

RENOVARE INTERNATIONAL, INC.

REVIEWING THE OPERATION OF GOLD ELECTROWINNING CELLS

RenoCell® Technical Bulletin



June 28, 2011

NOTICE

Renovare International, Inc. believes the information and recommendations herein to be accurate and reliable as the date of this document and that Renovare's products mentioned herein are reasonably fit for the recommended purposes. However, as use conditions are not within its control, Renovare does not guarantee results from use of such products or other information herein; no warranties, expressed or implied, are given. As governmental regulations and application or use conditions may change, it is the User's responsibility to determine the appropriateness of Renovare's products for User's specific end uses. Freedom from patents or trade secrets of Renovare or others is not to be inferred. For any information that may have been published subsequent to the document's date, contact Renovare International, Inc.

The footnotes (1-4) provide the result of an analysis that is associated with Equation 5 in Tables A through D. The Au concentration with Table A, with Au concentration over the range 0.2 incrementally to 2G/M³(footnote 1); Table B the range 2 to 20 in increments of 2 G/M³; Table C the range 20 to 200 increments of 20G/M³; Table D from 200 to 2000. The corresponding equilibrium potential is provided with each Au concentration.

REVIEWING THE OPERATION OF GOLD ELECTROWINNING CELLS

RENOCELL® TECHNOLOGY

The RenoCell® is an advanced, patented electrolytic cell design that is being used today for electrowinning (EW) metal recovery from process and waste water streams of a variety of precious and heavy metals. The RenoCell® consistently and efficiently reduces dissolved heavy (and all precious) metal to the sub-mg/L (ppm) concentration levels in a wide range of applications. The revolutionary performance of the RenoCell® is the result of a patented EW cell design that, for the first time, effectively utilizes a three-dimensional (3-D) cathode incorporating a porous carbon fiber plating element. The key to performance in any EW cell design is effective use of the surface area of the cathode available for electrodeposition of the dissolved metal ions. Since the porous carbon felt has at least a 500 times greater effective surface area than an equivalent 2-D planar cathode, and the RenoCell® design provides effective current and fluid flow distribution to this surface area, RenoCell® performance is greatly enhanced when compared to existing electrolytic cell designs.

The net result is that the RenoCell® can achieve much lower final metal ion concentrations using far less energy. This results in more metal removal in less time, and lower metal concentrations than has ever been achieved by EW technology to remove a given amount of metal from a metal-bearing solution. In general, RenoCell® is capable of a factor of 100 or lower final concentration of metal ions and three to ten or more times higher current efficiency than other electrolytic cells. RenoCell® is being used to achieve metal discharge effluent limits without further treatment; collects metals as elements ready for reuse or sale; use removable cartridges for ease of operations and maintenance; and improve cost effectiveness and reduce life cycle costs. RenoCell®'s enclosed cell design and small "footprint" allow the user substantial flexibility in placing a unit in a tight space.

A RenoCell® metal recovery system consists of the world's most efficient and highest performance electrowinning (EW) cell, a direct current (DC) power supply, and auxiliary equipment. Metal-bearing waste water or a process stream is electrolytically stripped of dissolved heavy metal ions as it passes through the RenoCell®. The metal ions are deposited as solid metal onto a specialized high surface area, carbon cathode. When the cathode is fully loaded, it is easily removed from the cell and replaced with a fresh one. The loaded carbon cathode can then be burned in a furnace or sold for its metal value.

1. INTRODUCTION

As mining operations strive to increase ore throughput and grade, it is becoming increasingly common for plant personnel to find plant solution tails rising. Often, this is a result of not moving the carbon through the adsorption circuit quickly enough. Inadequate stripping capacity, particularly in circuits using the Zadra elution process, is sometimes the limiting step. Within the stripping process it is often electrowinning (EW) performance that is determining maximum stripping frequency. With this in mind, it may be useful to review gold electrowinning and explore if and how electrowinning efficiency may be improved.

This technical paper will:

- Present some EW theory,
- Discuss the factors that can effect EW efficiency, and
- Discuss the EW RenoCell® technology and experience, as related to the more common EW cells.

To a great extent, the calculations made to size a standard gold electrowinning cells are based on data and models reported by Roger Paul of Mintek in SA. Extensive plant data collected and interpreted by Mike Costello (Australia) has been used to further enhance the methodology used to size common gold EW cells. Discussion presented is based on the “Mintek”-type cell and compared to the RenoCell® and others as available. Most comments, except for RenoCell®’s efficiencies and potential for Direct electrowinning (DEW) are relevant to other cell types.

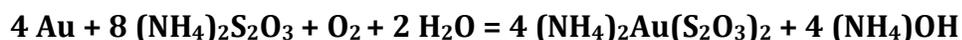
1.1 LEACH CHEMICAL PROCESS

The hydrometallurgical leaching of gold from gold-bearing ores or the dissolution of gold metal during the recycling of electronic and precious metal scrap is performed every day using hazardous chemicals. These chemicals represent risks for workers and threat for the environment. However, several other reagents are known to dissolve gold at the laboratory scale, none of these are used industrially. All of the hydrometallurgical gold extraction routes utilize a leaching step to produce a gold-bearing solution as an intermediate product while the recycling of secondary gold from the recycling of secondary gold from electronic and precious metal scrap using selective and fast dissolution of the precious metal constituents. Therefore, either leaching or dissolution operations require highly corrosive media due to the well-known chemical inertness of the noble metal toward most acids and bases.

Several reagents are known to leach gold from gold-bearing ores. It has been known for more than a century that alkaline solutions of alkali-metal cyanides (e.g., NaCN, KCN) dissolve gold under aerated conditions. The dissolution of metallic gold is due to the strong complexing capabilities of cyanide anions combined with the oxidizing properties of the dissolved molecular oxygen. Upon dissolution, gold forms the stable dicyanoaurate (III) complex anion $[\text{Au}(\text{CN})_2]^-$, as follows:



Other oxidizing compounds like cyanogen bromide (CNBr) can also be used to replace dissolved oxygen. Gold metal is also leached by aerated aqueous solutions of ammonium thiosulfate according to the overall reaction scheme given in the following formula:

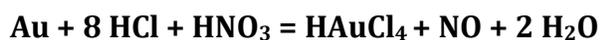


Finally, gold metal is dissolved by an aerated solution containing thiourea according to the following overall reaction:



However, only the cyanidation process is used industrially in hydrometallurgical processes. The optimized leaching conditions are usually a concentration of lixiviant of 0.1 - 0.2 mol·dm⁻³ NaCN. Enough NaOH must be present as neutralizer to maintain alkaline conditions at a constant pH of 11.

Several reagents can be used in the dissolution of gold metal from electronic and precious metal scrap. Among them, hot aqua regia is extensively used in small- and medium-scale operations. It is obtained by mixing three parts of concentrated hydrochloric acid (HCl) with one part of concentrated nitric acid (HNO₃). Moreover, it usually contains a halogen or even a certain amount of hydrogen peroxide to increase the dissolution rate. Upon dissolution in this media, gold forms the stable tetrachloroaurate (III) complexing anion (AuCl_4^-), in the following formula:



The main drawback of the treatment with aqua regia is the nitric oxide (NO) gas that evolves when the metal is digested. This noxious gas represents a major threat for the health and safety of the workplace. Apart from aqua regia, other corrosive reagents have been used or tested. For example, gold was dissolved into chlorine water (i.e., water saturated by chlorine gas) while bromine water has also been mentioned. It was the first metallurgical process to recover gold. Others studying the action of chlorine water onto gold, suggested that the dissolution mechanism is based on the reaction of molecular chlorine in water followed by a decomposition of a fraction of the hydrochloric acid,

yielding nascent chlorine. On the other hand, strong halohydric acids HX (e.g., HCl, HBr) in which the corresponding halogen X (e.g., Cl, Br) is dissolved have been known and used from several in the presence of both a strong oxidant and a halide anion under highly acidic solutions. Moreover, a hot solution of hydrochloric acid mixed with a hydrogen peroxide also dissolves gold by the following:



It has been shown that the dissolution of gold is facilitated by formation of the highly reactive nascent chlorine. However both the hydrometallurgical leaching of gold ores by cyanidation and the aqua regia process used for the secondary gold from waste electronics and precious metal scrap recovery are processes where both the lixiviant and reagent are hazardous chemicals that have serious health, safety, and environmental concerns but are widely used commercially because they are proven and have lower capital and, often, lower operating costs than competing techniques.

The hydrometallurgical leaching of gold from gold-bearing ores or the dissolution of gold metal during the recycling of electronic and precious metal scrap is performed every day using hazardous chemicals. These chemicals represent risks for workers and threat for the environment. However, several other reagents are known to dissolve gold at the laboratory scale, none of these are used industrially. All the hydrometallurgical gold extraction routes utilize a leaching step to produce a gold-bearing solution as an intermediate product while the recycling of secondary gold from the recycling of secondary gold from electronic and precious metal scrap using selective and fast dissolution of the precious metal constituents. Therefore, either leaching or dissolution operations require highly corrosive media due to the well-known chemical inertness of the noble metal toward most acids and bases.

1.1.1.1 CYANIDE LEACH CHEMISTRY

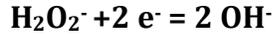
Cyanide leaching of gold (Au) is an electrochemical procedure that can be described by the following reactions:

Anodic:



Cathodic:





that yields:



In aqueous, alkaline cyanide leaches, Au oxidizes and dissolves forming Au (I) cyanide complexes in three stages where the species causes temporary passivation of the Au surface leading to a complex with free cyanide to form a $\text{Au}(\text{CN})_2^-$ ion and finally a passivating Au (III) oxide layer that only is available at a high positive potential that is not common.

2. MORE ELECTROWINNING THEORY

EW involves the exchange of electrons between a solid electrode and ions or molecules dissolved in solution. The rate of the reactions involved depends on the electrode potential, the electrode area and the rate of mass transport of the electroactive species to the electrode surface of interest.

If the cathode potential is sufficiently negative, all of the electroactive species undergo reduction to metal as soon as they reach its surface. The current at which this point is reached is known as the *limiting current*. Further increasing the cathode potential only results in the depletion, at the cathode surface, of the metal salt (ion) being reduced. At this point the transport of the ionic species through the Nernst boundary layer to the cathode surface becomes the rate-determining step. That is, the rate of metal reduction at the cathode has moved from electrochemical (kinetic) control to mass transport control. To increase the rate of the EW process under these conditions, it is necessary to increase either the electrode area (RenoCell®) or the rate at which the electroactive species are delivered (RenoCell®) to the cathode.

For the conditions noted, Tables A through F present the equilibrium electrode potential ($E_{\text{eq}}\text{SHE}$) for a number of reactions of the general form:

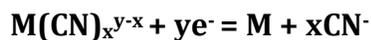


Table A: Equilibrium Potential for the Reduction of Metal-Cyanide Ions*

REACTION	METAL VALENCE	METAL CONC. (G/M ³)	E _{EQ} (V _{SHE})
(1) $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- = 4\text{OH}^-$	pH = 13	-	+0.45
(2) $\text{Hg}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Hg} + 4\text{CN}^-$	2	0.2	-0.448
(3) $\text{Pb}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Pb} + 4\text{CN}^-$	2	0.2	-0.498
(4) $\text{Ag}(\text{CN})_2^- + \text{e}^- = \text{Ag} + 2\text{CN}^-$	1	0.1	-0.568

(5) $\text{Au}(\text{CN})_2^- + e^- = \text{Au} + 2\text{CN}^-$	1	0.2	-0.514
(6) $\text{Cu}(\text{CN})_3^{2-} + e^- = \text{Cu} + 3\text{CN}^-$	1	0.06	-0.868
(7) $2\text{H}_2\text{O} + 2e^- = \text{H}_2(\text{g}) + 2\text{OH}^-$	pH = 13	-	-0.78
(8) $\text{Fe}(\text{CN})_6^{4-} + 2e^- = \text{Fe} + 6\text{CN}^-$	2	0.06	-1.108
(9) $\text{Ni}(\text{CN})_4^{2-} + 2e^- = \text{Ni} + 4\text{CN}^-$	2	0.06	-1.188
(10) $\text{Zn}(\text{CN})_4^{2-} + 2e^- = \text{Zn} + 4\text{CN}^-$	2	0.07	-1.338

* Metal ion concentration = 10^{-6} mol/liter; Free cyanide concentration = 0.2%

Table A has been carefully prepared to serve as a model for Tables B through F, with the only real difference being metal ion concentrations and their ion equilibrium potential reduction of metal-cyanide ions, focusing upon the Au ions in a variety of analyses, as follows:

Table B: Equilibrium Potential for the Reduction of Metal-Cyanide Ions*

REACTION	METAL VALENCE	METAL CONC. (G/M ³)	E _{EQ} (V _{SHE})
(1) $2\text{H}_2\text{O} + \text{O}_2 + 4e^- = 4\text{OH}^-$	pH = 13	-	+0.45
(2) $\text{Hg}(\text{CN})_4^{2-} + 2e^- = \text{Hg} + 4\text{CN}^-$	2	2.0	-0.389
(3) $\text{Pb}(\text{CN})_4^{2-} + 2e^- = \text{Pb} + 4\text{CN}^-$	2	2.1	-0.439
(4) $\text{Ag}(\text{CN})_2^- + e^- = \text{Ag} + 2\text{CN}^-$	1	1.1	-0.509
(5) $\text{Au}(\text{CN})_2^- + e^- = \text{Au} + 2\text{CN}^-$ ²	1	2.0	-0.572
(6) $\text{Cu}(\text{CN})_3^{2-} + e^- = \text{Cu} + 3\text{CN}^-$	1	0.6	-0.809
(7) $2\text{H}_2\text{O} + 2e^- = \text{H}_2(\text{g}) + 2\text{OH}^-$	pH = 13	-	-0.78
(8) $\text{Fe}(\text{CN})_6^{4-} + 2e^- = \text{Fe} + 6\text{CN}^-$	2	0.6	-1.049
(9) $\text{Ni}(\text{CN})_4^{2-} + 2e^- = \text{Ni} + 4\text{CN}^-$	2	0.6	-1.129
(10) $\text{Zn}(\text{CN})_4^{2-} + 2e^- = \text{Zn} + 4\text{CN}^-$	2	0.7	-1.279

¹ Au conc. G/M³: 0.02, 0.04, 0.06; 0.08, 0.1, 0.12, 0.14, 0.16, 0.18, 0.2

E_{EQ}: -0.456; 0.4783 -0.483, -0.491, -0.496, -0.500, -0.505, -0.5.8, -0.511, -0.517

² Au conc. G/M³: 0.2, 0.4, 0.59, 0.79, 0.99, 1.18, 1.29, 1.57, 1.77, 2.0

E_{EQ}: -0.517, -0.513, -0.541 -0.548, -0.554, -0.559, -0.563, -0.566, -0.569, -0.572

* Metal ion concentration = 10^{-5} mol/liter; Free cyanide concentration = 0.2%

Table C: Equilibrium Potential for the Reduction of Metal-Cyanide Ions*

REACTION	METAL VALENCE	METAL CONC. (G/M ³)	E _{EQ} (V _{SHE})
(1) $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- = 4\text{OH}^-$	pH = 13	-	+0.45
(2) $\text{Hg}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Hg} + 4\text{CN}^-$	2	20	-0.33
(3) $\text{Pb}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Pb} + 4\text{CN}^-$	2	20.7	-0.38
(4) $\text{Ag}(\text{CN})_2^- + \text{e}^- = \text{Ag} + 2\text{CN}^-$	1	10.7	-0.45
(5) $\text{Au}(\text{CN})_2^- + \text{e}^- = \text{Au} + 2\text{CN}^-$ ³	1	19.7	-0.63
(6) $\text{Cu}(\text{CN})_3^{2-} + \text{e}^- = \text{Cu} + 3\text{CN}^-$	1	6.3	-0.75
(7) $2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2(\text{g}) + 2\text{OH}^-$	pH = 13	-	-0.78
(8) $\text{Fe}(\text{CN})_6^{4-} + 2\text{e}^- = \text{Fe} + 6\text{CN}^-$	2	5.5	-0.99
(9) $\text{Ni}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Ni} + 4\text{CN}^-$	2	5.9	-1.07
(10) $\text{Zn}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Zn} + 4\text{CN}^-$	2	6.5	-1.22

* Metal ion concentration = 10^{-4} mol/liter; Free cyanide concentration = 0.2%

Table D: Equilibrium Potential for the Reduction of Metal-Cyanide Ions*

REACTION	METAL VALENCE	METAL CONC. (G/M ³)	E _{EQ} (V _{SHE})
(1) $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- = 4\text{OH}^-$	pH = 13	-	+0.45
(2) $\text{Hg}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Hg} + 4\text{CN}^-$	2	200	-0.271
(3) $\text{Pb}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Pb} + 4\text{CN}^-$	2	207	-0.321
(4) $\text{Ag}(\text{CN})_2^- + \text{e}^- = \text{Ag} + 2\text{CN}^-$	1	107	-0.391
(5) $\text{Au}(\text{CN})_2^- + \text{e}^- = \text{Au} + 2\text{CN}^-$ ⁴	1	197	-0.736
(6) $\text{Cu}(\text{CN})_3^{2-} + \text{e}^- = \text{Cu} + 3\text{CN}^-$	1	63	-0.691
(7) $2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2(\text{g}) + 2\text{OH}^-$	pH = 13	-	-0.78
(8) $\text{Fe}(\text{CN})_6^{4-} + 2\text{e}^- = \text{Fe} + 6\text{CN}^-$	2	55	-0.99

³ Au conc. G/M³: 2.0, 3.94, 5.91, 7.85, 9.85, 11.52, 12.50, 14.78, 16.85, 18.81, 19.7

E_{EQ}: -0.572, -0.589, -0.600, -0.607; -0.612; -0.617; -0.621; -0.624; -0.627; -0.633

⁴ Au conc. G/M³: 20;39.4;59.1, 78.5, 98.5, 115.2, 135.0; 158.5, 178.1, 197

E_{EQ}: -0.63;-0.648;-0.658;-0.665;-0.671;-0.675;-0.679;-0.682;-0.685;-0.688

(9) $\text{Ni}(\text{CN})_4^{2-} + 2e^- = \text{Ni} + 4\text{CN}^-$	2	59	-1.011
(10) $\text{Zn}(\text{CN})_4^{2-} + 2e^- = \text{Zn} + 4\text{CN}^-$	2	65	-1.161

* Metal ion concentration = 10^{-3} mol/liter; Free cyanide concentration = 0.2%

Table E: Equilibrium Potential for the Reduction of Metal-Cyanide Ions*

REACTION	METAL VALENCE	METAL CONC. (G/M ³)	E _{EQ} (V _{SHE})
(1) $2\text{H}_2\text{O} + \text{O}_2 + 4e^- = 4\text{OH}^-$	pH = 13	-	+0.45
(2) $\text{Hg}(\text{CN})_4^{2-} + 2e^- = \text{Hg} + 4\text{CN}^-$	2	2000	-0.212
(3) $\text{Pb}(\text{CN})_4^{2-} + 2e^- = \text{Pb} + 4\text{CN}^-$	2	2070	-0.262
(4) $\text{Ag}(\text{CN})_2^- + e^- = \text{Ag} + 2\text{CN}^-$	1	1070	-0.332
(5) $\text{Au}(\text{CN})_2^- + e^- = \text{Au} + 2\text{CN}^-$	1	19.7	-0.63
(6) $\text{Cu}(\text{CN})_3^{2-} + e^- = \text{Cu} + 3\text{CN}^-$	1	630	-0.632
(7) $2\text{H}_2\text{O} + 2e^- = \text{H}_2(\text{g}) + 2\text{OH}^-$	pH = 13	-	-0.78
(8) $\text{Fe}(\text{CN})_6^{4-} + 2e^- = \text{Fe} + 6\text{CN}^-$	2	550	-0.872
(9) $\text{Ni}(\text{CN})_4^{2-} + 2e^- = \text{Ni} + 4\text{CN}^-$	2	590	-0.952
(10) $\text{Zn}(\text{CN})_4^{2-} + 2e^- = \text{Zn} + 4\text{CN}^-$	2	650	-1.102

*Metal ion concentration = 10^{-2} mol/liter; Free cyanide concentration = 0.2%

Table F: Equilibrium Potential for the Reduction of Metal-Cyanide Ions*

REACTION	METAL VALENCE	METAL CONC. (G/M ³)	E _{EQ} (V _{SHE})
(1) $2\text{H}_2\text{O} + \text{O}_2 + 4e^- = 4\text{OH}^-$	pH = 13	-	+0.45
(2) $\text{Hg}(\text{CN})_4^{2-} + 2e^- = \text{Hg} + 4\text{CN}^-$	2	20000	-0.153
(3) $\text{Pb}(\text{CN})_4^{2-} + 2e^- = \text{Pb} + 4\text{CN}^-$	2	20700	-0.203
(4) $\text{Ag}(\text{CN})_2^- + e^- = \text{Ag} + 2\text{CN}^-$	1	10700	-0.273
(5) $\text{Au}(\text{CN})_2^- + e^- = \text{Au} + 2\text{CN}^{-5}$	1	197	-0.688
(6) $\text{Cu}(\text{CN})_3^{2-} + e^- = \text{Cu} + 3\text{CN}^-$	1	6300	-0.573
(7) $2\text{H}_2\text{O} + 2e^- = \text{H}_2(\text{g}) + 2\text{OH}^-$	pH = 13	-	-0.78
(8) $\text{Fe}(\text{CN})_6^{4-} + 2e^- = \text{Fe} + 6\text{CN}^-$	2	5500	-0.813

⁵ Au conc. G/M³: 197;394;591;758;986;1182

E_{EQ}: -0.688;-0.705;-0.716;-0.723;-0.726;-0.733

(9) $\text{Ni}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Ni} + 4\text{CN}^-$	2	5900	-0.893
(10) $\text{Zn}(\text{CN})_4^{2-} + 2\text{e}^- = \text{Zn} + 4\text{CN}^-$	2	6500	-1.043

* Metal ion concentration = 10^{-1} mol/liter; Free cyanide concentration = 0.2%

Table G: Equilibrium Potential for the Reduction of Metal-Cyanide Ions with Changing Temperatures*

REACTION	T C	Au (G/M ³)	E _{EQ} (V _{SHE})	Au (G/M ³)	E _{EQ} (V _{SHE})	Au (G/M ³)	E _{EQ} (V _{SHE})
$\text{Au}(\text{CN})_2^- + \text{e}^- = \text{Au} + 2\text{CN}^-$	20	0.2	-	1.97	-	19.7	-
	25	0.2	-0.54	1.97	-0.572	19.7	-0.63
	30	0.2	-0.59	1.97	-0.570	19.7	-0.63
	40	0.2	-0.506	1.97	-0.568	19.7	-0.63
	50	0.2	-0.501	1.97	-0.566	19.7	-0.63
	60	0.2	-0.497	1.97	-0.564	19.7	-0.63
	70	0.2	-0.493	1.97	-0.562	19.7	-0.63
	80	0.2	-0.490	1.97	-0.560	19.7	-0.63
	90	0.2	-0.485	1.97	-0.558	19.7	-0.63
	120	-	-	-	-	-	-

* All other ions concentration = 10^{-4} mol/liter (each); Free cyanide concentration = 0.2%

Table H: Equilibrium Potential for the Reduction of Metal-Cyanide Ions with Changing Temperatures*

REACTION	T C	Au (G/M ³)	E _{EQ} (V _{SHE})	Au (G/M ³)	E _{EQ} (V _{SHE})	Au (G/M ³)	E _{EQ} (V _{SHE})
$\text{Au}(\text{CN})_2^- + \text{e}^- = \text{Au} + 2\text{CN}^-$	20	19.7	-0.63	197	-0.688	1970	-0.746
	25	19.7	-0.63	197	-0.689	1970	-0.748
	30	19.7	-0.63	197	-0.690	1970	-0.750
	40	19.7	-0.63	197	-0.692	1970	-0.754
	50	19.7	-0.63	197	-0.694	1970	-0.758
	60	19.7	-0.63	197	-0.696	1970	-0.762
	70	19.7	-0.63	197	-0.698	1970	-0.764
	80	19.7	-0.63	197	-0.700	1970	-0.766

	90	19.7	-0.63	197	-0.702	1970	-0.700
	120	19.7	-0.63	197	-	1970	-

* All other ions concentration = 10^{-4} mol/liter (each); Free cyanide concentration = 0.2%

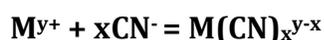
E_{eq} is calculated using the Nernst equation:

$$E_{eq} = E^0 + 0.059 \log \{M(CN)_{x^{y-x}} / [CN^-]^x\}$$

The standard reduction potential E^0 is calculated from the standard reduction potentials of the reaction:



with the equilibrium constant for the reaction:



As indicated in Tables A thru F above, cyanide complexes of mercury, lead, and silver will be electrodeposited in preference to gold. This is a very important point to note if you are electrowinning gold from an eluate with a high silver content since silver will be deposited (and hence will consume current) in preference to gold.

The reduction potentials for copper, nickel, iron and zinc are more negative than gold in cyanide chemistry. However, at the potential used in gold EW, the deposition of copper in particular is problematic depending on the copper concentration in the eluate. It is noted that every tenfold increase in copper concentration causes a positive shift of +0.059V in the copper equilibrium potential. Consequently, the equilibrium potential for 630 ppm copper in eluate will be approximately -0.63V, the same as gold at 20 ppm. As would be expected, copper recovery increases as the voltage (and consequently the current) applied increases.

2.1 INFLUENCE OF BASE METALS

Conventional electrowinning is best suited to the partial recovery of gold from solutions with high gold tenors. Furthermore, no foreign ions are introduced into the solution and it can also be efficiently operated at higher temperatures. High-grade gold can be produced that requires no further purification, provided that the solution to be treated does not contain metal ions that will be plated during EW. Unfortunately, this is an idealized assumption because base metals such as silver, copper, nickel, cobalt and iron typically occur with gold in the electrolyte as cyanide complex ions and may be plated out during EW. A major disadvantage of the conventional gold electrowinning process is its inability to produce discardable tailings. This is mainly due to the cathodic shift in the reduction potential of the $Au(CN)_2 / Au$ half reaction when the gold in solution decreases, resulting in

preferential deposition of base metals, and also a decrease in the mass transfer rate of aurodicyanide to the cathode surface, which may cause a significant decrease in the efficiency of conventional EW process.

As stated previously, base metals may influence the gold electrowinning process when present in high concentrations relative to that of gold or when too high overpotentials are applied. Base metals can adversely affect the EW process in terms of decreased current efficiencies, poor bullion fineness, and passivation of the cathode surface, and by influencing the morphology of the plated gold.

Much of these issues and problems are overcome by the RenoCell® electrowinning technology, either by producing discardable tailings and/or making direct electrowinning (DEW) and its positive features and extensive benefits available to the end user and operator.

The following electrochemical reactions are of relevance during the gold electrowinning process (E values quoted for metal ion concentrations of 10^{-4} mol.dm⁻³, NaCN concentration of 0.2% and NaOH concentrations of 2%).

The gold, which is present in the solution in the form of aurodicyanide ($\text{Au}(\text{CN})_2$), is reduced to metallic gold, according to Reaction (5) at potentials more negative than the reversible potential. Reaction (1), representing oxygen reduction in alkaline solutions, is another cathodic reaction competing with gold deposition. This is primarily because the electrolyte is typically saturated with oxygen due to the oxygen evolution occurring at the anode. Reaction (7) represents the evolution of hydrogen, which occurs at a significant rate at potentials more negative than $-0.9V_{\text{SHE}}$ when working at pH values above 10.1. The evolution of hydrogen should be under kinetic control at a significant range of potentials more negative than $-0.96 V_{\text{SHE}}$, and therefore may consume a high proportion of the cathodic current.

The major anodic reaction is the oxidation of water to oxygen, also indicated by Reaction (1) of the above tables. The reduction reaction of cuprous cyanide ($\text{Cu}(\text{CN})_3$) to metallic copper is indicated in Reaction (7). The more negative potential for the reduction of cuprous cyanide to metallic copper than that for the reduction of aurodicyanide to metallic gold signifies that gold should plate preferentially to copper at these conditions. However, copper may co-deposit with gold if high overpotentials are applied, or when the copper concentration is high relative to that of gold.

The kinetics of electrochemical reactions is typically studied by conducting polarization experiments in which the current required to change the potential of the electrode is determined. If the potential of the electrode is changed at a continuous rate, so-called potentiodynamic polarization diagrams are obtained. While it is relatively easy to obtain

polarization data, the interpretation is often difficult, as more than one reaction may contribute to the currents measured. Thus, it is preferable to first simplify the investigation of industrial scale systems by characterizing a purer electrolyte and then sequentially adding species that may contribute to further electrochemical reactions. In this way the contributions of the individual reactions may be isolated, if it can be assumed that interaction between the species will be minimal.

From an industrial point of view, it is typically essential with conventional EW to obtain loosely adherent precipitates that can be easily removed with high pressure water. If this cannot be achieved, some gold will get locked up inside the conventional electrowinning cells, which can result in electrowinning being uneconomical. This is not the case with the RenoCell® which allows all the captured value to be readily easily to be recovered by simply furnace processing of the metal coated carbon cathode by simple burning at ~600°C. Unlike the stainless steel cathodes, the electrolyte temperature, current density, and conductivity of the electrolyte have typically proved to be the main parameters that influence the adhesion of gold precipitates; co-deposition of base metals, such as copper, may also have an effect on the morphology and adhesion of the precipitate.

The electrodeposition of gold in industrial electrowinning cells is typically operated under mass transfer control. Various testing protocols have been developed over the decades to allow important operational parameters to be investigated and allow more effective cells to be investigated and compared, and RenoCell® is the world's premier example.

Synthetic solutions are prepared to simulate plant conditions. For example, the electrolyte may be prepared by adding 2 % caustic soda together with 0.1 % CN, to simulate conditions normally encountered in plant practice. Chemical compositions typically ranged from low to high copper and gold concentrations in order to determine at which concentrations the influence of copper became problematic. The influence of gold and copper at various concentrations is typically studied as is the morphology of the deposited metal with conventional EW.

The influence of the gold tenor on the polarization behavior of stainless steel electrodes is well established. A positive shift in the potential, where the gold reduction could be noticed, from -1.09 VSSE to -0.95 VSSE at a current density of 85 mA/m² can be observed when the gold in solution concentration is changed from 5 ppm to 1,000 ppm. This signifies that, during the electrowinning process, the potential for gold reduction will also shift to more negative potentials as the gold is removed from the solution. This may result in a change in the rate-limiting step of the electrochemical reaction from diffusion control to chemical control when a constant potential is applied

As mentioned, copper may co-deposit with gold when present in high concentrations relative to the concentration of gold. It is evident that copper present in concentrations of

200 ppm and higher will plate preferentially to gold present at 5 ppm. At these concentrations, the current density for the copper reduction reaction is higher than that for the gold reduction reaction at an applied potential of -1.0 VSSE. Copper will therefore plate at a faster rate than gold under these conditions. Although the current efficiency for gold electrowinning is expected to decrease as copper co-deposits with gold, the rate of gold electrowinning should remain the same, whether copper is present in the solution or not. This is because, at a specific applied potential, the limiting current for gold reduction should be independent of the copper concentration, assuming that the electrode potential will be such that the rate-determining step for gold deposition will be the mass transfer of aurocyanide to the reaction interface. Very loosely adherent precipitates were obtained when gold is plated from solutions containing only gold. On the other hand, copper plated from pure copper containing solutions proved to be moderate to highly adherent. Further discussion of gold and mixed Au-Cu for common EW used by the gold mining industry now is found in *A Study of the Influence of Copper on the Gold Electrowinning Process*, by J. Steyn and R.F. Sandenbergh.

Although copper will co-deposit with gold during the electrowinning process, relatively high-grade gold can still be produced by controlling the potential of the cathode. While the presence of copper will lead to a decrease in the current efficiency for gold recovery, the rate at which gold is recovered should remain unaffected if a constant potential is applied. Observations made indicated that the influence of copper on the adhesion of the obtained precipitate is of greater importance than its influence on the electrowinning performance in terms of the rate and current efficiency. Highly adherent precipitates were obtained when copper and gold were plated from solutions containing high copper concentrations, typically at concentrations higher than 500 ppm Cu. The level of adhesion of a gold precipitate obtained from a solution containing 100 ppm Au increased significantly when 1000 ppm Cu was added to the solution. Adhesion is not a factor with RenoCell®'s carbon cathodes, which are disposable and allow the lowest residual level of barren gold to be reached consistently.

Base metals may influence the gold electrowinning process when present in high concentrations relative to that of gold or when too high overpotentials are applied. Base metals can adversely affect the EW process in terms of decreased current efficiencies, poor bullion fineness, and passivation of the cathode surface, and by influencing the morphology of the plated gold.

Much of these issues and problems are overcome by the RenoCell® electrowinning technology, by producing discardable tailings and/or making direct electrowinning (DEW) and its positive features and extensive benefits available to the end user and operator.

Reaction (3) represents the evolution of hydrogen, which occurs at a significant rate at potentials more negative than $-0.9V_{SHE}$ when working at pH values above 10.1. The evolution of hydrogen should be under kinetic control at a significant range of potentials more negative than $-0.96 V_{SHE}$ and, therefore, may consume a high proportion of the cathodic current.

The major anodic reaction is the oxidation of water to oxygen, also indicated by Reaction (2). The reduction reaction of cuprous cyanide ($Cu(CN)_3$) to metallic copper is indicated in Reaction (4). The more negative potential for the reduction of cuprous cyanide to metallic copper than that for the reduction of aurocyanide to metallic gold signifies that gold should plate preferentially to copper at these conditions. However, copper may co-deposit with gold if high overpotentials are applied, or when the copper concentration is high relative to that of gold.

2.2 POLARIZATION DIAGRAMS

The kinetics of electrochemical reactions is typically studied by conducting polarization experiments in which the current required to change the potential of the electrode is determined. If the potential of the electrode is changed at a continuous rate, so-called potentiodynamic polarization diagrams are obtained. While it is relatively easy to obtain polarization data, the interpretation is often difficult, as more than one reaction may contribute to the currents measured. Thus, it is preferable to first simplify the investigation of industrial scale systems by characterizing a purer electrolyte and then sequentially adding species that may contribute to further electrochemical reactions. In this way the contributions of the individual reactions may be isolated, if it can be assumed that interaction between the species will be minimal.

2.3 MORPHOLOGY OF THE PLATED GOLD

From an industrial point of view, with conventional EW it is essential to obtain loosely adherent precipitates that can be easily removed with high pressure water. If this cannot be achieved, some gold will get locked up inside the conventional electrowinning cells, which can result in electrowinning being uneconomical. The electrolyte temperature, current density, and conductivity of the electrolyte have typically proved to be the main parameters that influence the adhesion of gold precipitates. Co-deposition of base metals, such as copper, may also have an effect on the morphology and adhesion of the precipitate.

The electrodeposition of gold in industrial electrowinning cells is typically operated under mass transfer control. Various testing protocols have been developed over the decades to allow important operational parameters to be investigated and allow more effective cells to be investigated and compared.

Synthetic solutions are prepared to simulate plant conditions. For example, the electrolyte may be prepared by adding 2 % caustic soda together with 0.1 % CN, to simulate conditions normally encountered in plant practice. Chemical compositions typically ranged from low to high copper and gold concentrations in order to determine at which concentrations the influence of copper became problematic. The influence of gold and copper at various concentrations is typically studied, as is the morphology of the deposited metal.

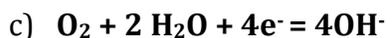
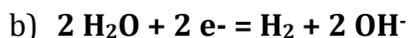
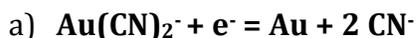
A decrease in the rate of gold electrowinning occurs when too-high overpotentials are applied. This is likely to be due to a decrease in the effective cathode area available for electrowinning because of the enhanced hydrogen evolution, as well as dislodging of the gold from the cathode surface due to the increased surface turbulence caused by the evolution of hydrogen gas. The optimum applied potential in conventional EW proved to be -1.2 VSSE, since the fastest electrowinning rate was obtained at this potential and a more loosely adherent precipitate can be expected than for gold plated at an applied potential of -1.0 VSSE.

2.4 OPERATIONS

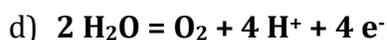
Although copper will co-deposit with gold during the electrowinning process, relatively high-grade gold can still be produced by controlling the potential of the cathode. While the presence of copper will lead to a decrease in the current efficiency for gold recovery, the rate at which gold is recovered should remain unaffected if a constant potential is applied.

During the EW of gold from an alkali cyanide electrolyte, the following reactions occur at the cathode and anode:

Cathode:



Anode:



Oxygen solubility in a hot eluate (electrolyte) is very low. Consequently, cathodic reaction (c) should not consume very much current. However, if the eluate linear flow rate is too high, oxygen generated at the anode may be carried into the cathode. Marsden and House report that the reduction of oxygen at the cathode can account for up to 50 % of the applied

current in some EW cells. Under conditions when gold EW from alkali cyanide electrolytes is mass transport controlled (that is, when the cathode potential is sufficiently negative), cathodic reaction (b) also occurs and hydrogen is evolved. It can be seen that both reactions (b) and (c) can generate hydroxide ion resulting in a localized increase in electrolyte pH at the cathode.

Gold deposition, reaction (a), is electrochemically controlled to a cathode potential of approximately $-1.0V$. At more negative cathode potential, the rate of gold reduction is typically mass transport controlled. Experience indicates that hydrogen evolution and gold reduction occur together until the limiting current is reached and the rate of gold deposition becomes mass transport controlled. Above the limiting current, the predominant reaction at the cathode is the evolution of hydrogen. When electrical energy is passed through a solution containing a metal salt, deposition of metal at an electrode will occur. The mass of metal deposited is dependent on the quantity of electrical energy passed through the solution. The quantity of electrical energy applied is measured in coulombs, where one coulomb is equal to one amp flowing for one second.

Assuming perfect current efficiency, the mass of metal deposited can be calculated using:

$$M = (I \times t \times A) / (Z \times F)$$

where M = mass of metal (grams)

I = current (amps)

t = time (seconds)

A = atomic mass of the metal

Z = metal valence in solution

F = Faraday's constant (96,500 coulombs)

In the case of gold, this formula indicates that the passage of 96,500 ampere seconds of electrical energy should result in the deposition of 197 g of gold. However, the generation of hydroxide ions, evolution of hydrogen, and reduction of other metals (such as Ag and Cu) that also occur at the cathode, consume most of the current applied. To take account of this inefficiency of the system, the term *current efficiency* (CE) is introduced. Data reported by Costello indicates that CE decreases as gold concentration in the eluate decreases. Based on operating plant data, Costello estimates that CE in a typical gold conventional EW cell is equal to approximately 15 % of the mean eluate gold grade. However, it is important to note that CE is also a function of current density. If the current density is too high, the CE will be poor regardless of the electrolyte gold concentration. In Australia, the current required by a gold EW system is generally calculated assuming an average CE in the range

8-12.5%. Corresponding values for RenoCell® are much higher and levels unreachable (<0.5mg/l and sometimes depending on system design <.02mg/l).

As noted in previously, the silver cyanide complex is more electropositive than gold. Consequently, it is reduced at the cathode in preference to gold during conventional EW. CE for silver deposition is generally assumed to be approximately 20%. RenoCell® is more efficient and also allows selective EW.

2.5 MINTEK EW CELL

The design of most EW cells used in the gold mining industry around the world has been derived from the Mintek cell. The Mintek cell is rectangular and consists of a series of alternately-placed anodes and cathodes arranged parallel to each other. In this type of cell, the direction of eluate flow is parallel to the direction of current flow. Typically, the anodes used are fabricated from stainless steel wire mesh or punched plate. The cathodes consist of a porous packed bed of very fine mild steel wire, or wool made by winding the steel wool around a cathode. Layers of woven stainless steel wire are also used as cathode material. Packed cathodes of steel wool or stainless steel wire provide a very high cathode surface area while maintaining good cathode porosity (trying to get improved performance like that reached by the RenoCell®).

In Mintek-type cells, the potential drop that occurs across the cathode bed limits its thickness. The rate at which the potential falls as the distance from the anode increases is dependent on the conductivity of the electrolyte. As the potential falls, the rate of gold reduction at the cathode surface moves from mass transport control to electrochemical (kinetic) control. If the cathode bed is too thick, the potential continues to fall until gold deposition stops and electrical bypassing occurs. Paul et al have noted that in the range – 1.0V to –1.3V, the deposition rate is determined by the electrode potential, while at potentials more negative than –1.3V, the rate is mass transport controlled.

A cathode is at its most electronegative on the two sides that face an anode. In these regions, the rate of gold reduction is mass transport controlled while in the other regions of this type of cathode, the rate of reduction is electrochemically controlled and in some parts of these regions, deposition does not occur. To ensure the region of mass transport control is maximized, the thickness of most packed bed cathodes is limited to between four and six centimeters. It is worth noting that there is a cathodic shift in the equilibrium potential for gold deposition of –0.12V for every tenfold decrease in gold concentration in the eluate. As a result, as gold concentration in the eluate decreases, an increasing proportion of the cathode becomes inactive for the reduction of aurocyanide ions to metallic gold in the Mintek-type cell.

For a gold EW cell utilizing packed bed cathodes, the cell design revolves around single pass extraction, E. Single pass extraction is defined as the fraction of an electroactive species removed from the eluate in a single pass through an EW cell. Single pass extraction is defined as:

$$E = 1 - c_{\text{out}} / c_{\text{in}} = 1 - \exp(-L/\lambda)$$

where c_{out} and c_{in} are the concentrations of the electroactive species entering and leaving a conventional EW cell respectively, L is the *total length* of packed bed cathode, and λ is known as the *characteristic length*.

The calculation of characteristic length (λ) that is dependent on the cathode surface area, the diffusion coefficient of aurocyanide, eluate linear flow rate, diffusion layer thickness, and voidage in the packed bed cathode. The characteristic length can be determined experimentally and varies proportionally with eluate linear flow velocity (u) and the thickness of the diffusion layer (δ) at the electrode surface. The value of δ is inversely proportional to the linear flow velocity raised to some power. As a result the value of the characteristic length can be expressed according to the equation $\lambda = ku^x$ where k , the mass transfer coefficient, is a constant. The value of the power, x , has been reported by various sources as having a value between 0.5 and 0.65. By assuming:

- Constant void space in the cathode bed,
- Constant cathode surface area, and
- An eluate flow rate approaching the practical flow limit (approximately 400 L/m²/min).

Paul has calculated a typical characteristic length to be approximately 31cm. From a practical viewpoint, it is important to note that characteristic length increases with the square root of the flow rate (approximately). The RenoCell[®] performance is optimized for low concentrations, which are expected from DEW from gold heap operation or other low concentration operation that allow single pass operations.

The reader is directed to the original Bulletin 2 to address the calculations and in depth discussion of optimization of convention EW and the various aspects of design of carbon systems and elution technology, none of which is required with RenoCell[®] EW technology.

3.1 INTRODUCTION AND BACKGROUND

A number of established techniques are available for the treatment of process and wastewater streams containing metal ions, including: electrodeposition, precipitation, ion exchange, adsorption and reverse osmosis. These methods have the disadvantages of the need for additional treatment technology to meet today's process water specifications and effluent discharge limits, and/or they produce a secondary effluent consisting of a more concentrated metal bearing solution or a mixed solid that requires further treatment, and they have high operational cost and complexity.

The technique of electrodeposition manifested in the RenoCell®⁶ technology can recover elemental metal directly from aqueous solution over a very wide range of metal ion concentration. In many cases, such as high value metals (e.g., Co, Ni) and precious metals (e.g., Au, Pt, Ag), this can allow the metal to be directly recycled. When the intrinsic toxicity of the metal (e.g., Cd, Hg) is the problem, removal of the metal from the waste stream in a single stage process is usually the most cost-effective solution. Where appropriate, electrochemical methods can also be used in conjunction with the other techniques to treat their secondary waste streams. A typical example is using RenoCell® to remove metal ions from ion exchange regenerant wastes allowing its reuse or neutralization and discharge.

3.2 PRINCIPLES OF OPERATION

Electrodeposition of a metal occurs at the cathode of an electrochemical cell while oxygen is produced at the anode due to the oxidation of water according to the following general reaction scheme (where M is a heavy or precious metal):

The performance of conventional electrochemical cells is limited at low metal ion concentrations. These devices are usually based upon metal plate or mesh cathodes in a tank with some means of mass transfer enhancement, e.g., by moving the electrodes or by achieving very turbulent solution flow. While this approach can be effective down to metal ion concentration levels of around 250 - 50 mg/L (often expressed as ppm, 1 ppm = 1 mg/L), effluent discharge limits are typically less than 5 mg/L and often below 1 mg/L (precious metals). Thus additional treatment would be required.

This problem has been addressed by Renovare by use of a patented electrochemical cell technology known as RenoCell® (see Figure 1). The RenoCell® design, for the first time,

⁶ RenoCell® is Renovare's registered trademarked name for the patented electrochemical deposition technology known as Porocell. Applicable U.S. patents include 5,690,806 and 6,162,333.

allows effective use of three-dimensional (3-D) cathode materials, in most cases a porous, carbon or graphite element⁷, via the flow path and current distribution embodied in the patent. The use of a 3-D cathode greatly enhances the performance of the cell since the carbon fiber element (~1000m²/g surface area) has a much larger effective surface area than a two-dimensional (2-D) electrode of the same nominal size. The design of the RenoCell® makes this very high surface area available for metal deposition at higher current efficiencies, lower current densities and higher deposition rates for a given nominal cell size than conventional cells with 2-D cathodes. The net result is that RenoCell® can achieve lower final metal ion concentrations while using less energy to remove a given amount of metal from a dilute metal-ion bearing solution. In general, RenoCell® is capable of a factor of 100 to 1000 lower final concentration of metal ions, and three to 10+ times higher energy efficiency than other commercial electrochemical cells.

The standard RenoCell® is constructed of high performance plastic that is mounted vertically to assure electrolyzed gases escape with effluent solution discharge. The RenoCell® can be mounted on a frame attached to a wall or a skid support structure, or within a cabinet housing.

The standard RenoCell® Model 500 for industrial applications consists of a cylindrical cathode enclosed in a 0.5m long polypropylene housing. The area of the cathode in this device, on a 2-dimensional basis, is approximately 0.1 m² while the actual plating area is at least 50 m². For certain applications, a variation of the standard Model 500 is used—the “divided” Model 500/D, which has a hydroscopic membrane (normally a cation-exchange membrane) positioned concentrically between the cathode and the anode. In this case, two electrolyte solutions, anolyte and catholyte, and consequent dual solution storage, circulation and control systems, are required. In most situations, the anolyte will consist of a small volume of compatible acid or salt solution. The divided cell system is applied to solutions containing chemical reactants that can be adversely oxidized at the anode or that would interfere with the cathodic deposition process, e.g., chlorine gas formation from chloride solution.

When the carbon element cathode is completely plated with metal to the point of reducing or blocking flow through the cell, as indicated by high pressure drop (typically about 0.7 bar) across the catholyte side of the cell, the cathode must be replaced. The spent cathode is removed from the RenoCell® by switching off the power supply and pumps, draining the cell of all fluids, disconnecting the outlet pipe or hose, removing the top end plate, and then extracting the metal-laden cathode cartridge assembly. A new cathode cartridge assembly

⁷ Other porous materials are utilized for special applications.

is then inserted into its locating position within the cell, the end plate, outlet hose and current feed connections re-attached, and the cell is ready for operation.

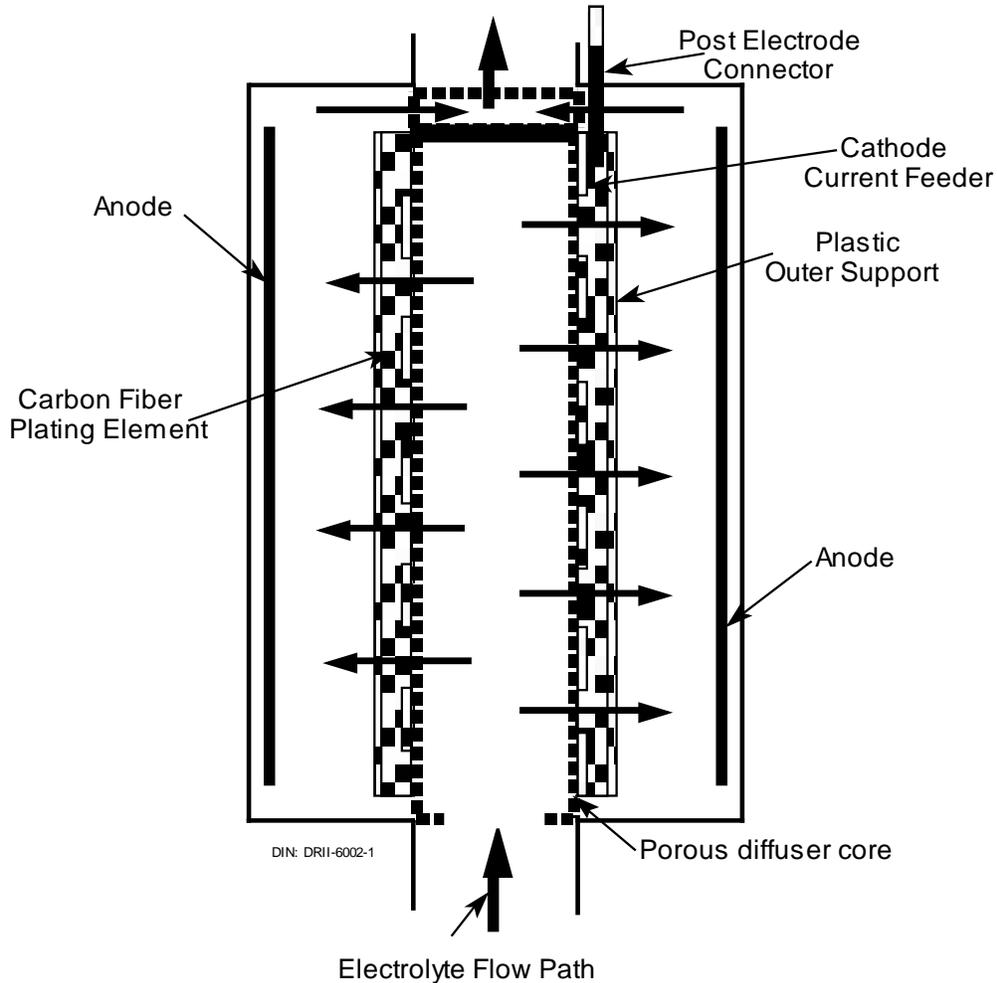


Figure 1: Schematic cross-section of standard RenoCell® (undivided)

The metal can be recovered from the cathode cartridge by removing the metal-laden carbon element and direct recovery in a furnace. The carbon is consumed in the furnace leaving only metal, and actually improves the quality of the melt by scavenging oxygen or other constituents that would otherwise reduce the final metal quality. As an alternate recovery methodology, the recovered metal can be re-dissolved anodically or chemically as a concentrated solution for: 1) recycling to the source process; 2) re-plating in a plate and frame type tank cell as a metal foil or sheet; or 3) precipitated as a salt. The cathode support and current feeder assembly can then be quickly refitted with a new carbon element and readied for reuse in subsequent cathode change-outs.

4.0 DIRECT ELECTROWINNING (DEW)

Direct electrowinning of precious metals directly from dilute (0.5 – 10 ppm Au) pregnant leach solutions. RenoCell® advanced electrowinning technology makes it commercially practical to directly electrowin precious metals from these mining and process solutions by providing significantly higher Faraday current efficiencies to recover precious metals concentrations to 0.1 ppm and below. The RenoCell's® patented design enables effective use of very high surface area three-dimensional (3-D) cathode materials. This unique design enables the economic recovery of gold, silver, and platinum group metals by direct electrowinning to below 0.1 ppm, often to less than 0.01 ppm, by providing:

- Porous cathode with very high active surface area,
- Replaceable cathode cartridge for easy metal recovery,
- Industry standard components in a compact, robust design,
- Optional divided cell configuration where required, and
- Significantly improved performance applicable to all electroplatable metals or electroprecipitable metal hydroxides and oxides.

RenoCells®, commercially used since 1998, are used successfully by the electronics, metal plating, and metal recovery industries in process and wastewater management applications. RenoCell® improves process quality and economics, and can meet metal effluent release limits in a single step. Base metals such as copper, cadmium, lead, tin, and zinc, and precious metals including gold, silver, palladium, platinum, and rhodium, in various leach or process electrolytes are being successfully removed and or recovered, often to below detection limits. Over 175 RenoCells® are in operation worldwide.

4.1 RENOCELL® PERFORMANCE

RenoCells® have been tested and are operating on a number of high-value metal recovery applications, primarily in the industrial process industries. The table below summarizes the recovery performance of the RenoCell® in four of these applications for precious metal recovery.

Table I: Typical RenoCell® Operating Experience

Source Stream	Metal	Initial (mg/L)	Final (mg/L)
Cyanide liquor	Au	380	< 0.1
Acidic liquors (simultaneous recovery)	Pt	24	1
	Pd	110	0.01
Acidic liquors	Pt	2000	0.5

Acidic liquors	Pd	500	< 0.5
----------------	----	-----	-------

In 18 test cases at a South African gold mine, the gold concentration in a carbon column eluant was reduced by the RenoCell® from ~350 mg/L Au to <1.0 mg/L Au in less than 30 minutes, and in most cases in less than 15 minutes. In several tests the end concentration was reduced to less than 0.1 mg/l, the lower detection limit for the assay method employed. By comparison, the recycle time in the existing electrolytic cells was about 12 hours with the terminal gold concentration about 16 mg/L.

Table J: South African Gold Mine Carbon Column Gold Elute Test Solution

Time (min.)	Au (mg/L)	pH
0	331	12.5
5	144	12.4
10	17.5	12.5
15	0.3	12.5
31	0.2	12.6
45	< 0.1	12.6

Overall current efficiency from 331 to 0.1 ppm was 13.3%.

Tests were also conducted on a printed circuit board line where a RenoCell® system was installed to recover gold from gold tab plating baths. The results of one test are shown below, and the photo shows gold deposited on the RenoCell® Model M100 cathode carbon element.

Table K: Gold Recovery from Process Solutions

Time (min.)	Au (mg/L)	CN ⁻ (mg/L)
0	480	150
15	24	69
25	0.8	60
35	0.5	55

Overall current efficiency from 480 to 0.8 ppm is 10.5% in 25 min.

Also note the rapid CN destruction via oxidation at the anode in an undivided RenoCell® (see Figure 2).



Figure 2: Loaded cathode

The RenoCell® attains major performance improvements through effective use of a unique 3D cathode design, including:

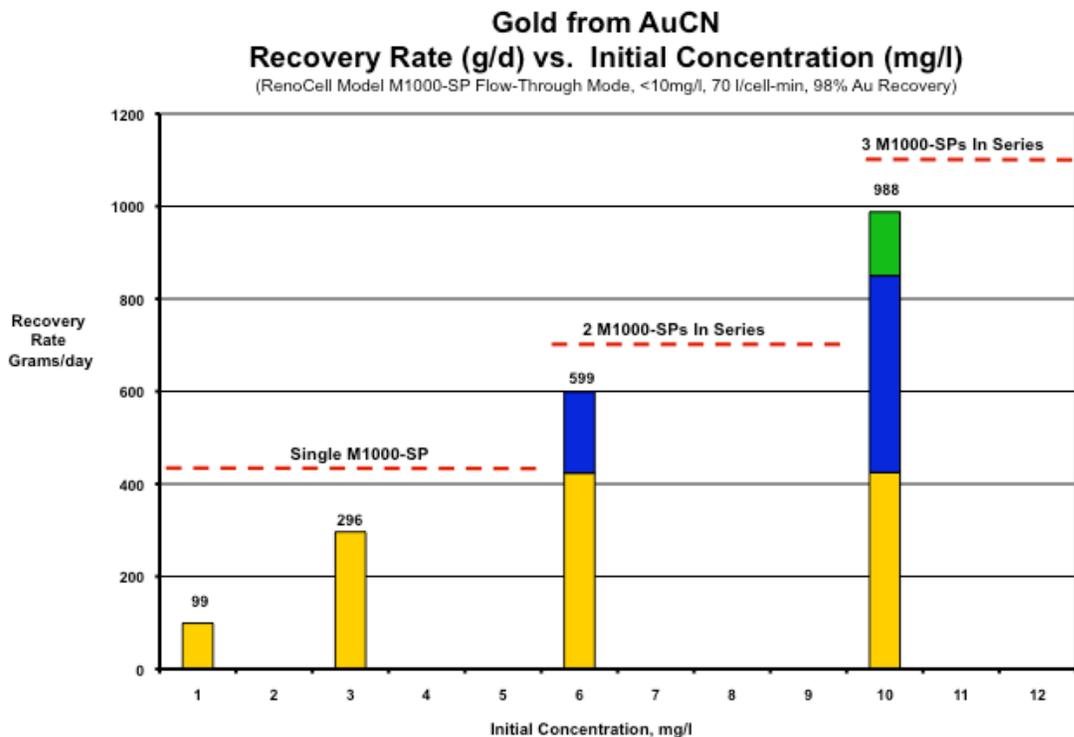
- High active cathode surface area produces compact design and efficient conversions even at low metal concentrations,
- High current efficiency to minimize energy use,
- High current density to allow rapid metal recovery,
- Ease of product removal,
- Safety and ease of control, and
- Lower operating and capital costs.

4.2 RENOCELL® DEW CASE STUDY

In a recent DEW Case Study with an Australian engineering firm for an Indonesian CN heap leach gold mining project, a series of performance and cost studies were conducted for a planned heap operation with the recovery of gold from ~2 ppm to 0.1 ppm at a flow rate of 100m³/hr.

The performance study revealed that this plant capacity could be provided by 24 Model M1000-SP (single-pass) RenoCells® operating at a flow rate of 70 liters per minute (Lpm) each. Each cell will operate at a current density (CD) of 150A/m² and voltage of ~10V. The 24 cells would be configured in modules of 6 (4 groups) and each module of 6

RenoCell's® cathodes would be changed every four days. Each cathode would contain four operating days of gold recovery or ~18.2 kg at 3 kg per cell.



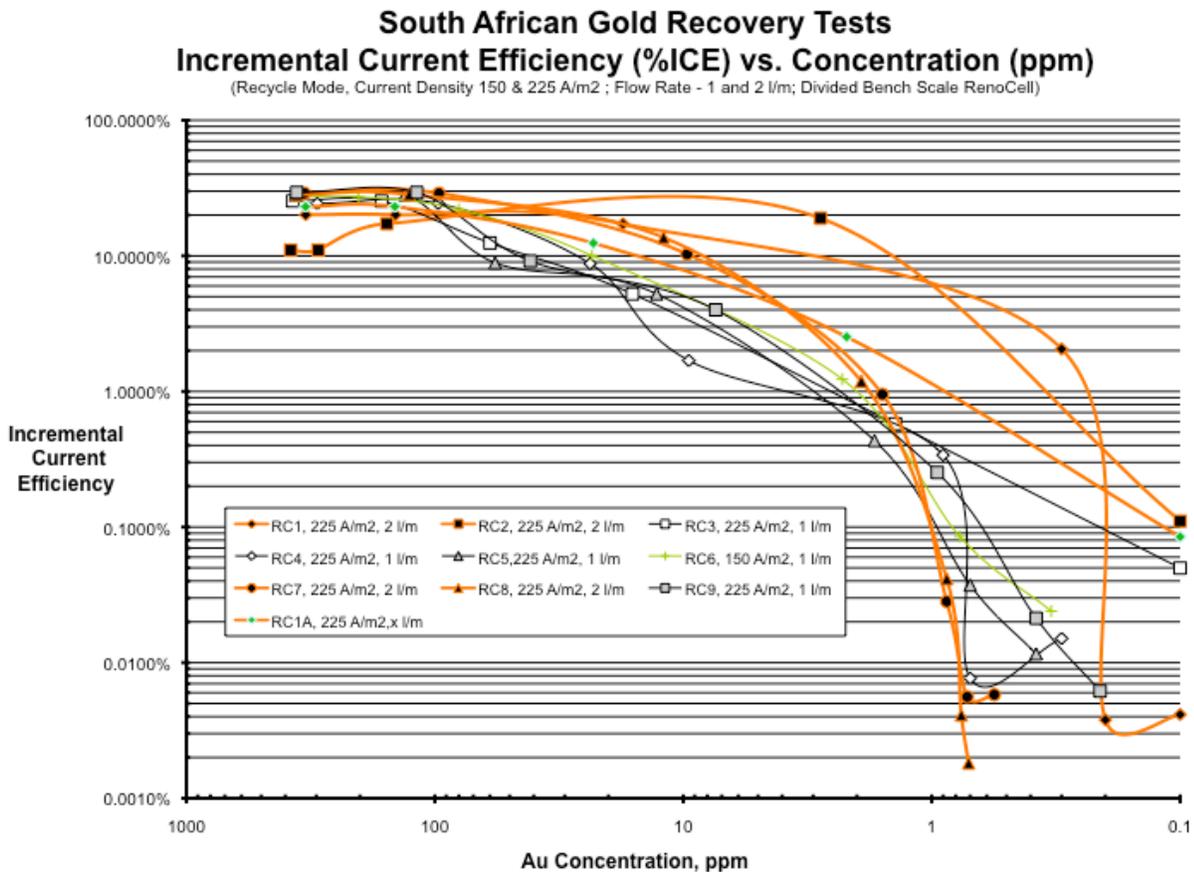
The capital and operating cost evaluation for three alternative recovery processes was carried out for the project. This included Case A - Carbon-In-Pulp (CIP), Case B - Carbon-In-Leach (CIL) and Case C - RenoCell® Direct electrowinning (DEW). The CIP and CIL activated carbon processes both included activated carbon adsorption, elution, goldroom, carbon regeneration, detox unit process operations, as well as working capital, etc. as required for each type of recovery plant. The Capex were within 20% of each other, while the Operating Costs were A - \$9/Toz, B - \$15/TOz and C - \$2.50/TOz.

Typical RenoCell® gold recovery rates in grams/day for metal concentrations ranging from 1 to 12 mg/l (= ppm) are shown below based upon an analysis of RenoCell® performance achieved during gold recovery tests conducted in South Africa using a RenoCell® bench scale system. For gold concentrations of 0.5 ppm, the M1000-SP is expected to recover about 40 g/day of gold based upon a 70 Lpm flow rate.

4.3 SOUTH AFRICAN GOLD RECOVERY TESTS

Recovery of Au from CN heap leach carbon column elute at a South African mine was evaluated using a RenoCell® bench scale system. The test series were conducted at 1 and 2 Lpm flow rates and 150 and 225 A/m² current densities. The results of 10 of these test

runs plotted as Incremental Current Efficiency versus Au Concentration in ppm are plotted below and show a consistent performance range for the RenoCell®, recovering from 300 to less than 1 ppm, at times to 0.1 ppm, in all cases with practical recovery efficiencies. The incremental current efficiencies (ICE) plotted are equivalent to what can be expected in single pass operations at concentrations below 6 – 10 ppm, and show CE values as high as 10% at 3 ppm and 0.1% at 0.1 ppm.



These tests also showed, as expected, somewhat better performance at the higher flow rate of 2 Lpm (orange curves) versus the lower 1 Lpm (black curves). It should also be noted that the 0.1 ppm end point is not necessarily representative of the RenoCell's® capabilities but rather the lower detection limit for the analytical method and AA mass spectrometer instrument used for analysis of the test samples. Overall current efficiencies (not shown) ranged from 5% to 10%, over the recovery range of 300 to less than 1 ppm.

4.4 RENOCELL® PGM RECOVERY TEST

A test program to determine RenoCell® recovery performance for a mixed Pt, Pd and Rh source stream resulting from the acid leach of scrapped automotive exhaust gas catalysts

was conducted using a RenoCell® bench scale test system. The test recovered 111.03 grams of material, assuming PGMs⁸, into the cathode. The cathode became quite stiff and noticeably heavier. The test solution, 40.7 gal., was contained in a 55 gallon drum. A MasterFlex pump delivered solution from the drum into the cathode feed tank of the bench system, and then the hose drain on the back of the bench unit was used to allow catholyte to return to the drum by gravity. The flow rate was about 1 liter/min to and from the drum to the catholyte tank of the bench system. The pump recirculation rate for the cathode side was 6 liters/min during the entire test. The anode side was maintained at 3 liters/min.

	Pt	Rh	Pd	Totals
Grams in Solution at Start	41.14 (267 ppm)	3.48 (22.6 ppm)	32.51 (211 ppm)	77.13
Grams in Solution at End	5.25 (34.1 ppm)	1.12 (7.3 ppm)	0.02 (0.13 ppm)	6.40
Grams Platted	35.89	2.36	32.49	70.73
% Platted	87.23	67.68	99.94	91.71



Figure 3: Comparison photograph of new cathode (left) and PGM-loaded cathode (right)

The electrolysis was run for 66 hours in constant current mode since there were no known other metals in solution. The current was set and maintained at 7.75 amps and voltage varied from a starting voltage of 2.27 to a 2.97 ending voltage. The electrolysis was run over a period of about 2 weeks at 8 hrs per day. It was not run during the night or weekends. The cell was drained each night and the cathode was rinsed in DI water and set aside till the following morning where it was reinstalled into the unit and exposed to electrolysis.

⁸ Other metals: Pb = 12.9% wt/wt, Cu = 4.52% wt/wt, unknown source – believed to have been in water source used in the leach chemistry.

For comparison, the use of sodium borohydride (SBH) precipitation in the existing production environment resulted in the recovery of 88% of Pt, 100% of Pd, and 34% of Rh from the leach solution. SBH is being replaced in the expanded production environment by EW using RenoCell® technology due to its equal or better recovery, much simpler and cleaner operations, and substantially lower operating costs. It should also be noted that the EW tests were not carried to completion but rather terminated for convenience. EW operations 24/7 and process optimization is expected to result in significantly improved performance with recovery in the ppb level for all metals.

5.0 'GREENER' ALTERNATIVE LIXIVIANTS

It was reported by Marsden (2006) that agitated cyanide leaching accounted for approximately 50% to 55% of gold extraction around the world. But pressure to ban or limit the operation of cyanidation is increasing due to a negative public perception about the environmental impact of the cyanide toxicity. An increase in the research into alternative lixivants has increased in last few decades. The alternative lixivants include thiourea, chlorine, bromine, iodine, and thiosulfate, among others.

In recent years thiourea has attracted considerable attention in hydrometallurgy of the precious metals, primarily gold. One of the reasons is the kinetic superiority of thiourea leaching compared to cyanide leaching. Another is thiourea's substantially less toxic nature compared to cyanide. Thus, thiourea may very well be used as a 'greener', more environmentally-sound substitute for cyanide in many hydrometallurgical applications. To recover gold and other PMs from precious metal-bearing materials including ores, leaching residues, flue dust, electronic scrap, jewelry scrap, etc., the gold and other PMs can be extracted from the precious metal-bearing materials with a thiourea solution to form a thiourea leach; the thiourea leach is then contacted with carbon to adsorb the gold and provide loaded carbon.

The use of thiourea as an alternative non-polluting reagent for gold leaching is very well known. The recovery process for removing precious metals from precious metal-bearing mixtures, such as silver-containing and gold-containing ores, commonly included crushing the ore, washing or frothing the crushed ore to eliminate clays and other contaminants, and then solubilizing the ore in an aqueous cyanide solution, an aqueous thiourea solution, an aqueous ammonium thiosulfate solution, or aqua regia. Thereafter, these solubilized (dissolved) precious metal-bearing solutions can be treated for recovery of the precious metals through methods such as carbon absorption, carbon-in-pulp absorption/desorption, amalgamation, ion exchange, electrowinning, or precipitation. However, the processes of gold recovering from thiourea solutions, particularly the electrowinning (EW) process, have received little attention.

Gold EW from thiourea solutions has been studied by others based upon standard EW techniques. For potentials more cathodic than 0 mV vs. SCE, gold reduction is typically mass transport-controlled and limited with standard EW. The estimated diffusion coefficient for the complex gold (I)-thiourea at 25°C was 1.0×10^{-5} , cm^2s^{-1} . Passivation due to thiourea adsorption on the electrode surface was observed at -300mV vs. SCE. Experiments show that gold reduction is favored by low thiourea and formamidine disulfide concentrations, and, thus, RenoCell® would be expected to perform better. Measurements indicated the presence of an adsorption step before the reduction of the complex gold (I) -thiourea, although the reduction of the species in solution is also feasible. This type of condition is often found with complex chemistry matrices such as Electroless Ni, and RenoCell® has been successfully employed. The influence of Current Density on the cathodic Current Efficiency and gold structure may be an issue. The influence of gold, thiourea and formamidine disulfide concentrations on the cathodic behavior of gold is the unknown with the RenoCell® (we need the Divided RenoCell®), but like other RenoCell® applications, the fact that other forms of EW have been successful, even with inadequate results, has always shown that the RenoCell® will perform better. This is especially the case for the more primitive forms of EW typically used to date for precious metals recovery.

For example, laboratory investigations by others on the kinetics of gold EW from acidic thiourea solutions obtained by gold elution from activated carbon in the processing of gold-bearing raw materials have been carried out as depending on temperature, current density, and the type of cathode material. It has been found that a high gold recovery could be obtained under suitable conditions, 45 mg/L Au in 6 g/L thiourea (especially at elevated temperature of 60C). The current efficiencies were as high as 0.5% to 1%, and the energy consumption can be less than 15 kW h kg⁻¹ of gold using a platinum mesh cathode. Our expectations for RenoCell® would be essentially ~100% gold recovery, and CE 10-30 times greater with no Pt cathode.

The step of contacting a loaded thiourea carbon bed with an alkaline solution of the thiosulfate ion with the loaded thiourea carbon involves desorbing the PMs from the carbon (thiourea apparently does not desorb loaded carbon.) An additional step often includes adding a salt to the aqueous thiosulfate solution; this includes protecting the thiosulfate ion from any oxidizing agents and is done by adding a reducing agent such as sodium sulfite to the thiosulfate solution.

When copper is present, removing the copper from the carbon is required prior to exposing the carbon to the thiourea solution containing the precious metal.

The hydrometallurgy techniques using thiourea share similarities to the already well known cyanidation techniques. In other words, thiourea can be used in similar types of unit operations that are used with cyanide as noted above. However, a significant difference

between thiourea and cyanide leaching techniques is the pH of the leach solutions that are used. Cyanide must be used in basic solutions to prevent evolution of toxic gaseous hydrogen cyanide. In contrast, thiourea is used in acidified solutions. The main unit operations are similar in a thiourea leaching method. In general, there has been very little work done on the elution of gold from activated carbon where the precious metals are loaded from thiourea solutions. We would expect to direct electrowin Au from the thiourea leach with the RenoCell® and bypass the use and recovery from carbon steps-all expensive and time consuming steps.

Au can be electrodeposited from acidic thiourea (and potentially thiocyanate and, of course, thiosulfate) solutions; however, a divided EW cell (such as the Divided RenoCell®) is required to avoid excess oxidation of the reagents at the anode as well as other deleterious reactions at the cathode in a standard EW cell involving sulfur species which may contaminate the solution and impact CE.

Even in the process of cyanidation of gold, the elution step has serious deficiencies, primarily with respect to kinetics. The elution of gold from a cyanide solution can last from 10 hours to 4 days. The reason for the slow elution rate of the cyanide metal complexes is the strong adsorption of gold cyanide complexes on activated carbon.

For example, a complex desorption process was reported in the literature wherein thiosulfate ion was employed for desorbing silver from carbon loaded from a cyanide solution. The first desorption step employs alkaline thiosulfate solution, and the silver is preferentially desorbed by three alkaline thiosulfate elutions leaving essentially all of the gold on the carbon. The gold is then desorbed by a second desorbing solution comprised of alkaline sodium cyanide. Although the principles described primarily in the context of recovering precious metals from raw materials which bear precious metals, it is understood that the same principles can be applied to the separation and recovery of precious metals generally.

More specifically, a thiosulfate elution step has been applied to the recovery of gold and silver from carbon loaded with a thiourea leach. Apparently, thiourea derivatives, instead of or in conjunction with generic thiourea, have also been explored. It is apparently expected that such thiourea derivatives would be used if they became less expensive and more readily available in the future. The important characteristics of the thiourea derivatives are that they dissolve both gold and other PMs in a precious metal-bearing material in an acidified solution and that they load carbon with gold and silver complexes that are leachable by thiosulfate. Some referenced thiourea derivatives include: N-methylthiourea, N-ethylthiourea, N-isopropylthiourea, N-(n-butyl)-thiourea, N-phenylthiourea, N-benzylthiourea, N-naphthylthiourea, N-tolylthiourea, N-(o-chlorophenyl)-thiourea, N-(p-hydroxyphenyl)-thiourea, N-(p-ethoxyphenyl)-thiourea, N-

(2,4-dimethylphenyl)-thiourea, N-acetylthiourea, N-benzoylthiourea, N,N-dimethylthiourea, N,N-diethylthiourea, N,N-dipropylthiourea, s-dimethylthiourea, s-diisopropylthiourea, s-di-n-butylthiourea, s-diphenylthiourea, s-ditolylthiourea, N,N-phenyltolylthiourea, N,N,N'-trimethylthiourea, N,N,N'-triethylthiourea, and N,N,N'-tripropylthiourea, among others.

The particular acid that is used for acidifying the thiourea is not critical; for example, sulfuric acid, hydrochloric acid, and nitric acid can be used and sulfuric would probably be preferable. This method for recovering is for such precious metals as gold, silver, palladium, platinum and rhodium from precious metal-bearing mixtures such as ores and tailings.

The affinity of activated carbon towards all other gold complexes is different. The effectiveness of activated carbon in removing gold complexes from aqueous solutions decrease in the following ligand order: $\text{SCN}^- > \text{SC}(\text{NH}_2)_2 > \text{CN}^- > \text{S}_2\text{O}_3^{2-}$. The gold thiosulfate complex has the lowest affinity to adsorb on the activated carbon, 15% to 17% gold recovery. Yen et al. (2002) reported that gold recovery from the thiosulfate solution was less than 20% when using 20 g/L or 40 g/L activated carbon. It requires 60 g/L carbon to recovery 95% gold with the loading of less than 2 mg Au/g, which is not feasible in the practical operation.

Gold thiosulfate complex differs from gold cyanide complex, which is easily adsorbed on activated carbon while gold thiosulfate complex cannot be satisfactorily recovered by activated carbon. However, gold thiosulfate could be recovered by activated carbon if cyanide is added into the thiosulfate solution. Thus, the potential of direct electrowinning with the RenoCell® would greatly reduce the complexity and potential of this greener leach technology.

Aurothiosulfate ions in the leach solution will migrate to the cathode and form a metallic gold deposit. The electroreduction of gold thiosulfate to gold is kinetically faster than the reduction of gold cyanide to gold; gold thiosulfate is reduced at -0.15 V vs SCE and is independent of pH for values of above 4. However the standard EW is especially problematic in the presence of a great excess of unwanted cupric and cuprous ions. Also, the oxidation and reduction reactions of $\text{S}_2\text{O}_3^{2-}$ occur at the anode and cathode surfaces as noted previously. Therefore, a standard EW process does not appear to be an attractive option for gold recovery. The RenoCell®, especially the Divided cell configuration, eliminates or reduces many of these issues and should allow direct electrowinning to be performed with substantial benefit in complexity and cost factors.

One alternative involves liquid-solid separation, in which the gold is recoverable by metal cementation or solvent extraction processes. At Zn/Au ratio of 30, 100% of gold is recovered and the barren solution can be recycled. The choice of solvent to extract gold is

esters, amines and the like. Ion exchange process can then extract the gold from either slurry or clear solution with strongly base anion resins. The gold can be recovered from the eluted solution by electrowinning or metal precipitation. Clearly, such complexity will nearly kill all projects either because of risks or high costs.

6.0 CONCLUSION

As operations strive to lower gold production costs, ore throughput and head grade are typically increased to limits imposed by the nature of the ore body and the capacity of plant equipment. Unless matched by an increase in the rate of gold removal, increased gold input results in elevated carbon loadings and a flattening of the carbon loading profile through the adsorption circuit. Ultimately, soluble gold losses tend to increase. To control soluble gold losses it is necessary to increase the rate of carbon advance through the adsorption and stripping circuits. It is not uncommon to find electrowinning cycle time dictating elution frequency.

In this paper, we have attempted to identify and discuss a number of issues that commonly impact on electrowinning efficiency. Our aim is to identify a new technology and improved EW cell that reduces the need for carbon and allows the promise of direct electrowinning (DEW) to be realized and reduce the cost of processing and extraction.

When the conditions are chosen so that the reduction of gold to gold metal is mass transport controlled over all the surface of three-dimensional cathode, the current is given by where the cathode potential is chosen so that the reduction of gold is mass transport controlled and no other reaction occurs or minimized, (b) the potential distribution is sufficiently uniform throughout the cathode and (c) the depletion of gold from solution during a single pass through the cathode is insignificant (except in the Single-pass RenoCell® 2 option).

It has been shown that it is feasible to electrowin gold from cyanide solutions, even with low ionic strength, to achieve gold levels below 0.2 ppm with reasonable cell performance using 3-D carbon cathodes. Furthermore, the power requirements and energy consumptions for the laboratory cell were low and a further improvement in performance has been realized with scale-up of the technology.

FOR MORE INFORMATION BE SURE TO VISIT OUR WEB SITE AT:

www.renovare.com

7. REFERENCES

- i. The Chemistry of Gold Extraction; Marsden and House
- ii. The Recovery of Gold from Concentrated Aurocyanide Solutions; Paul, Filmer and Nicol
- iii. Gold from Eluates; Paul
- iv. The Kinetics of the Elution of Gold from Activated Carbon; Adams and Nicol
- v. Practical Experience of Gold Electrowinning in Australia; Costello
- vi. Experience with the Use of Electrowinning Gold from Pregnant Eluates in the Gold Mining Industry in Australia; Costello
- vii. Actired Process – New Industrially Tested Process which Economically Improves Gold Elution; Duparque, Louis, Harvey and Van Lierde
- viii. Electrometallurgy and Electrochemistry Workshop; Paul, Costello, Ritchie and Spencer
- ix. The Electrowinning of Gold from Carbon-In-Pulp Eluates; Filmer
- x. A study of the influence of copper on the gold electrowinning process; Steyn and Sandenbergh