

Insolubilization of Cadmium in Paddy Field Using Atomized Iron Powder and Extracting Reagent

Kiyoharu NAKATANI,^{*†} Yuichi MAKINO,^{*} Yuki SHIMURA,^{*} Tomohiro FURUMURA,^{*} Keiichi MIZUSAWA,^{*} Jun USHIKU,^{*} Hisayo FUKUSHIMA,^{*} Tomonori KANEKO,^{*} Ayako TSUDA,^{*} and Masaru SAKAI^{**}

**Division of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan*

***Corda Limited Liability Company, Tsukuba, Ibaraki 305-0047, Japan*

The insolubilization of cadmium in the soil of a naturally cadmium-contaminated paddy field was studied using an atomized iron powder and an extracting reagent. Cadmium in the soil was extracted into the water phase by calcium chloride. The extracted cadmium was deposited on the iron powder. The deposition of cadmium was significantly influenced by calcium chloride, since the surface area of the iron powder increased with the increasing calcium chloride concentration. We discuss the potential of the technique and the insolubilization mechanism.

Keywords Iron powder, cadmium, paddy field, soil, rice

(Received July 5, 2013; Accepted September 19, 2013; Published November 10, 2013)

Introduction

The international standard value of a cadmium concentration allowed in rice is less than 0.4 mg kg⁻¹ (29th session of the Codex Alimentarius Commission, 2006). A removal or insolubilization technique of cadmium in a paddy field is necessary to decrease in the cadmium concentration in the rice. Several methods, such as soil washing, phytoremediation, and excavation/landfilling, have been used for the soil remediation of cadmium-contaminated paddy fields.¹⁻⁸ The soil remediation cost should be low compared with the harvest yield. Cadmium in soil has been frequently discussed on the basis of the chemical form, such as an exchangeable form, that bind to carbonates, and that bind to iron and manganese oxides.⁹ The cadmium dissolved only in the water phase is likely to absorb into the rice, so that the relatively soluble cadmium should be removed or insolubilized in the soil. The exchangeable cadmium will be readily dissolved into the water phase using an extracting reagent. However, harmful chemical reagents for the environment and for the growth of rice plants cannot be added into the soil, and highly concentrated cadmium cannot be poured directly into a river.

Iron powder can be used for the removal of heavy metal.^{8,10,11} A heavy metal ion, such as Cu²⁺, Pb²⁺ and Cd²⁺, is reduced and deposited as the metal, since the formal redox potential of the heavy metal/metal ion couple is greater than that of the Fe/Fe²⁺ couple. In a paddy field, on the other hand, iron powder has been scarcely used for the removal of cadmium. Frequently, the amount of cadmium dissolved in water from the paddy field soil is extremely low. Therefore, cadmium would not be efficiently

removed from the soil by the addition of iron powder alone. If cadmium is extracted into the water phase with an extracting reagent, the cadmium may be insolubilized on the iron powder in the paddy field.

Atomized iron powders containing various elements have been developed. Heavy metals in water and volatile organic compounds in soils have been reported to be efficiently removed.^{12,13} Such iron powders are low-cost. An appropriate amount of iron is expected to be harmless for the environment and for the rice plant growth. Therefore, soil remediation for a cadmium-contaminated paddy field using an extracting reagent and the atomized iron powder will be an effective technique. In the present paper, we report on a study of cadmium insolubilization in a cadmium-contaminated paddy field soil. The cadmium insolubilization could be performed by the extraction of cadmium and the deposition of the cadmium on the atomized iron powder. We discuss the potential of the technique and the insolubilization mechanism of cadmium.

Experimental

An atomized iron powder was gifted from Kobe Steel, Ltd. The grain size upon 50 or 80% accumulation in a cumulative grain size distribution of the iron powder was 50 – 60 or 80 – 100 μm, respectively. The content in the atomized iron powder used in the present study was determined to be iron of 98.3 ± 0.3%, sulfur of 1.5 ± 0.3%, and manganese of 0.2 ± 0.1% by electron-probe microanalysis (JEOL, JXA-8530F). Soil samples of naturally cadmium-contaminated experimental paddy fields from Niigata (P1) and Miyagi (P2 for the first experimental field, P3 for the second experimental field) prefectures in Japan were used. The soils were air-dried at 30°C (Yamato Scientific, IN604W), and were used after passing through a 2-mm mesh

[†] To whom correspondence should be addressed.
E-mail: nakatani@chem.tsukuba.ac.jp

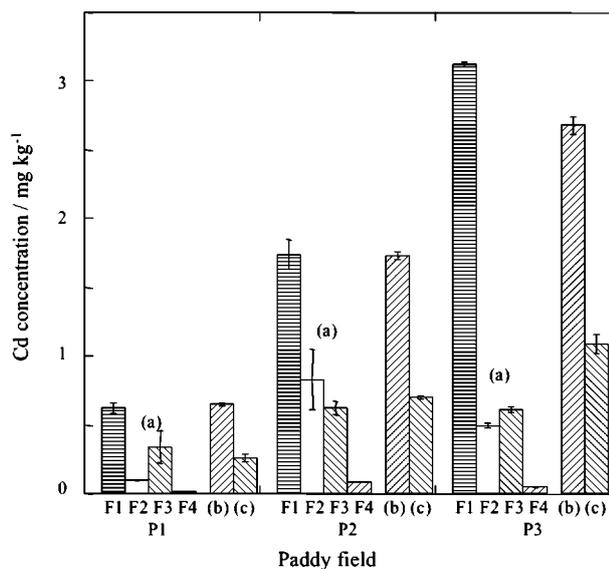


Fig. 1 Cadmium concentrations in soils for P1, P2 and P3 extracted by: (a) Tessier's method ($n = 3$ for P1 and P2, $n = 4$ for P3), (b) $0.1 \text{ mol dm}^{-3} \text{ CaCl}_2$ ($n = 5$ for P1, $n = 4$ for P2, $n = 3$ for P3), and (c) $0.025 \text{ mol dm}^{-3} \text{ CaCl}_2$ ($n = 4$ for P1 and P2, $n = 7$ for P3). Data are means \pm SD.

sieve. The soil pH in the soil (20.0 g)/water (50.0 cm^3) system was 5.1 for P1, 5.8 for P2, or 5.7 for P3.

The contents of cadmium in the soil were measured according to sequential extraction reported by Tessier *et al.*⁹ The total cadmium concentration was determined using a method reported by Asami *et al.*¹⁴ For insolubilization measurements of cadmium, a sample tube (glass tube of 100 cm^3 for shaking without soil, polypropylene tube of 250 cm^3 for that with soil) containing an aqueous solution (50 cm^3), the soil (0 or 10.0 g), and the iron powder (0, 0.10, 0.50 g) was shaken at 200 rpm (Yamato Scientific, MK161) (25°C). The sample was passed through a filter paper and a membrane filter (Millipore Millex-HN, pore size = 0.45 μm). The cadmium (228.802 nm) and iron (239.562 nm) concentrations in solution were determined by inductively coupled plasma atomic emission spectrometry (Shimadzu, ICPS-8100).

The surface area of iron powder was analyzed by a surface area and pore size analyzer (Coulter, SA-3100). The cadmium concentration in brown rice was determined on the basis of Ordinance No. 47 of 1971, Ministry of Agriculture and Forestry, Japan.

Results and Discussion

Insolubilization in soil samples

The insolubilization of cadmium was demonstrated using soil samples of naturally cadmium-contaminated paddy fields. The total cadmium concentrations in the soils for P1, P2, and P3 were 1.20 (mean) \pm 0.04 (standard deviation, SD), 3.36 ± 0.05 , and $4.09 \pm 0.08 \text{ mg kg}^{-1}$ (number of experiments, $n = 3$), respectively. By sequential extraction based on Tessier's method,⁹ the concentrations of cadmium in the soil as an exchangeable form (F1), that bound to carbonates (F2), that bound to iron and manganese oxides (F3), and that bound to organic matter (F4) were determined (Fig. 1). The cadmium concentration in the residual (F5), estimated from the total cadmium concentration in the soil, was smaller than 0.1 mg kg^{-1} .

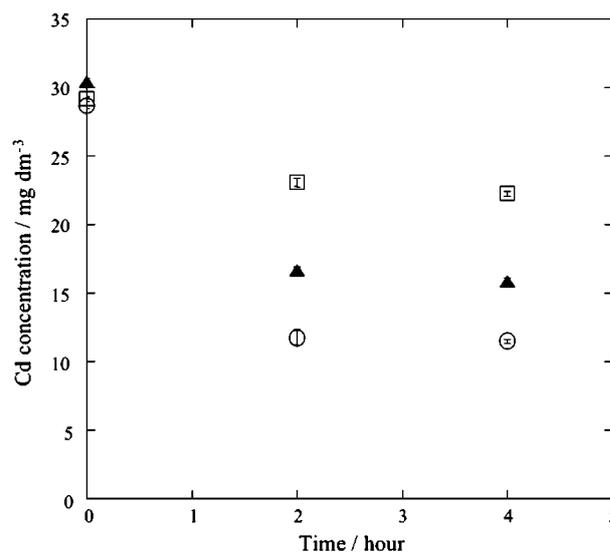


Fig. 2 Time dependence of the cadmium concentration in aqueous solutions of 0 (\square), 0.025 (\blacktriangle), and $0.1 \text{ mol dm}^{-3} \text{ CaCl}_2$ (\circ) in the presence of iron powder. Data are means \pm SD ($n = 3$).

In these soils, F1 was the main component, and was relatively soluble cadmium. We consider that the extraction of F1 and the successive insolubilization of F1 are indispensable.

To efficiently extract cadmium from soil, calcium chloride was used in the present system, since calcium chloride of low concentration is not harmful for the environment and for the growth of rice plants.^{2,3} The cadmium concentration extracted from soil into the water phase for 48 h (C_s) was measured in the soil (10.0 g)/ CaCl_2 solution (50 cm^3) system (Fig. 1). The calcium ion is expected to exchange with H^+ , Cd^{2+} and so forth adsorbed on the soil through cation exchange. A cation, such as H^+ , can also extract the cadmium in soil.² Furthermore, cadmium-chloride complex formation proceeds in the water phase by highly concentrated Cl^- . The logarithmic complex formation constant for $[\text{CdCl}]^+$ has been reported to be 2.0.¹⁵ Under the present experimental conditions, the contribution of $[\text{CdCl}]^+$ is significant. A relatively soluble cadmium, such as F1, is extracted into the water phase by CaCl_2 . Actually, C_s at $0.1 \text{ mol dm}^{-3} \text{ CaCl}_2$ agreed well with the cadmium concentration for F1 (Fig. 1).

When iron powder of 0.50 g was added to a soil (10.0 g)/ CaCl_2 solution (0.025 or 0.1 mol dm^{-3} , 50 cm^3) system, the cadmium concentration in the water phase was smaller than 0.01 mg dm^{-3} . Since $[\text{CdCl}]^+$ and Cd^{2+} are easily reduced to Cd using iron powder, cadmium in the water phase could almost be removed. A metal ion such as Zn^{2+} is frequently removed from an aqueous solution with an iron powder, as adsorption and coprecipitation with precipitated iron oxides.¹⁰ The cadmium ions may be removed by such coprecipitation in the presence of the iron powder. As a separate experiment, when an aqueous $\text{Cd}(\text{NO}_3)_2$ solution (27.1 mg dm^{-3} , 50 cm^3 , pH = 5.5) containing the iron powder (0.10 g) was shaken (6 h), the cadmium concentration in water decreased to 21 ± 2 (SD) mg dm^{-3} . Then, by the addition of $\text{Cu}(\text{NO}_3)_2$ (16.6 mg dm^{-3}), the cadmium and copper concentrations were changed to 27.2 ± 0.5 (SD) and $0.2 \pm 0.2 \text{ mg dm}^{-3}$ ($n = 3$, pH = 4.9 ± 0.2 (SD)), respectively (2 h). This result suggests that Cd on the iron powder is oxidized to Cd^{2+} by the redox reaction with Cu^{2+} . Therefore, the main reaction between the iron and the cadmium ions will be

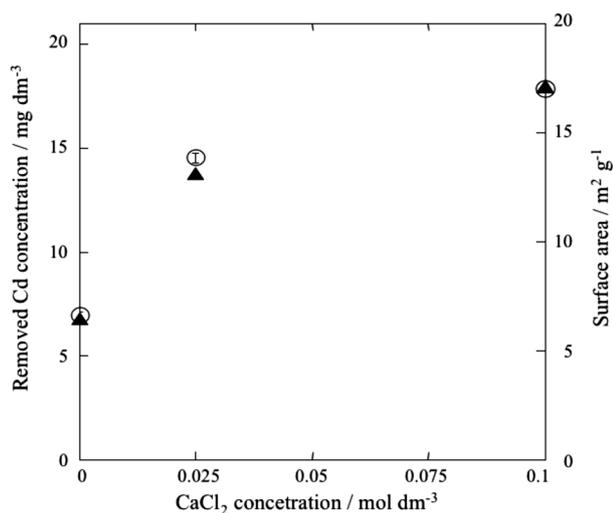


Fig. 3 Cadmium concentration removed in the aqueous solution (○) and surface area of iron powder (▲) at 4 h for 0, 0.025, and 0.1 mol dm⁻³ CaCl₂. Data of cadmium concentration are means ± SD ($n = 3$).

the redox reaction.

CaCl₂ effect on the redox reaction of iron powder

The calcium chloride concentration dependence of cadmium insolubilization with the iron powder (0.10 g) was analyzed in an aqueous Cd(NO₃)₂ solution at pH = 5.5 (50 cm³) in the absence of soil. Figure 2 shows the time dependence of the cadmium concentration in the aqueous CaCl₂ solution in the presence of iron powder. The cadmium concentration in the aqueous solution significantly decreased with increasing CaCl₂ concentration. The cadmium concentration removed from the aqueous solution at 0.1 mol dm⁻³ CaCl₂ was 2.5-times that without CaCl₂ (Fig. 3).

The surface area of the iron powder (BET surface area, correlation coefficient > 0.999) after addition into the solution (4 h) increased with the increasing CaCl₂ concentration (Fig. 3). The total pore volume and the pore volume with the pore diameter smaller than 80 nm of the iron powder after addition into the solution (4 h) were 0.028 and 0.025 cm³ g⁻¹ in the absence of CaCl₂, 0.129 and 0.106 cm³ g⁻¹ at 0.025 mol dm⁻³ CaCl₂, and 0.167 and 0.148 cm³ g⁻¹ at 0.1 mol dm⁻³ CaCl₂, respectively, indicating that the iron powder becomes porous due to CaCl₂. It is noteworthy that the increasing ratio of the surface area is in good agreement with that of the cadmium concentration removed from the aqueous solution (4 h) (Fig. 3). Therefore, since the surface area of the iron powder is directly proportional to the amount of cadmium removed from the solution, the cadmium insolubilization is influenced efficiently by the CaCl₂ concentration. The corrosion of iron has been reported to be induced by Cl⁻, which forms soluble complexes with iron leading to pit growth.¹⁶ In the present system, the redox reaction between the iron and the cadmium ions will proceed efficiently by such a complex formation of iron with Cl⁻ and pit growth.

Insolubilization mechanism in the soil system

To quantitatively analyze the insolubilization mechanism, we determined the cadmium concentration adsorbed on the iron powder. In this case, iron powder of 0.10 g was added into the soil of 10.0 g for P3 and an aqueous 0.025 mol dm⁻³ CaCl₂ solution of 50 cm³. After shaking the sample for 48 h (200 rpm,

Table 1 w_{Fe} , w_{Cd} , and estimated amount of cadmium insolubilized on iron powder (0.10 g) in soil samples (a, b, and c) of P3

Sample	w_{Fe}/mg	w_{Cd}/mg	Insolubilized Cd/mg
a	23.6	0.0078	0.033
b	31.4	0.011	0.035
c	26.6	0.0091	0.034

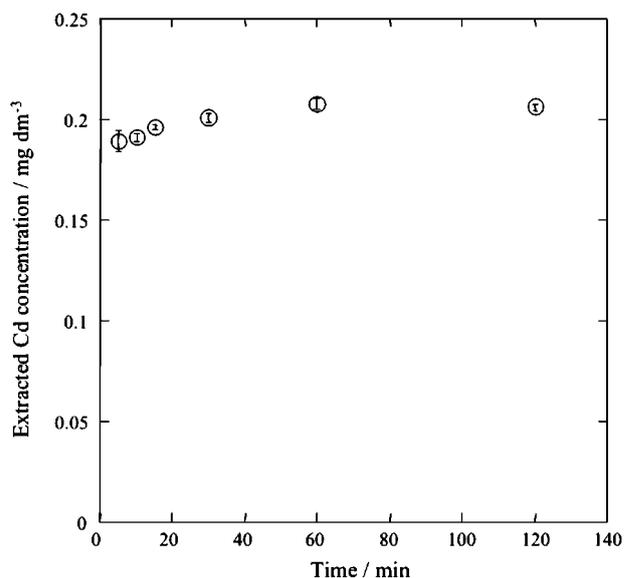


Fig. 4 Time dependence of the cadmium concentration in the water phase for the soil of P3 at 0.025 mol dm⁻³ CaCl₂. Data are means ± SD ($n = 3$ ($n = 2$ for 30 min)).

25°C), the iron powder was partially recovered from the sample by a magnet. After drying in a vacuum for 2 days, the iron powder was dissolved in hydrochloric acid of 2.5 cm³ for 15 min, and the cadmium and iron concentrations in the solution were determined. The residue of the iron powder was completely dissolved by a hydrochloric acid and nitric acid solution (1:1) of 5.0 cm³. Cadmium could not be detected in the residue. The amount of iron powder recovered from the sample (w_{Fe}) was assumed to be equal to that of the iron determined by the iron concentration in the HCl and HCl/HNO₃ solutions (Table 1). The ratio of w_{Fe} to 100 mg (iron powder added into the sample) ($w_{Fe}/100$) was ~0.3. Although the amount of cadmium adsorbed on the iron powder (w_{Cd}) was influenced by the sample, the amount of cadmium insolubilized on the iron powder of 100 mg can be estimated to be 0.034 mg from 100 w_{Cd}/w_{Fe} , independent of the sample (Table 1). In the absence of soil, an analogous experiment was demonstrated using an aqueous Cd(NO₃)₂ solution (cadmium concentration, 5.00 mg dm⁻³) at pH = 5.5 (50 cm³) containing 0.025 mol dm⁻³ CaCl₂ ($n = 2$). After shaking the sample (4 h), the iron powder was almost recovered from the sample by a magnet ($w_{Fe}/100 = 0.99 \pm 0.03$ (SD)). In this case, w_{Cd} was determined to be 0.236 ± 0.005 (SD) mg, the value of which agreed well with the amount of cadmium existing in the solution (0.250 mg). We consider that the cadmium ions in water can almost be insolubilized on the iron powder.

Figure 4 shows the extraction rate of cadmium from the soil of P3 (10.0 g) into the aqueous 0.025 mol dm⁻³ CaCl₂ solution (50 cm³). The concentration of cadmium extracted into the

water phase was saturated to 0.21 mg dm⁻³ at ~60 min; namely, 0.010 mg cadmium is extracted from 10.0 g soil (1.0 mg kg⁻¹, as shown in Fig. 1), and 80% of the saturated value was extracted during 5 min. In the presence of iron powder, however, cadmium deposition of 0.034 mg greater than 0.010 mg was estimated from an analysis of the iron powder (Table 1), indicating that F1 is almost extracted even in the 0.025 mol dm⁻³ CaCl₂ system (Fig. 1).

From these results, we propose the insolubilization mechanism of cadmium in the paddy soil system. Using CaCl₂ and the iron powder, cadmium of F1 in paddy soil is quickly extracted from the soil into the water phase as [CdCl]⁺ or Cd²⁺. The extracted cadmium is deposited on the iron powder because of the redox reaction with Fe. Since the cadmium concentration in the water phase decreases owing to cadmium deposition on the iron powder, further extraction of cadmium from the soil proceeds. Moreover, the increase in the surface area of the iron powder by CaCl₂ facilitates cadmium deposition.

Insolubilization in actual paddy field

In the cadmium-contaminated paddy field of P1, the insolubilization of cadmium by the present technique was demonstrated. Before 1 week of rice planting (rice variety, *Koshihikari*), iron powder of 74 or 1000 kg was dispersed in a 49 m² area (P1-1) or a 660 m² area (P1-2) of the paddy field, respectively. The iron powder could be homogeneously contained in the soil by soil puddling. As a control, the iron powder was not dispersed in a 660 m² area (P1-3) of the paddy field. Because the absorption of cadmium into the rice will proceed after ear emergence, calcium chloride of 27 kg was added in P1-1 23 days before harvesting (before ear emergence), and P1-1, P1-2 and P1-3 were filled with water within 1 week. As a water depth of 0.15 m, CaCl₂·2H₂O of 0.55 kg/m² (P1-1) corresponds to CaCl₂ of 0.025 mol dm⁻³ in the water phase. The cadmium concentrations in brown rice harvested from P1-1, P1-2, and P1-3 were 0.18, 0.27, and 0.27 mg kg⁻¹, respectively. The cadmium concentration in the rice for P1-2 was as high as that for P1-3, indicating that the cadmium in the soil cannot be insolubilized on the iron powder without the extraction of cadmium by CaCl₂ (P1-2). Using CaCl₂ and the iron powder, the removal efficiency of cadmium from the rice was 0.33 (= (0.27 - 0.18)/0.27). The soil could not be stirred after the addition of CaCl₂, so that the extraction of cadmium from the soil into the water phase would be limited. Furthermore, the activity of the iron powder would be decreased because of the long period between the dispersion of the iron powder and the addition of CaCl₂. Therefore, the cadmium insolubilization is expected to proceed efficiently by the addition of CaCl₂ and the soil puddling before rice planting. Nonetheless, the cadmium concentration absorbed in the rice was lowered by the present technique. Moreover, the cadmium concentration in new brown rice harvested from P1-1 after 2 years was 0.16 mg kg⁻¹, indicating that the cadmium deposited on the iron powder would not dissolve in P1-1 during 2 years.

Conclusions

Cadmium insolubilization in paddy-field soils could be

successfully demonstrated using atomized iron powder and CaCl₂. Cadmium as F1 could be extracted from paddy soil into the water phase by CaCl₂. The extracted cadmium was efficiently insolubilized because the surface area of the iron powder increased by the CaCl₂ effect. We consider that the present technique has sufficient potential to decrease the cadmium concentration in rice. Further studies on cadmium insolubilization at actual cadmium-contaminated paddy fields in several prefectures in Japan are now in progress in our laboratory.

Acknowledgements

The authors are grateful to Chemical Analysis Division, Research Facility Center for Science and Technology, University of Tsukuba, for allowing us to use the electron probe microanalyzer (JEOL, JXA-8530F), ICP atomic emission spectrometer (Shimadzu, ICPS-8100), and surface area and pore size analyzer (Coulter, SA-3100), and to Environmental Research Center Co., Ltd., in Japan for the quantitative analysis of cadmium concentration in brown rice.

References

1. T. Arao, S. Ishikawa, M. Murakami, K. Abe, Y. Maejima, and T. Makino, *Paddy Water Environ.*, **2010**, *8*, 247.
2. T. Makino, K. Sugahara, Y. Sakurai, H. Takano, T. Kamiya, K. Sasaki, T. Itou, and N. Sekiya, *Environ. Pollut.*, **2006**, *144*, 2.
3. T. Hayashi, T. Kida, M. Nanzyo, T. Takahashi, M. Honna, Y. Aikawa, and K. Yoshihara, *Soil Sci. Plant Nutr.*, **2007**, *53*, 720.
4. T. Makino, H. Takano, T. Kamiya, T. Itou, N. Sekiya, M. Inahara, and Y. Sakurai, *Chemosphere*, **2008**, *70*, 1035.
5. L. H. Wu, Y. M. Luo, P. Christie, and M. H. Wong, *Chemosphere*, **2003**, *50*, 819.
6. G. S. R. Krishnamurti, G. Cieslinski, P. M. Huang, and K. C. J. Van Rees, *J. Environ. Qual.*, **1997**, *26*, 271.
7. T. Makino, T. Kamiya, H. Takano, T. Itou, N. Sekiya, K. Sasaki, Y. Maejima, and K. Sugahara, *Environ. Pollut.*, **2007**, *147*, 112.
8. T. Watanabe, Y. Murata, T. Nakamura, Y. Sakai, and M. Osaki, *J. Plant Nutr.*, **2009**, *32*, 1164.
9. A. Tessier, P. G. C. Campbell, and M. Bisson, *Anal. Chem.*, **1979**, *51*, 844.
10. R. Rangsvivek and M. R. Jekel, *Water Res.*, **2005**, *39*, 4153.
11. J. Kumpiene, S. Ore, G. Renella, M. Mench, A. Lagerkvist, and C. Maurice, *Environ. Pollut.*, **2006**, *144*, 62.
12. H. Nakamaru, T. Ono, Y. Kato, and K. Ogura, *J. Japan Inst. Metals*, **2006**, *70*, 809.
13. T. Fujiura, S. Furuta, K. Haraguchi, and Y. Yakou, *Kobe Steel Engineering Reports*, **2009**, *59*, 25.
14. T. Asami and K. Kato, *J. Sci. Soil Manure*, **1977**, *48*, 335.
15. W. L. Lindsay, *“Chemical Equilibria in Soils”*, **1979**, Wiley-Interscience, New York.
16. M. F. Montemor, A. M. P. Simoes, and M. G. S. Ferreira, *Cem. Concr. Compos.*, **2003**, *25*, 491.