

ELECTROLEACHING PROCESS FOR REMEDIATION OF MERCURY CONTAMINATED SOILS

Ronaldo Luiz Correa dos Santos and Luis Gonzaga Santos Sobral
Centro de Tecnologia Mineral, CETEM/MCT
Rio de Janeiro Brazil

ABSTRACT

This paper presents some results for the treatment of mercury bearing residues, from the gold prospecting activities in the Tapajos basin region that uses elemental mercury to amalgamate gold in gravity concentrates, so as to recover and recycling the remaining elemental mercury. The utilized technique was the electroleaching which deals with the electrolysis of a residue suspension in a sodium chloride solution by using graphite electrodes. Additionally, some results of mercury recovery were presented inferring that, as the reaction goes on, gold particles present in the residue, in the ppm range, were also leached and codeposited on the cathode surface forming a gold amalgam. It was also shown the necessity of recycling the sodium chloride solution, after finishing the treatment of such residues, as it is a question of a high salinity effluent.

Key Words - electroleaching, amalgamation, graphite, salinity.

1. INTRODUCTION

The growth in industry and the changes in manufacturing processes have resulted in an increase in the volume and complexity of waste water discharges to the environment. Many traditional and new treatment processes are being modified and developed to try to eliminate the release to surface waters of the diverse chemical substances found in waste water discharges.

Biological methods are now being applied to an ever increasing range of effluent types^[1/2] However, sometimes these processes are impractical and are unable to be employed in the treatment of effluents containing biologically resistant substances.

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
Editors

Physical treatment processes, such as adsorption onto granular activated carbons, are effective at removing pollutants from water and such processes are quite adaptable over a wide range of process conditions^[3,4].

Physical-chemical treatment processes incorporate the addition of secondary chemicals to precipitate or react with the primary pollutants in the effluent. The use of high chemical doses to clean up an effluent often results in a discharge that itself remains unacceptable. Combined treatment processes are almost always required to treat a discharge in order to make it acceptable to Local Authorities. Such combined processes can be effective at eliminating pollution but usually require long contact times and larger areas to make them practical.

The interest in the use of electrochemical processes for treating waste waters is continuing to grow. The implementation of electrochemical processes in the treatment of such effluents can result in the destruction of the organic contaminant and lead to a total reduction in the COD (chemical oxygen demand) and BOD (biochemical oxygen demand) of the effluent^[5,7]. The method is simple and the process operating requirements and areas are significantly less than conventional treatment processes.

A major source of mercury-containing effluents has traditionally been the chlor-alkali industry. Although other sources such as mercury bearing residues, from the gold mine industry that uses elemental mercury to amalgamate gold in gravity concentrates, may also present significant environmental hazards. Conventional mercury recovery routes involve chemical precipitation, as sulphide^[10,11] or thiosulphate^[12], ion-exchange^[13], or cementation, using a copper-coated nickel^[14] or "base metal" fluidized bed^[15]. Other routes involve the use of hypochlorite^[13,16,17] to produce soluble Hg(II), either from insoluble mercury species or from elemental mercury, which can be reduced at the surface of different cathodes. Hypochlorite can be used, in the mercury dissolution process, as a chemical or being electrolytically generated in the reaction system.

This work presents a contribution to the extraction and recovery of mercury from mercury bearing materials. One of the object of the present work is to provide an improved and economical process

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
Editors

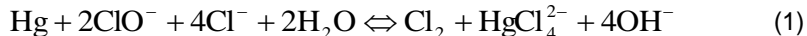
for the hydrometallurgical extraction and recovery of mercury that can be applied to low as well as high mercury content residues.

2. THEORETICAL CONSIDERATIONS

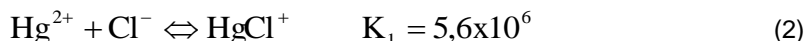
The disorderly use of mercury, during the gold recovery by treating gravity concentrates, has been generating high mercury content residues. Some experiments have been carried out so as to treat such residues by a pyrometallurgical process. During this process the mercury is volatilized, by increasing the temperature, and immediately condensed. The use of this route brings about some drawbacks, such as: the need of using big capacity equipment for treating great amount of residues, and the difficult task of dealing with mercury vapours, which requires sophisticated condensation systems to assure no leak to the environment.

The electrochemical process to recover mercury from residues takes place by the action of hypochlorite ions, generated during the electrolysis of a suspension made up of residue in an aqueous sodium chloride solution. The generation of hypochlorite ions is the result of the oxidation of chloride ions to elemental chlorine, which in contact with the aqueous solution produces such ions in charge of the elemental mercury dissolution.

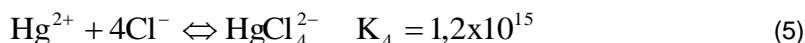
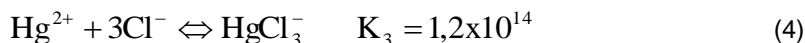
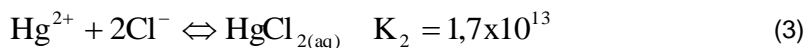
This process for treating residues with high mercury content, promotes the dissolution of mercury as HgCl_4^{2-} that is, immediately, deposited on the surface of graphite cathodes. The success of this process will depend, to some extent, on how effective is the chlorine reaction with the aqueous solution, generating the oxidising agent (ClO^-), which promotes the mercury dissolution according to the following reaction:



Mercury compounds are highly soluble in aqueous chloride solutions because of the complexation of mercuric ions. The following equilibrium reactions must be considered:^[18]



Roberto C. Villas Bôas, Christian Beinhoff, Alberto Rogério da Silva,
Editors



The total mercury concentration in the solution is given by:

$$C = [\text{Hg}^{2+}] + [\text{HgCl}^+] + [\text{HgCl}_{2(\text{aq})}] + [\text{HgCl}_3^-] + [\text{HgCl}_4^{2-}] \quad (6)$$

By substituting into Equation 6 the concentrations of HgCl^+ , HgCl_2 , HgCl_3^- and Hg^{2+} ions from the equilibrium expressions (2)-(5) respectively and rearranging, the relationship between the concentration of the HgCl_4^{2-} species and the total mercury concentration can be obtained:

$$\frac{[\text{HgCl}_4^{2-}]}{C} = \frac{K_4[\text{Cl}^-]^4}{1 + K_1[\text{Cl}^-] + K_2[\text{Cl}^-]^2 + K_3[\text{Cl}^-]^3 + K_4[\text{Cl}^-]^4} \quad (7)$$

According to Equation 7, when the chloride concentration is 0.86 mol dm^{-3} approximately 90% of the total mercuric ions will conform to the HgCl_4^{2-} species. The calculation procedure, based on the above equations, is only an approximate one as the activity coefficients were not taken into account. However, it is useful as it allows us to propose the following reaction



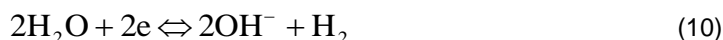
as the predominant reaction during the deposition of mercury from a solution containing chloride ions in high concentration. Reaction 8 has a reversible electrode potential, under standard conditions, of 0.4033 V(SHE). This potential was calculated from standard Gibbs energy data^[19].

In the situation where sodium chloride is used as the electrolyte the reaction occurring at the anode is

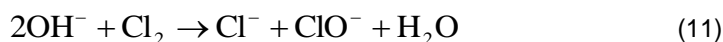


and the reaction taking place at the cathode is

Roberto C. Villas Bôas, Christian Beinhoff, Alberto Rogério da Silva,
Editors

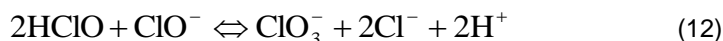


In a cell in which the anode and cathode products are not separated there is a measuring process which can be expressed by the following reaction:



Both the hypochlorite and the free chlorine can act as oxidising agents and are also chemically reactive in their own.

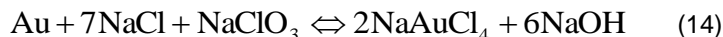
As the electrolysis goes on, the oxidising power of the reaction system increases due to the generation of chlorate ions (ClO_3^-) by two different ways, either by purely chemical reaction of the hypochlorite ion with hypochlorous acid in the bulk solution (chemical chlorate formation), according to the following reaction:



or by electrochemical oxidation of the hypochlorite at the anode under simultaneous oxygen evolution (anodic chlorate formation):



This reaction seems, in general, quite convenient regarding the treatment of mercury containing residues from the amalgamation process. Such residues contain, normally, low gold contents (### 1 ppm) which can be dissolved by chlorate ions, according to the following reaction:



The dissolved gold is codeposited with mercury generating an amalgam. The phase diagram of the system Au-Hg^[20] indicates that at ambient temperature, alloys with more than 5% of gold are solid and single phase. On the other hand, the mercury deposition from chloride solutions, at electrode surfaces where no reaction occurs among the elemental mercury and the electrode material, mercury droplets lost from the electrode cause calomel precipitation on the bottom of the cell by the following reaction:

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
Editors



As can be seen, in the reaction (15), a very insoluble mercurous compound (Hg_2Cl_2) is formed which will remain in the residue after the electroleaching process. Thus, is imperative to use some device able to collect those mercury drops, falling down from the cathode surface, extracting them from the reaction system.

In the early stage of the electroleaching process, hydrogen evolution occurs according to the reaction (10). This reaction is in charge of a pH rise. Subsequently, this pH rise occurs through the mercury and gold dissolution reactions, reaction (1) and (2) respectively.

During the electroleaching process, the solution pH has to be controlled in a safe range, between 4 and 9. When the solution pH goes down below 4, mercurous chloride (Hg_2Cl_2) is formed, which is very insoluble in chloride solution. On the other hand, if the solution pH goes up above 9 causes precipitation of a large amount of mercury oxide (HgO), as insoluble as mercurous chloride and will remain in the residue as such.

3. EXPERIMENTAL

All solutions used for voltametric studies contained 0.83 mol dm^{-3} NaCl (AnalaR) as supporting electrolyte and a mercury concentration of $5 \times 10^{-4} \text{ mol dm}^{-3}$ as mercuric chloride (HgCl_2). Solutions were made up using deionized distilled water and were de-aerated with oxygen-free nitrogen before steady state polarisation curves were recorded. A nitrogen flow was maintained over the solution, during the experiments, so as to avoid the oxygen to get into the cell.

The voltametric study was carried out by using a glassy carbon rotating disk electrode (area = $3.7 \times 10^{-5} \text{ m}^2$) embedded in a PTFE holder and attached to a rotating disc assembly (Oxford Electrodes - England). A conventional Pyrex cell assembly (Figure 1) was used, incorporating a saturated calomel reference electrode separated from the bulk solution by a Luggin capillary; a large platinum

Roberto C. Villas Bôas, Christian Beinhoff, Alberto Rogério da Silva,
Editors

foil (0.04 m x 0.04 m) in a separate compartment served as a counter electrode.

Linear potential scans were generated using a potentiostat (EG7G - Princeton Applied Research, model 363) in conjunction with a waveform generator (EG7G - Princeton Applied Research, Universal Programmer, model 175). The applied potential and the resulting current were stored in a PC computer through data acquisition software (Labtech Notebook) using a high-resolution data acquisition board (Mini-16-Strawberry Tree - Computer Instrumentation & Controls) and subsequently analysed.

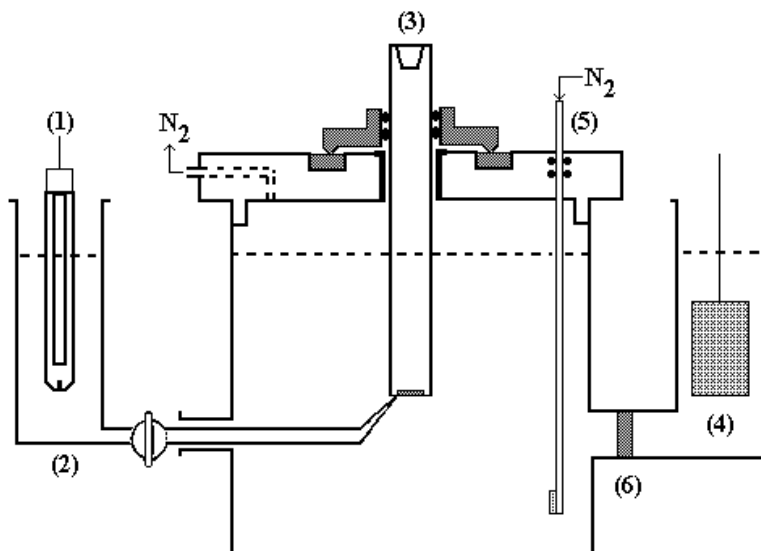


Figure 1 - Experimental cell design for experiments with rotating disc electrodes. (1) reference electrode, (2) Luggin capillary, (3) rotating disc electrode (working electrode), (4) platinum foil electrode (counter electrode), (5) nitrogen bubbler, (6) porous glass sinter.

Roberto C. Villas Bôas, Christian Beinhoff, Alberto Rogério da Silva,
Editors

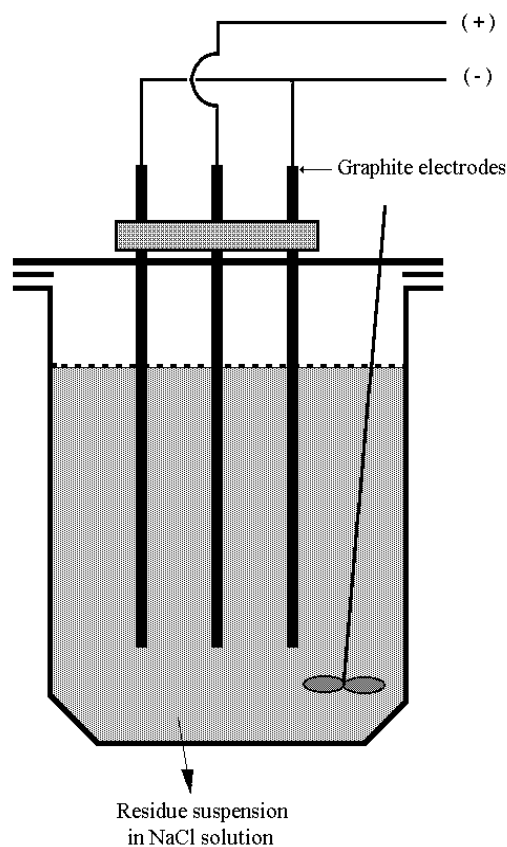


Figure 2 - Reaction system for electroleaching tests.

The reaction system shown in Figure 2, consists of one litre capacity Pyrex reactor. In each test 0.20 kg of residue was used, suspended in one litre of 0.86 mol dm^{-3} sodium chloride solution.

The residue used in this study is derived from Poconé region (Mato Grosso) which was generated during the amalgamation of gold from gravity concentrates. The average mercury and gold concentrations were $2.3 \times 10^{-4} \text{ mol kg}^{-1}$ (45.7 ppm) and $5.1 \times 10^{-6} \text{ mol kg}^{-1}$ (1 ppm) respectively.

Roberto C. Villas Bôas, Christian Beinhoff, Alberto Rogério da Silva,
Editors

4. RESULTS AND DISCUSSION

a- Kinetics of the mercury-chloride complex ion (HgCl_4^{2-}) reduction.

The reduction of HgCl_4^{2-} species (reaction 8) was studied with a rotating disk electrode by using the experimental conditions described before. Figure 3 shows some typical curves of current density as a function of the potential at different angular velocities, *i.e.* curves (a), (b), (c) and (d). Curve (e) corresponds to the hydrogen evolution on a mercury-coated vitreous carbon electrode and was obtained at 1000 rpm in the supporting electrolyte.

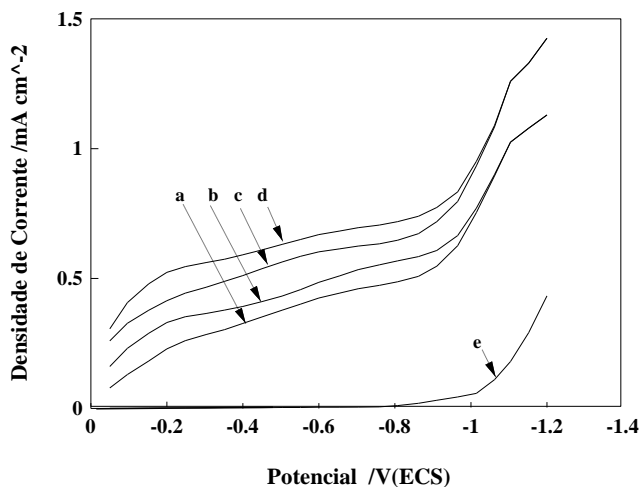


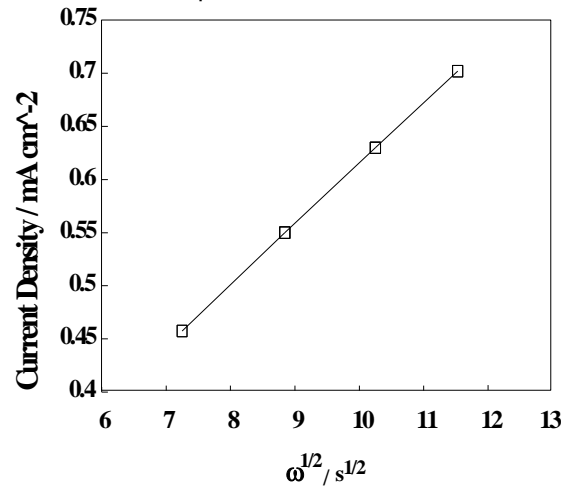
Figure 3 - Current density as a function of the electrode potential at different angular velocity. (a) 500 rpm, (b) 750 rpm, (c) 1000 rpm, and (d) 1250 rpm. Hydrogen evolution from a 50 g dm^{-3} NaCl solution at 1000 rpm.

Although the current is not really constant, the figure reveals that mercury reduction is mass-transfer controlled over a wide range of potentials; namely from about -0.3 V to -1.0 V(SCE) , where hydrogen evolution begins to increase considerably.

Roberto C. Villas Bôas, Christian Beinhoff, Alberto Rogério da Silva,
Editors

Likewise because of the low value of the limiting current density for the mercury reduction and in order to increase the space time yield of the reactor, it is necessary to increase the surface area where the reaction takes place. Therefore, several configurations of electrochemical reactors have been proposed. Williams and Olson^[21] showed the technical feasibility of removing traces of mercury by using extended surface electrolysis. Robertson *et al.*^[22] reduced the level of mercury to below the accepted concentration of 0.01 ppm in wastes by employing the swiss-roll cell with a cadmium coated stainless steel cathode. An industrial cell with a fluidized bed electrode was reported by van der Heiden *et al.*^[23], and Kreysa^[24] reported on experimental results obtained with a packed bed electrode. The use of graphite felt as an efficient porous electrode for the removal of traces of mercury ions from aqueous electrolyte solutions was investigated by Oren and Soffer^[25]. Matlosz and Newman^[26] investigated a flow-through porous electrode, made of reticulated vitreous carbon, for removal of mercury from contaminated brine.

Figure 4 shows a Levich-plot for mercury concentration of $5 \times 10^{-4} \text{ mol dm}^{-3}$, where the limiting current density were measured at a potential of 0.90 V(SCE). From the slope of the Levich-plot and using the literature value for the kinematic viscosity of $8.0 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ ^[27] the resultant diffusion coefficient is $2.21 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. This result is in close agreement with the reported value^[26].

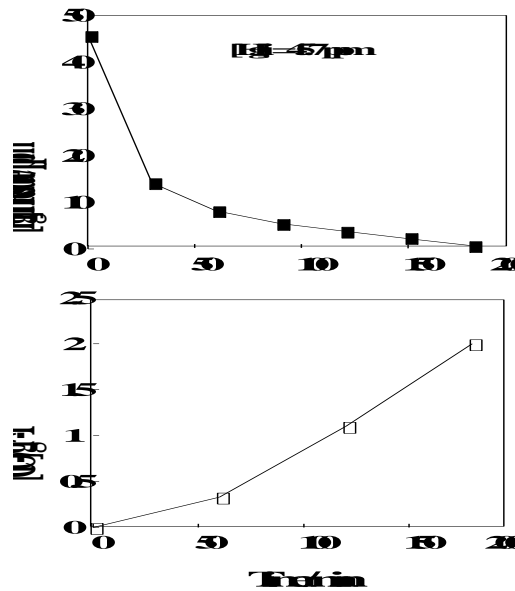


Roberto C. Villas Bôas, Christian Beinhoff, Alberto Rogério da Silva,
Editors

Figure 4. Limiting current density against square root of the electrode angular velocity. $[\text{Hg}^{2+}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$.

b- Mercury Electroleaching

Figure 5 shows some experimental results obtained with the reactor outlined in Figure 2. Analysing this figure, it can be seen that the mercury dissolution process occurs with high efficiency; after 3 hours of operation, under the conditions of the experiment, the mercury concentration was reduced from 45.7 ppm to 0.1 ppm which means an extraction over 99%. In addition, after finishing each test, the suspension was filtered and the residue did not suffer any washing process but dried before going to be analysed. This means that part of the mercury present in the electroleaching residue should come from the remaining solution after filtering process. The mercury concentration in the solution, after the leaching process, was, on average, of 0.09 ppm. Neither the mercury concentration in the solution nor in the residue were low enough to be considered as suitable for discharging, which indicates the necessity of extending the electrolysis time.



Roberto C. Villas Bôas, Christian Beinhoff, Alberto Rogério da Silva,
Editors

Figure 5 - Mercury concentration in the residue and hypochlorite concentration profiles, during the electroleaching test. $[\text{Hg}]_{\text{res.}} = 45.7$ ppm, $[\text{NaCl}]_{\text{sol.}} = 0.86 \text{ mol dm}^{-3}$, $i_a = 0.6 \text{ A dm}^{-2}$ and $i_c = 0.83 \text{ A dm}^{-2}$.

Figure 6 shows the effect of the ever increasing hypochlorite concentration on chlorate generation during the electrolysis.

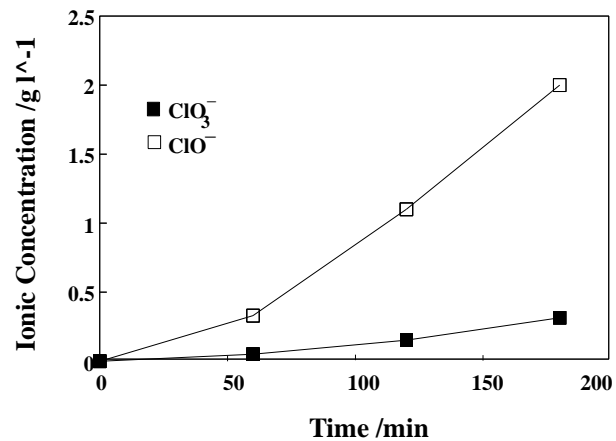


Figure 6 - Variation of hypochlorite and chlorate ions concentration. $[\text{Hg}]_{\text{res.}} = 45.7$ ppm, $[\text{NaCl}]_{\text{sol.}} = 0.86 \text{ mol dm}^{-3}$, $i_a = 0.6 \text{ A dm}^{-2}$ and $i_c = 0.83 \text{ A dm}^{-2}$.

As mentioned previously (item 2), during the electroleaching process there are two different ways to produce chlorate ions (Reactions 12 and 13) as the hypochlorite ion concentration builds up (Reaction 11). As the chlorate ion concentration builds up the oxidising power of the reaction system increases permitting not only the gold dissolution, present in the residue, but also to enhance the mercury dissolution process. The gold dissolution as well as its deposition were evidenced as long as the cathode surface was scraped, the shavings dissolved with aqua regia and the solution analysed for gold.

Figure 7 shows how the solution pH changes with the reaction time. The pH variation can be interpreted as a result of a continuous hydroxyl ions generation by the mercury and gold dissolution, as shown by reactions 1 and 14 respectively. This pH rise occurs very slowly, as shown in Figure 7, since the chlorate ion generation

reactions (Reactions 12 and 13), which occur in a less intensive way, tend to decrease the pH by the H^+ ions generation. During the performed tests, the leaching solution pH did not exceed the upper limit of the safe pH range (from 4 to 9).

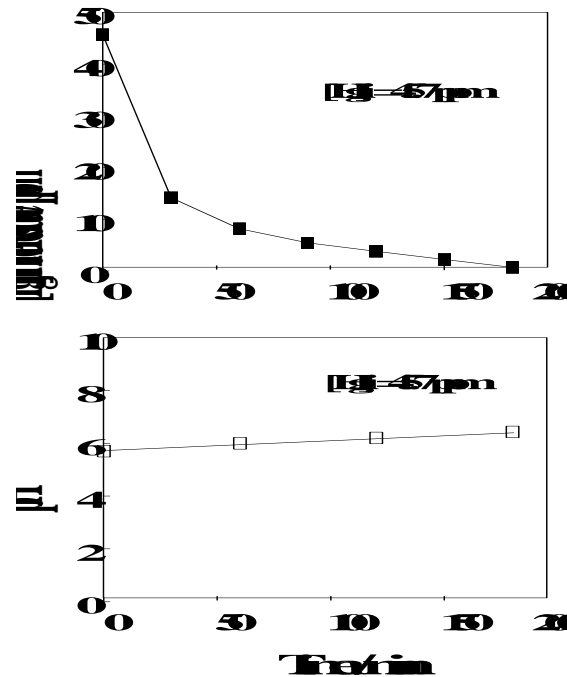


Figure 7 - Variation of pH with reaction time. $[Hg]_{res.} = 45.7 \text{ ppm}$, $[NaCl]_{sol.} = 0.86 \text{ mol dm}^{-3}$, $i_a = 0.6 \text{ A dm}^{-2}$ and $i_c = 0.83 \text{ A dm}^{-2}$.

5. CONCLUSIONS

The experimental results permit to conclude that, by choosing the suitable operational conditions, it was possible to reduce the mercury concentration to low values with high extraction efficiency (>99%), considering the utilised residue. The final mercury concentration was of 0.1 ppm, which is not low enough to be

Roberto C. Villas Bôas, Christian Beinhoff, Alberto Rogério da Silva,
Editors

considered as suitable for discharging, indicating the necessity of extending the electrolysis time.

The final leaching solution should not be discharged since it contains not only high salinity but also mercury concentration not suitable for discharging. It is recommended the recycling of this solution to the residue treatment process.

According to the low current densities obtained from the voltametric study, it is recommended the use of high surface area cathodes and provides good mass transfer conditions so as to enhance the reactor performance.

In case of dealing with higher mercury content residues (### 50 ppm), it is imperative to use special devices to extract the elemental mercury from the reaction system, accumulated on the cathode surface during the electroleaching process, so as to avoid the reaction between elemental mercury droplets and Hg^{2+} ions producing the quite insoluble mercurous chloride (Hg_2Cl_2) which remains in the residue.

It was evidenced the gold dissolution and its deposition, during the electroleaching process, by analysing the shavings scraped from the cathode surface.

REFERENCES

1. Moo-Young, M., *Int. Conf. Environ. Biotechnol. Waste Treatment and Recycling*, Hong Kong, 1992, p. 11.
2. Yu, P. H. F., *Int. Conf. Environ. Biotechnol. Waste Treatment and Recycling*, Hong Kong, 1992, p. 13.
3. Allen, S. J., McKay, G. & Khader, K. Y. H., *J. Coll. Int. Sci.*, **126** (1988), 517-24.
4. Allen, S. J., McKay, G. & Khader, K. Y. H., *J. Chem. Tech. Biotechnol.*, **45** (1989), 261-302.
5. Kaba, L., Hitchens, G. D. & Bockris, J. O###M., *J. Electrochem. Soc.*, **137** (1990) 1341-5.

Roberto C. Villas Bôas, Christian Beinhoff, Alberto Rogério da Silva,
Editors

6. Comninellis, C. & Plattner, E., *CHIMIA*, **42** (1988), 250-2.
7. Pletcher, D., Walsh, F. C., & White, I., *J. Chem. E. Symp. Ser.*, **116** (1990), 195-218.
8. B. Commoner, *Chem. Br.*, **8** (1972), 52.
9. R. Caban and T. W. Chapman, *AIChE J.*, **18** (1972), 892.
10. For example, *Chem. Abs.*, **81**, 82126e.
11. *ibid.*, **81**, 111188j.
12. Sumitomo Chemical Co. Ltd., German Patent 2 321 196 (1973).
13. W. C. Gardiner and F. Munoz, *Chem. Eng.*, **78** (1971), 57.
14. D. J. Flood and C. J. Kraynik, *Chem. Abs.*, **83** (1973), 65287g.
15. P. E. Waltrich, US Patent 3 704 875 (1972).
16. E. Wygasch and G. Weiss, US Patent 3 755110 (1973).
17. BP Chemicals Ltd., British Patent 1 336 084 (1973).
18. Latimer, W. M., The Oxidation States of the Elements and Their Potentials in Aqueous Solution, 2nd edn., Prentice-Hall, Inc., Englewood Cliffs, NJ, 1952, 181 pp.
19. Balej, J., Mercury. *Standard Potentials in Aqueous Solutions*, eds A. J. Bard, R. Parsons & J. Jordan. Marcel Dekker, New York, 1985, pp. 265-85.
20. M. Hansen, Constitution of Binary Alloys, McGraw-Hill, London (1958).
21. Williams, J. M. & Olson, M. C., *AIChE Symp. Ser.*, **73** (1976), 119-31.
22. Robertson, P. M., Scholder, B., Theis, G. & Ibl. N., *Chem. Ind.* (London), **1 July** (1978), 459-65.
23. van der Heiden, G., Raats, C. M. S. & Boon, H. F., *Eine, Chem-Ing-Tech.*, **51** (1979)651-3.
24. Kreysa, G., *Metalloberfläche*, **34** (1980), 494-501.
25. Oren, Y. & Soffer, A., *Electrochim. Acta*, **28** (1983), 1649-54.

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
Editors

26. Matlosz, M. & Newman, J., *J. Electrochem. Soc.*, **133** (1986), 1850-9.
27. Washburn, E. W. (ed), International Critical Tables of Numerical Data, Physics, Chemistry and Technology. McGraw-Hill, New York, 1929, Vol. III, 79 pp e Vol. V, 15 pp.

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
Editors