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Chemical treatment for treating cyanides-containing effluent from biological cokes wastewater treatment process

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Abstract

A pre-denitrification process has been used to treat cokes wastewater containing toxic compounds such as phenols, cyanides and thiocyanate in Korea, and has showed very good removal efficiencies in carbon and nitrogen removals. However, a considerable amount of cyanides in the form of ferricyanide remained in the effluent of biological treatment process. Though ferrous iron is known to be more efficient in removing ferricyanide than ferric iron, ferric chloride solution has been used as a chemical precipitant due to its low cost for a long time. In this study, ferrous sulfate and ferric chloride solutions were used to remove cyanides remained in the effluent of the pre-denitrification process. The optimum dosage of each iron solution was evaluated in batch experiments with or without PAC solution. In addition, the amount of produced chemical sludge and the settling performance of it were also examined numerically. In conclusion, economic assessment indicated that ferrous iron is more economically profitable than ferric iron in spite of its high cost.

Keywords: Cokes wastewater; Ferricyanide; Chemical processes; Precipitation; Coagulation; Sedimentation

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1. Introduction

The steel industries generate various wastewaters during the manufacture and processing of iron. Above all, cokes wastewater is considered as the most toxic one to be treated before being discharged into the environment [1,2]. This wastewater is mostly generated from cooling step after coking coals at high temperature (900–1100 °C) and liquid-stripping step of the produced coke oven gas, and contains various toxic compounds such as ammonia, thiocyanate, phenols and cyanides in high concentration range [1,2]. Traditional treatment of high-strength cokes wastewater utilizes expensive caustic treatment and steam stripping to reduce the contaminant load, followed by conventional biological treatment. Among various proposed processes [2,3], a biological nitrogen removal process, especially pre-denitrification process, has been operated to treat cokes wastewater in Korea, because of its simplicity and economic benefits.

The pre-denitrification process is a single-sludge system with recycle of nitrified effluent, and consists of two distinct microbial reactions under anoxic followed by oxic conditions (Fig. 1). In anoxic condition, heterotrophic denitrifying bacteria convert nitrite and nitrate into nitrogen gas using phenols as a carbon source, thus most of phenols are removed in this step [4]. Besides, very toxic free cyanide can be removed in some degree by anaerobes [5]. In oxic condition, autotrophic nitrifying bacteria convert ammonia into nitrite or nitrate, while autotrophic thiocyanate-degrading bacteria convert thiocyanate into ammonia, sulfate and bicarbonate [6]. These successive microbial reactions could completely remove most of toxic compounds within the cokes wastewater. However, final effluent from the biological process contained considerable amount of cyanides and fluorides, which must be legally removed below 1 mg/L and 15 mg/L in Korea, respectively.

Thermodynamically, free cyanide can easily form stable complexes with metals such as nickel, iron and cobalt [7–9]. The

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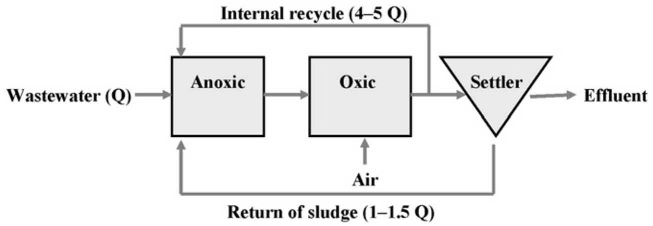

Fig. 1. Schematic diagram of the pre-denitrification process for treating cokes wastewater. *Q* represents liquid flow rate.

cokes wastewater contains cyanides in the form of free cyanide and ferricyanide, since it contains only iron in the form of ferric ion, but other metals below 0.1 mg/L (Table 1).

$$\mathrm{Fe}^{3+} + 6\mathrm{CN}^- \rightleftarrows \mathrm{Fe(CN)}_6^{3-} \qquad \log K = 43.9 \qquad (1)$$

It is well known that free cyanide is very toxic to microorganisms, but ferricyanide is essentially nontoxic except under UV-irradiating condition [8]. In spite of its acute toxicity, it has been reported that various aerobes and anaerobes can easily and rapidly degrade free cyanide [10]. However, ferricyanide is resistant to biodegradation due to its thermodynamic stability. For these reasons, only ferricyanide remained in the effluent of the pre-denitrification process. In order to remove residual cyanides and fluorides, thus, ferric chloride and poly aluminum chloride (PAC) solutions have been used in a chemical treatment process, after the biological treatment. The chemical treatment has successfully removed these compounds below regulation level, but numerous costs have been paid to purchase these chemical solutions. In fact, chemical cost was the main reason to choose ferric chloride solution instead of ferrous sulfate solution, since the former was more inexpensive than the latter to a half less in Korea. According to many reports, however, ferrous iron can more efficiently remove ferricyanide than ferric iron [7,9,11–16].

In this study, ferrous sulfate and ferric chloride solutions were used to remove cyanides remained in the effluent of the pre-denitrification process. The optimum dosage of each iron solution was evaluated in batch experiments with or without PAC solution. In addition, the amount of produced chemical sludge and the settling performance of it were also examined numerically. Eventually, the economic advantage of changing ferric chloride solution with ferrous sulfate solution was assessed on the basis of a chemical market price.

2. Experimental

2.1. Wastewater and chemical solutions

Cyanides-containing wastewater used in this study was collected from a settler of a full-scale wastewater treatment facility of a cokes-making plant in a steel company, Korea (Fig. 1). As shown in Table 1, the wastewater contained 98.3 mg/L of fluorides and 13.1 mg/L of cyanides in the form of ferricyanide, but there were no toxic compounds such as free cyanide, phenol, thiocyanate and ammonia due to the complete biodegradation of these compounds under anoxic followed by oxic conditions. Although high concentrations of chloride and sulfate ions existed in the wastewater, it was out of our concerns in this study.

One mole/litre of ferrous sulfate or ferric chloride solution was prepared by dissolving exact quantity of analytical grade $\mathrm{FeSO_4{\cdot}7H_2O}$ (Sigma) or $\mathrm{FeCl_3}$ (Sigma) with 1% $\mathrm{H_2SO_4}$ or HCl solution. Commercially available 17% (w/w) PAC solution and agglomerating agent were gained from the wastewater treatment facility and used in batch experiments.

2.2. Batch experiments

Batch experiments for precipitation reaction were carried out in 250-mL Erlenmeyer flasks filled with a 100 mL of the wastewater containing cyanides and fluorides. To evaluate removal performances of iron solutions or PAC solution for cyanides or fluorides, a desired volume of each solution was added into the wastewater. The flasks were agitated on a rotary shaker for 1 h, and then the supernatants were sampled to analyze cyanides and fluorides after centrifuging at 3500 rpm for 3 min. To examine the combined effect of PAC and iron solutions on cyanides removal, a following experiment was conducted successively: after adding each iron solution into the wastewater, it was mixed with PAC solution for 1 h, and then was adjusted to pH 6.5 by 5 mol/L of NaOH solution, finally, was mixed with agglomerating agent for 30 min. The chemical sludge formed by chemical treatment was settled in a 100 mL measuring-cylinder and the sludge volume was intermittently checked. Meantime, the supernatant was analyzed for cyanides concentration.

Table 1
Characteristics of the wastewater used in this study

COD	Phenols	Total N	$\mathrm{NH_4}^+$	$\mathrm{NO_2}^-$	$\mathrm{NO_3}^-$	SCN^-	Total CN
300	N.D.[a]	58	N.D.[a]	2.59	38.0	N.D.[a]	13.1

Free CN^-	Total organic carbon	Inorganic carbon	$\mathrm{PO_4}^{3-}$	$\mathrm{SO_4}^{2-}$	F^-	Cl^-	pH
N.D.[a]	80.3	24.6	3.2	1035	98.3	1150	7.15

Fe	Al	Ni	Cu	Co	Cr	Zn	Cd, Pb, K
5.13	0.37	0.08	0.05	0.02	0.02	0.01	N.D.[a]

[a] N.D. means ‘not detected’.

2.3. Analytical methods

Colorimetric method using a spectrophotometer (GENESYS TM 5, Spectronic Inc.) was used to measure the concentration of cyanides after distillation [13]. Fluorides concentration was analyzed by an ion chromatograph (DX–120, DIONEX Co.).

3. Results and discussion

3.1. Removal of cyanides by iron solutions

In order to evaluate the removal performance of cyanides by ferrous sulfate or ferric chloride solution, a desired volume of each solution was added into the wastewater (Fig. 2). When 0.5 mmol/L of ferrous iron was added into the wastewater, the color of it immediately turned from brown to blue, but any precipitate was not formed and cyanides was not removed at all. As added amount of ferrous iron was increased, a blue precipitate was formed, and residual cyanides concentration decreased. Ferrous iron above 1.5 mmol/L efficiently removed cyanides, but even 3.0 mmol/L of ferrous iron could not remove it below 1.5 mg/L of concentration. The solution pH decreased from 7.15 to 4.98 with increasing the added amount of ferrous iron due to the acidity (below pH 1) of ferrous sulfate solution. Meanwhile, adding ferric iron below 3.0 mmol/L of concentration did not turn the color of the wastewater, but an amount of brown precipitate was formed. The removal efficiency of cyanides by ferric iron was very poor below 3.0 mmol/L of it. However, it was very interesting that adding ferric iron above 4.0 mmol/L turned the color of the precipitate to slight dark-blue, and the removal efficiency of cyanides sharply increased with increasing added amount of ferric iron. Particularly, 6.0 mmol/L of ferric iron reduced cyanides concentration to 0.53 mg/L, but the solution pH was too much decreased to 2.7.

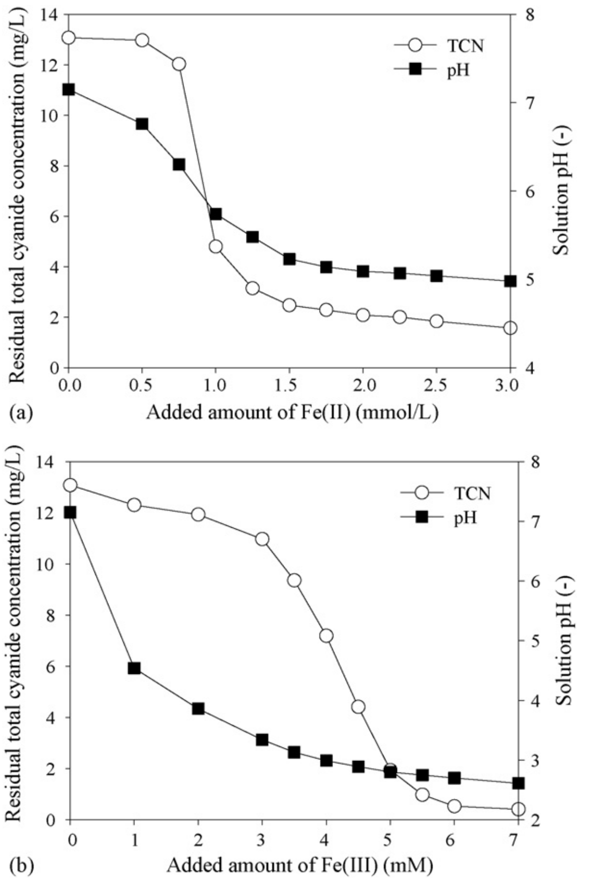

Fig. 2. Removal of cyanides by using (a) ferrous sulfate or (b) ferric chloride solution.

Iron cyanide solids are complex-coordination compounds that are produced and used in various commercial products and processes (Table 2). These solids are also present in environments as a result of disposal of cyanide-bearing materials into soils and groundwater containing iron. However, understanding of the precipitation and dissolution chemistry of iron cyanide solids is still in a nascent state [7]. According to report of Reguera et al. [15], a blue precipitate can be formed by mixing solutions of soluble ferric iron and ferricyanide as follows:

$$3\mathrm{Fe(II)}^{2+} + 2\mathrm{Fe(III)(CN)}_6^{3-} \rightarrow \mathrm{Fe(II)}_3[\mathrm{Fe(III)(CN)}_6]_2 \qquad (2)$$

However, this precipitate, i.e., ferrous ferricyanide, is unstable as the reducing $\mathrm{Fe(II)}^{2+}$ cation and the oxidizing $\mathrm{Fe(III)(CN)}_6^{3-}$ anion have an open path for electron transfer through the CN bridge. This fast internal process leads to the mixed valence ferrous–ferric ferrocyanide system according to Eq. (3):

$$\mathrm{Fe(II)}_3[\mathrm{Fe(III)(CN)}_6]_2 \rightarrow \mathrm{Fe(II)Fe(III)}_2[\mathrm{Fe(II)(CN)}_6]_2 \qquad (3)$$

The mixed valence species can be oxidized to a charged ferric ferrocyanide species by dissolved air or by ferricyanide in solution:

$$\mathrm{Fe(II)Fe(III)}_2[\mathrm{Fe(II)(CN)}_6]_2 \xrightarrow{\mathrm{O_2\ or\ Fe(III)(CN)}_6^{3-}} \{\mathrm{Fe(III)}_3[\mathrm{Fe(II)(CN)}_6]_2\}^+ \qquad (4)$$

Acquisition of an anion from solution to balance the charge leads to Turnbull's Blue (TB), i.e., $\mathrm{Fe(III)}_3\mathrm{A}[\mathrm{Fe(II)(CN)}_6]_2$, where A is Cl^-, $1/2(\mathrm{SO}_4)^{2-}$ and OH^- [15]. The Fe(II):Fe(III) ratio of 2/3 is different from that of Prussian Blue (PB), 3/4 or ferrous ferricyanide, 3/2. Accordingly, the blue precipitate formed in this study might be TB and the reason for the less satisfactory removal efficiency of cyanides by ferrous sulfate solution might be due to low concentration of anions for TB formation or high solubility of TB at high pE. It is known that TB is stable at low pE [7,11].

A brown precipitate can be formed by mixing ferricyanide with ferric iron of low concentration:

$$\mathrm{Fe(III)}^{3+} + \mathrm{Fe(III)(CN)}_6^{3-} \rightarrow \mathrm{Fe(III)}[\mathrm{Fe(III)(CN)}_6] \qquad (5)$$

This precipitate is designated as Prussian Brown (PBr) which is unstable compound in the presence of oxygen [7,11]. Besides, insoluble ferric hydroxide can be formed.

$$\mathrm{Fe(III)}^{3+} + 3\mathrm{OH}^- \rightarrow \mathrm{Fe(III)(OH)}_3 \qquad (6)$$

Namely, the mixtures of PBr and ferric hydroxide might be the brown precipitate observed in this study. The poor removal efficiency of cyanides by ferric chloride solution might be due to the instability of PBr or unexpected reactions such as ferric hydroxide formation. Meanwhile, other chemical reactions between ferricyanide and ferric iron can be occurred in the excess presence of ferric iron [12]. At acidic condition (perhaps, below pH 3), ferric iron can be reduced to ferrous iron in the presence of ferricyanide.

$$\mathrm{Fe(III)}^{3+} + \mathrm{e}^- \xrightarrow{\mathrm{Fe(III)(CN)}_6^{3-}} \mathrm{Fe(II)}^{2+} \qquad (7)$$

Then, the reduced ferrous iron can react with ferricyanide according to Eqs. (2)–(4), finally blue precipitate (TB) can be formed. It must be to note that Prussian Blue (PB) cannot be formed in this condition since ferricyanide cannot be reduced to ferrocyanide below pH 6 [12]. Since the solution pH was decreased below 3.0 by adding ferric iron above 4 mmol/L of concentration, the color of chemical precipitate could be turned from brown to blue due to the formation of TB in this study. The satisfactory removal efficiency of cyanides by ferric chloride solution might be due to enough supply of chloride ions or low solubility of TB at acidic condition [9,14].

3.2. Removal of cyanides by iron solutions with PAC solution: combined effect

As can be seen in Fig. 3, PAC solution could efficiently remove fluorides contained in the wastewater. An amount of chemical sludge was formed and its color was creamy. As increasing the added amount of PAC solution, the removal performance of fluorides by it increased and reached to 97.8%. However, the removal efficiency of cyanides by PAC solution only reached to 24%. It is well known that poly aluminum can effectively agglomerate with organic and inorganic pollutants [17,18]. Due to this advantage, PAC solution has been applied to final chemical treatment step of full-scale wastewater treatment facilities in spite of its expensive cost.

Fig. 4 shows the removal of cyanides by iron solutions with PAC solution. In the case of ferrous sulfate solution, there was ascending effect of PAC solution on cyanides removal by ferrous iron; 0.1 mmol/L of ferrous iron could remove cyanides to less than 1 mg/L of concentration with the aid of 700 mg–$\mathrm{Al_2O_3}$/L of PAC solution. The bright-blue color of chemical sludge indicated the existence of TB within the sludge. There has been no report on the combined effect of ferrous sulfate and PAC solution on cyanides removal. It might be due to that (i) poly aluminum could form stable agglomerate with ferrous ferricyanide. (ii) TB could be easily formed owing to excess presence of chloride ions originated from PAC solution. On the contrary, there was negative effect of PAC solution on cyanides removal by ferric iron. Even 7 mmol/L of ferric iron showed only 88.2% of removal efficiency for cyanides. The color of produced chemical sludge was not blue but bright brown. This result means that the sludge contains only PBr without TB. This negative effect of PAC solution might be due to that (i) the reduction of ferric iron into ferrous iron could not be occurred above pH 6, thus stable TB could not be formed even with 7 mmol/L of ferric iron. (ii) Since PBr was unstable above pH 6, it was difficult for poly aluminum to agglomerate with PBr.

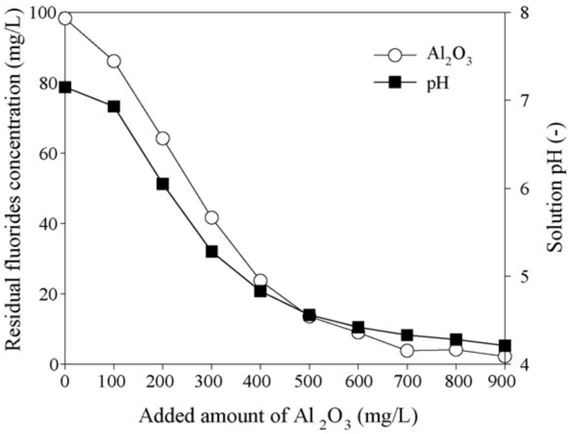

Fig. 3. Removal of fluorides by using PAC solution containing 17% (w/w) $\mathrm{Al_2O_3}$.

3.3. Advantages of using ferrous sulfate solution instead of ferric chloride solution

The use of iron and PAC solutions causes pH drop of the wastewater, thus it must be increased above pH 6.5 before being discharged into the environment. Fig. 5 shows the relation of solution pH and added amount of NaOH solution into the wastewater mixed with PAC or ferrous sulfate and PAC or

Table 2
Iron cyanide solids as reported in the literatures ([7,11,15])

Name	Chemical formula	Color	Thermodynamic stability
Prussian Blue (PB)	$\mathrm{Fe(III)_4[Fe(II)(CN)_6]_3}$	Blue	Stable at higher pE
Prussian Brown (PBr)	$\mathrm{Fe(III)[Fe(III)(CN)_6]}$	Brown	Unstable, turns to PB
Turnbull's Blue (TB)	$\mathrm{Fe(III)_3A[Fe(II)(CN)_6]_2}$[a]	Blue	Stable at lower pE
Ferrous ferricyanide[b]	$\mathrm{Fe(II)_3[Fe(III)(CN)_6]_2}$	Blue	Very unstable
Prussian Green (PG)	Not specified[c]	Green	No information available
Williamson's White (WW)	$\mathrm{Fe(II)_2[Fe(II)(CN)_6]}$	White	Unstable, turns to PB

[a] A is $\mathrm{Cl^-}$, $\mathrm{1/2(SO_4)^{2-}}$ and $\mathrm{OH^-}$.

[b] Many researchers had regarded ferrous ferricyanide as TB during last a hundred years.

[c] It is assumed as a mixture of PB and PBr.

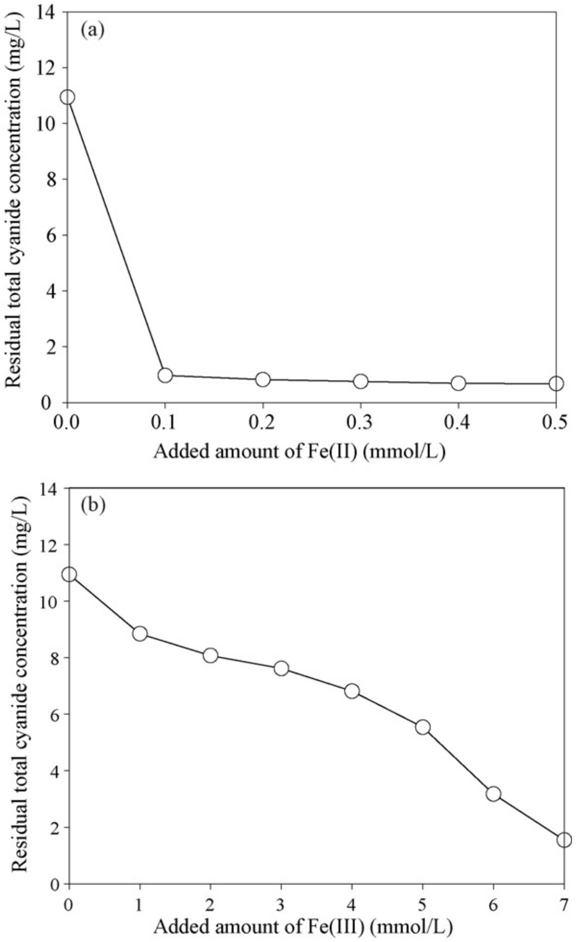

Fig. 4. Removal of cyanides by using (a) ferrous sulfate or (b) ferric chloride solution with PAC solution and agglomerating agent. PAC solution and agglomerating agent were added in the concentrations of 700 mg–Al_2O_3/L and 10 mg/L, respectively.

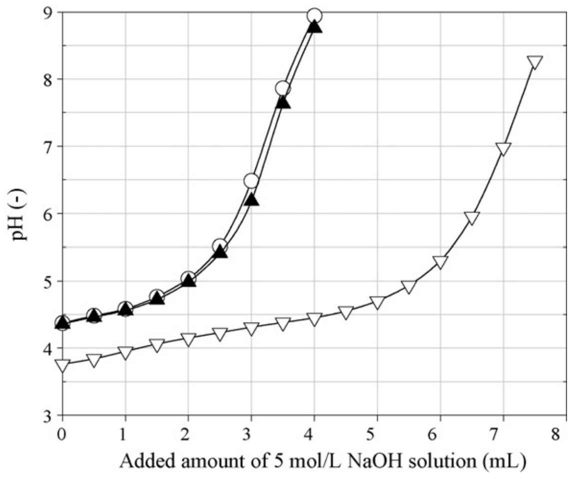

Fig. 5. Relation of solution pH and added amount of NaOH solution into 1 L of the wastewater mixed with iron or/and PAC solutions. Ferrous sulfate and ferric chloride solutions were added in the concentrations of 0.2 mmol/L and 6.0 mmol/L, respectively. Symbols: (○) adding only PAC solution; (▲) adding ferrous sulfate and PAC solutions; (▽) adding ferric chloride and PAC solutions.

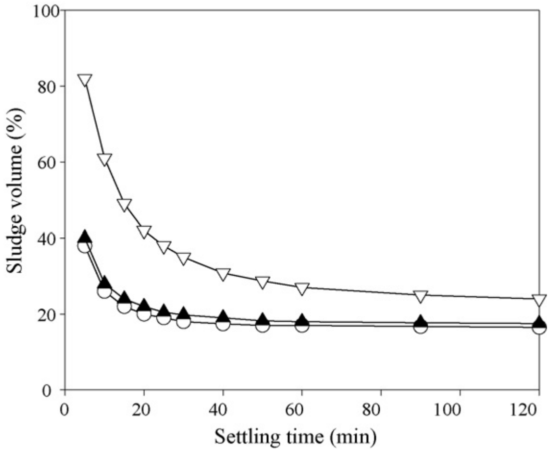

Fig. 6. Settling time of chemical sludge. Ferrous sulfate and ferric chloride solutions were added in the concentrations of 0.2 mmol/L and 6 mmol/L, respectively. Symbols: (○) adding only PAC solution; (▲) adding ferrous sulfate and PAC solutions; (▽) adding ferric chloride and PAC solutions.

ferric chloride and PAC solutions. Though adding PAC solution decreased the solution pH only to 4.37, 0.30% (v/v) of NaOH solution was needed for increasing it to 6.5 due to buffering capacity caused by poly aluminum. In the case of using ferrous sulfate and PAC solutions, 0.31% (v/v) of NaOH solution was consumed to increase pH from 4.36 to 6.5. On the contrary, the solution pH was decreased to 3.76 by adding ferric sulfate and PAC solutions, thus 0.68% (v/v) of NaOH solution was needed for increasing it to pH 6.5. These results indicate that the consumption of NaOH solution can be reduced to the half less by using ferrous sulfate solution instead of ferric chloride solution.

To examine settling capacity of produced chemical sludge, the sludge volume was measured by a measuring-cylinder according to settling time (Fig. 6). Settling rate of chemical sludge formed by ferrous iron was similar to that by only poly aluminum. However, the settling of chemical sludge formed by ferric iron was significant slower than others. In addition, 20% more amount of chemical sludge was formed by ferric iron than by ferrous iron. These results indicate that using ferrous iron is profitable for both sludge settling and sludge production.

3.4. Economic assessment on chemical treatment process for removing cyanides

As has been noted, ferrous sulfate solution has many advantages in removing cyanides than ferric chloride solution in spite of its high cost. At the moment, the economic aspect of using ferrous sulfate solution instead of ferric chloride solution should be considered for practical use in full-scale wastewater treatment process. Thus, the economic advantage of changing ferric chloride solution with ferrous sulfate solution was assessed on the basis of a chemical market price in Korea. As can be seen in Table 3, though the cost of ferrous sulfate solution was higher than ferric chloride solution, total cost for treating the wastewater was much lower in the case of using ferrous sulfate solution. Furthermore, operating cost can be also reduced in some degree

Table 3
Economic assessment on chemical treatment process for removing cyanides[a]

	Chemical cost[b]			Operating cost	
	6.4% $FeSO_4$	14.8% $FeCl_3$	45% NaOH	Settling performance	Sludge production
Using 0.2 mmol/L $FeSO_4$	12.12 \$ 194.01 \$[c]	0 \$	181.89 \$	Good	Small
Using 6.0 mmol/L $FeCl_3$	0 \$ 532.65 \$	133.66 \$	398.99 \$	Bad	20% larger

[a] For treating 1000 M^3 of the wastewater containing 13 mg/L of cyanides.

[b] Commercial costs of 6.4% $FeSO_4$, 14.8% $FeCl_3$ and 45% NaOH solution was 70, 59 and 132 \$/ton, respectively.

[c] Total chemical cost did not include costs for other chemicals such as PAC solution and agglomerating agent.

owing to improvement of sludge settling and decrease in sludge production.

4. Conclusions

In a full-scale pre-denitrification process for treating cokes wastewater, ferricyanide was not nearly removed biologically, thus chemical precipitation process had to be applied to remove residual ferricyanide after biological treatment. Though ferrous iron can efficiently remove ferricyanide than ferric iron, ferric chloride solution has been used as a precipitant due to its low cost for a long time. Thus, removal performance of each iron solution was evaluated by batch experiments in this study. Ferric iron could remove ferricyanide to less than 1 mg/L, but an amount of it was needed and solution pH was too much decreased. With the aid of PAC solution, 0.1 mmol/L of ferrous iron could remove ferricyanide to less than 1 mg/L, but even 6.0 mmol/L of ferric iron could not. Especially, economic assessment indicates that ferrous iron is more economically profitable than ferric iron in spite of its high cost. In conclusion, ferrous sulfate solution can replace ferric chloride solution for treating the wastewater containing cyanides, especially ferricyanide.

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