



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/AU90/00289 (22) International Filing Date: 5 July 1990 (05.07.90) (30) Priority data: PJ 5097 5 July 1989 (05.07.89) AU (71) Applicant (for all designated States except US): MINPROC TECHNOLOGY PTY. LIMITED [AU/AU]; 364 Albert Street, East Melbourne, VIC 3002 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only) : COSTELLO, Michael, Charles [AU/AU]; 15 Elmshurst Way, Greenwood, W.A. 6024 (AU). ROGERS, Douglas, Gordon [AU/AU]; 17 Ebro Way, Willetton, W.A. 6155 (AU). GUERNEY, Philip, John [AU/AU]; 29 Moorfields Street, Fig Tree Pocket, QLD 4069 (AU).		(74) Agent: OBERIN, Colin, James; Oberins, 66 Croydon Road, Croydon, VIC 3136 (AU). (81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i>
(54) Title: PROCESS FOR REDUCING THE CYANIDE CONTENT OF A SOLUTION (57) Abstract A process for treatment of waste aqueous process streams from industrial processes containing both cyanide ions and dissolved ammonia to reduce the cyanide content, comprising the consecutive steps: (a) adding a halogenating agent to the solution while maintaining the pH of the solution at greater than 7; (b) removing ammonia from the solution by aeration; (c) acidifying the solution to a pH of less than 7; (d) substantially neutralising the solution; and (e) removing the ammonia from the solution by aeration.		

DESIGNATIONS OF "DE"

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TITLE: PROCESS FOR REDUCING THE CYANIDE CONTENT OF A SOLUTION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for reducing the cyanide content of a solution.

10 The use of an alkaline aqueous solution of a cyanide salt for recovery of gold and/or silver values from ores, tailings and wastes has been well known and documented for a long period. While this process is well known and widely used for such precious metal recovery it is also to be understood that the waste water streams from such processes contain cyanide in solution which could be dangerous if allowed to enter the environment and particularly the water supply.

20 For this reason, waste aqueous process streams from gold treatment plants using alkaline cyanide solutions as the leachant must meet specific composition limits before they are discharged into the environment. In particular, the total cyanide and free cyanide concentrations must be below the maximum limits set by local, state and federal licensing authorities.

Similar requirements are imposed on the effluent discharged from cyanide production plants and from other industrial processes some of which produce waste water streams containing other species notably ammonia as well as cyanide ions.

2. Discussion of the Prior Art

30 A number of processes have been proposed to bring about the chemical breakdown of the total and free cyanide components of typical effluent streams. Some of the processes have been patented and several are presently used on the commercial scale.

High temperature hydrolysis brings about the total destruction of the cyanide ion, but the high temperatures and extended retention times required makes this process inefficient in cost terms. Some chemical reagents convert

the cyanide ion only to cyanate. In many localities, discharge of cyanate is not permitted. Further destruction of cyanate may be inefficient or costly in reagent consumption terms, or in fact require a different chemical reagent.

The complexity of cyanide destruction is compounded by the presence of other species in solution that interfere with the destruction mechanism and/or substantially increase the capital and operating costs. One such species is dissolved ammonia.

Treatment of an effluent or processing liquor containing, for example, an equivalent concentration of cyanide ions and dissolved ammonia, by the standard cyanide destruction methods is unsatisfactory in terms of additional reagent consumption, increased capital and operating costs and/or incomplete cyanide destruction. These methods include the use of hydrogen peroxide, chlorine, chlorine/calcium hydroxide, hypochlorite, or sulphur dioxide.

The applicants are aware, for example, of a proposal described in Australian Patent Application 73261/81 (PCT International Publication Number WO82/00288) for removing cyanide ions from solutions. This process provides for adjusting the solution to a pH of at least about 11 and to a halide content at least equivalent to the cyanide concentration. Electrolysis is performed using intense agitation of the electrolyte to result in deposition of solid carbon on the anode. Electrolytic methods generally require a readily available source of cheap electricity for economic operation and this is not always available in remote areas. Further, this proposal does not deal with any dissolved ammonia also present in the waste water stream.

Australian Patent Application 17053/88 (PCT International Publication Number WO 88/08408) relates to a method for separating by aeration a component such as cyanide from a liquid containing the component. The method comprises passing the liquid through an array of aeration columns arranged in stages so that the liquid flowing from one column

in a first stage is divided into two or more streams which are introduced into separate aeration columns in a successive second stage. However this process is likewise unsuitable for use in remote areas and does not effectively deal with any dissolved ammonia present in the waste water system.

Australian Patent Application 76929/81 relates to the chlorination of waste water containing ammonia, cyanide and phenol. This method involves adding a chlorinating compound to the waste water in a first vessel at pH 8.5 to 10, passing
10 the waste water to a second vessel at pH 6 to 8 and controlling the addition of the chlorinating compound in response to the redox potential in the second vessel so as to maintain the redox potential at +625 millivolts to +750 millivolts. This method requires close monitoring of redox potentials and is specifically directed at waste water containing phenol as well as ammonia and cyanide contaminants.

SUMMARY OF THE INVENTION

20 It is accordingly an object of the present invention to provide in one embodiment an improved process for reducing the cyanide content of a solution containing both cyanide and dissolved ammonia.

We have now found that the cyanide concentration of an effluent or process stream containing both cyanide and dissolved ammonia can be lowered to a level acceptable for discharge by a combination of steps. Accordingly, the present invention provides in one embodiment a process for
30 reducing the cyanide content of a solution containing both cyanide ions and dissolved ammonia, comprising the following consecutive steps:

- (a) adding a halogenating agent to the solution while maintaining the pH of the solution at greater than 7;
- (b) removing ammonia from the solution by aeration;
- (c) acidifying the solution to a pH of less than 7;
- (d) substantially neutralising the solution; and
- (e) removing the ammonia from the solution by aeration.

We have found that this combination of steps is effective in terms of both capital and operating costs and suitable for use in remote locations.

In step (a) the pH may be between 11 and 12 and most preferably about 12. The preferred reagent for raising the pH in step (a) and/or step (d) is sodium hydroxide.

In step (c) the preferred pH is less than 5 and most preferably from 3 to 4.

10 In step (d) the pH of the substantially neutralised solution may be about 7 and most preferably in the range 6 to 7.

The ammonia may be removed from the solution by aeration in the form of air stripping. Removed or stripped ammonia is preferably collected in a suitable gas scrubbing system.

20 The halogenation agent is preferably a chlorination agent. The chlorination agent may be any agent capable of generating and/or liberating chlorine in aqueous solution. Chlorine gas and agents capable of generating and/or liberating chlorine gas in the solution are particularly preferred for use as halogenation agents in accordance with the present invention. Hypochlorites such as sodium hypochlorite have been found suitable for use as chlorination agents in accordance with the present invention.

Where the chlorination agent is added in the form of gaseous chlorine the addition to the liquor may be achieved by means of a suitable gas sparging or bubbling system to oxidise the cyanide to cyanate.

30 In the process provided by the present invention, cyanide is converted by oxidation in step (a) to cyanate, which in step (c) is hydrolysed to ammonia and carbon dioxide. The carbon dioxide is readily removed from the reaction system. Step (c) may be considered as an acidification and hydrolysis step for converting the cyanate ion from the substantially ammonia free solution produced in step (b) to produce ammonia and carbon dioxide.

Steps (d) and (e) have the effect of re-neutralising the liquor derived from step (c) followed by removing the

dissolved ammonia produced by the acid hydrolysis of the cyanate ion. The final tail solution should be low in ammonia and contain little if any cyanide.

Each step may be carried out at temperatures close to ambient temperature (typically 15-30°C) and does not require the use of exotic materials of construction, nor the use of complex chemical engineering principles.

10 The present invention uses the effective combination of various known processes, none of which on its own, or in any other combination, would achieve the results achieved by the present invention by carrying out the present process, sequentially involving steps (a), (b), (c), (d) and (e). The process thus provides a unique method having substantial and unexpected advantages for treatment of waste waters.

20 More importantly, because the oxidation of cyanide to cyanate and the removal of dissolved ammonia are carried out separately, reagent consumption is minimised. This particularly applies to step (a), where tests show that complete oxidation of cyanide to cyanate is achieved by addition of typically 1.05 times the stoichiometric requirement of the halogenation agent.

Another significant advantage of the present process is that decomposition of cyanate to ammonia and carbon dioxide does not require the use of costly reagents.

EXAMPLES

The present invention is further described in the following non-limiting examples of illustrative embodiments.

Example 1

30 Initial laboratory scale testing of individual steps in the process of the invention were carried out to demonstrate under controlled conditions the operation of individual steps.

A. Examples of the Oxidation Step

As the source of chlorine, the laboratory testwork used as a chlorinating agent a solution of sodium hypochlorite with an equivalent free chlorine content of 13.1 g/L as determined

by titration against standard thiosulphate solution.

A solution (200 mL) containing 1000 ppm of cyanide ion (as sodium cyanide) and 1000 ppm of ammonia was treated with the above solution of sodium hypochlorite and the cyanide concentration was measured by ion selective electrode as a function of the added equivalent chlorine. In Test 1, shown in Table 1, the weight of chlorine sufficient to oxidise the amount of cyanide present in the solution to cyanate ion, was 0.54 g. The pH was 11.9-12.2 during the test.

10

Table 1

Test 1: Oxidation of Cyanide (1000 ppm) to Cyanate with Chlorine in the presence of Ammonia (1000 ppm)

	Chlorine Added (gms)	Cyanide Concentration (gms)
	0.26	311
	0.39	136
20	0.50	37
	0.52	17
	0.55	6
	0.59	0

Test 2 was carried out in the same way as Test 1 except that the initial solution was 100 mL in volume and contained 2000 ppm of cyanide ion and 2000 ppm of ammonia.

30

Table 2

Test 2: Oxidation of Cyanide (2000 ppm) to Cyanate with Chlorine in the presence of Ammonia (2000 ppm)

	Chlorine Added (gms)	Cyanide Concentration (gms)
	0.26	547
	0.39	241
	0.50	64
40	0.52	29
	0.55	6
	0.59	2

B. Examples of the Hydrolysis Step

As a pure source of cyanate ion, a solution of 3.1 g/L potassium cyanate was used.

In Test 3, 200 mL of this cyanate solution was treated with sufficient sulphuric acid solution to maintain pH 3.0 at room temperature. The increase in ammonia concentration as hydrolysis of cyanate proceeded was measured by specific ion electrode. The results are shown in Table 3.

10

Table 3

Test 3: Hydrolysis of Cyanate ion to Ammonia at pH 3.0

Time (min)	Ammonia Concentration (ppm)	Conversion to to Ammonia (%)
1	152	15
5	340	34
20	689	69
60	1,034	103

20

Test 4 was carried out in the same way as Test 3 except that the pH was maintained at pH 3.5

Table 4

Test 4: Hydrolysis of Cyanate ion to Ammonia at pH 3.5

Time (min)	Ammonia Concentration (ppm)	Conversion to to Ammonia (%)
1	124	15
5	195	20
20	483	48
60	759	76
105	1,027	103

40

Example 2

A test run was carried out on a prepared aqueous solution containing 2,000 mgm NH₃ per litre and 1200 mgm CN⁻ per litre to simulate a waste process stream from an industrial process

containing both cyanide ions and dissolved ammonia.

(a) Chlorination:

The solution was subjected to chlorination to oxidise all CN^- to CNO^- using the minimum Cl_2/OCl^- possible.

It was believed that a sharp rise in redox would occur at the 100% stoichiometric Cl_2 addition point i.e. where CN^- concentration < 1 ppm.

The pH during the chlorination was held at 11.9-12.0.

10 Chlorination was conducted by the addition of sodium hypochlorite. The results are summarised in Table 1 which shows that the stoichiometry at the mV rise was 100-105%.

Table 1

	TIME (mins)	HYPO ADDED (% Stoich)	REDOX (mV)	pH	CN^- (ppm)
20	0	0	+ 116	11.4	1,210
	2	11			
	10	22	+ 10	11.9	
	21	33			
	24				716
	29	44			
	37		- 46	11.9	
	38	56			
	47				384
	53	67			
30	78		- 92	11.9	
	79	78			
	95				105
	100	89			
	129		- 78	11.9	18
	134	100			
	148		- 15	11.9	
	157				4
	161	103			
	174		+ 5	12.0	
40	176	105			
	189				0.3
	191		+ 8	12.0	
	192	108			
	206		+ 20	12.0	

(b) First Aeration

The CNO^-/NH_3 mixture formed at around pH 12 in the chlorination step was passed through a packed column to remove the bulk of the NH_3 to atmosphere leaving a weak NH_3/CNO^- solution.

The column used for all aerations was a 7 m length of 300 mm Class 6 PVC pipe packed with 5 m of 1" tellerettes. Air flow was produced by fan suction with flow measured at the fan outlet using a digital turbine anemometer. Liquor flow was visually monitored via flow meter but physically measured by level change in the head tank.

Liquor flow was produced by a centrifugal pump running at - 2800 rpm.

Ammonia removal was 89% at an Air:Liquor ratio of 4900:1.

The area specific flow rates were:

$$\text{Liquor} = 0.55 \text{ l m}^{-2} \text{ sec}^{-1}$$

$$\text{Air} = 162 \text{ m}^3 \text{ min}^{-1} \text{ m}^{-2}$$

Exit gas assays via drager tubes indicated 450 ppm v/v NH_3 .

The drager tube reacts to NH_3 and other basic species (amines) in the sample gas, e.g. monochloramine, etc.

(c) (d) Acid Hydrolysis

The solution formed in the first aeration was made acidic to hydrolyse all CNO^- to NH_4^+ followed by caustic addition to raise the pH, converting NH_4^+ to NH_3 .

CNO^- destruction was very rapid, probably less than 30 minutes.

The acid and caustic requirements for this stage were about 6 kg $\text{H}_2\text{SO}_4 \text{ m}^{-3}$ for pH 12 to pH 3 and 5 kg NaOH m^{-3} to raise pH from 3 to 12. It was noted that some foaming occurs when pH falls below 7.

(e) Second Aeration

The NH_3 in the neutralised solution formed in the acid hydrolysis stage was removed to the atmosphere in a second aeration.

Ammonia removal during this second aeration was 92% at an Air:Liquor Ratio of 4750:1.

The area specific flow rates for this second aeration were:

$$\text{Liquor} = 0.57 \text{ l m}^{-2} \text{ sec}^{-1}$$

$$\text{Air} = 164 \text{ m}^3 \text{ min}^{-1} \text{ m}^{-2}$$

The drager tube sampling method was again used on the exit gas giving an indicated 200 ppm v/v NH_3 in the exit gas. Calculations based on air and liquor flows and the reduction in the solution NH_3 levels predict 170 ppm v/v NH_3 in the gas phase. Hence, the drager tubes appear to give realistic figures in this stage, at least.

10 The conclusion which can be drawn from this example is that chlorination of the CN^- can be achieved by near stoichiometric addition of chlorine. A small excess seems necessary, possibly due to reaction with ammonia at the lower CN^- levels.

Stripping of NH_3 from the alkaline solutions is very efficient with good tail solutions being obtained. Chlorinated amines in the exit gas would not appear to be a problem especially with accurate chlorination dosing control. Cyanate conversion is very rapid indeed and thus is not a
20 problem.

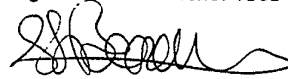
While it has been convenient to describe the invention herein in relation to particularly preferred embodiments, it is to be appreciated that other embodiments and arrangements are also considered as falling within the scope of the invention. Various modifications, alterations, variations and/or additions to the embodiments and arrangements described herein are also considered as falling within the scope and ambit of the present invention as defined by the claims.

CLAIMS

1. A process for reducing the cyanide content of a solution containing both cyanide ions and dissolved ammonia, comprising the following consecutive steps:
 - (a) adding a halogenating agent to the solution while maintaining the pH of the solution at greater than 7;
 - (b) removing ammonia from the solution by aeration;
 - (c) acidifying the solution to a pH of less than 7;
 - (d) substantially neutralising the solution; and
 - 10 (e) removing the ammonia from the solution by aeration.
2. A process according to Claim 1 wherein the aeration steps comprise air stripping for removal of ammonia from the solution.
3. A process according to Claim 1 or Claim 2 wherein the halogenation agent is a chlorination agent.
4. A process according to Claim 3 wherein the chlorination agent is chlorine gas.
5. A process according to Claim 4 wherein the chlorine gas is generated in solution.
- 20 6. A process according to any preceding claim wherein the pH is maintained at a level of between 11 and 12 during step (a).
7. A process according to any preceding claim wherein sodium hydroxide is used to raise pH in step (a) and/or step (d).
8. A process according to any preceding claim wherein ammonia removed from the solution is collected in a gas scrubbing system.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 90/00289

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6		
According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl. ⁵ C02F 9/00, 1/20, 1/66, 1/76, C22B 11/08		
II. FIELDS SEARCHED		
Minimum Documentation Searched 7		
Classification System	Classification Symbols	
IPC US Cl.	C02F 9/00, 1/20, 1/66, 1/76 210/904	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 8		
AU : IPC as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT 9		
Category*	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages 12	Relevant to Claim No 13
A	GB,A, 895741 (DEUTSCHE GOLD-UND-SILBER-SCHIEDEANSTALT VORMALS ROESSLER) 9 May 1962 (09.05.62)	(1)
A	GB,A, 1418743 (ELKEM-SPIGERVERKET A/S) 24 December 1975 (24.12.75) See example, figure.	(1)
A	US,A, 4029557 (CHRISTENSEN et al) 14 June 1977 (14.06.77) See claim 1, example.	(1)
A	US,A, 4070281 (TAGASHIRA et al) 24 January 1978 (24.01.78) See claims, examples.	(1)
A	US,A, 4105545 (MULLER et al) 8 August 1978 (08.08.78) See claims.	(1)
(continued)		
* Special categories of cited documents: 10 "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention		
"A"	document defining the general state of the art which is not considered to be of particular relevance	
"E"	earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search 4 October 1990 (04.10.90)		Date of Mailing of this International Search Report 11 October 1990
International Searching Authority Australian Patent Office		Signature of Authorized Officer  G.J. BROXAM

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	Derwent Abstract Accession no. 85591B/47, Class D15, SU,A, 650983 (NONFERR METAL RES.) 5 March 1979 (05.03.79)	(1)
A	Patents Abstracts of Japan, C-15, page 64, JP,A, 55-49191 (HITACHI PLANT KENSETSU KK) 10 March 1978 (10.03.78)	(1)
A	EP,A, 051967 (USS ENGINEERS & CONSULTANTS INC) 19 May 1982 (19.05.82) Claim 1, examples.	(1)
A	Patents Abstracts of Japan, C-226, page 164, JP,A, 32978 (KAWASAKI SETTETSU KK) 16 August 1982 (16.08.82)	(1)

V. [] OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE 1

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

- 1.[] Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:

- 2.[] Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

- 3.[] Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4 (a):

VI. [] OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 2

This International Searching Authority found multiple inventions in this international application as follows:

- 1.[] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
- 2.[] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

- 3.[] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. [] As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- [] The additional search fees were accompanied by applicant's protest.
 [] No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 90/00289

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Members			
GB	1418743	AU	51631/73	BE	794877
		CA	1005933	DE	2305457
		FR	2169928	GB	1418744
		JP	48084459	US	3950250
		US	4059514	BR	7300735
				ES	411034
				IT	974761
				ZA	7209010
US	4070281	DE	2534458	IT	1040320
		JP	51055774	JP	51121957
				JP	51017178
				JP	51025474
EP	51967	AU	76929/81	BR	8106874
		ES	8206389	JP	57132590
		US	4366064	ES	506690
				ZA	8107073

END OF ANNEX