



Elution and decomposition of cyanide in soil contaminated with various cyanocompounds

Mitsuo Matsumura^{a,1}, Toshinori Kojima^{b,*}

^a *Naito Kankyou-Kanri Co., 2051-2 Saitama-shi, Saitama, 336-0015, Japan*

^b *Department of Applied Chemistry, Faculty of Engineering, Seikei University, 3-1 Kichijoji-Kitamachi 3-Chome, Musashino-shi, Tokyo 180-8633, Japan*

Received 19 March 2002; received in revised form 15 August 2002; accepted 16 August 2002

Abstract

Standard soil samples contaminated with various standard cyanocompounds were prepared. Column elution experiments and analyses were conducted. Compounds with an easy capacity for dissociation to ions, such as KCN and potassium hexacyanoferrate(III), were found to be eluted by forming free cyanide even in fresh water. Hexacyanoferrate(II) salts, such as potassium hexacyanoferrate(II) and iron(III) hexacyanoferrate(II), were found not to be dissociated in water, but were dissociated and diffused under alkaline conditions (pH >13). Hexacyanoferrate(II) ion was found to be more easily dissociated in water with a higher pH.

Column tests as above were also conducted for soil samples taken from a former paint ink factory using iron(III) hexacyanoferrate(II), cyanogen chloride, potassium cyanate, copper cyanide, as well as potassium cyanide, as raw materials. It was demonstrated that iron(III) hexacyanoferrate(II) was dissociated and eluted under alkaline conditions. The elution rate was reduced when the contaminated soil was sandwiched with standard soil layers.

Further, it was found that the $\text{Fe}(\text{CN})_6^{4-}$ ion eluted with NaOH from hexacyanoferrate acid in soil, were easily decomposed into cyanic acid or other byproducts by UV with the addition of ozone and H_2O_2 .

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Soil; Cyanide; Hexacyanoferrate; UV; Oxidative decomposition

* Corresponding author. Tel.: +81-422-37-3750; fax: +81-422-37-3871.

E-mail addresses: mitsuo_matsumura@knights.co.jp (M. Matsumura), kojima@ch.seikei.ac.jp (T. Kojima).

¹ Tel.: +81-48-887-2590; fax: +81-48-886-2817.

1. Introduction

Cyanogen compounds are high toxicity materials, producing free cyanide ions that combine with cytochrome respiratory enzymes, including three-valent iron, and inactivate intracellular oxidase in the human body. Therefore, attempts have been made to substitute CN compounds. For example, methylenbromide compounds have recently been used as fumigants. But alternatives for CN compounds are rarely found or synthesized in many industries, and CN compounds are still used, not only in plating processes, mining and in metallurgical industries, but also as raw materials for fluorescent dyes in chemical industries. Cyanocompounds that have been improperly used, stored or discarded by industrial activities are a worrying problem as they can be leached by rainwater, to diffuse and to cause groundwater contamination. This kind of cyanide compound contamination is often a problem at former industrial plant sites. For example, heavy contamination has been reported in soil around plants that produced and supplied fuel gas made from coal and petroleum between 1800 and 1950, and around electric plating plants in The Netherlands [1–4]. As the free cyanide produced from potassium cyanide with a high dissociation constant has a high mobility and volatility, its toxicity is high and causes serious problems.

On sites of coal gasification plants, iron cyanide complexes have been discarded. Hexacyanoferrate, a chemical compound of cyanide with iron, is decomposed by microorganisms [5], and hexacyanoferrates such as $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$, have been evaluated as kinetically stable compounds [6], so cyanide or cyanometal compounds which can cause soil and groundwater pollution are usually treated to make an insoluble iron(III) hexacyanoferrate(II) by the addition of the three-valent iron salt [7]. However, iron(III) hexacyanoferrate(II) in soil and groundwater has been reported to be gradually decomposed under solar light or ultraviolet rays to produce free cyanide ions [8,9]. Furthermore, iron cyanide solids precipitated in the presence of excess dissolved iron was reported to show higher solubility than pure-phase iron cyanides [10]. Therefore, the possibility of the dissolution of hexacyanoferrates into groundwater should be evaluated to consider future risks, this even though it is generally regarded as being kinetically stable. Periods for their complete decomposition in soil should also be estimated from their stability constants and photolysis decomposition rates.

In Japan, the degree of the contamination with cyanocompounds is determined as follows. A soil sample is mixed with phosphoric acid to make pH lower than 2, distilled with ethylenediaminetetraacetic acid disodium salt and released hydrogen cyanide is recovered with sodium hydroxide solution to analyze by absorptiometry [7]. By the above Japanese standard method, it is not possible to assess the soil contaminated with stable cyanocompounds such as iron(III) hexacyanoferrate(II). Therefore, no site contaminated with iron(III) hexacyanoferrate(II) has so far been reported in Japan.

In the present study, we conducted column elution experiments and analyses using standard soil samples contaminated with various cyanocompounds, and with soil actually contaminated with iron(III) hexacyanoferrate(II) in Japan. Further, we discuss the method for hexacyanoferrate decomposition by UV rays [11] with the addition of ozone and H_2O_2 . Finally, the possibility of the application of the present findings to the remediation of the contaminated soil was discussed.

Table 1
Chemical composition of standard soil

	Content (wt.% dry)
Moisture	21
Ig, loss (600 °C)	11
T-CN	<0.5
T-Hg	<0.3
Cd	<0.9
Pb	<60
Cu	49
Zn	90
Fe	70100
Mn	954
As	11
T-Cr	15

2. Experimental

2.1. Reagents and standard soil

Commercial reagent grade chemicals of potassium cyanide, potassium hexacyanoferrate(II), potassium hexacyanoferrate(III) and iron(III) hexacyanoferrate(II), and distilled water were used in the present study. The standard soil, air-dried under 2 mm mesh, used in the present study was commercially available soil suitable for growing grass. [Tables 1 and 2](#) show the chemical composition of and composition of elute from the standard soil (standard soil:distilled water = 1:10). For homogeneity, it was pulverized with an agate mortar.

Table 2
Composition of elute from standard soil (standard soil:water = 1:10)

	Content (mg dm ⁻³)
T-CN	<0.1
T-Hg	<0.0005
Cd	0.001
Pb	<0.001
Cr ⁶⁺	0.005
As	<0.001
Se	<0.001
B	<0.1
F ⁻	0.1
Cl ⁻	4.1
Br ⁻	0.1
SO ₄ ²⁻	0.7
NO ₂ ⁻	0.1
NO ₃ ⁻	13
PO ₄ ³⁻	0.5
pH	5.5 (26 °C)

2.2. Column test with standard reagents for contaminated soil model

Distilled water with 2.505 g of dissolved potassium cyanide was added to 100 g of the standard soil pretreated as above. After the sample had completely dried, a small amount of water was added and the sample was agitated and dried again. After this operation was repeated three times, the sample was left to be completely dried for 28 days at room temperature. The cured sample was then pulverized and dried under atmospheric conditions and sieved to 2 mm or less. A pretreated sample of 10 g was packed with quartz wool in a 40 mm long 15 mm diameter glass column. The procedure as described above was also carried out for potassium hexacyanoferrate(II) (2.110 g), potassium hexacyanoferrate(III) (2.360 g) and iron(III) hexacyanoferrate(II) (1.835 g). Distilled water, 0.1, and 0.5 mol/dm³ sodium hydroxide solutions were used as eluents. The eluents were injected with a micro pump so that the water level of the eluent would always be 2 cm above the standard soil sample surface in the column. The tip of the introduction tube was kept under the water level of the eluent. The flow rate of the effluent was adjusted with a column cock to 100 ml/30 min (± 5 min). The experiments were conducted over periods of several hours to 1 day. Total cyanide concentration and pH of every 100 ml effluent sample taken were measured.

2.3. Column test for soil samples from contaminated site

The contaminated soil samples A–D used in the present study were taken from a former paint ink factory using iron(III) hexacyanoferrate(II), cyanogen chloride, potassium cyanate, copper cyanide, as well as potassium cyanide, as raw materials, though the authors were not informed of the detail differences among the sites. The same column tests were also carried out for samples A–D as above for soil sample contaminated with a standard iron cyanocomplex reagent. Flow experiments for a column with triple layers were also conducted as follows. First, the column was filled with 30 g of the standard soil sample as the lowest layer, next 10 g of the soil sample from the site contaminated by iron(III) hexacyanoferrate(II) was added as the middle layer, and then 20 g of the standard soil sample was added as the top layer. The cyanogen fraction was examined using the 0.1 mol/dm³ sodium hydroxide solution.

2.4. Quantitative analysis

Quantitative analysis for total cyan concentration was conducted basically according to Japan Industrial Standard (JIS) K0102 [12]. The 100 ml of effluent was neutralized with a phosphoric acid solution, and then a further excess of phosphoric acid, 10 ml, was added. Then 0.05 mol/dm³ potassium permanganate solution was added as an oxidizing agent along with 10% EDTA solution; it was then diluted with water to 250 ml. The hydrogen cyanide was separated by distillation, and recovered in a trap filled with 20 ml of 2% sodium hydroxide solution. The heating temperature was adjusted beforehand in order that the distillatory solution quantity became 100 ml after a distillation time of 40 min. Preparative isolation and dilution were carried out after the distillatory solution was well mixed, and adsorption spectrophotometry by the 4-prigineacid-pirazorone method was carried out for quantitative analysis. The same analyses were also conducted for the remaining contaminated

soil samples, by adding 100 ml of distilled water to 10 g of the soil. The concentration of total cyanide ions in the decomposition liquid of hexacyanoferrate(II) and (III) ions was measured directly by ion chromatography.

2.5. Decomposition of cyanide and hexacyanoferrate(II) ions

The samples employed for the decomposition experiments were potassium hexacyanoferrate(II) and potassium cyanide. A 1.1775 g of potassium hexacyanoferrate(II) was weighed, dissolved in distilled water and then diluted with water to 200 ml. A total of 20 ml of this solution was collected and mixed with 10 ml of 1.0 mol/dm³ sodium hydroxide solution. In an experiment, 10 ml of 30% hydrogen peroxide solution was added. Then it was diluted to 350 ml with distilled water.

In case of potassium cyanide, 1.0914 g was weighed, dissolved in 25 ml of 1.0 mol/dm³ sodium hydroxide solution and diluted to 200 ml with distilled water. Then, 20 ml of the solution was collected and diluted to 350 ml with distilled water.

The UV radiation set-up (internal irradiation type with 100 V AC/400 W stabilized power, main peaks are 184.9 and 253.7 nm) employed is shown in Fig. 1. The samples were placed in an internal cylinder and were photo-decomposed by irradiating with ultraviolet rays for 120–240 min, under an ozone flow at 2 g/h (total flow rate; 120 l/h). Before and after photodecomposition, the concentration of total cyanide and pH were measured.

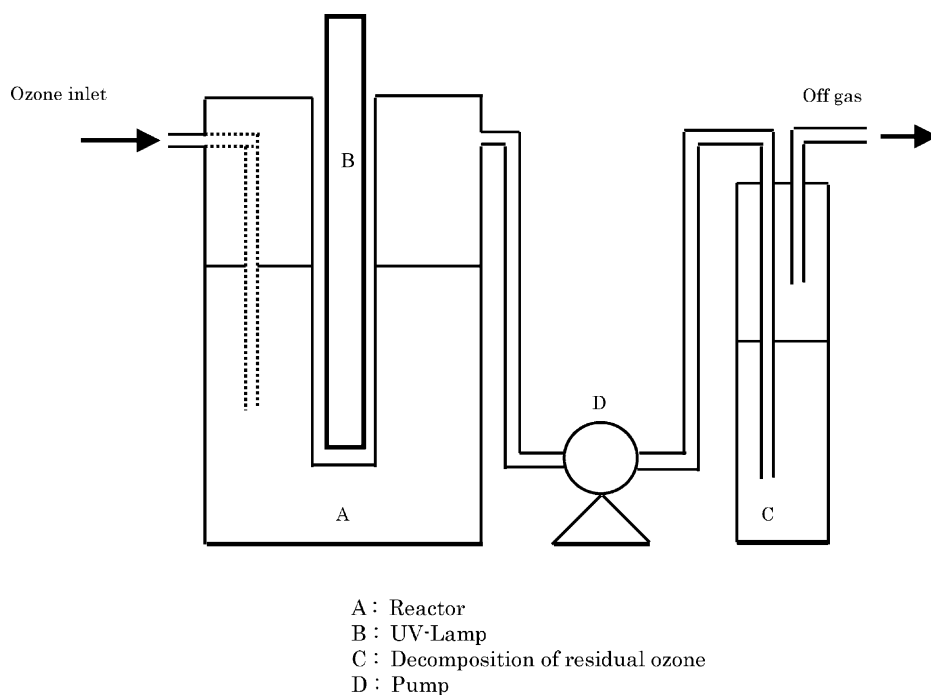


Fig. 1. Experimental setup: (A) reactor; (B) UV-lamp; (C) decomposition of residual ozone; (D) pump.

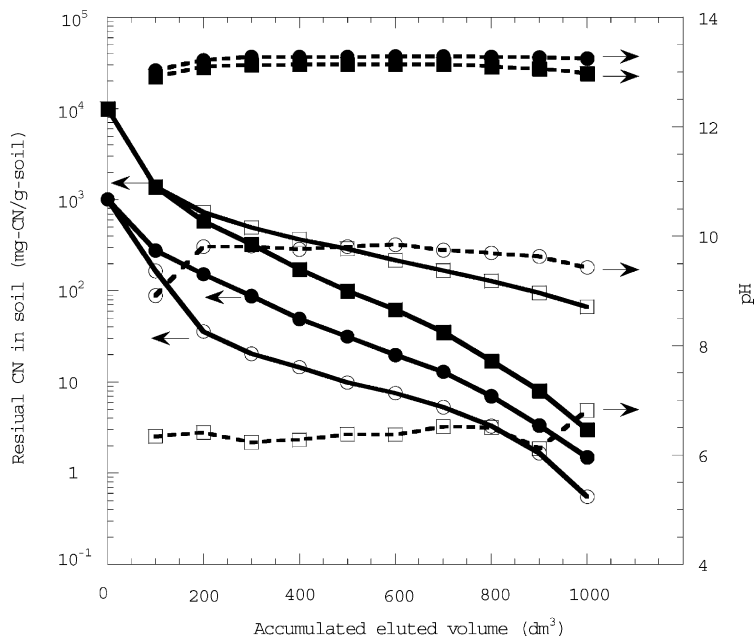


Fig. 2. Column elution test for KCN and $K_3Fe(CN)_6$ contaminated soil: (—) residual CN; (···) pH; eluted with 0.1N NaOH ((●) KOH, (○) KOH); eluted with H_2O ((■) $K_3Fe(CN)_6$, (□) $K_3Fe(CN)_6$).

3. Results and discussion

3.1. Column test for model of standard soil contaminated with standard reagents

The results for a column elution test for standard soil contaminated with cyanocompounds are shown in Figs. 2 and 3. Cyanogen amounts remaining in the potassium cyanide mixed soil were 0.0 mg (nil) in the cases in which distilled water and the 0.1 mol/dm³ sodium hydroxide solution were used as eluents. The potassium cyanide in the soil was thought to have been dissociated into free cyanide even at low pH.

It was also demonstrated that all of the added cyanogen was eluted from the standard soil mixed with potassium hexacyanoferrate(III) with both the distilled water and the 0.1 mol/dm³ sodium hydroxide solutions, as in the case of potassium cyanide. It is considered that potassium hexacyanoferrate(III) also easily dissociated to cyanoferrate ion with relatively high mobility even at low pH.

On the other hand, in the case of a standard soil contaminated by potassium hexacyanoferrate(II), 40% of the added cyanogen remained in the soil after elution with the distilled water, but all of the added cyanogen was eluted from the soil by the 0.1 mol/dm³ sodium hydroxide solution. It is considered that the potassium hexacyanoferrate(II) was dissociated by the addition of the sodium hydroxide to form hexacyanoferrate(III) ions with high mobility only at high pH.

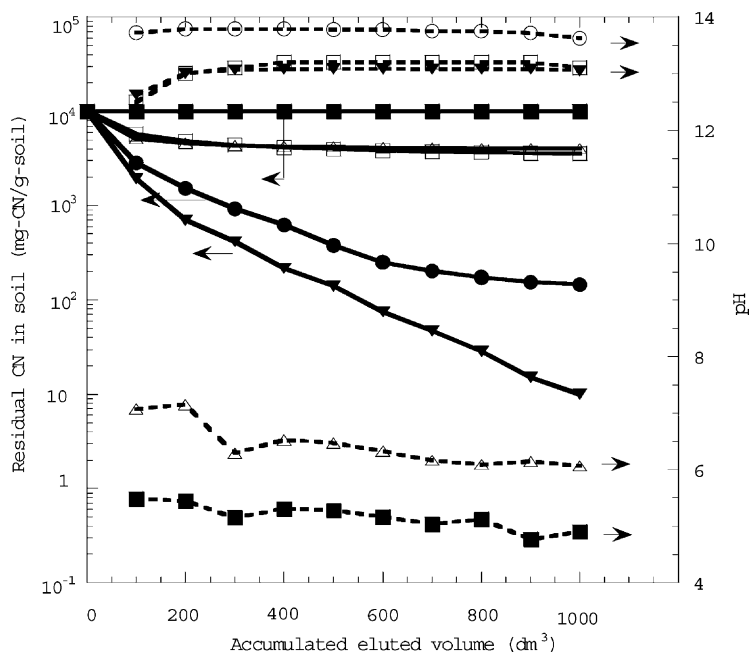


Fig. 3. Column elution test for $K_4Fe(CN)_6$ and $K_4[Fe(CN)_6]_3$ contaminated soil: (—) residual CN; (···) pH; eluted with 0.1, 0.5N NaOH ((▼) 0.1N $K_4Fe(CN)_6$, (■) 0.1N $Fe_4[Fe(CN)_6]_3$, (●) 0.5N $Fe_4[Fe(CN)_6]_3$); eluted with H_2O ((□) $Fe_4[Fe(CN)_6]_3$, (○) $Fe_4[Fe(CN)_6]_3$, (△) $K_4Fe(CN)_6$).

In the case of a standard soil added with iron(III) hexacyanoferrate(II), 99.9% of the cyanogen remained in the soil after elution with the distilled water, but 98.5% of the added cyanogen was eluted from the soil by elution with the 0.1 mol/dm^3 sodium hydroxide solution, i.e. at high pH.

To summarize, compounds with a high dissociation into ions capacity, such as KCN and potassium hexacyanoferrate(III), were found to be eluted even in fresh water. However, hexacyanoferrate(II) salt compounds such as potassium hexacyanoferrate(II) and iron(III) hexacyanoferrate(II) were found to not dissociate in water, but were dissociated and diffused under alkaline conditions (pH >13).

3.2. Column test for soil samples from a contaminated site

The results of the column elution test of the soil samples from a site actually contaminated by an iron cyanocomplex are shown in Fig. 4. For all contaminated soil samples, the cyanogen fraction remaining, after 1000 ml (100 ml 10 times) of elution with distilled water, was as high as 99%. However, the cyanogen fraction remaining, after 1000 ml elution with 0.1 mol/dm^3 sodium hydroxide solution, was 0.0% for samples A–C, and 24.5% for sample D. In order to elute all of the cyanogen in the sample, a longer elution time and/or the use of a higher concentration of alkali as an eluent seemed to be required. The results

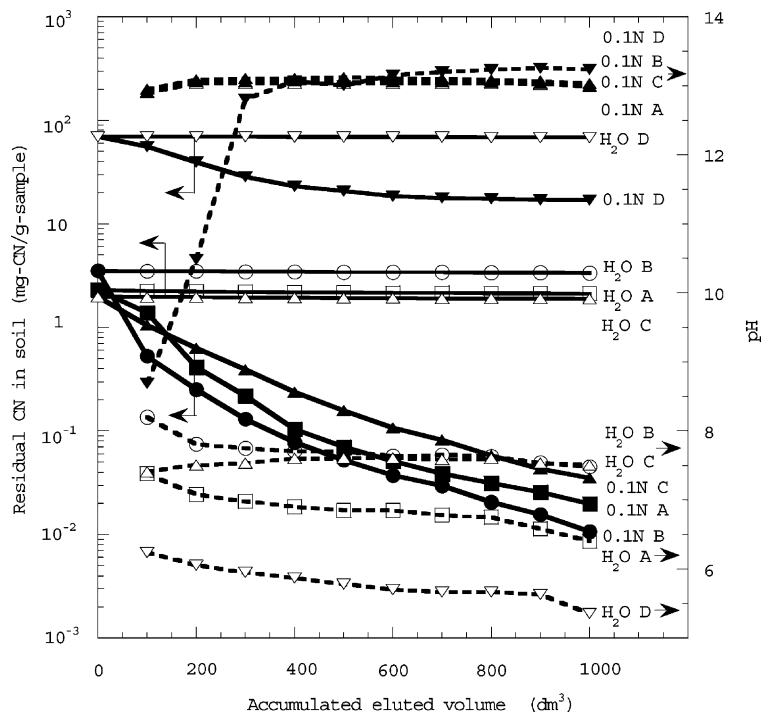


Fig. 4. Column elution test for cyanide contaminated soil-1: (—) residual CN; (---) pH; eluted with 0.1, 0.5N NaOH (■) sample A, (●) sample B, (▲) sample C, (▼) sample D; eluted with H₂O (sample A (○), sample B (△), sample C (▽), sample D).

using 0.5 mol/dm³ sodium hydroxide solution as an eluent, i.e. at high pH, are shown in Fig. 5 and show the recovery rate of cyanogen in the contaminated soil to be about 98% with an elution volume of ten times the 100 ml solution, and 100% for an elution volume of 13 times the 100 ml solution elution. The color of the effluent was blue at the beginning, then tended to fade to yellow from brown with an increase in the elution fraction number using the alkaline eluent. The present results also support the concept that iron(III) hexacyanoferrate(II) is dissociated into the hexacyanoferrate ion by the addition of the sodium hydroxide, i.e. at high pH.

3.3. Flow experiment for a column with triple layers

The results on flow experiment for a column with triple layers, i.e. the soil sample from the site contaminated by iron(III) hexacyanoferrate(II) sandwiched with upper and lower layers of standard soil are shown in Fig. 6. The relations between the accumulated eluted volume, the residual amount of cyanogen in the soil, and its concentration in the eluant are shown in the figure. The dissolution rate was faster and the concentration in the eluant decreased more rapidly for the single layer than that for the triple layer, for the same amount of soil contaminated with iron(III) hexacyanoferrate(II). Therefore, in the case where the high

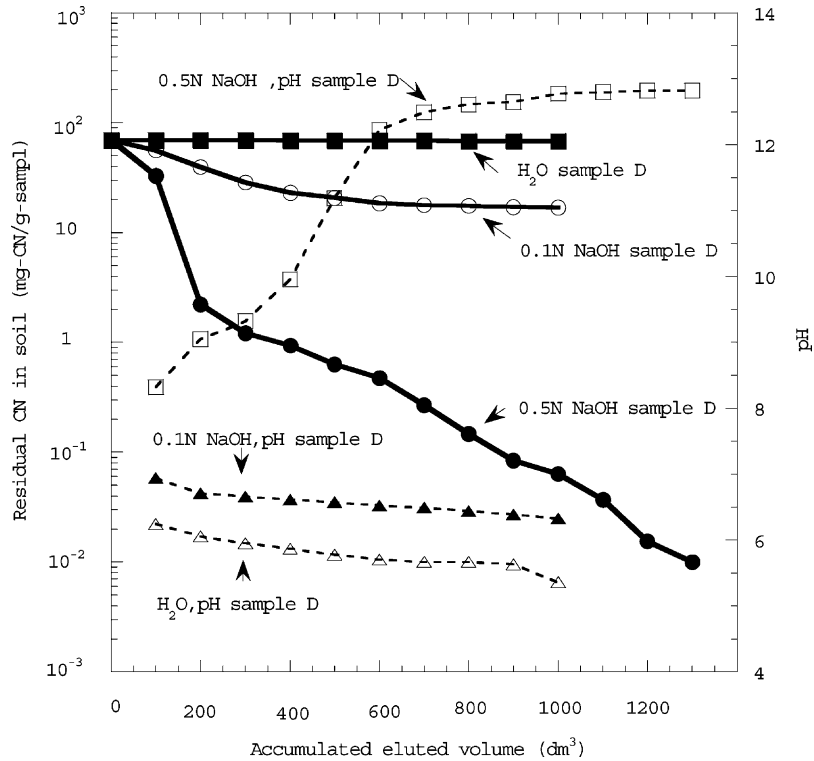


Fig. 5. Column elution test for cyanide contaminated soil-2.

cyanogen concentration is located in the upper part in the soil, only the highly contaminated soil should be recovered from the soil body and separately treated to elute the cyaniferous ion and to efficiently remedy the situation.

3.4. Discussion on the effect of the equilibrium constant on the dissolution rate

Though concentration profiles of cyanogen exist in the actual column, the following simple analyses were conducted to compare elution behavior between various conditions. The simplest assumptions of uniform concentration and equilibrium between soil and eluate in the column lead to the following equations

$$\ln \left(\frac{C}{C_0} \right) = -\frac{kV}{W} \tag{1}$$

from

$$W \, dm = -C \, dV \tag{2}$$

$$C = km \tag{3}$$

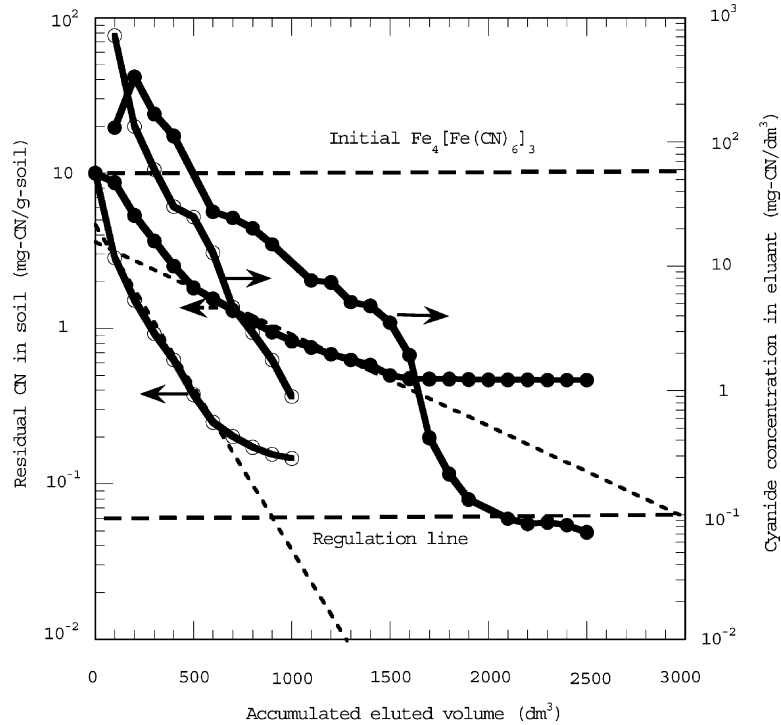


Fig. 6. Column elution test for $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ contaminated soil: (○) single layer, (●) triple layers.

where C ($\text{mg CN}/\text{m}^3$ eluate) is the cyanogen concentration in the eluate, m ($\text{mg CN}/\text{g soil}$) is the cyanogen concentration in the soil, k ($\text{g soil}/\text{m}^3$ eluate) is the apparent distribution coefficient, W (g) is the total soil weight, and V (m^3) is the cumulative amount of eluate. The results of calculations for the column test of standard soil with the addition of a standard chemical reagent solution are shown in Table 3. The distribution coefficient, k , of iron(III) hexacyanoferrate(II) was much lower than those of potassium cyanide, potassium hexacyanoferrate(II), and potassium hexacyanoferrate(III), when water was used as an eluent. However, the distribution coefficient drastically increased when NaOH solution

Table 3
Apparent distribution coefficient, K (kg/m^3)

Reagent	NaOH		
	Distilled water	0.1 mol/dm ³	0.5 mol/dm ³
KCN	56.9	56.9	–
$\text{K}_3\text{Fe}(\text{CN})_6$	29.5	55.9	–
$\text{K}_4\text{Fe}(\text{CN})_6$	0.2	54.0	–
$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	0.0	2.2	30.2

Table 4
Decomposition of free CN and K_4FeCN_6 by UV ray with addition of ozone and H_2O_2

Reagent	Decomposition method	Initial CN (mg/dm ³)	Final CN (mg/dm ³)	Residue CN (wt.%)	Initial pH	Final pH	Reaction time (h)
KCN	UV + O ₃	124.6	0.016	0.013	12.6	12.5	2.0
	UV + O ₃	124.6	0.103	0.083	13.0	13.0	2.0
$K_4Fe(CN)_6$	UV + O ₃	124.6	0.071	0.057	13.0	12.6	4.0
	UV + O ₃ + H ₂ O ₂	124.6	0.025	0.020	13.0	9.4	2.5

was employed as an eluent. When 0.5 mol/dm³ of NaOH was employed as the eluent, the value was comparable to the values for potassium cyanide, potassium hexacyanoferrate(II), and potassium hexacyanoferrate(III) when water or 0.1 mol/dm³ of NaOH was used. It is recommended that the pH of the eluent be more than 13 for soil highly contaminated with iron(III) hexacyanoferrate(II).

3.5. Oxidative decomposition of hexacyanoferrate(II) ion by UV rays

The results on chemical decomposition of the eluted hexacyanoferrate(II) with ozone and ultraviolet rays are shown in Table 4 comparing the effects of adding hydrogen peroxide. The release of free cyanogen was prevented by the addition of 1.0 mol/dm³ sodium hydroxide solution.

It was found that cyanogen in potassium cyanide was decomposed by 99.99%, with only ozone and UV for 2 h. However, in the case of potassium hexacyanoferrate(II), the residual cyanogen after decomposition with ozone and UV rays for 2 h was more than 0.103 mg/dm³ (0.08%), and that after 4 h it was still more than 0.071 mg/dm³ (0.05%). By adding hydrogen peroxide, the value was reduced to 0.025 mg/dm³ (0.02%) after 2.5 h, and the pH of the residue of 9.4 supports its decomposition to acids other than cyanogen.

From these results, it was suggested that potassium cyanide could be decomposed by only using UV rays with ozone in the oxidation, and that the addition of hydrogen peroxide could promote the oxidation reaction of potassium hexacyanoferrate(II). Hexacyanoferrate salt, as $Fe(CN)_6^{4-}$ in the eluent from soil contaminated by a sodium hydroxide solution, was also found to be decomposed using hydrogen peroxide in addition to ozone with UV rays.

4. Conclusion

Compounds with the capacity for easy dissociation to ions, such as KCN and potassium hexacyanoferrate(III), were found to be eluted by forming free cyanide even in a medium of fresh water. However, hexacyanoferrate(II) salts such as potassium hexacyanoferrate(II) and iron(III) hexacyanoferrate(II) were found to not dissociate in water, but were dissociated and diffused under alkaline conditions (pH > 13). The above tendency was also demonstrated for in.

It was found that the $Fe(CN)_6^{4-}$ ion is eluted by NaOH from the soil samples from a site contaminated by iron(III) hexacyanoferrate(II). The elution rate of Iron(III) hexacyanoferrate(II) was reduced when the contaminated soil was sandwiched with standard soil layers.

It was also demonstrated that the eluted ion was more easily decomposed into other acids than cyanogen by UV rays with ozone and the addition of H₂O₂.

References

- [1] J.C.L. Meeussen, M.G. Keizer, W.H. Riemsdijk, in: F. Arendt, M. Hinesveld, W.J. Van den Brink (Eds.), *Proceedings of the Third International Tfk/TNO Conference on Contaminated Soil*, Karlsruhe, vol. 1, Kluwer Academic Publisher, Dordrecht, The Netherlands, 1990, pp. 367–374.
- [2] N.S. Shifrin, B.D. Beck, T.D. Gauthier, S. D. Chapnick, G. Goodman, *Toxicology Pharmacology* 23 (1996) 106–116.
- [3] T.L. Thels, T.C. Young, M. Haug, K.C. Knutsen, *Environ. Sci. Technol.* 28 (1994) 99–106.
- [4] R.S. Ghosh, D.A. Dzombak, R.G. Luthy, D.V. Nacjles, *Water Environ. Res.* 71 (1999) 1205–1216.
- [5] K.L. Cherryholes, W.J. Cornils, D.B. McDonald, C. Splinter, *ASTM Spec. Tech. Pub. No. 854* (1985) 502–505.
- [6] M.G. Meeuseen, W.H. Keizer, A.M. Van Rlemsdijk, *Environ. Sci. Technol.* 26 (1992) 1832–1838.
- [7] Environment Agency, Japan, *Japanese Standard (Kankyocho Kokuji Dai 46 Gou, Kaisei Kankoku Dai 19 Gou, Kankoku Dai 25 Gou)*, 1991, 1993, 1994.
- [8] A.G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, 1st edn., Academic Press, New York, 1976.
- [9] A.G. MacDiarmid, *Complex Cyanide–Simple Cyanide Exchange Systems*, PhD thesis, University of Wilconsin, 1953.
- [10] R.S. Ghosh, D.A. Dzombak, R.G. Luthy, D.V. Nackles, *Environ. Eng. Sci.* 16 (1999) 293–313.
- [11] S. Asperger, *Trans. Faraday Soc.* 48 (1952) 617–624.
- [12] Ministry of International Trade and Industry, Japan, *Industrial Standard, JIS K 0102*, 1995.