

SÉRIE TECNOLOGIA AMBIENTAL

**Recovery of defective Discs in the production of New
Real coins by intensive Cyanidation**

PRESIDÊNCIA DA REPÚBLICA

Dilma Vana Rousseff

Presidente

Michel Miguel Elias Temer Lulia

Vice-Presidente

MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E INOVAÇÃO

Marco Antonio Raupp

Ministro da Ciência, Tecnologia e Inovação

Luiz Antonio Rodrigues Elias

Secretário-Executivo

Arquimedes Diógenes Ciloni

Subsecretário de Coordenação das Unidades de Pesquisa

CETEM – CENTRO DE TECNOLOGIA MINERAL

Fernando Antonio Freitas Lins

Diretor

Andréa Camardella de Lima Rizzo

Coordenador de Planejamento, Acompanhamento e Avaliação

Arnaldo Alcover Neto

Coordenador de Análises Minerais

Carlos César Peiter

Coordenador de Apoio Tecnológico à Micro e Pequena Empresa

Claudio Luiz Schneider

Coordenador de Processos Minerais

Cosme Antônio de Moraes Regly

Coordenador de Administração

Ronaldo Luiz Correa dos Santos

Coordenador de Processos Metalúrgicos e Ambientais

SÉRIE TECNOLOGIA AMBIENTAL

ISSN 0103-7374

ISBN 978-85-61121-96-9

STA - 63

Recovery of defective Discs in the production of New Real coins by intensive Cyanidation

Paula Franco Cabral do Nascimento

Chemist

Luis Gonzaga Santos Sobral

Chemical Engineer, PhD

Carlos Eduardo Gomes de Souza

Industrial Chemist

Priscila Martins da Rocha

Chemist

Diogo de Oliveira Padrão

Chemist

CETEM/MCTI

2012

SÉRIE TECNOLOGIA AMBIENTAL

Luis Gonzaga Santos Sobral

Editor

Andréa Camardella de Lima Rizzo

Subeditora

CONSELHO EDITORIAL

Marisa B. de M. Monte (CETEM), Paulo Sérgio Moreira Soares (CETEM), Saulo Rodrigues P. Filho (CETEM), Silvia Egler (CETEM), Vicente Paulo de Souza (CETEM), Antonio Carlos Augusto da Costa (UERJ), Fátima Maria Zanom Zotin (UERJ), Jorge Rubio (UFRGS), José Ribeiro Aires (CENPES), Luis Enrique Sánches (EPUSP), Virgínia Sampaio Ciminelli (UFMG).

A Série Tecnologia Ambiental divulga trabalhos relacionados ao setor minero-metalúrgico, nas áreas de tratamento e recuperação ambiental, que tenham sido desenvolvidos, ao menos em parte, no CETEM

O conteúdo desse trabalho é de responsabilidade exclusiva do(s) autor(es).

Valéria Cristina de Souza

Coordenação Editorial

Vera Lúcia Espírito Santo Souza

Programação Visual

Andrezza Milheiro

Revisão

Produção de novas moedas do real por cianetação intensiva /
Paula Franco Cabral do Nascimento [et al.]. —Rio de Janeiro:
CETEM/MCTI, 2012.

27p. (Série Tecnologia Ambiental, 63)

1. Cianetação intensiva. 2. Recuperação de discos. 3. Aço carbono. I. Centro de Tecnologia Mineral. II. Nascimento, Paula Franco Cabral do III. Sobral, Luis Gonzaga Santos.. IV Rocha.. Priscila Martins da. V. Padrão, Diogo de Oliveira. VI. Souza, Carlos Eduardo Gomes de, Série.

CDD – 669.2

CONTENTS

RESUMO _____	7
ABSTRACT _____	8
1 INTRODUCTION _____	9
1.1 Brazilian Coins Standard _____	11
2 OBJECTIVE _____	13
3 EXPERIMENTAL _____	14
3.1 Intensive Cyanidation _____	14
3.2 Copper-tin Dissolution Process _____	16
3.3 Characterization _____	17
4 RESULTS AND DISCUSSION _____	18
5 CONCLUSIONS _____	23
REFERENCES _____	24

RESUMO

Este estudo teve como objetivo a recuperação de discos defeituosos da produção das moedas de R\$ 0,10 (dez centavos) da nova família do Real (a moeda atual brasileira), posta em circulação no ano de 2002, que utiliza um substrato de aço carbono submetido a um acabamento superficial na liga cobre-estanho por processo eletrolítico. A recuperação desses discos defeituosos foi realizada por cianetação intensiva, com adição simultânea de peróxido de hidrogênio (H_2O_2) e ar comprimido como agentes oxidantes, utilizando um sistema reacional que era composto de um tambor rotatório, totalmente perfurado, imerso em solução alcalina de cianeto de sódio (NaCN). O processo mostrou-se eficaz na remoção/dissolução da liga cobre-estanho, depositada indevidamente no substrato de aço carbono, sem comprometer a superfície desse substrato e, conseqüentemente, as suas dimensões, o que acenou para a possibilidade de reutilização desses discos, isentos da liga cobre-estanho, no processo de revestimento eletrolítico para produzir novas moedas.

Palavras chaves

Cianetação intensiva, recuperação de discos, aço carbono

ABSTRACT

This study aimed at recovering defective R\$ 0.10 disks of the new family of the Real (The actual Brazilian currency), implemented from 2002 onwards, which uses mild steel blanks as metallic substrate submitted to a surface finishing with an electrolytic deposit of a copper-tin alloy. The recovery of these defective discs was accomplished by intensive cyanidation, with simultaneous addition of hydrogen peroxide (H₂O₂) and blowing air as oxidizing agents, using a reaction system consisting of a rotating drum, completely perforated and immersed in sodium cyanide alkaline solution (NaCN). The process proved effective in removing/dissolving the copper-tin alloy out of the defective disks without compromising the surface of the mild steel substrate and, consequently, their dimensions, which waved to the possibility of re-use those blanks in the electrolytic coating process for producing new coins.

Keywords

Intensive cyanidation, blanks recovery, mild steel.

1 | INTRODUCTION

The concept of metals plating is used to define the electrolytic reduction of an element, in ionic form, on the surface of metallic substrate or conductive nature, as a result of the migration of metallic ions of interest (under the influence of an electric current), in aqueous solution, with the purpose of protecting the less noble substrate against the corrosive processes that are submitted, as well as to add the necessary surface finishing to reach commercial values. In the plating process, an electrolytic cell is used containing an electrolyte, constituted of ionic salts of the metal to be plated, also known as bath. The baths are essentially inorganic ones, as the one of copper, chrome, tin, nickel, zinc, noble metals (gold, silver, rhodium, platinum etc.), and copper/tin, zinc/iron, zinc/nickel and zinc/cobalt alloys. The demand of this technique is in the diversity of finishes, allowing its application, as in the aesthetic part (such as in the production of jewels), as in the corrosion area (tools and automotive pieces).

Among the protection processes for mild steel substrate, the copper plating occupies a prominence place. In many cases it constitutes a good intermediate layer for subsequent nickel plating: deposits of copper-nickel-chrome on mild steel provide remarkable protection and aesthetics, which justifies nowadays its wide use. The protection of the plated copper on iron is of cathodic character. The copper layer should be thick and compact, which means with minimum porosity, to provide the maxim protection.

The copper plating is quite used as intermediate layer for further depositing nickel, silver, gold, in aluminium and its alloys, in zinc and its alloys, and in the high-lead or antimony contents alloys,

on which it would not be possible the plating of other metals without compromising their adherence.

Currently, the process of plating copper and its alloys on mild steel is widely used by various plating industries. The concept of plating metals is usual for defining the electrolytic reduction of a given element, initially in ionic form, on the surface of a metal or conductive nature substrate, as a result of the migration of interest metal ions, in aqueous phase, with the purpose of protecting those less noble substrates against deterioration, such as the corrosive processes that are submitted such metal structures, as well as to assign the surface finish required to aggregate commercial values. In the Brazilian Mint (CMB) this process is used in the production of coins through the coating of mild steel blanks with copper, for producing the currencies of R\$0.01 and US\$0.05 and in the copper-tin alloy for R\$0.10 and US\$0.25 ones and the ring of the R\$1.00 one.

The electroplating of copper may be accomplished by using solutions where it is in the cupric (Cu^{2+}) or cuprous (Cu^{1+}) states. These solutions may be termed as baths, in the former case one uses, usually, sulphate bath (the most common), fluorborate bath, sulphamate bath etc.; in the other case are cyanide baths 2-4. The sulphate baths have the advantage of low cost, good chemical stability and are relatively easy to work, since they are less toxic. But, despite these advantages, the cyanide baths continue to be chosen due to deposits of copper be highly adherent, relatively uniform, and morphologically more coherent (finer grains). The copper cyanide baths are potentially more poisonous, requiring strict safe measures to deal with them.

Bearing in mind to verify the resistance of the metallic coatings, tests are accomplished, in which the piece is put in a closed camera with a spray of sodium chloride solution (Camera of Salt-spray) or sulphurous anhydride (SO₂) (Camera of Kesternich), simulating highly aggressive atmospheres.

The thickness of the coating (deposited layer) and their properties depend on several factors: used current density, concentration of salts, bath temperature, presence of additive, nature of the base metal, bath stirring, pH etc.8-11. The amount of plated metal determines the mass and the final dimensions of the treated pieces. Therefore, the amount of metal deposited has to be controlled within very restricted tolerances for the final pieces to be under their specifications.

1.1 | Brazilian Coins Standard

The coins that circulate at a country are called under circulation coins, which are manufactured in high production scale. Those coins can be made out of solid alloy blanks (type I), disks with covering of the "sandwiches" type or "clads" (type II) and with plated blanks (type III).

The United States and now the European Community use the type II coins that have advantages such as: high safety against frauds and falsifications due to the exclusiveness of the three-layer material and to the format of exclusive disk for using in automatic vending machines, mainly for coins of high denomination.

The type I disks were already the most common in Brazil. In the period around 1899 up to 1998, several metallic alloys and isolated metals were used as, for instance: gold, silver, copper

alloys (bronze, brass, copper-nickel, bronze-aluminum), nickel, aluminum and stainless steel. The disks of the type III were released in Brazil in July of 1998, in the second generation of "Real" coins. This disk type was issued in the seventies, in Canada. Among the main advantages, one can mention: a) smaller risk of coating pilling off, as the coins are manufactured with a substrate of mild steel immobilizing less than 10% w/w of non-ferrous metals such as copper, nickel, tin, said of great strategic value; b) easier in distinguishing the facial values of the coins for the color variety for the old people and visual deficient; c) acceptance of the coins with recommended minimum thickness of plated layer for using in automatic vending machines; d) larger safety against frauds and falsifications.

The baths used at the Brazilian Mint are: a) the cyanide baths for the ones of copper for the coins rates of R\$ 0.01 and R\$ 0.05 and b) the one of copper-tin, also cyanide bath, for the coins rates of R\$ 0.10 and R\$ 0.25 and of R\$ 1.00 (in this case, only for the ring). The coins of R\$ 0.01 and of R\$ 0.05 have 35 micrometers layers (specification) of copper, whose substrates are mild steel blanks SAE 1006/1008.

The decision for using cyanide baths was ruled mainly in the quality of the deposits that should be obtained. Another relevant argument is that this bath type is more known, spread and practiced at the main Mints of the world. The choice of copper and bronze deposits sought mainly to obtain coins with a beautiful aspect and different of the previous series (made out of stainless steel).

2 | OBJECTIVE

This technical contribution aimed at recovering the defective discs from an inappropriate electroplating process and industrial misspecifications, using a suitable way of removing the copper-tin alloy and re-incorporating the recovered mild steel blanks in the production of new coins.

3 | EXPERIMENTAL

3.1 | Intensive Cyanidation

The defective discs, for running the bench scale tests, were the ones used for producing the R\$0.10 coins, made available by CMB (the Brazilian Mint). One of the objectives of this study was to recover the defective discs, while producing the new Real coins, via intensive cyanidation, and, still, use the resulting solution out of this treatment in volume settings of the electrolytic cells since evaporation takes place during the production process of those mild steel plated blanks due to the temperature at which these baths are used (60 °C).

The Figure 1, below, shows a picture of a sample of those defected discs and rings (from R\$1.00 coins) out of a poorly controlled electroplating process. On the other hand, the Figure 2 shows the reaction system used for the intensive cyanidation tests that is composed of a cubic polycarbonate cell with 22:22:22 (LxWxD) cm, manufactured by Plasmetal Plastics and Metals, with useful capacity of 5 litres and a six perforated face rotatory drum, manufactured in polypropylene and driven by a 220V and 1/2HP engine. This drum, duly loaded with 100g of defective discs, was submerged in the alkaline cyanide solution, in a rotating movement providing an effective contact between the metal parts and the cyanide solution with the continuous addition of distinct oxidizing agents, blowing air and adding hydrogen peroxide solution, so as to dissolve the copper-tin alloy previously plated.



Figure 1. Samples of defective blanks and rings.

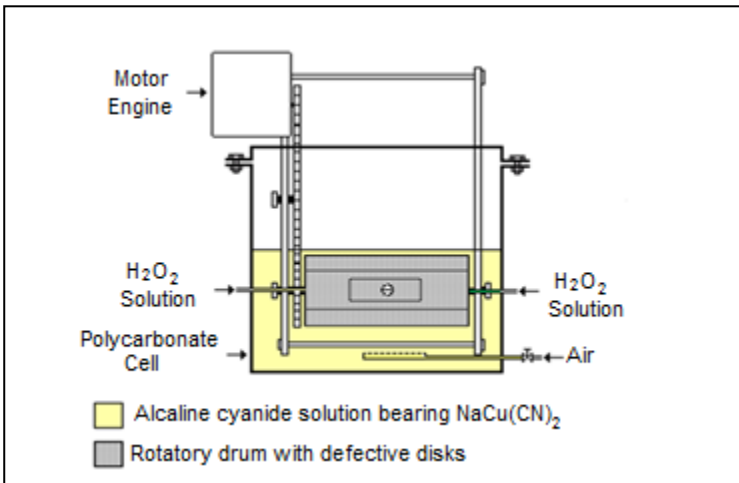


Figure 2. Reaction system used in the intensive cyanidation tests.

The Figure 3, as follows, shows the photos of the drum in operation and open for loading it with the defective discs to be treated.

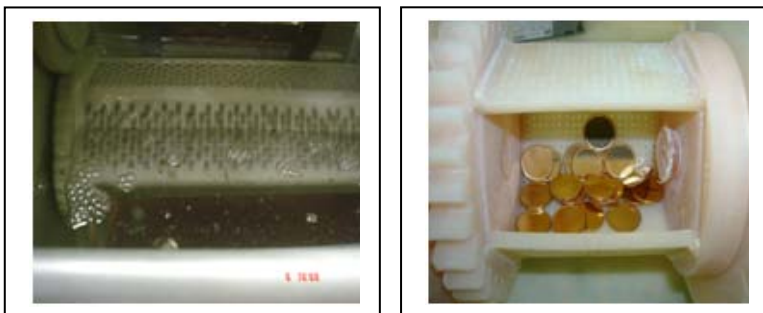
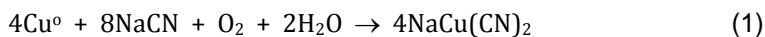


Figure 3. Rotating drum in operation and open to be loaded.

3.2 | Copper-tin Dissolution Process

The reactions that take place during the copper-tin alloy dissolution process, during the intensive cyanidation, using as oxidizing agents the oxygen out of the atmospheric air and hydrogen peroxide, are:

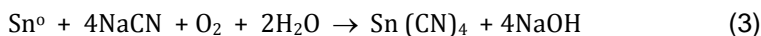
Oxidation of copper by oxygen (O_2)



Oxidation of copper by Hydrogen Peroxide (H_2O_2)



Oxidation of tin by oxygen (O_2)



Oxidation of tin by Hydrogen Peroxide (H_2O_2)



3.3 | Characterization

Aliquots were taken from the reaction system so as to analyze the free cyanide, by titration with silver nitrate (AgNO_3) and rhodamine as indicator, and for determining the copper and tin concentrations, by atomic absorption spectrometry.

The dimensional measurement of discs were accomplished in triplicate using a micrometer Mitutoyo, where it was possible to verify the dimensional integrity of the edge, diameter and between faces of the blanks after the intensive cyanidation process.

The precipitate formed during the tests for recovering the blanks was characterized by X-rays diffraction (XRD) using a Bruker equipment-D4 From Endeavor, under the following operation conditions: radiation $\text{Co K}\alpha$ (35 kV/ 40mA); speed of the goniometer of 0.020° per step with counting time of 1 second per step and collected from 4° to 80° . The qualitative interpretations of the spectrum were performed by comparison with standards contained in the database PDF02 (ICDD, 2006) in software BrukerDiffrac Plus.

4 | RESULTS AND DISCUSSION

The dissolution of electrolytic metal deposit by the proposed method starts when the contact of the rotating drum, properly loaded with the defective discs, with the alkaline cyanide solution takes place. Then, air starts to be blown, adding, periodically, hydrogen peroxide solution. This gradual injection of peroxide aimed at using it as oxidizing agent for dissolving the copper-tin alloy, as shown in reactions 2 and 4. On the other hand, when using just the oxygen present in atmospheric air, the oxidation reactions are not as effective during the dissolution process, due to the decrease of oxygen solubility as the salinity of the aqueous phase increases caused by metallic salts produced, which does not happen while using the hydrogen peroxide.

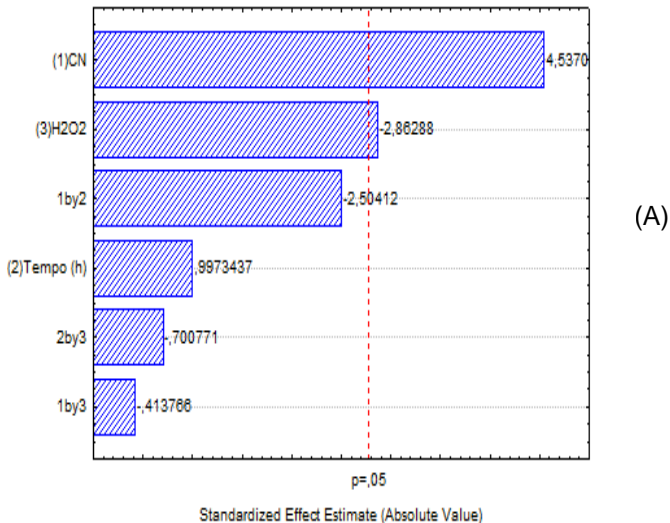
A full factorial design was done in two levels with three variables: concentration of the alkaline cyanide solution, the volume of hydrogen peroxide added as oxidant agent and cyanidation time.

Table 1. Experimental design

Experimental design		
NaCN (g/L) Concentration	Volume of H ₂ O ₂ (mL)	Cyanidation Time (h)
10	49	4
20	63	6

The analyzed metals were copper and tin. The experimental data were processed using Statistica (StatSoft, Inc., 2004, version 7). The Pareto diagrams (Figure 4) show the effects that are statistically significant within the studied levels. The effects

whose rectangles are to the right of the dividing line ($p=0.05$) should be considered significant. The results obtained from the experimental design indicated that the cyanide concentration in solution was the factor under study that showed the greatest statistical significance. On the other hand, hydrogen peroxide was marginally significant in the dissolution of Cu (Figure 4A). For the tin dissolution process, the hydrogen peroxide showed greater statistical significance, while the cyanide solution concentration was considered marginally significant in such dissolution process (Figure 4B). The interaction between the initial cyanide and hydrogen peroxide concentrations proved to be important in reducing the free cyanide concentration in solution (Figure 4C), since something of free cyanide is oxidized to cyanate (CNO^-), not only by hydrogen peroxide added as well as, to a lesser extent, by dissolved oxygen in aqueous phase.



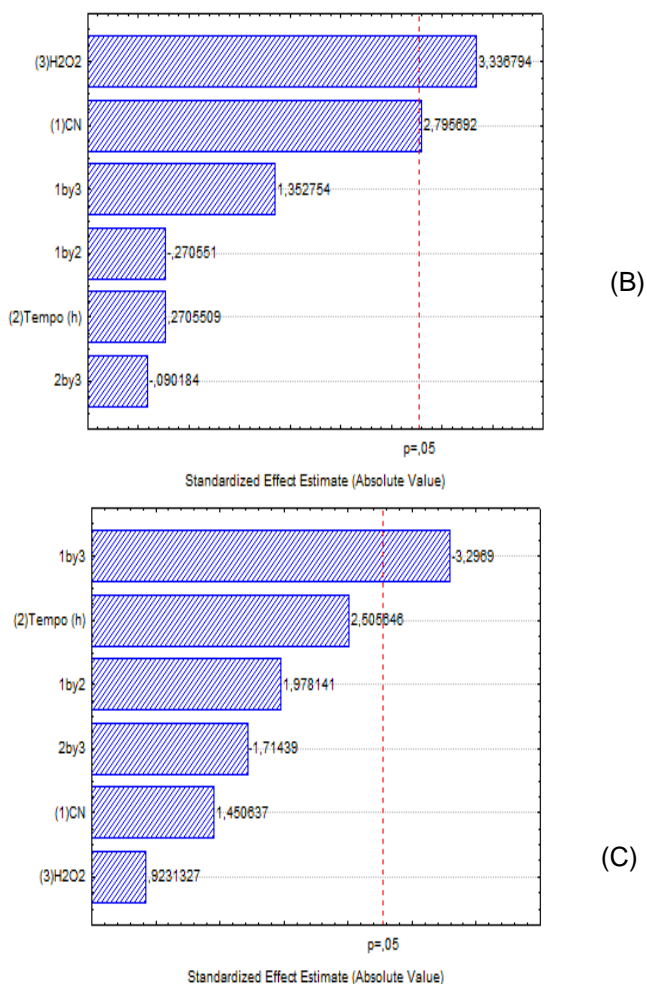


Figure 4. Pareto diagram for Copper (A), tin (B) and Cyanide (C).

The presence of oxidizing agents can also cause the oxidation of copper cyano- complex, generated during the copper oxidative process out of the disks copper-tin coatings layer, releasing cyanate ions and copper (II) hydroxide (Cu(OH)₂) as insoluble compound. The reactions 5, 6 and 7 show how these oxidative processes take place:



The dimensional analysis of diameter, edge and between faces, made in virgin mild steel blanks and those just reclaimed, shows, as seen in Table 2, that the dissolution of the copper-tin alloy coating, through the proposed intensive cyanidation process, as well as, the abrasion suffered by the discs as a result of the rotating drum bearing the defective ones, did not provide significant changes in their dimensions when compared with those of virgin mild steel blanks.

Table 2. Dimensional analysis of R\$0,10 rate recovered blanks.

Tested Disos	Diameter		Edge		Between faces	
	Average	Standard Devistion	Average	Standard Devistion	Average	Standard Devistion
	Mm	Mm	mm	mm	mm	
1	19.603	0.006	2.213	0.012	1.930	0.012
2	19.623	0.029	2.197	0.035	1.930	0.010
3	19.597	0.015	2.207	0.040	1.947	0.018
4	19.637	0.061	2.220	0.010	1.930	0.011
5	19.590	0.022	2.223	0.031	1.937	0.018
6	19.597	0.015	2.197	0.015	1.927	0.015
7	19.590	0.026	2.230	0.017	1.947	0.030
8	19.577	0.012	2.230	0.020	1.933	0.026
9	19.597	0.021	2.203	0.050	1.930	0.019
10	19.612	0.014	2.213	0.020	1.931	0.022
11	19.592	0.020	2.202	0.012	1.921	0.012
12	19.618	0.017	2.223	0.018	1.905	0.018
Virgin Mild Steel Blanket	19.620	0.010	2.190	0.035	1.900	0.029

5 | CONCLUSIONS

The experimental design indicated that the concentration of cyanide and hydrogen peroxide were the most significant variables in the copper and tin dissolution processes, out of the coating alloy composing the new R\$0.10 coins.

The mild steel substrate, free from the copper-tin alloy, kept the characteristics of the virgin mild steel blanks as regards, mainly, to dimensional aspects as well as surface features, as the intensive cyanidation process proved quite effective in dissolving the deposited alloy without compromising the integrity of the mild steel blanks. However, it was detected the appearance of brown particles in suspension, only in the test carried out under conditions of higher level of the three variables studied, due to the formation of ferricyanide ions ($[\text{Fe}(\text{CN})_6]^{3-}$), as a result of the metallic substrate oxidation (mild steel blanks) that decomposes in the presence of light forming ferric hydroxide precipitate ($\text{Fe}(\text{OH})_3$).

The recovered discs are fit to be returned to the production process of new coated discs for subsequent minting for issuing new coins.

Finally, it is worth noticing that the intensive cyanidation process, used for recovering the R\$0.10 defective coins, applies, also, to the defective R\$0.01 and R\$0.05 coins, which are only coated with copper, as well as to the R\$0.25 ones and ring of the R\$1.00 coins, as they are, also, coated with copper-tin alloy.

REFERENCES

- A. S. M., "Heating Treating, Finishing and Cleaning of Metals", Metals Handbook, vol. 2, pp. 432 – 445, 1968.
- BERTORELLE, E., Tratados de Galvanoplastia, 4ª edição, 1974, vol. 3 Cap. III pp. 437-521.
- GEDULD, H. Practical problems in copper cyanide plating. Metal Finishing, vol.65, nº 8, p. 52-56, Agosto de 1967.
- DUDEK, D. A.; FEDKIW, P. S., Electrodeposition of copper from cuprous cyanide electrolyte, vol. 474, Issue 1, 16 September 1999, pages 16-30.
- SINITSKI, R.E., SRINIVASAN, V. And HAYNES, R., J. Electrochem. Soc. 127 (1980), p. 47.
- CRIBB, J. – Eyewitness Guides – Money – Dorling Kindersley Limited – London 1990. (Aventura Visual – Dinheiro – Editora Globo 1990).
- DELBROUCK, U. – Technical Report of Six Experimental Years In The Manufacture of Electropalated Blanks. XX Mint Director's Conference – África do Sul -1998.
- ELECTROPATED COINS – The British Royal Mint – XV1 Mint Director's Conference – Londres – Junho de 1990.
- JACKE, H. Dr. – Electroplating of Coins Blanks – The Clad and Electroplated Low Carbon Steel Process At Deutsche Nickel – XX Mint Director's Conference – África do Sul -1998.
- KUTZELNIGG, A – Ensayo de Recubrimiento Metálico – Editorial River Madrid, 1967.
- LAS 100 MEJORES PIEZAS DEL MONETARIO DEL MUSEO ARQUEOLÓGICO NACIONAL - Ministério de Educación Cultura y Desporte – Espana – Julio de 2003.

MANUAL DE OPERAÇÃO; WESTAIN, Canadá, DVED 001/5, 2000.

MARTINEZ, J. C. C.; OGANDO, R. O.; SATLHER, L.; SOBRAL L. G. S. and SANTOS R. L. C.; Avaliação da Resistência à corrosão e à abrasão das moedas brasileiras, 56º Congresso Anual da Associação Brasileira de Metalurgia e Materiais. Belo Horizonte, Minas Gerais, 2001.

SÉRIES CETEM

As Séries Monográficas do CETEM são o principal material de divulgação da produção científica realizada no Centro. Até o final do ano de 2010, já foram publicados, eletronicamente e/ou impressos em papel, mais de 200 títulos, distribuídos entre as seis séries atualmente em circulação: Rochas e Minerais Industriais (SRMI), Tecnologia Mineral (STM), Tecnologia Ambiental (STA), Estudos e Documentos (SED), Gestão e Planejamento Ambiental (SGPA) e Inovação e Qualidade (SIQ). A Série Iniciação Científica consiste numa publicação eletrônica anual.

A lista das publicações poderá ser consultada em nossa homepage. As obras estão disponíveis em texto completo para download. Visite-nos em <http://www.cetem.gov.br/series>.

Últimos números da Série Tecnologia Ambiental

STA-61 - **Avaliação ecotoxicológica de efluentes da indústria carbonífera.** Zuleica Carmen Castilhos, Silvia Gonçalves Egler, Hudson Jean Bianchini Couto, Silvia Cristina Alves França, Jorge Rubio, Cristiane Moreira dos Reis Pereira, Patricia Correa Araujo, 2011.

STA-60 - **Mecanismos, técnicas e aplicações da agregação no tratamento mineral e ambiental.** Cristiane Oliveira, Jorge Rubio, 2011.

STA-59 - **Influência do Níquel na Biorremediação de Solo Tropical Multicontaminado com Hidrocarbonetos de Petróleo e na Estrutura da Comunidade Microbiana.** Natália Franco, Rodrigo Gouvêa Taketani, Selma Gomes Ferreira Leite, Andrea Camardella de Lima Rizzo, Siu Mui Tsai e Cláudia Duarte da Cunha, 2010.

INFORMAÇÕES GERAIS

CETEM – Centro de Tecnologia Mineral
Avenida Pedro Calmon, 900 – Cidade Universitária
21941-908 – Rio de Janeiro – RJ

Geral: (21) 3867-7222

Biblioteca: (21) 3865-7218 ou 3865-7233

Telefax: (21) 2260-2837

E-mail: biblioteca@cetem.gov.br

Homepage: <http://www.cetem.gov.br>

NOVAS PUBLICAÇÕES

Se você se interessar por um número maior de exemplares ou outro título de uma das nossas publicações, entre em contato com a nossa biblioteca no endereço acima.

Solicita-se permuta.

We ask for interchange.