the adsorbents.



Yukiya HAKUTA

Graduated from the Department of Chemistry, School of Engineering, Tohoku University in 1988. Withdrew from the Department of Chemistry, Graduate School of Engineering, Tohoku University in 1993. Assistant, School of Engineering, Tohoku University in 1993. Joined AIST in 2001. Researcher, Supercritical Fluid Research Center. R&D Staff, Chemicals Division, Manufacturing Industry Bureau, Ministry of Economy, Trade and Industry in 2007. Senior Researcher, Research Center for Compact Chemical Process, AIST in 2008; Senior Researcher, Nanosystem Research Institute in 2010; and currently, Group Leader, Nanoparticle Structure Design Group, Nanomaterials Research Institute in 2015. In this paper, was in charge of the demonstration at the pilot plant for incinerated ash decontamination.



Akira TAKAHASHI

Graduated from the Faculty of Engineering, Kyoto University in 2009. Completed the master's course at the Department of Materials Science and Engineering, Graduate School of Engineering, Kyoto University in 2011. Joined AIST in 2011. Researcher, Green Technology Research Group, Nanosystems Research Institute in 2011. Started the doctor's course at the Department of Chemistry, Graduate School of Science, the University of Tokyo in 2013 while maintaining position at AIST. Researcher, Nanoparticle Functional Design Group, Nanomaterials Research Institute, AIST in 2015. In this paper, was in charge of the synthesis of adsorbents and study of its physical properties.



Durga PARAJULI

Obtained the Masters of Science and Technology in Physical Chemistry at the Tribhuvan University (Nepal) in 2002. Completed the doctor's course at the Saga University in 2006. Doctor (Engineering). Postdoctoral Researcher, Graduate School of Science and Engineering, Saga University in 2006. Postdoctoral Researcher, Quantum Beam Science Center, Japan Atomic Energy Agency from 2008 to 2011. Researcher, Nanosystem Research Institute, AIST in 2011; Researcher, Green Technology Research Group, Nanosystem Research Institute in 2014; and Researcher, Nanoparticle Functional Design Group, Nanomaterials Research Institute in 2015. In this paper, was in charge of the development of cesium elution method from incinerated ash and the development of adsorbents.



Kimitaka MINAMI

Completed the doctor's program at the Department of Chemical Engineering, Graduate School of Engineering, Tohoku University in 2005. Research Center for Compact Chemical Process, AIST in 2005; Institute of Multidisciplinary Research for Advanced Materials, Tohoku University in 2006; Advanced Institute for Materials Research, Tohoku University in Nov 2007; and Assistant, New Industry Creation Hatchery Center, Tohoku University in 2010. Engaged in researches on supercritical fluid and nanoparticle synthesis. Joined the Nanosystem Research Institute, AIST in March 2012; and Senior Researcher from Oct 2013. In this paper, was in charge of the design of the pilot plant.



Tetsuo YASUTAKA

Graduated from the Department of Agricultural and Environmental Engineering, Faculty of Agriculture, Kyoto University in 2000. Completed the master's program at the Graduate School of Agriculture, Kyoto University in 2002. Joined the Kokusai Kogyo Co., Ltd. in 2002. Completed the doctor's program at the Graduate School of Environment and Information Sciences, Yokohama National University in 2007. Researcher, Research Institute for Geo-Resources and Environment in 2011; and Senior Researcher in 2013. In this paper, was in charge of the development of monitoring technology and on-site application.



Tatsuya UCHIDA

Graduated from the Department of Fermentation Technology, Faculty of Engineering, Yamanashi University in 1970. Joined Hitachi Chemical Co., Ltd. in 1970. Worked on the environmental restoration integrated with the production facilities, R&D for Waste Material Recycling Division, and helped export overseas plants. Manager of Design, Household Equipment Division in 1995; Managing Plant Director; and Director, CSR Department and Quality Assurance General Manager, Environmental Safety



Department, Cooperate Business Strategy Headquarters in 2004. Member, Recycling Committee, Japan Nuclear Fuel Ltd. from 2005. Established the Uchida Professional Engineer Office in 2008. Technical Support Advisor, AIST in 2011; and Visiting Researcher from 2015. In this paper, was in charge of the design of the pilot plant.

Discussion with Reviewers

1 Overall

Comment (Toshimi Shimizu, AIST)

This paper discusses the decontamination technology for incinerated ashes by using the Prussian blue nanoparticles, in response to the urgent demand against the radioactive material leakage accident at the Fukushima Daiichi Nuclear Power Plant of the Tokyo Electric Power Company. It presents typical nanotechnology in which wide-ranging scales are linked seamlessly from nanoparticles, adsorbents, adsorption systems, to plant construction. Of particular interest is the description of the related technologies that were built under specific environments and conditions, from over-viewing the total issue, creating the original research strategy, to collaborating and making adjustments with various stakeholders including the researchers of different fields, Japanese government, local governments, and local residents. I think this paper is suitable for publication in *Synthesiology*.

Comment (Naoto Kobayashi, Waseda University)

This paper describes the results of R&D that has provided solutions in an extremely short period of time using PB nanoparticles, for the urgent issue of decontaminating the leaked radioactive materials from the Fukushima Daiichi Nuclear Power Plant of the Tokyo Electric Power Company due to the Great East Japan Earthquake. It is a significantly useful paper that presents the attainment of the final goal of verification and practical use through collaboration with companies. I believe it is suitable for publication in *Synthesiology*. On the other hand, there seems to be a lack of scientific explanation on the effectiveness of decontamination by PB nanoparticles, which is the essential technology, and additional explanation is recommended.

2 Figure to present the R&D organization

Comment (Toshimi Shimizu)

The explanations of elemental technologies and the integration scenario for synthesiological discussion are presented in Figs. 2 and 4, Table 2, and others. On the other hand, in this research, the stakeholders are the central government, local governments of prefectures, cities, towns, or villages, and local residents, as well as technology users and product manufacturers. It can be positioned as a specific R&D in which the urgent problems had to be solved in a situation where related laws were still lacking. The research was conducted in the restriction of compliance and involved diverse and complex collaboration and interrelationships, but I feel such complexity and difficulty are not sufficiently expressed in the present figures.

For example, I remember that the industry-academia-government collaboration framework was formerly categorized into three forms in AIST, one-to-one collaboration such as regular joint research or subcontracted research, one-to-many such as research consortiums and platforms, and many-to-many such as research associations and research bases. I think the general readers will find it interesting to know how the one-to-one or one-to-many collaboration framework that started from the development of adsorbents and PB nanoparticle mass production through corporate joint research had shifted to some other

collaborative structure, and whether there was a new collaborative framework different from the above three categories. If possible, could you create a schematic illustration to show how the environment surrounding this R&D (including the stakeholders) changed over time? If this is not possible, could you present a schematic illustration that shows the R&D framework (including the stakeholders) at the final stage?

Answer (Tohru Kawamoto)

We decided it was difficult to represent this in a figure, so we added the new subchapter, “3.4 Flow of corporate collaboration and collaboration with the government and local government,” in the manuscript.

3 Ways of collaborating with the companies

Question & Comment (Naoto Kobayashi)

In this paper, “3.1 Transferring strategy” was very well written and it is very important. I think it is useful for researchers who will be involved in the “bridging research” or translational research in the future, including those at universities. However, in reality, industry-academia collaboration often does not work very well. If you know any “secrets” in transferring to companies based on your experience, please tell us.

Answer (Tohru Kawamoto)

Thank you for your encouraging comments. For the practical utilization based on the technology originated in the research institute, the important points are described below. Please note that the situation would be different in the case where the research demand is raised by companies. Basically, It would be necessary to establish Table 2 as formal knowledge. Specifically, it is as follows:

- (1) Visualization of the business image is the most important, even if it is just an expectational diagram. In general, the researcher in the research institute thinks that the companies should create their business models. However, if we think so, the project will fail regardless of whether the technology is good or bad when the companies cannot achieve their business model. Of course, the companies are responsible for their final business models. However, at the start of the R&D, when the companies know no details, construction of the draft of the model by the institute-side would be important for discussion.
- (2) The design of the supply chain is also important. If the partner company is large, it would cover all of the supply chain on its own. But a small and medium-sized company often cannot do that. When a small and medium-sized company establishes the business model, the research institute needs to suggest some material supplier, for example.
- (3) Consideration for handling of intellectual properties are also important. At least, when you aim for commercialization involving multiple companies as in this case, AIST is required to keep the basic intellectual property to make the companies follow our vision.

Although I focused on topics other than research, specialty of the technology is the most important, as described in Subchapter

3.4.

Note that we have not yet reached our research goal, unfortunately. I think we are out of the “valley of death” because the companies succeeded in commercializing the adsorbents and the products has been recommended in the government agency manuals. On the other hand, for true contribution to society, we must overcome the “Darwinian sea”. Currently, we have not achieved industrialization, one of the reason being that the progress of the cesium decontamination by the government has gone slightly differently from our initial plan. Although this is totally the role of the companies, “what the research institution can do in this stage?” is an issue to be considered.

4 Storage of the adsorbents

Question & Comment (Naoto Kobayashi)

In “2.2.4 Investigation of the storage and disposal of the waste material,” you describe the establishment of a mild oxidation method using heated steam. Since this is an extremely important technology in your R&D, it is recommended to show the reference for published papers, if any. If this is the first description, you should provide more explanation including figures about the “large amount of oxidative heat.”

Answer (Tohru Kawamoto)

It is cited as Reference [51] as a paper on it has been published on March 25, 2016.

5 Science of hexacyanoferrate

Question (Toshimi Shimizu)

In the cesium adsorption using hexacyanoferrates, are there any scientific experiments on what kinds of structural factors affect the adsorption performance? For example, do different metals such as iron, cobalt, nickel, copper, zinc, or others, or the different composition of iron/cyanoferrate group/water have great effect on that? In practical application, the adsorbent needs to be used under various and complex aqueous conditions (temperature, coexistence of various ions, presence of other molecular compounds, pH, concentration, etc.). From the perspective of analytical chemistry, are the optimal metal species and compositions for each adsorption under various conditions clear? Or, is it necessary to conduct an adsorption test for each adsorbent on site? Please explain from the scientific view of analytical chemistry.

Answer (Tohru Kawamoto)

I think the optimal solution at the academic paper level is mostly known, e.g. concerning the capacity of the cesium adsorption or high-pH resistance by changing the metal species. However, there isn't a lot of work for the detailed dependence on the composition ratio of each metal species. We have determined the chemical composition with intensive investigation such as the elution properties after adsorption. However, Prussian blue has different properties compared to other analogues. Its mechanism of cesium adsorption is not completely understood. This issue will be discussed elsewhere, since this discussion is beyond the scope of this paper.