CHEMICAL AND BIOLOGICAL CYANIDE DESTRUCTION AND SELENIUM REMOVAL FROM PRECIOUS METALS TAILINGS POND WATER

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Abstract

The Bureau of Mines, U.S. Department of the Interior, is investigating chemical and biological decontamination of complex wastewaters such as tailings pond water containing 280 ppm CN and 5 ppm Se as well as significant concentrations of arsenic, copper, iron, silver, and zinc. The most effective chemical procedure involves cyanide oxidation using hydrogen peroxide or sodium hypochlorite followed by selenium reduction using ferrous hydroxide. The effluent contains $\leq$1 ppm CN and 20 ppb Se; concentrations of other major contaminants meet EPA drinking water standards. Preliminary research indicates that biological cyanide oxidation is possible even in highly alkaline solutions (pH 10.5) containing high cyanide concentrations; indigenous bacteria destroyed 85 pct of the cyanide. Exploratory research shows that other bacteria removed up to 79 pct of the selenium from chemically oxidized, low-cyanide water. These promising results may lead to a final processing scheme that involves a combination of chemical and biological techniques.

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Introduction

Management of mine drainage and mineral processing waste systems is a serious problem that could have major impacts on the U.S. mineral industry. Recent legislation (established by the Superfund Amendments and Reauthorization Act of 1986) provides that preferred remedial actions are those treatments that permanently and significantly reduce the volume, toxicity, or mobility of the hazardous substance. However, in many cases, treatment technology to meet stringent discharge requirements for toxic anions and heavy metals does not exist. The Bureau of Mines has a long history of research on minerals waste management and related environmental problems and policies. The Bureau now has a unique opportunity to develop or adapt mineral processing technologies to remediate site-specific contaminated mining and milling wastes and then apply these technologies to sites with similar problems.

A major remediation problem involves disposal of cyanide waste solutions. Researchers at the Salt Lake City Research Center are investigating chemical and biological decontamination of complex wastewaters such as tailings pond water from an operating silver mine. The objective of the Bureau research is to reduce the concentrations of contaminants to levels that meet EPA drinking water standards.

Several methods have been developed for treating cyanide waste solutions including a wide variety of chemical and biological oxidation processes, acidification-volatilization-reneutralization, biodegradation, ion flotation, solvent extraction, and ion exchange (1-4). Since industry prefers oxidation processes, research concentrated on effective, relatively simple, chemical oxidation treatments such as sodium hypochlorite ($NaOCl$) and hydrogen peroxide(H_2O_2) addition. Because of the relatively high costs associated with these chemical treatments, the Bureau also conducted extensive biological research in which bacteria, indigenous to precious metals tailings pond water, were used to oxidize the cyanide.

Following the oxidation step, the primary contaminant remaining in the water is selenium [present as selenate (SeO_4^{-2}) and selenite (SeO_3^{-2})]. Off-the-shelf technology is not available for selenium removal from mining and milling wastewaters; however, several methods have been investigated for treating agricultural wastewaters. These treatments generally involve the reduction of SeO_4^{-2} to elemental selenium using either chemical reduction with ferrous hydroxide [$Fe(OH)_2$] (2) or biological reduction using an indigenous bacteria (3-4). These techniques were applied to the tailings pond water. Since no selenium-reducing bacteria were found in the tailings pond water, bacteria isolated from agricultural waters were used.

Description of Precious Metals Tailings Pond Water

The Bureau obtained a 200-gal water sample from the tailings pond of an operating silver mine. The principal silver mineral at this mine is naumanite (Ag_2Se) which occurs with acanthite (Ag_2S). The mineralization is relatively iron and manganese free and is readily amenable to cyanidation. The sample was pumped from the edge of the tailings pond (at a depth of 2 to 3 ft) and had a cyanide concentration of 280 ppm (200 ppm free CN and 80 ppm complexed CN) at a pH of about 10.5. The sample also contained, in parts per million, 3.2 Ag, 0.2 As, 4.5 Cu, 10 to 16 Fe, 5 Se, and 130 to 160 Zn. Silver, copper, iron, and zinc are probably present as cyanide complexes with arsenic occurring as arsenite or arsenate (the cyanide and arsenic species have not been identified). About one-half the selenium is present as selenite. Selenate is also present; however, the relatively high sulfate concentration (150 ppm) has prevented an accurate determination of the selenate concentration. A portion of the selenium may be present as metal-selenium bonded complexes, also known as selenocyanates ($SeCN^-$) (5); cyanide solutions are known to dissolve selenium from selenides such as naumanite with the subsequent formation of selenocyanates (5).

Sample Analysis

The determination of total cyanide involved reflux distillation of a strongly acidified sample. The hydrogen cyanide (HCN) gas formed in the distillation was purged into an absorption solution containing sodium hydroxide (NaOH). Titrimetric or selective ion electrode methods were used for determining the free alkali cyanide. Free cyanide in the tailings pond water was determined by titrimetric or selective ion electrode procedures. Complexed cyanide was calculated as the difference between total and free cyanide.

Cations such as copper, iron, and zinc were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Atomic absorption spectrophotometry (AA) was used to analyze arsenic and silver. Low levels of arsenic were determined using a graphite furnace AA technique. Total selenium and selenite were determined using a hydride generation AA procedure. The selenate in the tailings pond water was identified using an ion chromatograph; selenate in the chemically oxidized water was calculated as the difference between total selenium and selenite. The presence of selenocyanate in this tailings pond water has yet to be established by analytical techniques; however, cyanide leaching of selenide ores is known to produce selenocyanates (5).

Experimental Procedures and Results

The primary decontamination steps involved cyanide decomposition followed by selenium reduction and/or coprecipitation. The concentrations of other contaminants were generally decreased to acceptable levels as a result of cyanide and selenium removal.

Several cyanide decomposition procedures were investigated, including the following: (1) catalytic oxidation using activated carbon with a copper catalyst, (2) oxidation using NaOCl, H_2O_2, or a combination of the two, and (3) biological oxidation using bacteria indigenous to the tailings pond water.

The following selenium removal methods were studied: (1) reduction of selenate and selenite to elemental selenium using $Fe(OH)_2$ in oxidized low-cyanide (<2 ppm CN) water, and (2) reduction of selenate and selenite to elemental selenium in chemically oxidized water using bacteria indigenous to agricultural drainage waters.

Catalytic Oxidation of Cyanide

Activated carbon, with the addition of cupric ion (added as $CuCl_2 \cdot 2H_2O$) and oxygen, has been demonstrated to be an effective treatment for cyanide-containing wastewaters (6). The adsorption capacity of activated carbon is about 1 to 5 mg CN per gram carbon; however, with this technique, the cupric ion increases the adsorption capacity to 25 mg CN per gram carbon, and dissolved oxygen continuously regenerates the adsorption sites. Limited research indicates that for this method to be applicable to precious metals tailings pond water, metal contaminants, particularly iron

(15 to 20 ppm), would have to be removed in a pretreatment step. Apparently, metal contamination prevents continuous regeneration of adsorption sites. If the adsorption sites cannot be continuously regenerated, the carbon will have to be chemically regenerated or discarded and replaced with fresh carbon. Further research is needed to determine if this technique would effectively remove cyanide from precious metals tailings pond water following the removal of metal contaminants.

Chemical Oxidation of Cyanide

Cyanide can be effectively decomposed using a strong oxidant. The most commonly employed method, alkaline chlorination (1), involves the addition of chlorine gas and NaOH or the direct addition of a hypochlorite such as NaOCl. Hypochlorite addition is the more expensive option; however, it was used in these studies to keep the process as simple as possible. The probable reactions involved when using NaOCl are analogous to the reactions with chlorine gas in an alkaline medium (1) as shown in equations (1) and (2). These reactions are generally carried out at a pH of about 8.5. The cyanide is oxidized to nitrogen and carbon dioxide which forms a bicarbonate in solution.

$$NaCN + NaOCl \rightarrow NaCNO + NaCl \qquad (1)$$

$$2NaCN + 5NaOCl + H_2O \rightarrow N_2 + 2NaHCO_3 + 5NaCl \qquad (2)$$

Sludge formation nearly always accompanies chlorination. This sludge is composed primarily of precipitated metal hydroxides or possibly as ferrocyanides or ferricyanides (1). An advantage of chlorination is that the cyanide is decomposed to nitrogen and carbon dioxide; no other contaminants, such as ammonia, are produced.

Hydrogen peroxide is also used to decompose cyanide. Several H_2O_2 processes have been investigated and patented by industry (7-8). In many cases, a soluble metal compound catalyst, such as a copper compound, is added to increase the reaction rate. Decomposition proceeds by the following reactions:

$$NaCN + H_2O_2 \rightarrow NaCNO + H_2O \qquad (3)$$

$$NaCNO + 3H_2O \rightarrow NH_4OH + NaHCO_3 \qquad (4)$$

Hydrogen peroxide will decompose copper, nickel, and zinc cyanide complexes with the formation of a hydroxide sludge. A disadvantage of H_2O_2 treatment is the formation of ammonia; subsequent treatment will probably be required to reduce the ammonia concentration to EPA drinking water standards.

Extensive research was conducted to determine the effects of reagent type and dosage, pH, and retention time on cyanide decomposition in tailings pond water. The oxidants used were liquid bleach containing 5.25 wt pct NaOCl and 30 pct H_2O_2 solution; these reagents were added directly to the tailings pond water and agitated.

Sodium Hypochlorite Treatment. Tests were conducted to determine the effects of pH and NaOCl dosage on cyanide decomposition in tailings pond water. A summary of preliminary data is presented in Table I. The NaOCl dosage used in these tests ranged from 0.29 to 1.1 times the stoichiometric NaOCl (10 to 40 mL NaOCl/L of tailings pond water) required in reactions (1) and (2). The most effective dosage was 15 mL/L; this is the stoichiometric NaOCl dosage needed in equation (1) to produce cyanate

(cyanate assays were not obtained for these solutions because of the interferences caused by other anions present).

TABLE I. - Effect of NaOCl dosage and retention time on cyanide decomposition at pH 8.5 to 9[1]

NaOCl dosage, mL/L	Retention time, hr[2]	Final pH	Effluent CN, ppm
10	3	9.0	68
15	3	9	7
25	3	9	36
40	3	8.8	35
10	5	8.5	67
15	5	8.5	10
25	5	8.6	35
40	5	8.7	40

[1] The head solution contained about 280 ppm CN. The pH was adjusted to between 8.5 and 9 using HCl prior to NaOCl addition.

[2] Retention times were randomly chosen.

Subsequently, a two-step procedure was studied; the total NaOCl dosage of 40 mL/L was 1.1 times the stoichiometric NaOCl needed in equations (1) and (2). Test data, shown in Table II, indicate that a two-step treatment was effective if the initial NaOCl dosage was below 20 mL/L. The solution was filtered between steps to remove the metal hydroxides which precipitate during cyanide oxidation (1). Retention times used in these tests were chosen at random.

TABLE II. - Effect of two-step NaOCl addition on CN decomposition[1]

NaOCl dosage,[2] mL/L	Retention time, hr	Final pH	Effluent CN, ppm
5	3	8.6	150
35	4	8.1	.28
10	3	8.6	56
30	4	8.1	.11
15	3	8.6	10
25	4	8.8	.12
20	3	8.6	32
20	4	8.7	30

[1] The head solution contained 280 ppm CN. The pH was adjusted to 8.5 with HCl following NaOCl addition.

[2] NaOCl was added in two steps. The solution was filtered between steps.

A test series was also conducted to determine the effect of pH on cyanide decomposition when using a two-step NaOCl addition. Test results, presented in Table III, show that this procedure was more effective as the pH decreased. Adding NaOCl to tailings pond water at the natural pH of 10.5 yields an effluent pH of 8.5 to 9. Therefore, pH adjustment will not be required for NaOCl treatment.

TABLE III. - Effect of pH on CN decomposition when using a two-step NaOCl addition[1]

NaOCl dosage,[2] mL/L	Retention time, hr	pH[3]	Effluent CN, ppm
15	3.5	[4]11.7	45
25	2	[5]11.7	29
15	3.5	[4]10.8	41
25	2	[5]10.6	35
15	3.5	[4]9.9	3.1
25	2	[5]9.3	.64
15	3.5	[4]8.8	5.2
25	2	[5]8.6	.14

[1] The head solution contained 280 ppm.

[2] NaOCl was added in two steps. The solution was filtered between steps. The total NaOCl dosage was about 1.1 times stoichiometric.

[3] The pH was maintained by adding NaOH or HCl as required.

[4] Initial pH.

[5] Final pH.

Overall, data indicated that a two-step NaOCl treatment effectively decreased the cyanide concentration in tailings pond water to <1 ppm. The total NaOCl dosage of 40 mL/L was 1.1 times the stoichiometric amount needed to oxidize the cyanide to nitrogen and carbon dioxide. The effluent concentrations of the primary contaminants following NaOCl treatment are presented in Table IV. Arsenic, copper, iron, and zinc met EPA drinking water standards; the effluent concentrations of selenium and silver did not meet the standards. Copper, iron, and zinc precipitated as hydroxides (1). Arsenic, selenium, and silver were also identified in the sludge. Metal hydroxides are known to coprecipitate and/or adsorb arsenic from solutions (9); iron hydroxides are reported to reduce selenite and selenate to elemental selenium which subsequently precipitates (2). Silver is probably also removed by a coprecipitation mechanism. The reagent cost for this treatment would be about $8.00 per 1,000 gal of tailings pond water treated to produce an effluent containing <1 ppm CN. Although an effective process, the cost may be prohibitive, especially when treating large volumes of wastewater. Thus, research was conducted using H_2O_2 treatment which is reported to be less expensive (1).

TABLE IV. - Solution analyses following NaOCl treatment

	Concentration, ppm		
Contaminant	Feed	Effluent	EPA dws
As.........	0.2	0.01	0.05
Cu.........	4.5	<.5	1.0
CN.........	280	.1	.05
Fe.........	16	.15	.3
Se.........	5	4	.01
Ag.........	3.2	.2	.05
Zn.........	157	<4	5

dws Drinking water standards.

Hydrogen Peroxide Treatment. Extensive research was conducted to determine the effects of H_2O_2 dosage, pH, and retention time on cyanide decomposition in tailings pond water. Test series were also conducted with cupric ion additions to determine if the cupric ion would act as a catalyst to increase the reaction rate. Recommended operating conditions for H_2O_2

processes include a pH range of 8.3 to 12.5 and an H_2O_2:CN mole ratio of 0.6 to 3.0 (1).

Data from a detailed test series, presented in Tables V through VII show the effects of H_2O_2 dosage, pH, and retention time on cyanide decomposition. From these data, the following observations were made:

1. Hydrogen peroxide can be used to treat tailings pond water without pH adjustment.
2. The required retention time depends on the H_2O_2 dosage.
3. An effluent cyanide concentration of 2 to 3 ppm appears to be the lower limit at a practical H_2O_2 dosage.

TABLE V. - Effects of H_2O_2 dosage and retention time on CN decomposition at pH 9[1]

H_2O_2 dosage,[2] mL/L	Retention time, hr	Final pH	Effluent CN, ppm
1	1	8.9	213
	5	8.9	163
	23	8.6	38
	47	8.5	5.4
	71	8.7	4.9
2.5	1.5	8.9	165
	5	8.5	24
	23	8.7	3
	119	8.8	5
5	1.5	8.7	97
	5	8.8	1.5
	23	8.9	1.5
	119	9	3
10	1	8.7	37
	3.5	8.9	4.3
	22.5	9.1	1
	99	9.2	1

[1] The head solution contained about 280 ppm CN. Initial pH was adjusted to 9 with HCl.

[2] The H_2O_2 dosage ranged from 1 to 10 times stoichiometric.

TABLE VI. - Effects of H_2O_2 dosage and retention time on CN decomposition at pH 10.5[1]

H_2O_2 dosage,[2] mL/L	Retention time, hr	Final pH	Effluent CN, ppm
1	72	9.5	27
	262	9.2	22
2.5	4	10.0	95
	70	9.4	3.1
	264	9.1	2.8
5	4	9.8	21
	70	9.5	3.6
	264	9.2	2.4
10	2	9.7	9
	4	9.6	3.5
	21.5	9.7	1
	73	9.6	1

[1] The head solution contained about 280 ppm CN. Initial pH was 10.5.

[2] The H_2O_2 dosage ranged from 1 to 10 times stoichiometric.

TABLE VII. - Effects of H_2O_2 dosage and retention time on CN decomposition at pH 11.25[1]

H_2O_2 dosage,[2] mL/L	Retention time, hr	Final pH	Effluent CN, ppm
1	1	10.25	217
	94	10.1	29
2.5	4	10.5	126
	25	9.8	3.3
	47	9.5	<3
5	1	10.8	153
	94	9.8	3.2
10	1	10.8	75
	72	9.8	1

[1] The head solution contained about 280 ppm CN. Initial solution pH adjusted to 11.25 with NaOH.

[2] The H_2O_2 dosage was 1 to 10 times stoichiometric.

Research was also conducted in which $CuCl_2 \cdot 2H_2O$ was added to the tailings pond water to determine if cupric ion acts as a catalyst in the cyanide decomposition reaction (1). The test procedure involved adding H_2O_2 to the tailings pond water at the natural pH of 10.5 followed immediately by cupric ion addition. The solution was agitated for 2 h; solution pH was maintained with NaOH. Test results, presented in Table VIII, indicate that cupric ion does not enhance but actually retards cyanide decomposition at the conditions tested; apparently, a stable cyanide complex is formed that H_2O_2 does not decompose.

Table VIII.- Effect of cupric ion addition on cyanide decomposition at pH 10.5[1,2]

H_2O_2 dosage,[3] mL/L	Cupric ion dosage, g/L	Final pH	Effluent CN, ppm
1	0.0	10.1	62
1	.187	10.5	117
1	.373	10.5	158
1	1	10.5	152

[1] The head solution contained about 280 ppm CN.

[2] The solutions were agitated for 2 hr.

[3] H_2O_2 was added first followed immediately by $CuCl_2 \cdot 2H_2O$. NaOH was added throughout the test to maintain pH.

The data in Tables V through VIII indicate that the cyanide concentration in tailings pond water can be decreased to 2 to 3 ppm using an H_2O_2 dosage of about 2.5 times stoichiometric (2.5 mL/L); a dosage of 10 times stoichiometric decreases the effluent level to 1 ppm. The effluent concentrations of the primary contaminants following H_2O_2 treatment (2.5 mL/L dosage) are presented in Table IX. The effluent concentrations of arsenic, copper, iron, and zinc met EPA drinking water standards; the effluent levels of selenium and silver were well above the standards. As in the NaOCl tests, copper, iron, and zinc precipitated as hydroxides; arsenic, silver, and a portion of the selenium were precipitated and/or adsorbed by these hydroxides. The retention time required to attain the low cyanide levels depended on the amount of H_2O_2 used. The procedure was effective at the natural pH of the water (pH 10.5). Cupric ion did not improve the efficiency of cyanide decomposition.

TABLE IX.- Solution analyses following H_2O_2 treatment

Element	Concentration, ppm		
	Feed	Effluent	EPA dws
As......	0.2	<0.05	0.05
Cu......	4.5	<1	1
CN......	280	3	.05
Fe......	16	<.015	.3
Se......	5	4	.01
Ag......	3.2	1	.05
Zn......	157	<1	5

dws Drinking water standards.

The reagent cost for an H_2O_2 dosage of 2.5 times stoichiometric, which produces an effluent cyanide concentration of 2 to 3 ppm, would be about $5.00 per 1,000 gal of tailings pond water treated. A dosage of 10 times stoichiometric is required to produce an effluent cyanide concentration of about 1 ppm, H_2O_2 reagents would cost about $20.00 per 1,000 gal. The reagent cost of H_2O_2 treatment to attain an effluent cyanide concentration of 1 ppm or less was much higher than with the NaOCl procedure ($8.00 per 1,000 gal).

H_2O_2-NaOCl Treatment. Tests were also conducted to determine if H_2O_2 treatment followed by NaOCl addition could be used to reduce reagent costs. Reagent additions of 1 to 5 mL H_2O_2/L followed by 2 to 10 mL NaOCl/L were tested. Results indicate that adding 2 mL H_2O_2/L to precious metals tailings pond water at pH 10.5 (natural pH of the tailings pond water) decreased the effluent cyanide concentration to between 3 and 5 ppm. An NaOCl addition of 5 to 10 mL/L was then used to decrease the cyanide level to 0.5 to 1 ppm. The concentrations of the remaining contaminants were comparable to those effluent levels shown in Tables 4 and 9. Total retention time was 1 to 3 days with no pH adjustment. The reagent cost of this procedure would be $5.00 to $6.00 per 1,000 gal of water treated; less expensive than either single chemical treatment tested.

Biological Oxidation of Cyanide

Chemical oxidation of cyanide is expensive regardless of the technique used. An alternative procedure involves biological decomposition using bacteria indigenous to the tailings pond water. The fact that certain micro-organisms, such as fungi and bacteria, can metabolize cyanide is well-known. Certain microbes use cyanide, thiocyanate, and cyanamide in their cellular metabolisms to synthesize amino acids. These compounds can also be used as nitrogen and carbon sources. For example, *Bacillus megaterium* converts potassium cyanide (KCN) to asparagine, asparatic acid, and carbon dioxide (10); whereas, *Pseudomonas paucimobilis mudlock* oxidizes free and complexed cyanide to carbonate and ammonia (11).

Several biological processes have been studied for cyanide decomposition from wastewaters including trickling filters (12-13), activated sludge (14), fluidized bed reactors (15), and rotating biological contactors (RBCs) (16). In general, these processes have been operated at a neutral or slightly basic pH and cyanide concentrations less than 200 ppm. Very little research has been conducted on solutions with a pH and cyanide concentration as high as this tailings pond water (pH 10.5 and >250 ppm CN).

A full-scale biological treatment facility (RBC process) is currently being used to treat cyanide wastewaters at Homestake Mining Co., Lead, SD (16);

the wastewater, a mixture of mine water and tailings impoundment water generally contains <6.5 ppm total CN at a pH of 7 to 8.5. The bacteria used in this operation were isolated from process waters and gradually acclimated to increased cyanide and thiocyanate concentrations to produce a bacterial strain with increased capacity to degrade cyanides. These bacteria oxidize free and complexed cyanide to carbonate and ammonia; metals are adsorbed, ingested, and precipitated as in equation (5).

$$M_xCN_y + 4H_2O + O_2 \xrightarrow{\text{bacteria}} \text{M-biofilm} + 2HCO_3 + 2NH_3 \qquad (5)$$

Research was conducted to determine if a similar technique could be used to treat tailings pond water. Preliminary experiments with bacteria isolated from tailings pond water indicated that these organisms were able to survive in solutions containing up to 280 ppm CN in the pH range of 9.5 to 11. In addition, these bacteria, which are gram-negative rods and oxidase positive, degraded the cyanide. Using Roche identification tubes, the bacteria were identified as a Pseudomonas species. Subsequently, a fatty-based technique was used to identify the bacterial strains as Pseudomonas pseudoalcaligenes and Pseudomonas diminuta. These bacteria belong to the same family as those used in the Homestake process.

Tests were conducted in a single-pass, trickling reactor consisting of three glass columns (2.54-cm ID by 61-cm high) packed with 0.635-cm quartz chips leaving a 10-cm headspace; the columns were connected in series with a reservoir at the bottom of each column. The columns were seeded with a mixture of 50 pct PGY broth (5 g/L peptone, 2.5 g/L glycerol, and 0.5 g/L yeast) and tailings pond water; this mixture was inoculated with cyanide-degrading bacteria (Pseudomonas sp. isolated from tailings pond water). To build up biomass, the initial feed to the reactor consisted of tailings pond water with 10 pct PGY and a small inoculant of Pseudomonas sp. Subsequently, tailings pond water with no additives was fed downflow through the reactor system at 0.12 mL/min for 111 days; the retention time in each column was 90 min. Feed and effluent samples were analyzed periodically for cyanide as well as copper, iron, selenium, and zinc.

Cyanide concentrations for feed and effluent solutions at various time intervals are presented in Figure 1; the effluent cyanide concentrations are labeled C1-E (column 1), C2-E (column 2), and C3-E (column 3). The feed concentration varied from 82 to 249 ppm CN because of periodic dilution with varying amounts of nutrient solution. Effluent concentrations from C3-E ranged from 9 to 41 ppm CN. The average cyanide removal through the system for the 111-day test was 87 pct regardless of feed concentration.

The feed and effluent solutions were also analyzed for ammonia since ammonia is a product of cyanide degradation (equation 5); the ammonia concentration in the water increased from a feed concentration of 56 ppm to an effluent concentration of 136 ppm which indicates that the bacteria are oxidizing the cyanide. In addition, the nitrite concentration decreased from 29.5 to 21.3 ppm; the nitrate concentration increased from 135 to 172 ppm indicating that the bacteria in the system may be oxidizing the ammonia to nitrite and then to nitrate as seen in the Homestake process (16). The effect of this cyanide degradation system on other water contaminants is shown in Table X. The solution assays indicate that most of the iron and zinc are removed in this system; however, copper and selenium are not removed. The iron and zinc probably precipitate as hydroxides after the cyanide is destroyed.

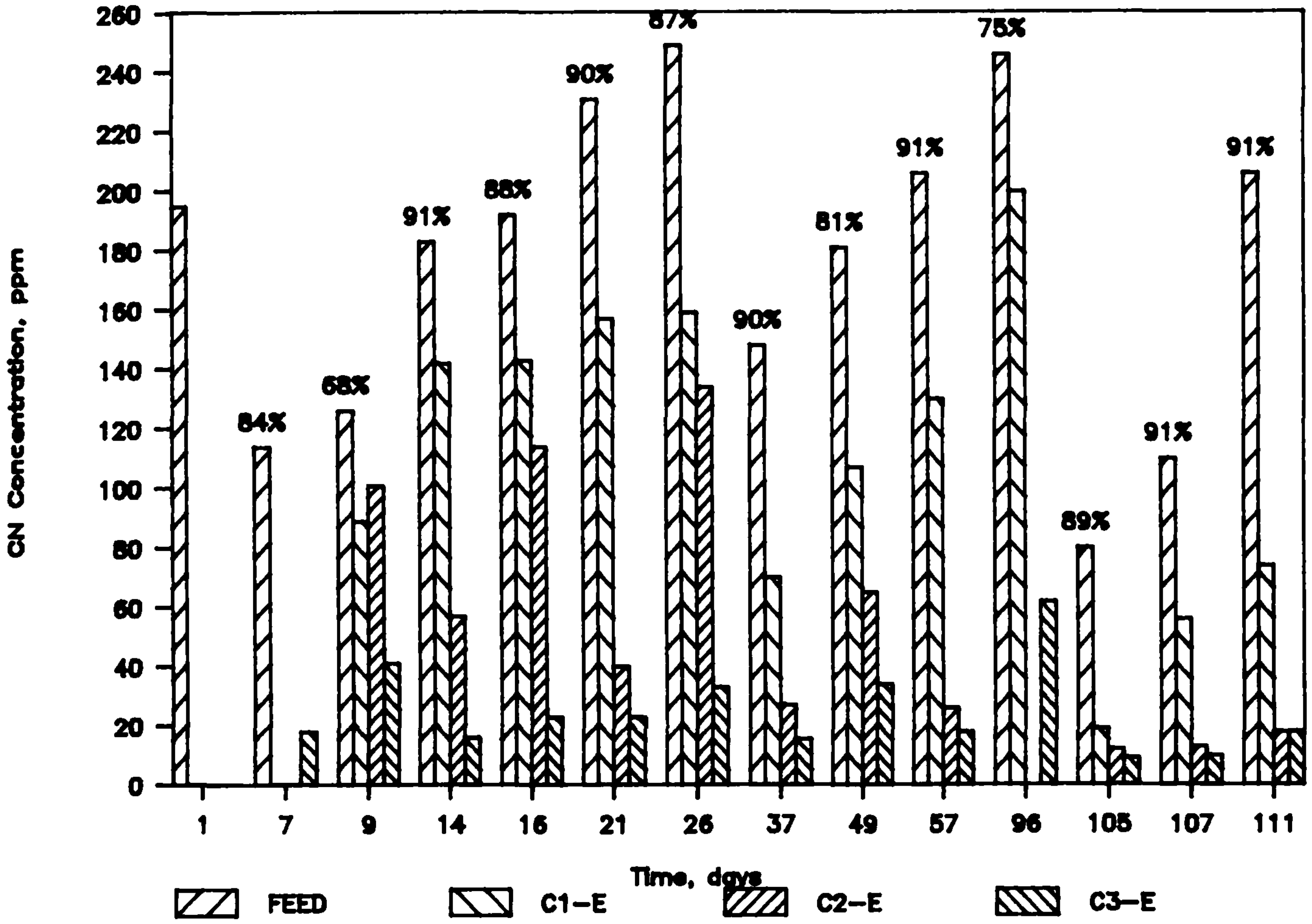

Figure 1. - Bacterial cyanide removal by three-column, single-pass, trickling reactor.

TABLE X. - Solution analyses from the three-column trickling reactor system

Element	Concentration, ppm		
	Feed	Column 1 effluent	Column 3 effluent
Cu.....	4.3	4.47	5.18
CN.....	231	157	23
Fe.....	9.54	<.22	<.22
Se.....	5.1	5.4	5
Zn.....	131	132	8.5

Chemical Reduction of Selenium

Following chemical oxidation of the cyanide (using the H_2O_2-NaOCl oxidation method), the primary contaminants remaining in the water are selenium (4 ppm), silver (0.1 to 0.6 ppm), and cyanide (0.5 to 1 ppm). Limited research with radioactive selenium tracers, together with AA analysis, indicates that selenium in this treated water is present as selenate (3.5 ppm) and selenite (0.5 ppm). A method developed by the Bureau of Reclamation (BOR) for removing selenate and selenite from agricultural drainage waters involves chemical reduction with $Fe(OH)_2$ (2). The proposed reaction stoichiometry for selenate reduction is shown in equations (6) and (7) (2); selenite reduction is believed to occur by a similar mechanism.

$$Na_2SeO_4 + 9Fe(OH)_2 \rightarrow Se^0 + 3Fe_3O_4 + 2NaOH + 8H_2O \quad (6)$$

$$Na_2SeO_4 + 6Fe(OH)_2 \rightarrow Se^0 + 3Fe_2O_3 + 2NaOH + 5H_2O \quad (7)$$

Recommended operating conditions include a pH of about 9 with a large excess of $Fe(OH)_2$ (at least 200 times stoichiometric). The $Fe(OH)_2$ is produced by adding ferrous sulfate ($FeSO_4 \cdot 7H_2O$) or ferrous chloride ($FeCl_2 \cdot 4H_2O$) plus NaOH to the solution (2). The results of a test series in which $Fe(OH)_2$ dosages ranged from 4 to 620 times stoichiometric are presented in Table XI; $Fe(OH)_2 \cdot 7H_2O$ was used in all tests. The data indicate that an effluent selenium concentration of as low as 0.02 ppm was achieved using large reagent dosages; selenium removal was based on AA assays. Maximum selenium removal was generally attained with a 5- to 10-min retention time regardless of reagent dosage. The effluent silver concentration was 0.05 to 0.1 ppm using this procedure; the effluent cyanide concentration was <0.5 ppm. To attain an effluent selenium concentration of 0.1 ppm, the cost of $Fe(SO)_4 \cdot 7H_2O$ (25 g/L) would be $5.00 to $15.00 per 1,000 gal of tailings pond water treated.

TABLE XI. - Selenium removal from chemically oxidized tailings pond water by chemical reduction[1]

$FeSO_4 \cdot 7H_2O$, g/L	pH[2]	Effluent Se, ppm
[3]0.5	9.0	3.0
5	8.8	2.9
10	8.6	2.4
15	8.8	2.1
25	9	.1
30	9	.1
35	8.9	.09
40	8.8	.08
50	9.15	.05
[4]75	9.1	.02

[1] The chemically oxidized water used in these tests contained from 3.6 to 4.0 ppm Se and <1 ppm CN.

[2] The pH was maintained using NaOH.

[3] This reagent dosage is four times the stoichiometric amount required to reduce selenate to elemental selenium.

[4] This reagent dosage is 620 times the stoichiometric amount required to reduce selenate to elemental selenium.

Biological Reduction of Selenium

Chemical techniques exist for selenium removal from contaminated waters; however, because of the large reagent dosages required, chemical treatment may be prohibitively expensive, especially when treating large volumes of contaminated water. Research involving the selenium-contaminated waters of the Kesterson Reservoir (located in the San Joaquin Valley of California) showed that biological reduction is a viable alternative to chemical treatment for selenium removal, when the selenium is present as selenate (3-4). Several selenium-reducing bacteria were isolated from Kesterson waters and identified using common bacterial identification techniques such as gram stains, growth on selective media, and standard biochemical tests.

Fifteen bacterial species were isolated; the predominate family was Pseudomonadaceae, followed by Enterobacteriaceae. The most active selenium reducers used in laboratory experiments, either as isolates or mixed cultures were (1) Pseudomonas alcaligenes, (2) Pseudomonas fluorescens, (3) Pseudomonas aeruginosa, (4) Citerobacter freundii, (5) Enterobacter aerogenes, (6) Enterobacter agglomerans, (7) Enterobacter cloacae, and (8) Klebsiella oxytoca (3).

Studies revealed that bacterial selenium reduction occurs by at least a two-step reaction process, in which selenate is reduced to selenite then possibly to Se(II) and eventually to elemental selenium which precipitates from solution. A mixed bacterial culture removed up to 96 pct of the selenium from agricultural drainage waters (simulated and actual water samples from the Kesterson area) in a small-scale, continuous, plug-flow reactor; the selenium concentration in these waters ranged from 0.15 to 0.61 ppm (3).

Selenium-reducing bacteria were not found in the precious metals tailings pond water because of the high cyanide concentration and high pH. Thus, bacteria isolated from Kesterson waters were cultured in the tailings pond water following chemical oxidation of the cyanide (using the H_2O_2-NaOCl oxidation technique). The oxidation step renders the solution amenable to selenium-reducing bacteria by (1) destroying the toxic cyanide, (2) reducing the alkalinity from a toxic pH 10.5 to a livable pH 8.5, and (3) converting the selenium in the tailings pond water to primarily selenate. Samples of the chemically treated water contained 0.5 to 1 ppm CN, 4 ppm Se, and up to 0.6 ppm Ag.

Exploratory Batch Tests. Exploratory shaker tests demonstrated that Pseudomonas sp. bacteria removed up to 72 pct of the selenium from chemically oxidized tailings pond water. Bacterial cell growth was excellent at 2.5 to 4 by 10^9 cells/mL; 5 g/L peptone was added as a nutrient source. A series of batch tests was also conducted to investigate the effect of cyanide concentration on bacterial selenium reduction. Test results indicated that cell growth occurred in solutions containing up to 30 ppm CN; however, selenium was extracted only in the low cyanide sample (about 2 ppm CN) (3). Pseudomonas sp. bacteria did not reduce the selenium concentration in biologically oxidized tailings pond water; either the cyanide concentration was too high (10 ppm) or the selenium in the tailings pond water had not been oxidized to selenate.

Continuous Testing in Columns. Continuous testing was conducted in a 2.54-cm-diam glass column packed with 0.635-cm ceramic saddles; the measured bed volume was 255 mL. Sterile, chemically oxidized tailings pond water, to which 5 g/L peptone had been added as a nutrient source, was circulated upflow through the column; the column was then inoculated with Pseudomonas alcaligenes bacteria. After approximately 1 week of circulation, the recycle tubing was removed and fresh chemically oxidized tailings pond water, containing 4 ppm Se and 2 ppm CN, was pumped upflow through the column on a single-pass basis at a rate of 0.84 mL/min (5.1-h retention time). Half the feed solution was sterilized and the other half was non-sterile; the sterilized solution contained 10 g/L peptone as a nutrient source. Up to 79 pct of the selenium was extracted during approximately 1 month of operation. Following a brief shutdown for repairs, the test continued for another month; selenium reduction was maintained at a level between 53 and 67 pct (3).

Determination of Selenium-Reducing Mechanism. Batch tests were conducted to determine if selenium reduction in chemically oxidized tailings pond water follows the same two- or possibly three-step reaction proposed for agricultural drainage waters in which selenate is reduced to selenite then possibly to Se(II) and eventually to elemental selenium. This reaction mechanism was established by varying the amount of air supplied to selenium-contaminated agricultural waters that had been inoculated with Pseudomonas sp. (predominately Pseudomonas alcaligenes). The tests were conducted in a 3-L reactor vessel containing 2.1 L of solution at 25° C; 5 g/L peptone was added as a nutrient. The total gas flow into the reactor vessel was 50 mL/min; the amount of air added was regulated by mixing with nitrogen (3). The same procedure was used to study the reaction mechanism in oxidized tailings pond water. Test data are presented in Figures 2A-D. As with the agricultural drainage waters, the most effective selenate reduction was observed with a gas flow of 40 mL/min N_2 and 10 mL/min air producing about 2 ppm dissolved oxygen in solution (Fig. 2C). In this test, the total selenium concentration was reduced from 3.9 to 0.16 ppm in 48 hr. In the presence of excess air (Fig. 2A), selenate reduction was slow; about one-third of the selenate was converted to elemental selenium after 72 hr.

Figure 2B shows that a 25-mL/min N_2-25-mL/min air mixture was not effective with less than one-half the selenium being removed. In the nitrogen test, the selenate was only reduced to selenite; however the total selenium concentration was not reduced. Overall, these data show that the reaction mechanism for selenate reduction in oxidized tailings pond water is similar to that described for the agricultural drainage waters with the selenate being reduced to selenite which is reduced to elemental selenium.

Discussion

Test results showed that strong oxidants, such as NaOCl or H_2O_2, will decompose cyanide in precious metals tailings pond water to ≤ 1 ppm; however, the reagent costs are prohibitive for large volumes of contaminated water. Biological oxidation using indigenous bacteria shows promise with cyanide removal consistently at 85 pct over a long operating time period. If a low-cost nutrient can be found, the overall cost of a biological system should be much lower than chemical treatment. An option which deserves study involves biological oxidation to remove most of the cyanide followed by a chemical polishing step to reduce the cyanide concentration to acceptable levels. (The EPA drinking water standards for total cyanide is 0.05 ppm. With many cyanide-contaminated waters, including tailings pond water, the standards will be difficult, if not impossible, to meet because of the stable cyanide complexes present. Standards may have to be established on a "case-by-case" basis with separate standards established for free and complexed cyanides.)

Selenium removal, by chemical or biological means, was also investigated. Chemical removal involved reduction of selenate and selenite to elemental selenium using $Fe(OH)_2$ following a cyanide oxidation step. Effluent selenium levels of 0.02 ppm were achieved using a large reagent excess. As seen in the cyanide research, reagent costs of chemical treatment may be prohibitive. Biological reduction of selenate was also studied using selenium-reducing bacteria isolated from agricultural drainage waters and cultured in low-cyanide tailings pond water. Effluent selenium levels of as low as 0.16 ppm were attained in batch testing; in continuous tests, selenium effluent concentrations of about 1 ppm were achieved. The costs of a biological system should be much lower than chemical treatment provided a low-cost nutrient can be found and solid-liquid separation problems are solved. Biological treatment alone, however, may not reduce the selenium effluent concentrations to EPA drinking water standards (0.01 ppm). A combination biological-chemical procedure may be required.

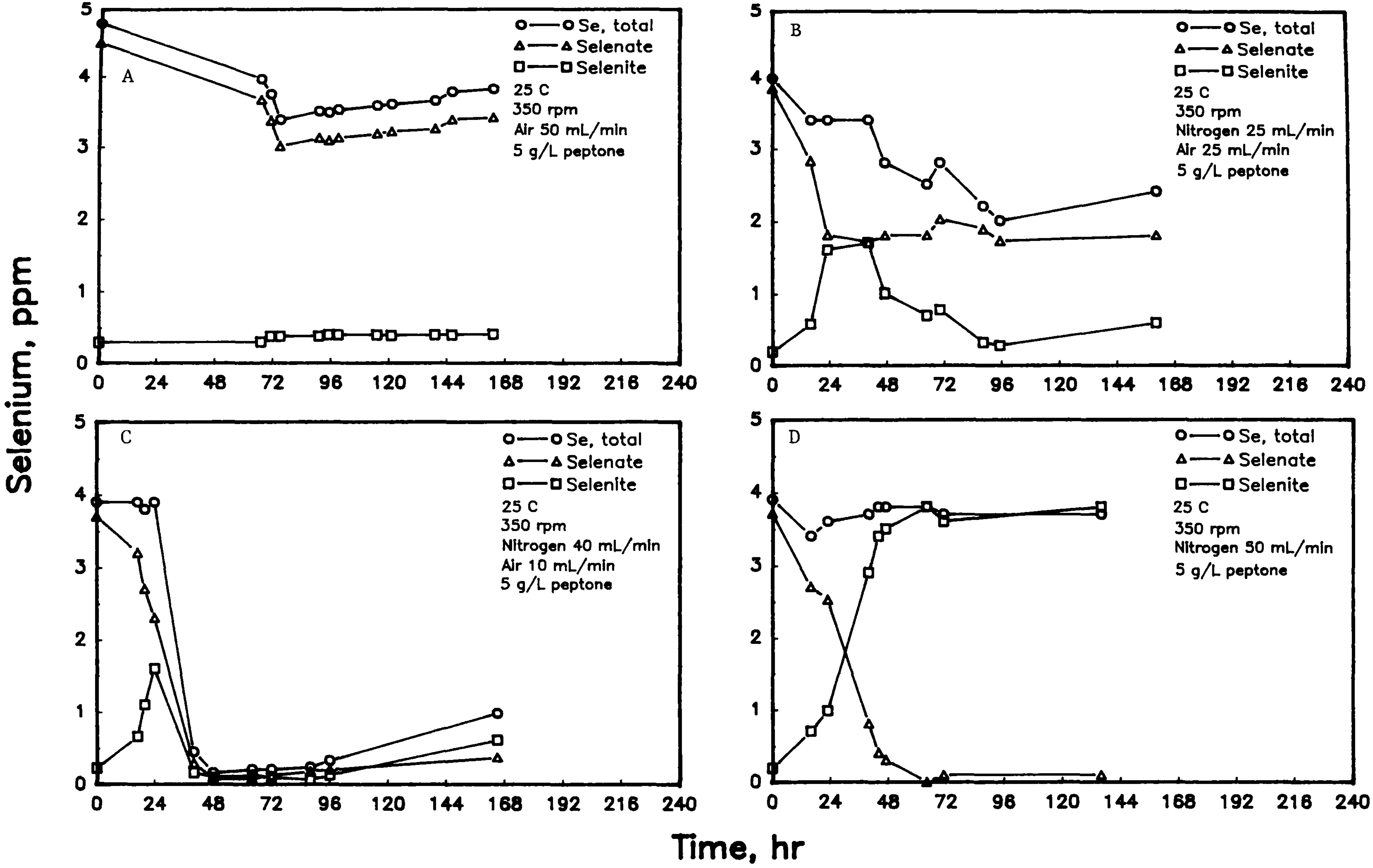

FIGURE 2A-D. Test results showing mechanism involved in bacterial reduction of selenium from chemically oxidized tailing pond water.

References

1. R. W. Watson, "Cyanide Removal From Water," Pollution Control in Metal Finishing, Noyes Data Corp., (1973), 147-178.

2. P. M. Murphy, "Removal of Selenate From Water by Chemical Reduction," Industrial Engineering Research, 27, (1988), 187-191.

3. P. B. Altringer, D. M. Larsen, and K. R. Gardner, "Bench-Scale Process Development of Selenium Removal From Wastewater Using Facultative Bacteria," (Paper presented at the International Symposium on Biohydrometallurgy, Jackson Hole, WY, 17 August 1989) 16; available upon request from the Salt Lake Research Center, Salt Lake City, UT.

4. D. M. Larsen, P. B. Altringer, and K. R. Gardner, "Biologically Assisted Control of Selenium in Process Waste Waters," Biotechnology in Minerals and Metals Processing, B. J. Scheiner, F. M. Doyle, and S. K. Kawatra, eds. (SME-AIME, 1989), 177-185.

5. V. Krishnan, and R. A. Zingaro, "Coordination Compounds in Which Selenium Functions as the Donor Atom," Selenium, R. A. Zingaro, and W. C. Cooper, eds., (Van Nostrand Reinhold Co., 1974), 337-407.

6. F. W. McQuiston, Jr., and R. S. Shoemaker, "Gold and Silver Cyanidation Plant Practice," 2 (SME-AIME, 1981), 165-170.

7. O. B. Mathre (assigned to E.I. du Pont de Nemours and Co.), "Destruction of Cyanide in Aqueous Solutions," U.S. Pat. 3,617,567, Nov. 2, 1971.

8. B. C. Lawes, and O. B. Mathre (assigned to E.I. du Pont de Nemours and Co.), "Cyanide Removal From Waste Waters," U.S. Pat. 3,617,582, Nov. 2, 1971.

9. A. Mehta, "A Survey on Arsenic Literature," (U.S. EPA Grant R 804595010, Mineral Research Center, Montana College of Mineral Science and Technology Foundation), (1977), 143.

10. K. F. Castric, D. A. McDevitt, and P. A. Castric, "Influence of Aeration on Hydrogen Cyanide Biosynthesis," Current Microbiology, 5, (1981), 223-226.

11. T. I. Mudder, and J. L. Whitlock, "Biological Treatment of Cyanidation Wastewaters," paper in Proceedings of the 38th Industrial Waste Conference, Purdue University, (1983), 279-287.

12. Zenon Environmental Inc, "Biological Destruction of Cyanide in Canadian Mineral Processing Effluents," DSS File No. 15SQ.23440-4-9184, Burlington, Ontario, (1985), 185.

13. J. A. Porter, and P. H. Dutch, "Phenol-Cyanide Removal in a Plastic-Packed Trickling Filter," Journal WPCF, 32, (1960), 622-631.

14. D. Harden, D. D. Jones, and J. J. Gauthier, "Adaptation of an Industrial Activated Sludge Process to the Removal of Cyanide," paper in proceedings of the 38th Industrial Waste Conference, Purdue University, (1983), 289-298.

15. S. G. Nutt, H. Melcer, I. J. Marvan, and P. M. Sutton, "Treatment of Coke Plant Wastewater in the Coupled Pre-Denitrification Fluidized Bed Process," paper in proceedings of the 37th Industrial Waste Conference, Purdue University, (1982), 527.

16. J. L. Whitlock, and T. L. Mudder, "The Homestake Wastewater Treatment Process: Biological Removal of Toxic Parameters From Cyanidation Wastewaters and Bioassay Effluent Evaluation," Fundamental and Applied Biohydrometallurgy, R. W. Lawrence, R. M. R. Brannion, and H. G. Ebner, eds., (Elsevier, 1986), 327-339.

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