

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 July 2003 (31.07.2003)

PCT

(10) International Publication Number
WO 03/062498 A1

(51) International Patent Classification⁷: C25C 01/12

(21) International Application Number: PCT/AU03/00056

(22) International Filing Date: 21 January 2003 (21.01.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PS 0095 23 January 2002 (23.01.2002) AU

(71) Applicant and

(72) Inventor: EVERETT, Peter, Kenneth [AU/AU]; 9/2a Palmer Street, Cammeray, NSW 2062 (AU).

(74) Agent: BALDWIN SHELSTON WATERS; 60 Margaret Street, Sydney, NSW 2000 (AU).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,

GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

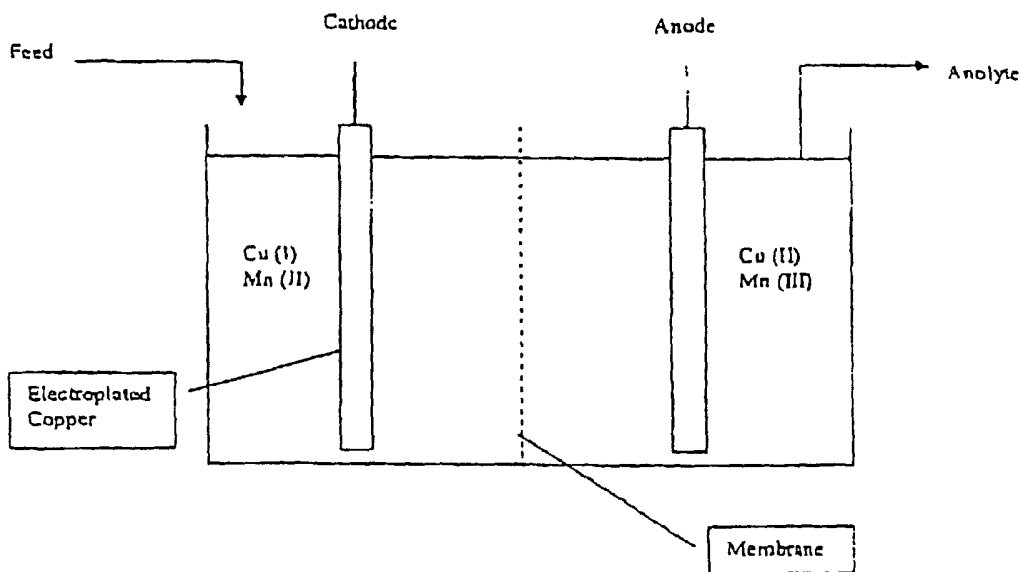
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations
- of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ANODIC ENERGY STORAGE IN ELECTROLYSIS OF A SINGLE HALIDE SOLUTION



(57) Abstract: The present invention describes a process for the electrolytic recovery of a metal, such as copper, from a single halide solution, wherein the single halide solution includes a variable valence ion, such as manganese, which does not contaminate the cathodically recovered metal. The ratio of the halide to the variable valence ion is controlled such that the solution can reach an E_h close to but less than that at which evolution of halogen gas occurs. The electrolyte recovered from this process may be used subsequently for the electrochemical leaching of metals, such as gold.



WO 03/062498 A1

Anodic Energy Storage in Electrolysis of a Single Halide Solution

Field of the Invention

5 The present invention relates to the electrowinning and leaching of base and precious metals, typically metals that have been leached into the solution in a halide leaching stage. More particularly, the invention relates to the storage of anodic energy in a soluble form as a result of electrolysis of the halide solution, which stored anodic energy can subsequently be used in the leaching of a mineral or metal.

10

Background to the Invention

 Internationally, energy costs and greenhouse gas emissions are taking on increased significance. Many prior art mineral leaching and electrolytic recovery processes do not make use of the anodic energy generated during the electrolysis process and rather allow this energy to effectively be wasted. The most common way in which this energy is wasted is the generation in the electrolysis process of oxygen at the anode, which is then dispersed to the atmosphere. This dispersion of oxygen can actually contribute to gas emissions, when the oxygen released is impure.

20 Some leaching/electrolysis processes use pressurised oxygen in the oxidation stage of the leaching process to enhance leaching, and this can further increase the release of oxygen to atmosphere during the process, together with noxious or greenhouse gases.

 Another disadvantage that occurs with the anodic generation of oxygen, for example by the electrolysis of water at the anode, is that an acid mist is normally generated. As water is broken down in the electrolysis process it produces half a molecule of oxygen and two hydrogen ions. When sulphur is present in the mineral that has been prior leached, this often results in a strong sulphuric acid solution. Some of this acid can be entrained in the oxygen leaving the process and be exhausted to atmosphere (producing acid rain).

30 Australian patent No. 669906 discloses a process known as the Intec Process. In the Intec process, bromide ion is added to a chloride electrolyte and, during electrolysis, anodic energy can be stored in a halide complex formed at the anode at a

high solution E_h (eg. 100 to 200 millivolts below the potential for chlorine evolution). Typically the energy is stored in the halide complex at a level below the evolution of chlorine gas. The resultant halide complex has sufficiently high oxidation potential such that it can be used subsequently to leach gold from difficult to leach mineral ores.

5 Thus, the halide species produced has the capacity to replace cyanide leaching.

In the Intec Process for copper, metal is deposited on the cathode by reduction of copper ions in the feed solution. This is commonly referred to as electrowinning. At the anode, cupric (Cu^{II}) ions are formed by oxidation of cuprous (Cu^{I}) ions. Also at the anode, oxidised bromide ions combine with chloride ions to form compounds such as
10 BrCl_2^- . This species has been observed to not contaminate the metal recovered at the cathode (eg. copper). Formation of this species is responsible for the high anolyte solution E_h obtained. Hence, the anolyte may be used subsequently for the electrolytic leaching of gold and other precious metals (*e.g.* platinum, palladium *etc.*) into solution.

However, the Intec process has several disadvantages. During the
15 electrowinning step, the BrCl_2^- formed in solution at the anode has an equilibrium with dissolved BrCl (bromine chloride). Bromine chloride is a volatile gas which can, to some extent, be released during electrolysis, and which therefore must be scrubbed or otherwise removed to prevent its release to the atmosphere.

Furthermore, the presence of bromide ions can interfere with the recovery of
20 leached gold from solution after the leaching stage. For example, where the leached gold is adsorbed onto activated carbon, the bromide ion can interfere with this process by complexing with the gold.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

25

Summary of the Invention

The present invention provides a process for the electrolytic recovery of a metal from a single halide solution, wherein the single halide solution includes a variable
30 valence ion which does not contaminate the cathodically recovered metal, and the ratio of the halide to the variable valence ion is controlled such that the solution can reach an E_h close to but less than that at which evolution of halogen gas occurs. Typically, this process is known in the art as electrowinning.

In the present invention, reference to a "single halide" allows for small amounts of other halides to be present, such as those which might be present in the leachate of a leached mineral.

In the present invention, when it is stated that the variable valence ion does not
5 contaminate the cathodically recovered metal, this statement allows for the presence of small quantities of contaminant, but at a level which does not affect the end use of the metal product. Preferably, the level of contamination in the cathodically recovered metal is less than 5 ppm, more preferably less than 3 ppm. Melting may further reduce contamination.

10 In the present invention, where reference is made to "an Eh close to but less than that at which evolution of halogen gas occurs", it is meant an E_h which is preferably within 500 mV, more preferably within 300 mV, and more preferably within 100-200 mV of the E_h at which evolution of halogen gas occurs.

Advantageously, the electrowinning process of the present invention does not
15 produce any volatile gases at the anode. In particular, there is no vapour pressure of, for example, bromine chloride above the cell. Since the process of the present invention does not produce any harmful volatile gases, the cell may be operated with an open anode chamber.

Preferably, the amount of halide ion is greater than the amount of variable
20 valence ion. Preferably the molar ratio of halide to the variable valence ion is high and is in range of 20:1 to 2:1, more preferably 7:1 to 4:1. More preferably, the molar ratio of halide to the variable valence ion is approximately 6:1.

In a most preferred form, the variable valence ion is a cation, because of the ease of control of the oxidation state thereof in solutions, however it is possible that the
25 variable valence ion may also be a complex anion. When the variable valence ion is a cation, a number of possible cations may be used. However, a suitable cation is manganese which is relatively abundant and inexpensive. In this regard, typically the anodic energy is stored in the form of a manganic (Mn^{3+}) ion which is sufficiently stable in strong halide solution, and which is also stable without the presence of an additional
30 complexing agent.

Preferably the single halide is chloride because of its ease of handling and abundance, but other single halides may be used.

Preferably, the process of the present invention is carried out under acid

conditions. Preferably, the pH of the electrolyte is less than 3.

Typically the process is used as part of the electrolytic recovery of copper (amongst other metals). Copper has the advantage that it can also absorb anodic energy (ie. the cuprous ion (Cu^+) along with the manganous ion (Mn^{2+}) get converted to cupric (Cu^{2+}) and manganic (Mn^{3+}) forms respectively). However, with appropriate
5 modification, the process can also be used for recovery of metals such as zinc, nickel, lead etc.

Advantageously, the process of the present invention can be used to generate a higher oxidation state of the variable valence ion, which can thereby increase the E_h of
10 electrolyte. The electrolyte having a high E_h may be used subsequently to leach gold and other precious metals from a mineral. Thus, the anodic energy is not wasted (eg. in the generation of oxygen or sulphuric acid). Typically the electrolyte having a high E_h is the anolyte. The anolyte may be separated from the catholyte by a membrane in the cell.

Accordingly, in a second aspect the present invention provides a process as
15 described above that forms part of a closed loop combined electrolytic/leaching process, such that the electrolyte from the electrolysis process is returned to the leaching stage, including the halide ion in solution at a high E_h and the variable valence ion in solution at a high oxidation state. This return electrolyte then functions as a lixiviant in the
20 leaching process and has been observed to oxidise difficult to leach metals such as gold and other precious metals into solution.

In another aspect, the present invention provides an electrochemical leaching process including the steps of:

- (a) conducting the process as described above;
- 25 (b) recovering the electrolyte (preferably the anolyte); and
- (c) adding a metal to be leached to the electrolyte.

The metal to be leached include any precious metal, such as gold, palladium, platinum, ruthenium, rhenium, rhodium, iridium *etc.* Preferably, the metal to be leached includes gold. Recovery of, for example, leached gold from solution is a facile and well known
30 process. Typically, recovery of gold from solution is conducted by adsorption of the gold onto activated carbon.

The leaching process of the present invention is advantageous because it avoids the use of harmful cyanide in the leach. Moreover, the absence of bromide ions

in the leach is advantageous, because bromide ions can interfere with subsequent recovery of gold from the leach.

It is envisaged that the present invention will be useful in recovering metals from many different types of ores and/or scrap metal. A particularly preferred
5 embodiment is where the feedstock includes gold-rich copper concentrates.

Brief Description of the Drawings

A preferred embodiment of the invention will now be described, by way of example
10 only, with reference to the accompanying drawings in which:

Figure 1 illustrates a diaphragm electrochemical cell used in the electrowinning process of the present invention.

Figure 2 shows the E_h of the anolyte solution over time during electrowinning.

Figure 3 shows the concentration of leached gold in solution increasing during
15 electrochemical leaching, and the E_h of the anolyte correspondingly decreasing.

Figure 4 shows a Pourbaix diagram for manganese and chloride ions in solution.

Modes for Carrying out the Invention

20 Notwithstanding any other forms which may fall within the scope of the invention, a preferred form of the invention will now be described, by way of example only with reference to the following non-limiting examples.

Example 1 – Electrowinning of Copper

25

An electrolyte of 150gm per litre sodium chloride 85°C was prepared. This electrolyte was electrolysed in an electrolytic cell by passing a current of approximately 700 Amps per square metre through the electrolyte. Passage of current led to the evolution (formation) of copious quantities of chlorine gas (as readily identified by the
30 noxious smell).

To this electrolyte 20 grams per litre of Mn^{2+} ion was added. It was observed that this addition stopped the evolution of chlorine gas. Further, to this solution, 30 grams per litre of Cu^{2+} ion was added, resulting in a brown solution resulting from the

formation of a cupric chloride complex. The preferred ratio of chloride ion to manganese ion was approximately 6 to 1, and it was observed that when the Cu^{2+} ion was added the solution could be controlled to reach an E_h close to but not greater than that at which chlorine gas evolved. The resultant E_h was approximately 1000 mV (with
5 respect to the standard Ag/AgCl electrode).

Thereafter, the addition of metallic copper to this solution resulted in the solution becoming clear, as the oxidant was consumed. The reaction is: $\text{Mn}^{3+} + \text{Cu}^0 \rightarrow \text{Mn}^{2+} + \text{Cu}^+$.

During electrolysis, and most surprisingly, there was no evidence of formation
10 of MnO_2 on the anode in the electrolytic cell. The formation of MnO_2 is a problem in a conventional zinc sulphate cell, and the absence of this problem was attributed to the high ratio of chloride ion to Mn^{2+} and Mn^{3+} ion. Thus, during electrolysis, the chloride ion was able to be maintained in solution, Mn^{2+} was oxidised to Mn^{3+} without the formation of MnO_2 at the anode, and a pure metal (copper) was able to form at the
15 cathode, which was observed to be substantially free of manganese impurity. Figure 4 illustrates the various oxidation states of manganese in solution over a range of pHs.

It was observed with the absence of a second halide such as Br^- in the electrolyte, that apart from the process being cheaper, no volatile halogen gas complex was formed which would have otherwise had a deleterious affect on plant hygiene and
20 which would have to have been removed (ie. scrubbed) from any gas leaving the process.

Example 2

25 (i) Electrowinning of Copper

A diaphragm electrochemical cell (diagram 1) was used which consisted of 1 plate anode (15cm X 9cm) and 2 cathodes made from prepared copper pipe. The solution was stirred and heated to 70°C. The cell was operated at 6A or 220A/m² based
30 on the estimated cathode surface, not including the deposited dendrites. From a mass balance of the system 13.5 g Cu would be reduced from the solution, giving an approximate flow rate to the cell of 0.3 l/hr of feed. The feed composition is given below.

Table 1: Feed Concentration

Component	Concentration (g/l)
Cu(I) Chloride	80
Mn(II) Chloride	20
NaCl	150

The feed solution was made by the addition of the required components.

5 Copper powder was added to ensure that the copper (I) chloride was formed.

The cell was first filled with 3 litres of feed solution at the beginning of the experiment. The liquor composition was 30 g/l Cu, 20g/l Mn and 150g/l NaCl. The cell was turned on for 15 minutes before the feed to the cell was started. This was to form Cu(II) in the anode chamber before any anolyte solution was to be taken off the
10 cell. The cell was operated for 30 minutes before the anolyte solution was collected for the second phase of the experiment.

At each sampling time, temperature, E_h (vs. a Ag/AgCl standard electrode), pH, current and voltage were measured. The solution and copper product were analysed for copper, manganese and gold by ICP-AES (Inductively Coupled Plasma –
15 Atomic Emission Spectroscopy).

The feed solution was made from copper (II) chloride, manganese chloride and sodium chloride at the respective concentrations required. It was required that copper (II) chloride was to be reduced to copper (I) chloride. To achieve this a large amount of copper powder was added (1kg) to reduce copper (II) to copper (I). While the solution
20 was in contact with air, the copper was oxidised to copper (II) compounds. It was observed that the pH of the feed solution increases over time. To maintain the desired pH of approximately 1.5, a large amount of concentrated hydrochloric acid was added over the week when the feed solution was made. Fine precipitates were also formed within the solution. To avoid fouling the cell membrane, the feed solution was filtered
25 before the experiment was carried out.

The cell was operated for 4 hours with a voltage drop of 2.51V and the current through the cell was 6A. Feed flow rate to the cell was 300ml/hr at a temperature of 70°C. Table 2 below shows an example of the concentrations of the feed to the cell and

the anolyte solution leaving the cell.

Table 2: Concentration of Copper and Manganese entering and leaving the cell

Time(min)	Anolyte Concentration (g/l)		Feed Concentration (g/l)	
	Cu	Mn	Cu	Mn
60	18.8	4.0	38.8	3.6
120	21.4	3.1	36.5	3.5
180	22.7	3.3	36.0	3.5
240	21.9	3.2	38.7	3.5

5 With time the E_h of the anolyte solution increased showing that the copper (I) was converted to copper (II). Manganese (II) was also oxidized to manganese (III). Figure 2 shows the E_h of the anolyte solution with time. The E_h reported was based on the silver/silver chloride reference electrode, with the maximum E_h reaching 1V after 1 hour of the cell running.

10 Samples of reduced copper product were taken at every hour to monitor the quality of copper produced. Samples were taken from the electrode and washed with distilled water to remove any electrolyte solution. The samples were dried to remove water and an approximate sample of 0.2g were taken and digested with 50ml of aqua regia. From the analysis below, manganese was present only in trace levels (Table 3),
15 and could be expected to be further reduced on melting of the copper.

Table 3: Copper purity and manganese levels within the copper sample

Sample	Mn content in copper product (ppm)
1 hour	2.95
2 hour	1.29
3 hour	1.11
4 hour	0.09
Composite	1.19

(ii) Leaching of gold

A 500ml anolyte solution was taken from the cell and brought to temperature (75°C). Approximately 0.1g of gold powder was added to the solution and 1ml samples
5 were taken to observe the gold dissolution. The E_h of the solution was monitored as the solution was brought up to temperature. As the temperature was increased, the E_h increased from 0.710V to 0.794V and the pH dropped from 0.55 to -0.24.

Gold was leached into the solution as shown in Figure 3 and the E_h correspondingly dropped. Within the 8 hour period the concentration of gold increased
10 to 193.2 ppm Au (corresponding to 90% dissolution) showing that the anolyte solution can leach gold.

The E_h of the anolyte was actually lower than when it was firstly made. This could be due to the decomposition of manganese (III), the active oxidant in the anolyte.

15 In summary, the Examples demonstrate the following advantages of the present invention:

- the electrolyte is cheap
- the electrolyte is non-volatile
- an open anolyte chamber may be employed
- 20 - the absence of bromide ions allows facile precipitation of gold and other precious metals.

Whilst the invention has been described with reference to a preferred embodiment, it should be appreciated that the invention can be embodied in many other forms.

Claims

1. A process for the electrolytic recovery of a metal from a single halide solution,
5 wherein the single halide solution includes a variable valence ion which does not contaminate the cathodically recovered metal, and the ratio of the halide to the variable valence ion is controlled such that the solution can reach an E_h close to but less than that at which evolution of halogen gas occurs.
- 10 2. A process according to claim 1 wherein the variable valence ion is a cation.
3. A process according to claim 2 wherein the cation is a manganese cation.
4. A process according to any one of the preceding claims wherein the variable
15 valence ion is manganese (II) ion.
5. A process for the electrolytic recovery of a metal from a single halide solution, including the step of adding to the solution a manganese (II) ion, wherein the ratio of the halide to the manganese (II) ion is controlled such that the solution can reach an E_h
20 close to but less than that at which evolution of halogen gas occurs.
6. A process according to any one of the preceding claims wherein the amount of halide ion is greater than the amount of variable valence ion.
- 25 7. A process according to claim 1 wherein the molar ratio of the halide to the variable valence ion is approximately 6 to 1.
8. A process according to any one of the preceding claims wherein the halide is chloride.
- 30 9. A process according to any one of the preceding claims wherein the metal to be recovered includes copper.

10. A process according to any one of the preceding claims which produces an electrolyte including the variable valence ion in a high oxidation state.
11. A process according to claim 10 wherein the electrolyte includes manganese
5 (III) ions.
12. A process according to claims 10 or 11 wherein the electrolyte is the anolyte, said anolyte being separated from the catholyte by a membrane.
- 10 13. A process as claimed in any one of the preceding claims that is part of a closed loop electrolytic/leaching process, such that the electrolyte returned to the leaching stage includes the halide ion in solution at a high E_h , and the variable valence ion in solution at a high oxidation state.
- 15 14. A leaching process including the steps of:
- (a) conducting the process according to any one of claims 1 to 12;
 - (b) recovering the electrolyte; and
 - (c) adding a metal to be leached to the electrolyte.
- 20 15. A leaching process according to claim 14 wherein the metal to be leached includes gold.
16. A process for the electrolytic recovery of a metal from a single halide solution substantially as herein described with reference to the Examples.
- 25 17. A process for leaching a metal substantially as herein described with reference to the Examples.

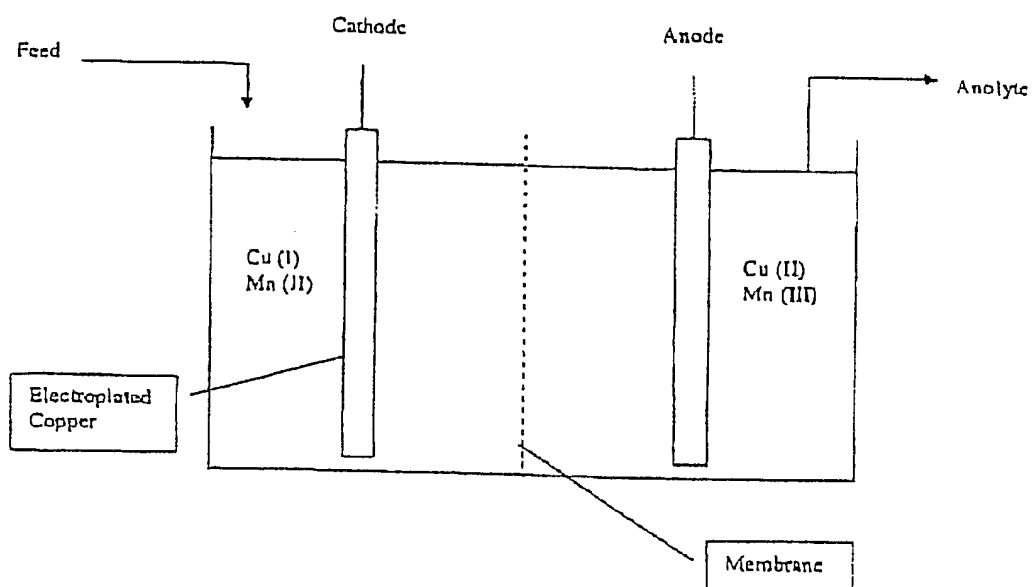


FIGURE 1

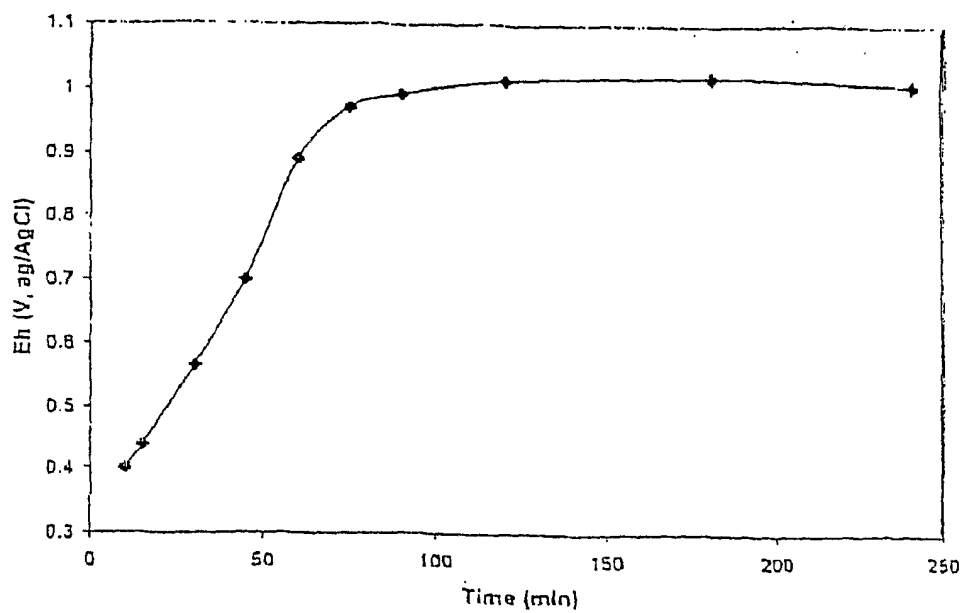


FIGURE 2

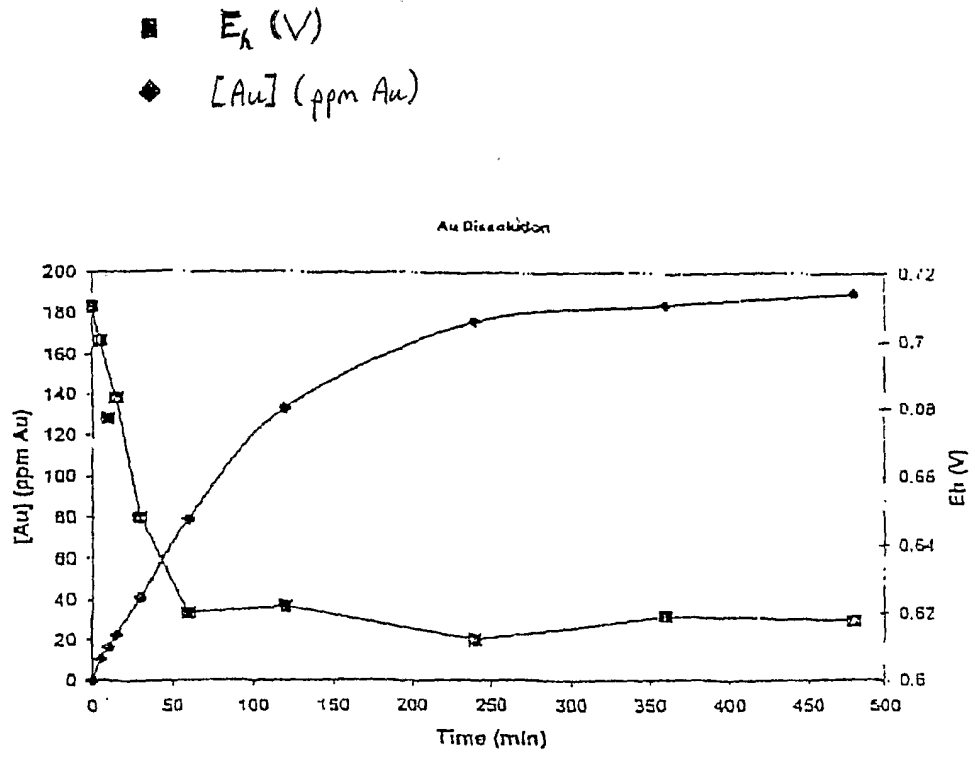
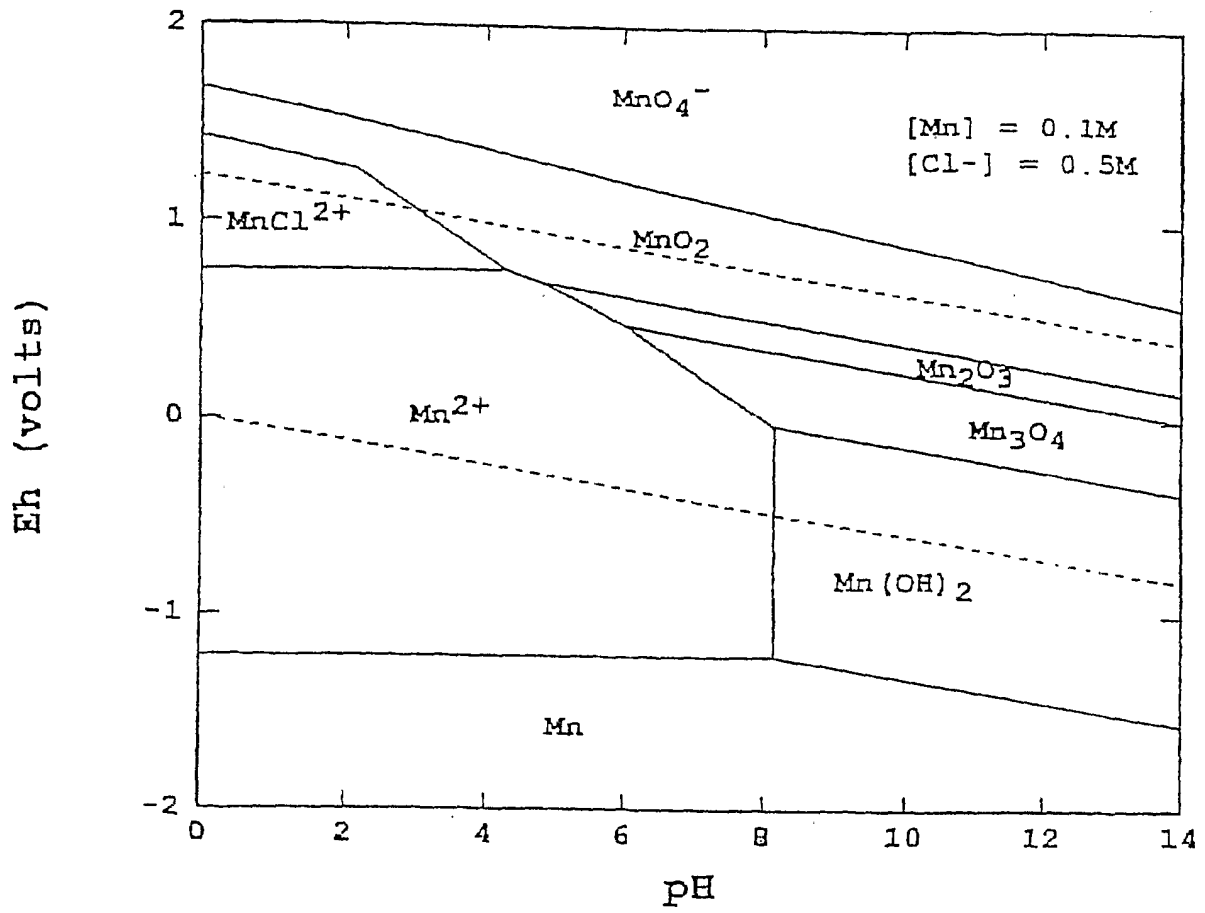


FIGURE 3

FIGURE 4



INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU03/00056

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : C25C 01/12		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DWPI: C25C 01/12 and keywords: halid+, halogen, chlorid+		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	Derwent Abstract Accession No. 84-153142/25, Class V04 & DE 3245-474 A (NAUMOV J I) 14 June 1984 See abstract	1-12 13-17
X	US 5837123 A (WONG et al) 17 November 1998 See columns 2 and 3	1-2, 8-9
X	US 6179988 B1 (PECKHAM et al) 30 January 2001 See claims 13-19	1-2, 9
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent 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 when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search 18 February 2003		Date of mailing of the international search report 26 FEB 2003
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustrialia.gov.au Facsimile No. (02) 6285 3929		Authorized officer THARU FERNANDO Telephone No : (02) 6283 2486

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU03/00056

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 3738996 A (ROBOTRON VEB K (DD)) 30 June 1988 See English abstract	1-17
A	Derwent Abstract Accession No. 2002-675656/73, Class M25 (M24) CN 1189541 A (UNIV DONGBEI) 5 August 1998 See abstract	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU03/00056

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 Member
DE 3245474	NONE
US 5837123	AU 27102/95
US 6179988	AU 81454/98 WO 9911842
DE 3738996	BR 9806138 DD 264824 EP 937163
CN 1189541	NONE
END OF ANNEX	