Rapid Communication

Treatment of Water Contaminated with Radiocesium Using Novel Complexes between Prussian-Blue and Bivalent Transition Metal Hydroxides

Hisashi UBARA [1,*], Eiji YUKI [1], Kazuki TSUKIYAMA [1], Masato KAMIZAWA [1], Koichi SENOH [1], Kohei OHTA [1], Fumio SHIMAMOTO [1] and Nariyuki OHTA [1]

[1] *Mie Plant, Mie Chuo Kaihatsu Co., Ltd., 4713 Hachiya, Yono, Iga-shi, Mie 518-1152, Japan*

A variety of technologies are applied to the decontamination of radiocesium from water using inorganic adsorbents such as zeolites, Prussian blue (PB) and its analogues. However, these adsorbents are difficult to apply. Although zeolites work as good adsorbents for cesium (Cs) in freshwater, their adsorption ability is extremely low in seawater and fly ash extracts with a high salt concentration. In contrast, PB and its analogues maintain their selective adsorption ability for Cs even in water containing salts, but a high level of cyan remains in the treated water. In this study, we introduce a new technology that utilizes complexes between PB and hydroxides of transition metals (PB-X) for the decontamination of Cs from water and report results of demonstration tests on simulated seawater and fly ash extract. Furthermore, the excellent results of the PB-X method applied to the extracts from fly ash contaminated with radiocesium (more than 8,000 Bq/kg) are also shown. It has been proved that radiocesium activities are not only below the detection limit (<10 Bq/kg) and the content of cyan can be controlled under the regulation value of tap water in the water treated with PB-X.

KEYWORDS: Prussian blue, PB, PB-X, radiocesium, Cs, cyan, decontamination, zeolite, transition meal seawater, fly ash extract

I. Introduction

Various treatment technologies have been developed and applied that use non-organic adsorbents such as zeolites or Prussian blue (PB) [1-3] and its analogs to decontaminate water containing radiocesium (Cs). Unfortunately, these adsorbents present several troublesome problems. For example, zeolite exhibits excellent Cs-adsorbing performance in contaminated water with low concentrations of sodium or potassium salts. However, in contaminated water with a high salt content, such as seawater, its adsorption performance is significantly degraded [6)].

Burnable radioactive wastes, such as vegetation, are disposed of by incineration to reduce the volume of waste. After this process, a large quantity of fly ash is generated that exceeds

---

* Corresponding author, E-mail: ubara8379@dinsgr.co.jp

DOI : 10.15669/fukushimainsights.Vol.4.308

Originally published in Transactions of the Atomic Energy Society of Japan (ISSN 1347–2879), Vol. 13, No. 4, p.127–135 (2014) in Japanese. (Japanese version accepted: August 30, 2014)

the radioactive limit designated for waste material (8,000 Bq/kg) because the radioactive Cs migrates to the fly ash and condenses 7). Thus, a study of the decontamination of fly ash by cleaning is required. However, the decontamination of fly ash contaminated with radioactive Cs by water extraction and treatment using zeolite is not efficient because of the high concentrations of Na^+, K^+, and Ca^{2+}.

On the other hand, PB maintains its excellent selectivity for Cs adsorption from contaminated water containing salts; however, because of its ultrafine particle size (100 nm and below), the discharge limit for the total cyanide concentration (T-CN) (<0.5 mg/L) stipulated by Fukushima Prefecture code may be exceeded because of the elution of soluble PB 8). Furthermore, when PB is used as a particulate or powder, a long time is required before adsorption equilibrium is reached (as for zeolite) because of the slow diffusion in the crystal lattice, which limits the rate of Cs adsorption.

In this study, we report a new processing technology for Cs-contaminated water that insolubilizes the soluble PB by quickly adsorbing Cs at the molecular level during the synthesis of PB in contaminated water. Subsequently, the synthesis of metal (Me) hydroxide ($Me(II)(OH)_2$) with divalent transition metals (Me(II): Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II)) occurs, forming a new complex, PB-X. Using this method, the direct discharge of treated water is possible. In summary, the process shows (1) quick and highly efficient Cs adsorption and (2) a total cyanide concentration in the treated water below the discharge limit stipulated by the Fukushima Prefecture code.

Possible insolubilization mechanisms for soluble PB by the PB-X material are insolubilization by the interaction of the d-orbitals of the Me(II) ion of $Me(II)(OH)_2$ or the d–π interactions of the cyano ligand of PB. Alternatively, insolubilization by the intercalation of soluble PB in the lamellar structure of $Me(II)(OH)_2$ 12, 13) is possible because $Me(II)(OH)_2$ has a hexagonal crystal form with a lamellar structure 9-11). A survey of time-dependent Cs removal by PB-$Me(II)(OH)_2$ treatment was conducted with simulated contaminated seawater and fly ash extract water containing stable Cs. The relationship between the $Me(II)(OH)_2$/PB molar ratio and the T-CN concentration in the treated water and the influence of K^+ on the Cs removal were investigated. The radioactive Cs concentration in the treated water was lower than the stipulated limit (<10 Bq/L). Furthermore, after the purification of fly ash extract water containing a high concentration of K^+ (2%) and a radioactive Cs concentration exceeding 8,000 Bq/kg, the T-CN concentration was in compliance with the limit stipulated by Fukushima Prefecture. In this paper, "X" in PB-X represents $Me(II)(OH)_2$.

II. Experimental

In this study, commercial special grade chemicals were used unless noted.

1. Cs removal from Contaminated Simulated Seawater using Stable ^{133}Cs

(1) Preparation of simulated seawater contaminated with ^{133}Cs

Cs-contaminated simulated seawater was prepared by adding cesium chloride (^{133}CsCl, 12.7 mg) to simulated seawater (1 L) prepared from distilled water containing sodium chloride (NaCl, 3.0%), magnesium chloride ($MgCl_2$, 0.5%), and potassium chloride (KCl, 0.05%). This yielded a concentration of stable ^{133}Cs of 10 mg/L (0.075 mmol/L).

(2) Treatment of ^{133}Cs-contaminated simulated seawater using PB-X

Sodium ferrocyanide decahydrate (0.85 mmol, $Na_4Fe(II)(CN)_6 \cdot 10H_2O$) obtained from Alfa Aesar was added to 500 mL of simulated seawater and stirred. Then, ferric chloride hexahydrate (0.9 mmol, $Fe(III)Cl_3 \cdot 6H_2O$) was added, resulting in the formation of PB. The pH of the treatment liquid was adjusted with an aqueous solution of sodium hydroxide (5 mol/L, NaOH) to 6–8, and the solution was stirred for 10 min.

Next, a Me(II) salt (1.7 mmol), which is twice the molar concentration of $Na_4Fe(II)(CN)_6 \cdot 10H_2O$, was added. Thus, $Me(II)(OH)_2$ was prepared by hydrolytic degradation induced by adjusting the pH to 7–9 with 5 mol/L aqueous NaOH. The solution was stirred for a specified period, and the time-dependent Cs removal was recorded. Subsequently, the pH was adjusted to 7–8, and 1 mL of a 0.1% aqueous anionic polymer flocculant (A-115/MT Aqua-Polymer Inc.) was added; this resulted in the deposition of a coarse floc while gently stirring the mixture. After leaving the solution under static conditions, the treated liquid was filtered through a 5 C filter paper with a 1-mm mesh, and the filtrate and filtered residue were obtained. The time from the synthesis of PB until the formation of the coarse floc on the addition of the polymer flocculant was defined as the processing time. The Cs concentration and T-CN of the filtered liquid were measured.

The Me(II) salts for insolubilizing the PB used were chlorides or hydrosulfates of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II). In the cases of Fe(II) and Mn(II), the dissolved oxygen was removed using sodium sulfite (Na_2SO_3) to prevent oxidation to Fe(III), Mn(III), or Mn(IV), and the treatment was conducted in the presence of bubbling nitrogen gas. For comparison with Fe(II), the insolubilization of PB was conducted using $Fe(III)Cl_3$.

In addition, a commercially available PB pigment (0.8 g, 2.8 mmol, MILORI BLUE, Dainichiseika Color & Chemicals Mfg., $NH_4Fe(III)Fe(II)(CN)_6$) was added to 500 mL of simulated seawater, and the time-dependent variation in the Cs concentration in the treated water was recorded.

(3) Influence of molar ratio of $Me(II)(OH)_2/Na_4Fe(II)(CN)_6 \cdot 10H_2O$

The treatments were conducted under similar conditions as II-1-(2) with a fixed amount of added $Na_4Fe(II)(CN)_6 \cdot 10H_2O$ (0.85 mmol) but varying amounts of added Me(II) salt, and the relationship between the molar ratio $Me(II)(OH)_2/Na_4Fe(II)(CN)_6 \cdot 10H_2O$ and the concentration of Cs and T-CN were investigated.

2. Test of Cs Removal from Simulated FLy Ash Extract Water Containing Stable ^{133}Cs

The following experiments were conducted on the simulated fly ash extract water having different K^+ concentrations, to investigate the inhibiting effect of K^+ on Cs removal.

(1) Preparation of ^{133}Cs-contaminated simulated fly ash extract water

Four simulated fly ash extract samples were prepared by adding NaCl (1.2%, Na^+: 0.47%), $MgCl_2$ (0.2%, Mg^{2+}: 0.05%), $CaCl_2$ (0.83%, Ca^{2+}: 0.3%), and KCl to distilled water to yield four different K^+ concentrations of 0.05%, 0.1%, 0.5%, and 1.0% respectively. Cs-contaminated simulated fly ash extract water was prepared by adding 12.7 mg of ^{133}CsCl to 1 L of each simulated fly ash extract sample to yield a stable ^{133}Cs concentration of 10 mg/L (0.075 mmol/L).

(2) Treatment of ^{133}Cs-contaminated simulated fly ash extract

$Na_4Fe(II)(CN)_6 \cdot 10H_2O$ (1.0 mmol) was added to the four simulated fly ash extract samples with different K^+ concentrations (500 mL) and stirred. Then, ferric chloride anhydride (1.2 mmol, $Fe(III)Cl_3$) was added to yield PB. The pH of the treatment liquid was adjusted to 6–8 with a 5 mol/L aqueous NaOH solution and stirred for 20 min. Next, manganese sulfate hydrate (2.1 mmol, $Mn(II)SO_4H_2O$) or copper sulfate anhydride (2.1 mmol, $Cu(II)SO_4$) was added, and the pH was adjusted to 7–9 with 5 mol/L aqueous NaOH solution and stirred for 20 min. Subsequently, the pH was adjusted to 7–8, and 1 mL of 0.1% aqueous A-115 polymer flocculant solution was added, resulting in the deposition of a coarse floc on gentle stirring. After leaving in a static condition, the treated liquid was filtered through a 5C filter paper with a 1-mm mesh and the filtrate and filtered residues were acquired. The Cs and T-CN concentrations of the filtered liquid were measured.

(3) Elution test of filtered residue according to Notification No. 13 from the Ministry of the Environment 14)

The filtered substance was weighed wet, soaked in 10 times as much distilled water, and elution was conducted for 6 h in a shaker. Then, the eluted liquid was filtered through a 5C filter paper with 1-μm screen mesh, and the filtered liquid was acquired. The Cs and T-CN concentrations of the filtered liquid were measured.

3. Radioactive Cs-Contaminated Fly Ash Extract

The purification treatment was conducted on fly ash extract with a radioactive concentration of over 8,000 Bq/kg provided by Tokyo Power Technology Ltd. under the conditions described in Cases 1–3.

(1) Case 1: Radioactive concentration of 8,900 Bq/kg

After the pH of the fly ash cleaning water (500 mL, pH 10.7) had been adjusted to pH 6.9 with 2 mol/L sulfuric acid, 1.75 mmol of $Na_4Fe(II)(CN)_6$. $10H_2O$ was added while stirring. Next, 1.75 mmol of $Fe(III)Cl_3$ was added and stirred for 20 min while adjusting the pH of the treated liquid to 6.8–7.5 with 5 mol/L aqueous NaOH solution.

Next, 3.5 mmol of $Cu(II)SO_4$ was added, and the hydrolytic degradation of $Cu(II)SO_4$ was conducted for 20 min while adjusting the pH to 7.0–8.0 with 5 mol/L aqueous NaOH solution. Subsequently, 1 mL of 0.1% A-115 polymer flocculant was added, and a coarse floc deposit was formed on gentle stirring. The treated liquid was filtered through the 5C filter paper, and the filtrate and filtered residues were acquired.

(2) Case 2: Radioactive concentration of 9,200 Bq/kg

After the pH of the fly ash extract water (500 mL, pH 11.1) had been adjusted to pH 4.1 with 2 mol/L H_2SO_4, 1.75 mmol of $Na_4Fe(II)(CN)_6 \cdot 10H_2O$ was added while stirring. Next, 1.75 mmol of $Fe(III)Cl_3$ was added and stirred for 20 min while adjusting the pH of the treated liquid to 7.0–8.0 with a 5 mol/L aqueous NaOH solution.

Next, 4.0 mmol of $Cu(II)SO_4$ was added and stirred for 20 min while adjusting the pH to 7.0–8.0 with 5 mol/L aqueous NaOH solution. Then, 0.2 g of PGα21Ca polymer flocculant provided by Nippon Poly-Glu was added, and a coarse floc deposit was formed on gentle stirring. The treated liquid was filtered through the 5C filter paper, and the filtrate and filtered residues were acquired.

(3) Case 3: Radioactive concentration of 13,000 Bq/kg

First, 2.0 mmol of $Na_4Fe(II)(CN)_6 \cdot 10H_2O$ and 2.0 mmol of $Fe(III)Cl_3$ were added in series to 500 mL (pH 5.4) of fly ash water and stirred for 20 min while adjusting the pH to 7.0–8.6 with 5 mol/L aqueous NaOH solution. Next, 4.0 mmol of Cu(II)SO_4 was added. The solution was stirred for 20 min while adjusting the pH to 7.0–8.0 with 5 mol/L aqueous NaOH solution. After that, 1 mL of 0.1% A-115 polymer flocculant was added, and a coarse floc deposit was formed on gentle stirring. The treated liquid was filtered through the 5C filter paper, and the filtrate and filtered residues were acquired.

(4) Elution test according to Notification No. 13 from the Ministry of the Environment

An elution test was conducted on the filtered residue obtained using Case 1 according to Notification No. 13 from the Ministry of the Environment [14)]. Here, 90% of the weight of the filtered residues was moisture, 1 g in 3.8 g of solid content was the active material, and the residues were insoluble components such as supernatant that coprecipitated with the active material and $CaSO_4$. Because a quantity of specimen was required for the measurement of T-CN and radioactivity, the filtered residues were used for elution tests with the contained moisture.

4. Analysis Methodology

(1) Quantitative analysis of ^{133}Cs in simulated test water

The $^{133}Cs^+$-ion concentrations of the eluted liquid obtained from elution tests of the filtered water and the filtrates acquired after PB-X treatment of the ^{133}Cs-contaminated simulated seawater and simulated fly ash extract were measured using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7000x). The lower limit for determination was set to 0.001 mg/L.

(2) Ion analysis of radioactive Cs-contaminated fly ash extract

After diluting the fly ash extract water by 1,000, a quantitative ion analysis was conducted. The positive ions were measured by ICP-MS (Agilent 7000x) and negative ions were measured by ion chromatography (ICS2000, Dionex).

(3) Total cyanide analysis

The measurement of the T-CN of the treated water was conducted in accordance with methods 38.1.2 and 38.2 of JIS K0102. The lower limit for determination was set to 0.05 mg/L.

(4) Measurement of radioactive Cs concentration

The measurement of the concentrations of radioactive Cs (^{134}Cs and ^{137}Cs) were conducted on the radioactive-Cs-contaminated fly ash cleaning water, its PB-X treated filtrate, and the eluted liquid of elution test for filtered residues under the following conditions.

(a) Measuring device: germanium semiconductor detector (GR3019-7935-7F-RDC-4-2002C(S/N6516)/Canberra, Japan).

(b) Measuring methodology: γ-ray spectrometry using germanium semiconductor detector (Ministry of Education, Culture, Sports, Science and Technology, Science and Technology Policy Bureau, Revised in 1992).

III. Results and Discussion

1. PB-X treatment of ^{133}Cs-contaminated Simulated Seawater and Simulated Fly Ash Cleaning Water

(1) Cs-contaminated simulated seawater

(a) Time dependent change in Cs concentration in the simulated seawater during PB-X treatment

Figure 1 shows the time-dependent fluctuation in Cs concentration of simulated seawater in the treated water using PB-Fe(III)(OH)$_3$ and PB pigment for comparison with that treated with PB-Me(II)(OH)$_2$.

If the 20-min PB synthesis process during PB-X treatment is considered, the adsorption removal rate for Cs in the simulated seawater should reach the highest value within 1 h for both processes. It is thought that the Cs adsorption by PB proceeds in molecular level because the PB is synthesized in aqueous solution. On the other hand, for the PB pigment, 24 h were required to reach equilibrium because of the slow adsorption speed of the PB pigment. One possible reason for this is that the Cs$^+$-ion adsorption speed is controlled by the diffusion of Cs$^+$ ions in the PB crystal lattice in the case of PB pigment particles. **Table 1** Concentration of Cs in the finished water and Cs removal ratio after 1 h treatment of the simulated seawater using PB-Me(II)(OH)$_2$, PB-Fe(III)(OH)$_3$, and PB dye.

The Cs concentration and Cs removal rate from treated water with treatment time (1 h) are shown in **Table 1**. The order of Cs removal rates is Co(II)-Ni(II) > Cu(II)-Mn(II) > Fe(II) > Zn(II) ≫ Fe(III) > PB pigment.

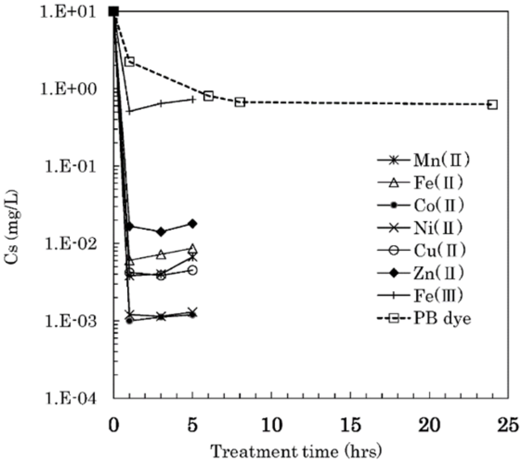

Figure 1 Change in Cs concentration in the filtrates of the simulated seawater treated with PB-Me(Ⅱ)(OH)$_2$ and PB dye with respect to treatment time

Table 1 Concentration of Cs in the finished water and Cs removal ratio after 1 h of treatment of the simulated seawater using PB-Me(II)(OH)$_2$, PB-Fe(III)(OH)$_3$, and PB dye

Me(II)	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Fe(III)	PB dye
Cs (mg/L)	0.004	0.006	0.001	0.001	0.004	0.017	0.51	2.2
Removal ratio (%)	99.96	99.94	99.99	99.99	99.96	99.83	94.91	77.69

The distribution coefficient (K_d), an index of the adsorption performance of Cs, is expressed by the ratio of Cs concentration in solid phase to that in the liquid phase. Here, the volume of Cs-contaminated water is V (mL), the Cs concentration before and after treatment are C_0 and C_1 (mg/L or Bq/L), respectively, and the quantity of adsorbent is defined as w (g). K_d is expressed by equation (1):

$$K_d = \{(C_0 - C_1)/w\}/(C_1/V)\ (\mathrm{mL/g}) \quad (1)$$

In the PB-X treatment, two moles of Me(II) salt were added per mole of PB. Some $\mathrm{Me(II)(OH)_2}$ generated as a result of hydrolytic degradation of the Me(II) salt is dissolved, depending on the solubility product; here, using equation (1) the molecular formula of the active material that insolubilizes the soluble PB was determined to be $\mathrm{NaFe(III)Fe(II)(CN)_6{\cdot}2Me(II)(OH)_2}$. **Table 2** shows the K_d values of the active materials after 1 h of PB-X treatment. The K_d values are high, 10^6 to 10^7 mL/g, except for that of Zn(II). On the other hand, the K_d values of PB-$\mathrm{Fe(III)(OH)_3}$ and PB-dye are low, 22,000 and 2,200 mL/g.

(b) Concentration of T-CN and transition metal (Me) in treated water

In the PB-X treatment, T-CN was not detected (<0.005 mg/L) in any of water samples treated for 1 h. On the other hand, the T-CN concentrations of water treated with PB-$\mathrm{Fe(III)(OH)_3}$ and PB pigment were 110 and 1.8 mg/L, respectively, thus exceeding the discharge limit (0.5 mg/L) stipulated by the Fukushima Prefecture code. The inferior performance of $\mathrm{Fe(III)(OH)_3}$ with respect to Cs adsorption and T-CN concentration compared to those of $\mathrm{Fe(II)(OH)_2}$ can be explained by the difference in affinity of Fe(II) and Fe(III) for the PB ion $[\mathrm{Fe(III)Fe(II)(CN)_6}]^-$.

According to the HSAB rules, Fe(III) is classified as a harder acid than Fe(II). Because the PB ion is a soft base, a hard acid like Fe(III) cannot form a sufficiently strong interaction with the PB ion for insolubilization. That is, part of $\mathrm{Fe(III)(OH)_3}$ may be eluted by disassociation even if the PB ion is insolubilized by attractive forces. On the other hand, for $\mathrm{Fe(II)(OH)_2}$, the interactions between the d-orbital of the soft acid (Fe(II)) and the π-electrons of the soft base ($\mathrm{CN^-}$) contribute to the insolubilization of soluble PB. In addition, the difference in the physical structures of $\mathrm{Fe(II)(OH)_2}$ and $\mathrm{Fe(III)(OH)_2}$ should be mentioned 19). A possible mechanism for the insolubilization is via the intercalation of soluble PB in $\mathrm{Fe(II)(OH)_2}$, which has a hexagonal crystal structure with a lamellar structure. For example, according to a report by Takahashi et al 13)., when the Zn(II) salt is hydrolyzed under the presence of anions, the coprecipitation of zinc hydroxide $\mathrm{Zn(II)(OH)_2}$ occurs with the intercalation of the anions between layers. The distance between layers varies according to the molecular length of the coprecipitated anion. For example, the layer distance is 12 Å in coprecipitation with succinic acid, which has an ion length of 7.6 Å, while coprecipitation with dodecanedioic acid ion increases the layer distance to 18 Å. Consequently, the layer distance will also be increased to more than 5 Å, the ion length of the co-present PB ion, in the case of $\mathrm{Fe(II)(OH)_2}$, which has a lamellar structure; thus, the intercalation of PB ions seems possible.

Table 2 Distribution coefficient (K_d) for Cs of the active materials, $\mathrm{PB{\cdot}2Me(II)(OH)_2}$

Me(II)	Kd (mL/g)
Mn(II)	3,100,000
Fe(II)	1,600,000
Co(II)	12,000,000
Ni(II)	12,000,000
Cu(II)	2,400,000
Zn(II)	710,000

On the other hand, the structure of $Fe(III)(OH)_3$ is amorphous, and it forms gel-like colloid particles, adsorbing the PB ion with weak coulombic interactions on the particle surfaces. Therefore, some PB can become disassociated, eventually being detected in the T-CN.

Table 3 shows the quantity of eluted Me(II) ions in the water treated with PB-X for 1 h. PB-$Co(II)(OH)_2$ and PB-$Ni(II)(OH)_2$ show excellent Cs removal rate, but the quantities of Co and Ni eluted in the treated water were high (20 and 26 mg/L, respectively), and the treated water was slightly colored. The eluted quantity of Me(II) corresponds to the solubility product (K_{sp}) of $Me(II)(OH)_2$ 15), and the PB-X-treated water using $Cu(II)(OH)_2$ showed the lowest metal elution, 0.03 mg/L.

In our process, Cs is removed from solution by the synthesis of PB from ferrocyanide and Fe(III) salts in the contaminated water, followed by insolubilization of the soluble PB with $Me(II)(OH)_2$. The mechanism can be expressed by formulas (2)–(6)

$$Na_4Fe(II)(CN)_6 + Fe(III)Cl_3 \rightarrow NaFe(III)Fe(II)(CN)_6 + 3NaCl \quad (2)$$

Cs^+ ions are captured by PB by the ion exchange reaction with Na^+ ions in PB, as indicated in formula (3).

$$Cs^+ + NaFe(III)Fe(II)(CN)_6 \rightarrow CsFe(III)Fe(II)(CN)_6 + Na^+ \quad (3)$$

Next, $Me(II)(OH)_2$ is synthesized through hydrolytic degradation, as shown by formula (4).

$$Me(II)X_{2-n}^{(n+1)-} + 2NaOH \rightarrow Me(II)(OH)_2 + 2Na^+ + X_{2-n}^{(n+1)-} \quad (4)$$

Here, when n = 0, the anion is univalent, and, when n = 1, the anion is bivalent.

The hydrolytic degradation of Me(II) salts is achieved through the pH adjustment of reaction liquid. When the Me(II) salt is added with a molar ratio, x, of Me(II) salt/$NaFe(III)Fe(II)(CN)_6$, a novel complex $NaFe(III)Fe(II)(CN)_6 \cdot yMe(II)(OH)_2$ is generated, as indicated in the reaction formulas (5) and (6), and it is considered that this insolubilizes the soluble PB. When the solubility of $Me(II)(OH)_2$ is small, x = y.

$$xMe(II)(OH)_2 \rightleftarrows yMe(II)(OH)_2 + (x-y)Me(II)^{2+} + 2(x-y)OH^- \quad (5)$$

$$M(I)Fe(III)Fe(II)(CN)_6 + yMe(II)(OH)_2 \rightarrow \underset{(PB-X)}{M(I)Fe(III)Fe(II)(CN)_6 \cdot yMe(II)(OH)_2} \quad (6)$$

Here, M(I) is Na or Cs.

Table 3 lists the y values of the novel complex in reaction formula (6) calculated from the Me(II) concentration in the treated water. If the Me(II) concentration is low, y is equal to x. The value y for Mn(II) that shows the maximum elution of 57 mg/L is y = 1.4, but y = 2 for Cu(II) because of the low concentration (0.03 mg/L) in the treatment water. The relationship of the y value of the novel complex and the T-CN concentration of the treated water are discussed in the next section.

Table 3 Me(II) concentrations in the treated water of the simulated seawater treated with PB-X, the solubility product (K_{sp}) 15) of $Me(II)(OH)_2$, and the y value in the active PB-yMe $(II)(OH)_2$ complex

Me (II)	Mn	Fe	Co	Ni	Cu	Zn
Concentration (mg/L)	57	3.4	20	26	0.03	2.9
K_{sp} at 25°C	1.9×10^{-13}	8.0×10^{-16}	1.6×10^{-15}	2.0×10^{-15}	2.2×10^{-20}	1.2×10^{-17}
y	1.39	1.96	1.80	1.74	2.00	1.97

(c) $Me(II)(OH)_2$/PB molar ratio, y, and the Cs concentration and T-CN of the treated water

In the PB-X treatment, the T-CN concentration of the treated water is decreased by the insolubilization of soluble PB by $Me(II)(OH)_2$. The effect is related to the molar ratio, y, of $Me(II)(OH)_2$ and PB. The relationship between the Cs concentration and T-CN concentration of the treated water with respect to y for the case of Me(II) = Cu(II) in the PB-X treatment is shown in **Figure 2**. The Cs concentration of the treated water is approximately constant with respect to y, but the T-CN concentration decreases as y increases. From Figure 2, $y \geqq 1.2$ is necessary to satisfy the Fukushima Prefecture T-CN discharge limit (<0.5 mg/L) by insolubilization through the interaction of $Cu(II)(OH)_2$ and soluble PB. This is also true for other Me(II) species, such as Mn(II).

Unlike T-CN, the Cs concentration in the treated water shows almost no change with respect to y. This implies that the T-CN eluted from the treated samples is derived from the PB that did not adsorb Cs, and the PB that adsorbed Cs is insoluble. Presumably this is attributable to the nature of the affinity of Na^+, K^+, Ca^2, and Cs^+ for the PB ion ($[Fe(III)Fe(II)CN)_6]^-$). This can be explained by the HSAB rules.

According to the HSAB rules, chemical species can be classified as acids or bases and hard and soft species. The hard acids and hard bases or soft acids and soft bases form stable interactions, but the hard acid and soft base or soft acid and hard base do not form stable interactions.

Cs is an alkali metal in period six, and the lowest unoccupied atomic orbital (LUAO) of Cs^+ is the 6s orbital. It is classified as an easily polarized soft acid compared to Na^+ (3s) and K^+ and Ca^{2+} (4s). The order of softness of the cations is Cs^+ (soft) $\gg K^+ > Na^+ > Ca^{2+}$ (hard).

On the other hand, the PB ion ($[Fe(III)Fe(II)(CN)_6]^-$) is a soft base that will tightly bond with soft acid Cs^+, but the bonding of hard acids Ca^{2+}, Na^+, K^+, and $[Fe(III)Fe(II)(CN)_6]^-$ is weak. As a result, these complexes disassociate in aqueous solution. According to Klopman[17)], the formation of interactions between soft acid Cs^+ and soft base PB ion is dominated by the interaction of the LUAO and the frontier molecular orbitals of the highest unoccupied molecular orbital (HOMO) of the PB ion; presumably, the Cs-PB bond has some covalent character and may form insoluble particles.

(2) Simulated fly ash extract

Mn(II) and Cu(II) showed the same Cs removal rates in the PB-X treatment of simulated seawater, and a PB-X treatment was conducted on the simulated fly ash extract water containing

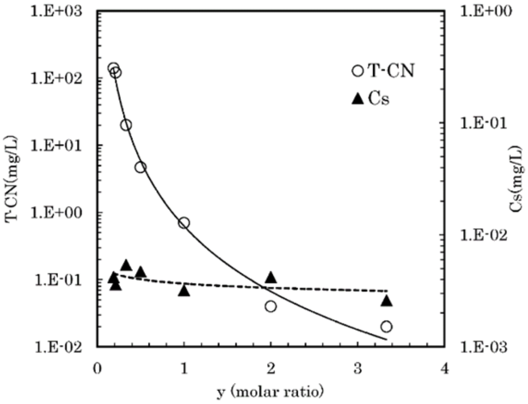

Figure 2 Effect of the $Cu(II)(OH)_2$/PB molar ratio (y) on the T-CN and Cs concentrations in the simulated seawater treated with PB-$Cu(II)(OH)_2$

four levels of K^+ content: 0.05%, 0.1%, 0.5%, and 1.0%. The results acquired for the treated water and filtered residue are summarized in the next section.

(a) Influence of K^+ content in simulated seawater on Cs adsorption performance

The concentrations of Cs in the PB-X-treated water with Me(II) = Mn or Cu, T-CN concentration, and K_d of the active materials under these treatment conditions are listed in **Tables 4** and **5** respectively. Furthermore, the change in the Cs concentration in the treated water and K_d with regard to K^+ content are shown in **Figure 3**.

The K_d is 10^4 to 10^5 mL/g for Cs in zeolite in pure water, and the inhibitory effect on Cs adsorption by Na^+ or K^+ have been reported [6, 7].

Table 4 Concentrations of metal ions and T-CN in the finished water and K_d for Cs of $PB\cdot 2Mn(II)(OH)_2$ with respect to K^+ content in the simulated fly ash extract

K Contents in the extracts (%)	Concentration of metals and T-CN in the finished water								
	Na	Mg	K	Ca	Mn	Fe	Cs	T-CN	K_d
				(mg/L)					(mL/g)
0.05	4,500	450	380	590	93	0.13	0.004	0.08	2.7×10^6
0.1	4,500	450	820	580	91	0.06	0.015	0.11	7.1×10^5
0.5	4,400	440	4,500	590	98	0.03	0.039	0.05	2.7×10^5
1.0	4,500	440	9,100	590	106	0.05	0.058	<0.05a)	1.8×10^5

a) An inequality sign in the table indicates a value less than lower detection limit.

Table 5 Concentrations of metallic ions and T-CN in the treated water, and K_d for Cs of $PB\text{-}2Cu(II)(OH)_2$ with respect to K^+ content in the simulated fly ash extracts

K Content in the extracts (%)	Concentration of metals and T-CN in the finished water								
	Na	Mg	K	Ca	Cu	Fe	Cs	T-CN	K_d
				(mg/L)					(mL/g)
0.05	4,800	470	460	600	0.02	0.03	0.005	<0.05	2.1×10^6
0.1	4,700	460	900	590	0.01	0.04	0.007	<0.05	1.5×10^6
0.5	4,600	440	4,600	590	0.03	0.02	0.008	<0.05	1.3×10^6
1.0	4,600	450	9,300	590	0.01	0.04	0.012	<0.05	8.6×10^5

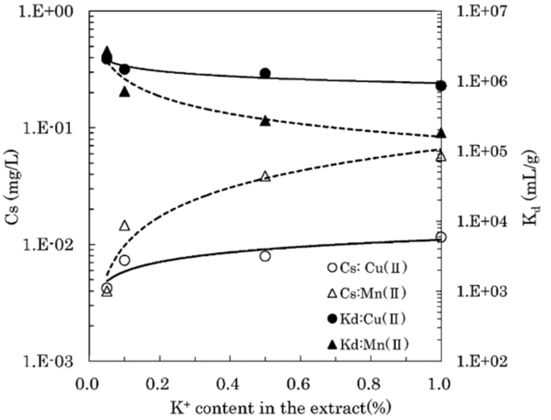

Figure 3 Effect of K^+ content in the simulated fly ash extracts on the concentration of Cs in the treated water, and the distribution coefficient (K_d) of Cs for $PB\cdot 2Cu(II)(OH)_2$ and $PB\cdot 2Mn(II)(OH)_2$

For example, the K_d of fly ash cleaning water containing Na^+ (1,500 mg/L), K^+ (2,800 mg/L), and Ca^{2+} (1,300 mg/L) treated for 24 h using zeolite is 800 (mL/g), and the adsorption performance is extremely inhibited by Na^+ and K^+. The concentration of cations other than K^+ in the simulated fly ash extract water in this study are high (Na^+: 5,000 mg/L, Mg^{2+}: 500 mg/L, and Ca^{2+}: 3,000 mg/L), and even at a K^+ content of 1% (10,000mg/L) a high level K_d of Cs, more than 10^5 (mL/g), can be maintained through PB-X treatment as shown in Figure 3. In particular, when Me(II) = Cu, the inhibition of Cs adsorption by K^+ is lower than that with Mn^+, and it showed excellent Cs adsorption performance ($K_d = 8.6 = 10^5$ mL/g and a Cs removal rate of 99.88%) for the simulated fly ash extract with a K^+ concentration of 1.0%. Based on these results, PB-X is an excellent material for the treatment of Cs-contaminated water containing a high concentration of salts.

(b) Elution test on PB-X treated filtered residues

Elution tests were carried out according to notification No. 13 from the Ministry of the Environment [14] on the residues acquired by filtration of PB-X treated simulated fly ash extract. The results are shown in **Table 6** and **Figure 4**. The weight of the filtered residues decreased to approximately 1 g when dried. To maintain the quantity of the analyzed specimen, the elution tests were conducted in the wet state (moisture content approximately 90%) using distilled

Table 6 Effects of K^+ content in the simulated fly ash extract on K, Cs, T-CN, and transition metal (Cu or Mn) concentrations in the leachates in leaching tests

Me(II)	K, Cs, T-Cn, Cu, Mn	K^+ content (%)			
		0.05	0.1	0.5	1.0
Cu(II)	K (mg/L)	68	101	398	851
	Cs (mg/L)	0.001	0.002	0.001	0.002
	T-CN (mg/L)	<0.05	<0.05	0.05	<0.05
	Cu (mg/L)	0.001	0.005	0.003	0.006
Mn(II)	K (mg/L)	40	94	460	981
	Cs (mg/L)	0.001	0.003	0.006	0.011
	T-CN (mg/L)	1.0	0.57	0.52	0.06
	Mn (mg/L)	15.8	17.1	11.6	11.4

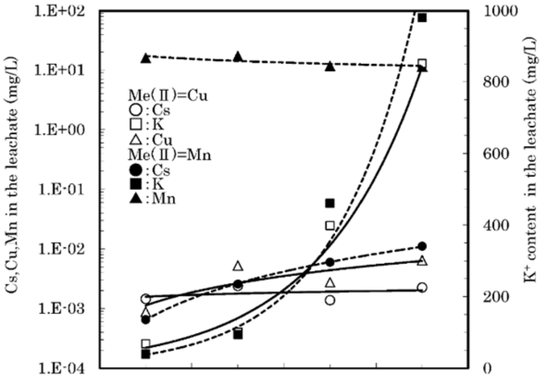

Figure 4 Relationship between K^+ content in the simulated fly ash extracts and the leachability of Cs, transition metals (Mn, Cu), and K^+ in the leachates of the filtration residues obtained after PB-X(Me(II) = Cu, Mn) treatment

water (10 times as much as the filtered residues).

In the elution test of the PB-X-treated filtered residues, the elution of Cs and CN^- was inhibited more by the presence of Cu(II) than Mn(II). Furthermore, the elution Cu(II) was very low, especially compared to that of Mn. The quantity of Cs eluted from the PB-X-treated filtered residues was low (0.001–0.002 mg/L) for Me(II) = Cu, and the presence of K^+ did not have an effect on the Cs elution quantity. Furthermore, the T-CN was very low, indicating stable fixation of insolubilized Cs and soluble PB through the formation of PB•2Cu$(OH)_2$.

When Me(II) was Mn, the presence of K^+ in the elution liquid affected the quantity of Cs eluted. The reason for the high T-CN elution is considered to be the inhibited insolubilization of soluble PB by the interaction of soluble PB molecules and Mn(II)$(OH)_2$ because some portion of the Mn(II) was oxidized to Mn(III) or Mn(IV) during the 6-h shaking in the elution test. Furthermore, when the d–π interactions of the d-orbitals of Mn(II) and Cu(II) and the π-electrons of CN of PB are compared, the d–π interaction of Cu(II)-CN is expected to be stronger than that of Mn(II)-CN based on the HSAB rules 16). Thus, the superiority of using Cu over Mn in the PB-X treatment can be explained based on the assumed stronger interaction of PB with Cu(II) $(OH)_2$ than Mn(II)$(OH)_2$.

2. PB-X Treatment of Radioactive-Cs-contaminated Fly Ash Extract

In the purification test of radioactive-Cs-contaminated fly ash extract, the PB-X treatment used Cu(II) salts based on the results obtained using the simulated fly ash extract water.

The results are as follows:

(1) Radioactive Cs-contaminated fly ash extract

The measurement of radioactivity for Cases 1–3 of the radioactive-Cs-contaminated fly ash extract water are listed in **Table 7**, and the concentrations of ion species contained in the cleaning water are listed in **Table 8**.

The fly ash extract samples have high K^+ content (1.9–2.4%), which could inhibit Cs adsorption, and the rubidium ion (Rb^+) is content is about 70 mg/L.

(2) Analysis of treated water

Table 9 lists the concentrations of radioactive Cs, T-CN, Fe, and Cu in the treated water acquired in Cases 1–3 of PB-X(Me(II) = Cu) treatment of fly ash extract water.

Table 7 Radioactive Cs concentration in the fly ash extracts

Fly ash extracts	^{134}Cs (Bq/L)	^{137}Cs (Bq/L)	Total Cs (Bq/L)
Case 1	2,720 ± 56	6,190 ± 64	8.910
Case 2	2,540 ± 39	6,000 ± 62	8,540
Case 3	4,000 ±49	9,000 ±76	13,000

Table 8 Ion concentrations in the fly ash extracts contaminated with radiocesium

Fly ash extract	Na	Mg	K	Ca	Rb	Sr	^{133}Cs	Cl	NO_3	SO_4
	(mg/L)									
Case 1	3,200	510	24,000	1,320	72	22	0.63	23,000	280	5,000
Case 2	2,570	830	22,900	1,580	68	31	0.60	21,000	280	8,600
Case 3	2,760	520	19,000	1,350	79	24	0.78	18,000	280	6,200

Table 9 Concentrations of radiocesium, T-CN, Fe, Cu, and ^{133}Cs in the filtrates obtained by PB-X treatment of the fly ash extract

Filtrates	^{134}Cs (Bq/L)	^{137}Cs (Bq/L)	Total Cs (Bq/L)	T-CN (mg/L)	Fe (mg/L)	Cu (mg/L)	^{133}Cs (mg/L)
Case 1	<5	<8	<10	0.08	0.14	7.0	<0.001
Case 2	<5	<7	<9	<0.05	0.06	6.8	<0.001
Case 3	<4	<6	<8	<0.05	0.05	1.8	<0.001

Table 10 Concentrations of radiocesium, T-CN, and heavy metals in the leachate from the leaching test of the residue obtained after PB-X treatment of Case 1

^{134}Cs (Bq/L)	^{137}Cs (Bq/L)	Total Cs (Bq/L)	T-CN (mg/L)	Fe (mg/L)	Cu (mg/L)
<5	<7	<9	<0.05	0.08	2.8

Cases 1 and 2 are the PB-X treatment using the fly ash extract water having similar ion concentrations or radioactive Cs concentrations. These were used to observe the reproducibility of the decontamination effect by adjusting the amount of added $NaFe(II)(CN)_6 \cdot 10H_2O$ and $Cu(II)SO_4$ required to form 3.5 mmol/L (1.7 g/L) of active material for Cs adsorption, i.e., $PB \cdot 2Cu(II)(OH)_2$.

The radioactive Cs in the treated water was not detected in Cases 1 and 2, and the discharge limit (<0.5 mg/L) of Fukushima Prefecture code was satisfied. In Case 3, the treatment of water contaminated with radioactive Cs (13,000 Bq/kg) resulted in the removal of Cs and T-CN at an active material concentration of 4 mmol/L.

The K_d of the active material material for Cs was calculated to exceed 9.5×10^5 mL/g. Excellent Cs adsorption performance of PB-X treatment was also demonstrated for the contaminated water containing a high concentration of salts. The eluted Cu concentration in the treated water was higher than that of the simulated fly ash extract. All treated water in Cases 1–3 showed a high chemical oxygen demand (COD), and the amber color was easily removed using active charcoal. We believe that a lignin decomposition component was contained in the simulated fly ash extract water. Consequently, it is considered that the formation of a complex of lignin with Cu increased the Cu elution in the treated water.

(3) Analysis of filtered residues

The concentrations of radioactive Cs, T-CN, Fe, and Cu in the eluted liquid from the elution tests were determined based on notification No. 13 from the Ministry of the Environment and are listed in **Table 10** for Case 1. Neither radioactive Cs nor T-CN was detected in the eluted liquid, and it was confirmed that Cs was firmly fixed on the $PB \cdot 2Cu(OH)_2$, the active material, and, thus, the PB molecule was insoluble

IV. Summary

A quick and highly efficient method for the removal of Cs from contaminated water was confirmed, via the synthesis of PB-X, a novel complex of PB and the hydroxide of a bivalent transition metal ($Me(II)(OH)_2$).

Furthermore, for the case where Me(II) = Cu(II), it was demonstrated that the T-CN concentration of the treated water was below the discharge limit stipulated by Fukushima Prefecture.

This was achieved by adjusting the $Cu(II)(OH)_2$/PB molar ratio, y, to above 1.2.

For the case of Me(II) = Cu in PB-X, we found that the Cs removal inhibition effect was mitigated by K^+. The radioactive concentration in the treated water was below the detectable level (<10 Bq/L). This was also true for the fly ash water with a K^+ concentration of 2% and radioactive concentration of 13,000 Bq/L. The K_d of the $PB{\cdot}2Cu(II)(OH)_2$ active material exceeded 9×10^5 (mL/g). Additionally, CN^- was not detectable (<0.05 mg/L).

Furthermore, neither Cs nor T-CN were detectable in the eluted liquids prepared from the elution tests conducted on the filtered residues of PB-X treatment carried out in accordance with notification No. 13 from the Ministry of the Environment, and it was confirmed that Cs was stably trapped by PB-X, and no elution of PB molecules took place.

Based on the above results, the PB-X treatment is a quick and excellent adsorption process with high selectivity (better than zeolite) for Cs removal from water, also quickly reducing the T-CN of treated water to under the environmental limit, a result that powdered PB did not achieve. Consequently, the PB-X treatment is a promising Cs-removal technology for incineration fly ash cleaning water obtained after the burning of vegetation containing a high concentration of salts such as Na^+ and K^+, seawater, as well as refuse leachate.

Currently the possibility of the application of the PB-X principle to ferrocyanide complexes of Mn(II), Co(II), Ni(II), Fe(II), Cu(II), and Zn(II), the so-called “PB analogs” is under investigation.

In addition, the PB-X was granulated and used in the study of Cs removal using the column method. Additionally, to clarify the Cs adsorption mechanism, a structural analysis of PB-X has been conducted, and the results will be reported soon.

Finally, the purification demonstration test for radioactive Cs-contaminated fly ash cleaning water in this study was conducted in Kawauchi Village, Fukushima Prefecture from October 30 until November 1,2013. The fly ash cleaning water was obtained and the measurement of radioactive Cs and T-CN was conducted by kind cooperation with Tokyo Power Technology, Ltd. We would like to take this opportunity to express our sincere appreciation to the people of Kawauchi Village and Tokyo Power Technology, Ltd. who understood, cooperated, and gave us permission for the reported experiments.

References

1) IAEA Report of United Nations Project E 11, *The Use of Prussian Blue to Reduce Radiocaesium Contamination of Milk and Meat Produced on Territories Affected by the Chernobyl Accident* February 1997.
2) V. Nigrovic, “Enhancement of excretion of radiocaesium in rats by ferric cyanoferrate (II),” *Int. J. Radiat. Biol.*, 7, 307–309 (1963).
3) N. L. Torad, M. Hu, M. Imura et al., “Large Cs adsorption capability of nanostructured Prussian blue particles with high accessible surface areas,” *J. Mater. Chem.*, 22, 18261–18267 (2012).
4) L. L. Burger, D. A. Reynolds, W. W. Schulz et al., *A Summary of Available Information on Ferrocyanide Tank Wastes*, October 1991, Prepared for the U.S. Department of Department of Energy. http://www.osti.gov/scitech/servlets/purl/6126105.
5) A. Omura, Y. Moritomo, Cs^+ Trapping in size-controlled nanospaces of hexacyanoferrates, *Appl. Phys. Express*, 5, 057101, (2012). http://www. tsukuba.ac.jp/public/press/120413.pdf.
6) Y. Ban, I. Yamagishi, Y. Morita, “Adsorption properties of Cs by inorganic adsorbents in sodium chloride solution,” *JAEA Res.*, 2011-037. [in Japanese]
7) NIES, *Center for Material Cycles and Waste Management Research, Technical data*, Fourth edition March 28th, 2014. Adequate Treatment of Radioactive Wastes from the Standpoint of Behavior of Radioactive Substances. http://www.nies.go.jp/shinsai/enpdf/hrfba3000009yxpa-att/techrepo_r4_140328.pdf. [in Japanese]
8) S. Inamori, R. Inamori, N. Murata, K. Kakazu, “The effectiveness of radioactive cesium removal

measures using Prussian blue non-woven fabric proposed by International Research Institute for Nuclear Decommissioning," *Yousui Haisui*, 56, 231–237 (2014). [in Japanese]

9) *Encyclopaedia Chimica*, 1993.
10) Z. Liu, M. Osada, T. Sasaki et al., "Selective and controlled synthesis of A- and B-cobalt hydroxides in highly developed hexagonal platelets," *J. Am. Chem. Soc*., 127, 13869–13874, (2005).
11) J. Yuan, K. Laubernds, Q. Zhang, S. L. Suib, "Self-assembly of microporous manganese oxide octahedral molecular sieve hexagonal flakes into mesoporous hollow nanospheres," *J. Am. Chem. Soc*., 125, 4966–4967, (2003).
12) S. Ida, D. Shiga, M. Koinuma, Y. Matsumoto, "Synthesis of hexagonal nickel hydroxide nanosheets by exfoliation of layered nickel hydroxide intercalated with dodecyl sulfate ions," *J. Am. Chem. Soc*., 130, 14038–14039, (2008).
13) S. Takahashi, T. Iwasa, Y. Kanazawa, "Formation of organic anion-pillared layered zinc hydroxides by coprecipitation," *Nippon Kagaku Kaishi*, 7, 502–507, (1997). [in Japanese]
14) Ministry of Environment Minister's Secretariat Waste Management and Recycling Department, *Analysis Operation Manual regarding the Industrial Waste Verification Method: Revised Version*, May 2013.
15) Chemistry 112 HP, Reference Materials, Solubility Product Constants near 25 C, http://bilbo.chm.uri.edu/CHM112/tables/Ksp Table.htm.
16) R. G. Pearson, "Hard and soft acids and bases," *J. Am. Chem. Soc*., 85, 3533–3539, (1963).
17) G. Klopman, "Chemical reactivity and concept of charge- and frontier-controlled reactions," *J. Am. Chem. Soc*., 90, 223–234, (1968).
18) H. Ubara, K. Tsukiyama, M. Kamizawa et al., Method for Processing of Radioactive Cs Contaminated Water, *Japanese Pat*. No. 5352853. [in Japanese]
19) J. D. Bernal, D. R. Dasgupta, A. L. Mackay, "The oxide and hydroxides of iron and their structural interrelationships," *Clay Miner. Bull*., 4, 15–30, (1959).
20) Dainichiseika Color & Chemicals Mfg. Co., Ltd. Product Brochure, http://www.daicolor.co.jp/products_i/pro_i pig/miloriblueqa.html.