ANNUAL ACTIVITY REPORT 2009 - 2010



National Institute of Science and Technology on Mineral Resources, Water and Biodiversity

INCT-ACQUA Annual Activity Report 2009 - 2010

Expedient

Editors	Virginia S. T. Ciminelli — <i>EE/UFMG</i> Claudia L. Caldeira — <i>EE/UFMG</i> Marcelo B. Mansur — <i>EE/UFMG</i> Helio A. Duarte — <i>ICEx/UFMG</i>
Proofreader	Virginia S. T. Ciminelli — <i>EE/UFMG</i> Claudia L. Caldeira — <i>EE/UFMG</i> Marcelo B. Mansur — <i>EE/UFMG</i> Helio A. Duarte — <i>ICEx/UFMG</i> Francisco A. R. Barbosa — <i>ICB/UFMG</i> José G. Tundisi — <i>IIEGA</i> Ângela M. F. Guimarães — <i>CEFET/MG</i> Ana Cláudia Q. Ladeira — <i>CDTN/CNEN</i> Jaime W. V. Mello — <i>UFV</i>
Production	Editora Cubo
Management	Rafael Mozeto and Larissa Orlandi
Credits	Max Barroso/FUNDEP intervention in a photograph by Marcus Desimoni/Agência Nitro (Cover, Summary and Publication background)
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Instituto Nacional de Ciência e Tecnologia em Recursos Minerais, Água e Biodiversidade



Telephone E-mail Home Page

Headquarters

Universidade Federal de Minas Gerais – UFMG Escola de Engenharia – Bloco II Depto. de Engenharia Metalúrgica e de Materiais Av. Antonio Carlos, 6627 – 31270 - 901 Belo Horizonte – MG, Brazil +55 (31) 3409-1825 / 1810 inct.acqua@demet.ufmg.br www.acqua-inct.org

Management Committee

Coordinator Virginia S.T. Ciminelli – DEMET/UFMG, chair Vice-Coordinators Francisco A. R. Barbosa – ICB/UFMG, co-chair José Galizia Tundisi – IIEGA/SP, co-chair Ângela M. F. Guimarães – CEFET/MG Ana Claudia Q. Ladeira – CDTN Jaime W. V. Mello – UFV Hélio A. Duarte – ICEx/UFMG

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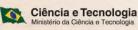
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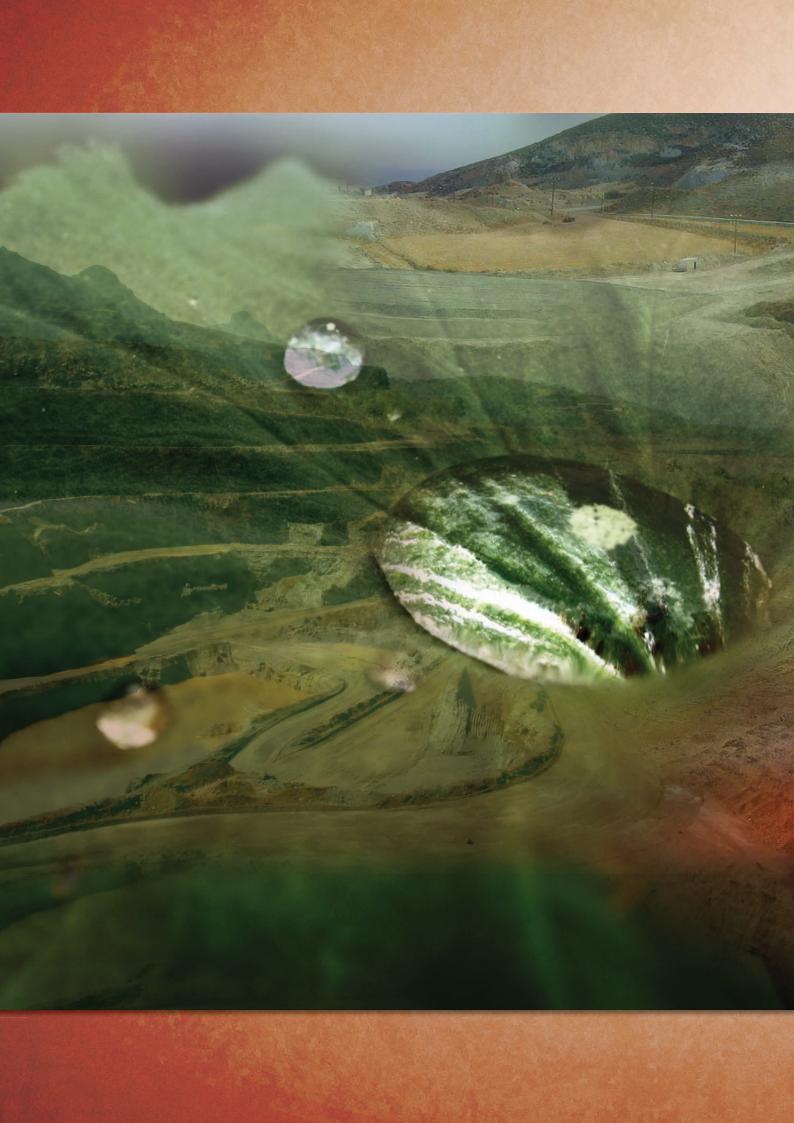














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introduction

National Institute of Science and Technology on Mineral Resources, Water and Biodiversity – INCT-ACQUA

Instituto Nacional de Ciência e Tecnologia em Recursos Minerais, Água e Biodiversidade

Mineral Production, Conservation of Water Resources and Biodiversity – Challenges for Integration

Mineral wealth, abundant water resources and rich biodiversity – competitive advantages for the economic development of Minas Gerais State and Brazil – are the focus of the work of INCT-Acqua. By combining and integrating Mineral Resources, Water and Biodiversity, the Institute adopts a new paradigm, where water is the common denominator of the initiatives focused on innovation, scientific development, social and sustainable regional development. The integration among these topics is still incipient in Brazil and abroad, and it is one of the most original aspects of the present proposal. A systemic approach is needed to fully assess the environmental and territorial implications resulting from a significant, worldwide increase in mineral production.

The research activity of the INCT-Acqua encompasses two major areas.

The first comprises the assessment of the impact of mining activities on the quality of water, soil and conservation of biodiversity. Within this context, the priorities are: the development of advanced technologies for the study and evaluation of ecotoxicity, the use of innovative methodologies using neotropical species as bioindicators and the identification and characterization of water quality standards to be used as reference for future recovery studies at impacted areas. The broader objectives are: the contribution towards the minimization of the environmental impacts of the mineral industry, the selection of remediation techniques, and, particularly, the conservation and recovery of aquatic biodiversity.

The second research area consists of adding value and environmental performance to mineral-based products and processes. The mineral production processes should consider the sustainable use of all natural resources involved (e.g., water, energy and mineral resources), exploring the synergy with regional production chains, which promotes the development of local communities. The industrial processes are "re-designed" to minimize emissions, to transform waste into products and to add more value to the products, thus providing the basis for better biodiversity conservation.

Main Approaches

From Molecular Level to Industrial Processes: Scientific Fundamentals as Drivers of New Environmental Paradigms for the Mineral Industry

Advanced scientific tools are used to investigate chemical and biological systems in detail. The association of molecular modeling techniques (e.g., computational chemistry and spectroscopic techniques, including those which use synchrotron light radiation) allows the identification of the nature of chemical bonding and distribution of contaminants in soils and other substrates. The understanding of the mechanisms that explain the environmental impact will contribute to the development of functionalized, tailor-made materials for the removal of harmful species at traces and ultra-trace levels. The expansion of knowledge boundaries promotes a better and more accurate evaluation of environmental impacts, making it possible to develop environmentally sustainable extraction processes and to identify new ways of mitigating and remediating the impacted areas.

Biodiversity in Mining Areas: New Possibilities for Environmental Remediation

The inventories of biodiversity/richness of species, particularly of aquatic organisms, have not yet received the attention they deserve in view of their ecological, economic and social importance. The understanding of the dynamics of metal species in aquatic environments requires the knowledge of their interaction with the biological communities. INCT-Acqua seeks to identify microorganisms and plants (from the contaminated sites), which are capable of removing toxic elements, as well as to elucidate their mechanisms of tolerance. This initiative focuses on contributing towards the identification of species to be used in bioremediation/phytoremediation techniques. In addition to contributing towards the removal of polluting/ contaminating elements, it is expected that the identification of these species will allow the development of more sustainable alternatives for remediation of impacted areas.

Changing the Present Attitude towards a New Development Model for Mining Regions

The Institute calls for joined initiatives with the partnership of the public and industrial sectors

as well as the organized society. The generation and dissemination of scientific and technological fundaments aim at supporting the development of public policies and the increase of industrial competitiveness, with main focus on capacity building.

Environmental education will be directed to communities in the mining areas. An ambitious plan is being carried out aimed at introducing the concepts of INCT-Acqua in environmental education programs, enhancing and supporting particularly those already existing. Videos, printed material, interactive games and other educational tools will contribute towards the construction of a new ethical perspective of sustainability.



recursos minerais biodiversidade

Research Topics

- Evaluation of water/environmental quality and aquatic biodiversity, aiming at the proposition of restoration and conservation strategies for mining areas;
- Modeling and simulation of hydrometallurgical processes, optimized to achieve a better environmental performance;
- Design and application of natural and synthetic materials for separation, fixation or encapsulation of chemical species;
- Metal sulfide oxidation applied to metal extraction and control of acid mine drainage.

Vision

To become International and National reference in:

- Fundaments and modeling of water-based, metal extraction and remediation processes;
- Monitoring, diagnosis of environmental and water quality in mining and metallurgical districts;
- Mitigation of impacts, biodiversity conservation and value-added to water in mining areas;
- Proposal and use of innovative, systemic and sustainable approaches for the mineral sector by a joined academic, public and industrial sectors effort.

MANAGEMENT COMMITTEE

Virgínia S. T. Ciminelli – DEMET-UFMG, chair José Galizia Tundisi – IIEGA-SP, co-chair Francisco A. R. Barbosa – ICB-UFMG, co-chair Ângela Mello Guimarães – CEFET/MG Ana Claudia Q. Ladeira – CDTN Jaime W. V. Mello – UFV Hélio Anderson Duarte – DQ-UFMG

LEADING INSTITUTIONS

Universidade Federal de Minas Gerais – UFMG Instituto Internacional de Ecologia e Gerenciamento Ambiental – IIEGA Universidade Federal de Viçosa – UFV Centro de Desenvolvimento da Tecnologia Nuclear – CDTN Centro Federal de Educação Tecnológica de Minas Gerais – CEFET-MG

ASSOCIATED NATIONAL INSTITUTIONS

Universidade Federal do Ceará – UFCe

Universidade Federal de Juiz de Fora – UFJF

Universidade Federal de São João del-Rei – UFSJ

Universidade Federal dos Vales do Jequitinhonha e Mucuri – UFVJM

Secretaria de Estado de Ciência, Tecnologia e Educação Superior - SECTES Pólo de Excelência Mineral e Metalúrgico e Pólo de Excelência Recursos Hídricos

INDUSTRY AND STATE GOVERNMENT COLLABORATION

ANGLO GOLD ASHANTI

EIP – Espaço Israel Pinheiro IGAM – Instituto Mineiro de Gestão das Águas INB – Indústrias Nucleares do Brasil IEF-MG – Instituto Estadual de Florestas de Minas Gerais LAPOC – Poços de Caldas Laboratory OSCIP VERDE NOVO PETROBRAS KINROSS – Paracatu VALE VM – Votorantim Metais

INTERNATIONAL COLLABORATION

Centro Atômico Constituintes, Comisión Nacional de Energía Atómica – Argentina Forschungszentrum Karlsruhe – Alemanha Jacobs University – Alemanha Ohio University – EUA Technical University-Dresden – Alemanha The Pennsylvania State University – EUA University of Queensland – Australia

- Forschungszentrum Karlsruhe (Germany)
- Technical University-Dresden (Germany)
 Jacobs University (Germany)

• The Pennsylvania State University (EUA) Ohio University (EUA)

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• Universidade Federal do Ceará (UFCe)

- EIP Espaço Israel Pinheiro (GO)
- VM Votorantim Metais (GO)

• INCT-ACQUA

- Universidade Federal de Minas Gerais (UFMG)
- Universidade Federal de Viçosa (UFV)
- Universidade Federal de Juiz de Fora (UFJF)
- Universidade Federal de São João del-Rei (UFSJ)
- Universidade Federal dos Vales do Jequitinhonha e Mucuri (UFVJM)
- · Centro de Desenvolvimento da Tecnologia Nuclear (CDTN)
- · Centro Federal de Educação Tecnológica de Minas Gerais (CEFET-MG)
- Instituto Estadual de Florestas de Minas Gerais (IEF-MG)
- Instituto Mineiro de Gestão das Águas (IGAM)
- Pólo de Excelência Mineral e Metalúrgico
- Pólo de Excelência Recursos Hídricos
- ANGLO GOLD ASHANTI LAPOC – Poços de Caldas Laboratory
 OSCIP VERDE NOVO

- PETROBRASKINROSS Paracatu
- VALE
- VM Votorantim Metais

· Indústrias Nucleares do Brasil (INB)

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· Instituto Internacional de Ecologia e Gerenciamento Ambiental (IIEGA)

· Centro Atômico Constituintes, Comisión Nacional de Energia Atómica (Argentina)



INCT-ACQUA Network



facts and figures

Knowledge and Technology Transfer Indicators

6 Events in Communities, Elementary and Secondary Schools

2 Patent Deposits

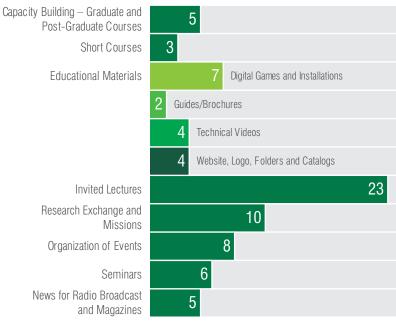
10 Projects with Industries and Others

5 Interaction with Other Projects

Research Indicators: Publications

Books	2
Book Chapters	6
Journals	65
Proceedings Books	11

Education and Outreach Activities Indicators



Capacity Building Indicators

	Current	Concluded
Undergraduate Students	7	-
M.Sc and PhD Students	26	20
Post-Doctorates	9	1
Technical Level	2	-

national and international partnership

The INCT-Acqua has received many foreign visitors, from companies and universities. Visiting professors offered seminars, short-courses and interacted with the Brazilian researchers. INCT-Acqua participated and sponsored in the creation of SANAP – South America Network for Acid Mine Prevention, a South American division of the INAP – International Network on Acid Mine Prevention, established this year. The Institute is part of the network on sustainability research under the State program of the Mineral and Metallurgical Pole of Excellence/ Secretariat of Science and Technology-SECTES/MG. Various initiatives to contribute to environmental education at all levels, taking advantage of ongoing initiatives, are also under development. The relevance of the topics addressed by the INCT-Acqua has been validated and reinforced by foreign visitors and specialists or executives from private companies.

Organization of Events

1st workshop of the INCT-ACQUA. July 13-14, 2009.

Cycle of Conferences – Brazilian Academy of Sciences/ UFMG/FAPEMIG – A Crise da Água e o Desenvolvimento Nacional: um Desafio Multidisciplinar, Belo Horizonte, October 30, 2009. José G. Tundisi and Francisco A. R. Barbosa. – Organizing committee.

XVI Brazilian Meeting on Mössbauer Spectroscopy, Fortaleza – CE, November 24-27, 2009. *Igor F. de Vasconcelos (UFCE) and José D. Fabris (UFMG). – Organizers.*

WinterSchool – Computational Chemistry and Physics in the Nanoscale. 2009.

Joswig, Jan-Ole; Duarte, Hélio A.; Heine, Thomas; Kleinekathöfer, U.; Seifert, Gotthard; Cavalcanti, W. – Organizers.

XVI Brazilian Symposium on Theoretical Chemistry. 2009. *Duarte, Hélio A.; de Abreu, Heitor A. – Organizers.*

International Workshop on Density Functional Theory – Present and Future Challenges and X deMon Developers Workshop. 2010.

Duarte, H. A.; Abreu, Heitor A.; Salahub, Dennis R.; Koster, A. – Organizers.

International Symposium Improving Access to Safe Water: Perspectives from Africa and the Americas – São Carlos. September 13-17, 2010. *IIEGA (Jose G. Tundisi). – Organizer.*

Seminar "INCTs: challenges and perspectives for science in Brazil". October 28-29, 2010. *IEAT-UFMG/ FAPEMIG. – Francisco A. R. Barbosa and Santuza Teixeira. – Organizers.*

Seminars

"Bioavailability of Metal Contaminants in Soils: Estimating True Human Exposure". School of Engineering, UFMG. February 11, 2009. Beverley Hale (University of Guelph, Canada) "The Development of soil adsorption models for metal contaminants". School of Engineering, UFMG. February 11, 2009. *Leslie Evans (University of Guelph,Canada)*

"Acid Mine Drainage and Environmental Monitoring". School of Engineering, UFMG. April, 2009. Massimo Gasparon (University of Queensland, Australia)

"Physical, chemical and biological mechanisms of acid mine drainage". UFMG and CDTN. July, 2009. *Dina Lopez (Ohio University, USA)*

"Aqueous Processing: Minerals, Materials, and Environmental Systems". October, 2009. *K. Osseo-Asare (Pennsylvania State University, USA)*

"Biomineralization by bacteria in subsurface environments". May 24, 2010. *Susan Glasauer (University of Guelph, Canada)*

Researchers Exchange and Missions

Virgínia S. T. Ciminelli; Francisco A.R. Barbosa; Wander L. Vasconcelos Flávio M. Vasconcelos; Renato Ciminelli – UFMG, SANAP, SECTES, Brazil. University of Queensland, Australian Academy of Science, The National Science and Technology Centre, Sustainable Minerals Institute (SMI), JK Centre and CRC Mining, Institute of Applied Ecology (University of Canberra), Centre for Advance Wastewater, The Australian Groundwater Centre. Australia. September 4-17, 2009.

Wander L. Vasconcelos – UFMG, Brazil. University of Queensland. Australia. December/2009 to January/2010.

Virginia S.T. Ciminelli – UFMG, Brazil. National Cheng Kung University, Tainan – Taiwan. May, 2010.

Thomas Heine – Jacobs University, Germany. Chemistry Department, UFMG. May 13-18, 2010.

Helio A. Duarte – UFMG, Brazil. Molecular Modeling group of Curtin University, Nanochemistry Institute. Australia. July 15-24, 2010.

Regina P. de Carvalho – UFMG, Brazil. American Association of Museums Conference. Los Angeles, USA. May 23-26, 2010 – and visit to The Exploratorium. San Francisco, USA. May 27-29, 2010.

Dina Lopez - Ohio University, USA. UFMG, CDTN and INB (Nuclear Industries of Brazil). Poços de Caldas - MG. July/2009 and March-July/2010. Dr. Agnieska Kuc - Jacobs University, Bremen-Germany. Chemistry Department, UFMG. August 1-28, 2010.

Dr. Augusto Faria de Oliveira - TU, Dresden, Germany. Chemistry Department, UFMG. August 1-28, 2010.

Hélio A. Duarte - UFMG. Brazil. Mission to Jacobs University – Bremen, Germany, INCT and PROBRAL projects. December 6-17, 2010.



Left: Internal. Symp. Improving Access to Safe Water: Perspectives from Africa and the Americas, São Carlos, September 13-17, 2010. Right: 1st Workshop INCT-ACQUA.

Invited Lectures

XI Congresso Brasileiro de Ecotoxicologia – XI ECOTOX. Round Table: Acid drainage and arsenic geochemistry – environmental and research perspectives in Brazil. Bombinhas - SC. September 19-23, 2010. Jaime W. V. Mello

2nd Annual Meeting of CICITEM – Center of Scientific and Technological Investigation for Mining, Antofagasta – Chile. June, 2009. - INCT-Acqua - Minerals and Biodiversity. National Institute of Science and Technology. Virgínia S. T. Ciminelli

XVI Brazilian Meeting "Jacques Danon" on Mössbauer Spectroscopy. "The mineral iron as a contaminant of the product or processes of the mineral industry: challenges and opportunities for scientific and technological advances. Fortaleza, Brazil. November 24-27, 2009.

Virgínia S. T. Ciminelli

XVI Brazilian Meeting "Jacques Danon" on Mössbauer Spectroscopy. "Chemistry of the sulfide mineral surfaces from theoretical calculations - the challenge of the chalcopyrite". Fortaleza, Brazil. November 24-27, 2009. Hélio A. Duarte

XVI Brazilian Meeting "Jacques Danon" on Mössbauer Spectroscopy. "Sulfide oxidation and acid mine drainage mineralogy". Fortaleza, Brazil. November 24-27, 2009. Enver Murad

XVI Brazilian Meeting "Jacques Danon" on Mössbauer Spectroscopy. "Acid rock drainage and geochemical of arsenic – environmental implications and research perspectives". Fortaleza, Brazil. November 24-27, 2009. Jaime W. V. Mello

Cycle of Conferences Brazilian Academy of Sciences - ABC/UFMG/FAPEMIG. "Water, Mineral Industry and Environment". ABC/UFMG/FAPEMIG. Belo Horizonte - MG. October 30, 2009. Virgínia S. T. Ciminelli

II Symposium of Mining and Water Resources – Invited lecture: Geochemical background in mining. May 30-June 2, 2010. Flávio de M. Vasconcelos

Workshop on Cooperative Research Opportunities in Mining – Mining in Chile. Technological Center of Minas Gerais - CETEC, Belo Horizonte. "INCT-Acqua - Minerals and Biodiversity. National Institute of Science and Technology". September 24, 2009. Virgínia S. T. Ciminelli

Il Symposium of Mining and Water Resources - Round Table "Acid drainage a challenge for water resources management". Belo Horizonte - MG. May 31, 2010. Virgínia S. T. Ciminelli (Moderator)

II Symposium of Mining and Water Resources – Conference: SANAP – South America Network for Acid Prevention. May 30-June 2, 2010. Jaime W. V de Mello and Flávio de M. Vasconcelos (Chairman)

Water in Mining 2009. Keynote Speaker. Perth, Australia. September 15-17, 2009. Virgínia S. T. Ciminelli

Symposium of Sustentable Mining and Enviroment. UFMG, IGC. Evaluation of environmental impacts from mining activities. Belo Horizonte – MG. July 14-15, 2010. Ana Claudia Q. Ladeira

 3^{rd} Workshop Iron Quadrangle 2050 – Panel: Strategy for Development of Mining Territories. Presentation of cases designed to minimize the impacts of interruption of activities in areas with mineral and metallurgical activities, as well as to establish proposals that seek the support of the local population. Ouro Preto – MG. June 8-10, 2010. Virgínia S. T. Ciminelli

6th Technology Innovation exhibition – Expominas. Initiatives of National Institute of Science and Technology on Mineral Resources, Water and Biodiversity. Minas Gerais, Brazil. October 8-10, 2010. Hélio A. Duarte

Structural, electronic and mechanical properties of chemical systems of mineral industry and environmental interest – A computational approach. Nanochemistry Research Institute Curtin University of Technology. Perth, Australia. July 21, 2010. Hélio A. Duarte

Seminar at Chemistry Department, UFMG. "X-Ray absortpion fine structure (XAFS). October 20, 2010. Igor F. de Vasconcelos

Biodiversity and Development Sustaintable Seminar – UFMG. Conhecimento e Cultura 2010. "Mining, watershead and biodiversity". October 22, 2010.

Virgínia S. T. Ciminelli and Francisco A. R. Barbosa

III Seminar on Electronic Structure and Molecular Dynamics – SEEDMOL. Structural properties of nanotubes of modified aluminosilicates, SCC-DFTB. Brasilia – DF. October 13-17, 2010. Hélio A. Duarte

Nanomaterial derivated from imogolite: aluminophosphate nanotubes, 23rd Regional Meeting of the Brazilian Chemical Society – 23^o ERSBQ. Juiz de Fora – MG. October 30-November 2, 2009. Hélio A. Duarte

Structural Properties of Aluminosilicate Nanotubes: A SCC-DFTB study. XXXV Congress of Theoretical Chemists of Latin Relevance, QUITEL. San Andrés – Colombia. September 18-22, 2009. Hélio A. Duarte

Retention of arsenic in gibbsite and nanostructures of aluminosilicates, Day of Chemist. Department of Chemistry, CCEN-UFPB. João Pessoa – PB. June 18, 2009. Hélio A. Duarte

Structural Properties of Aluminosilicate Nanotubes Seminar invited by Prof. Itamar Borges Jr., Militar Institute of Engineering – IME. April 2, 2009. Rio de Janeiro – RJ. Hélio A. Duarte

Interactions with Other Projects

BRA 3013 International Agency for Atomic Energy – Workshop on Environmental Remediation – IAEA TC Project BRA3013 – "Providing Practical Guidance for the Implementation of a Decommissioning and Remediation Plan for the Minas Gerais Uranium Mining and Milling Production Centre". November 23-27, 2009. Poços de Caldas – MG, Brazil.

CICITEM – Center of Scientific and Technological Investigation for Mining. July 29-30, 2009. Antofagasta, Chile. **CIAM Project (Brazil, Mexico, Canada)** – 2010-2012 in the field of Advanced Materials coordinated by Prof. Hélio A. Duarte – Agency: CNPq/CONACYT/NRC – Period: 2009-2011 – participants Prof. Hélio A. Duarte (Brazil), Andreas Koster (Mexico), Dennis R. Salahub (Canada).

CYTED/Iberoarsen network, (I) Dra. Marta Litter e Dr. Jochen Bundschuh, 3º International Congress on Arsenic in teh Environment (As2010), National Cheng Kung University, Tainan – Taiwan, may 17 – 21, 2010. (II) 3ª Conferência Hemisférica sobre Geologia Médica. October 12-16, 2009. Montevidéu, Uruguai.

SMI – Sustainable Minerals Institute and AMIRA. Chris Moran – University of Queensland. July, 2010.

Additional Funding

Following the initiatives of the Mining and Metallurgical Pole of Excellence (Secretariat of Science and Technology and Superior Education/ MG) – INCT-Acqua, it has been established a 2-million dollar, Fapemig/University of Queensland agreement to support research projects in the INCT-Acqua scope. This call is unique as the funds will support not only exchange of researchers, but will cover consumables, equipment, international undergraduate exchange, and other activities. Funds from the private sector should also be mentioned; these projects have contributed to expand the group's exposure to industrial problems and to technical information that is not available in scientific publications.

CAPES/DAAD (PROBRAL) – ICEX/UFMG. Exchange program with Jacobs University.

CAPES/DAAD (PROBRAL) – EE/UFMG – CEFET/MG. Exchange program with Karlsruhe Forshungzentrum.

PELD - MCT/CNPq - ICB/UFMG.

PELD = Long Term Ecological Research Program -Phase II – Ecological processes and the conservation of biological diversity of the Atlantic Forest in the middle Rio Doce Watershed, Minas Gerais. (2009-2012).

VALE – EE/UFMG.

Fitoextraction of nickel and cobalt from laterites ores (2010).

VALE - EE/UFMG.

Assessment of Acid Rock Drainage in the Amazon Region – Copper and Nickel Mines. – Projects Cristalino, Alemão, Polo, Jaguar (2005–2010).

VALE - EE/UFMG.

Aplication of the Biotic Ligand Model for water quality analyses in the copper mining areas – Carajas, Para. (2007-2009).

KINROSS PARACATU - EE/UFMG.

Arsenic release from flotation tailings – after dessulfurization processes (2009-2010).

KINROSS PARACATU – EE/UFMG – UFV – University of Queensland.

Environmental and human health impact assessment of arsenic contamination associated with the Morro do Ouro Mine, Paracatu, Brazil (2010).

VOTORANTIM METAIS - EE/UFMG.

Evaluation of laterites for Ni and Co extraction by Caron Process, Niquelandia, Brazil (2007-2010).

VOTORANTIM METAIS – IIEGA.

Revitalization of the river S. Fco. and study the contamination of the sediment, water and aquatic biota (2008-2010).

PETROBRAS - ICB/UFMG.

The environmental quality of the sub-basins of the rivers Ibirité and Pintados: a proposal of integrated management policies for Ibirité reservoir, municipality of Ibirité, Minas Gerais state, South-east Brazil.(2007–2010)

Partnership with the Public Sector and Society

Renato Ciminelli, chair, The Mineral and Metallurgic Pole of Excellence

The Mineral and Metallurgic Pole of Excellence is an innovation. It is a knowledge-driven program launched by the State Secretariat of Science, Technology and High Education of Minas Gerais in October 2007, aiming to consolidate a world-class intelligence matrix to structure and reinforce groups of R&D, promote strategies of innovation, anchor territorial sustainability, bring competitiveness, promote value-added and entice new businesses to the mineral and metallurgic production chain.

The Institute calls for joined initiatives with the partnership of the public and industrial sectors, as well as the organized society. The Mineral and Metallurgic Pole of Excellence, within the context of the INCT-ACQUA, provides a complementary



XVI Brazilian Meeting "Jacques Danon" on Mössbauer Spectroscopy, Fortaleza – Brazil. November 24-27, 2009.

network of relationships linking the Institute and the various social, industrial, governmental, scientific and press segments related to mining, metallurgy and territorial developments. This platform has regional, national and international dimensions.

The institutions below constitute the management consortium of the Mineral and Metallurgic Pole of Excellence as its basic network background, which is shared with the INCT-ACQUA.

Six major achievements of the Mineral and Metallurgic Pole of Excellence are anchored on the cooperation with the INCT – AQUA:

- Avenues of International Cooperation to Australia, Chile, Portugal and France;
- The Mineral and Metallurgic Consortium of Professional Formation and Training as a privileged link with the major mining, metallurgic and associated logistic companies;
- A New Network of 10 R&D Groups Working with Sustainability Issues;
- Two major state and municipal driven Mining Territories Development Policies implemented in the 'Quadrilatero Ferrifero';
- The Geopark Quadrilatero Ferrifero (www. geoparkqf.org), to be recognized by UNESCO, is an initiative for the sustainability of mining territories;
- A package of social, industrial, scientific and governmental mobilization events.

Research and Education Institutions

UFMG – Universidade Federal de Minas Gerais. **UFOP** – Universidade Federal de Ouro Preto.

CETEC – Fundação Centro Tecnológico de Minas Gerais.

CEFET – Centro Federal de Educação Tecnológica de Minas Gerais.

PUC MINAS – Pontifícia Universidade Católica de Minas Gerais.

UFSJ – Universidade Federal de São João del-Rei. **CDTN/CNEN** – Centro de Desenvolvimento de Tecnologia Nuclear.

Industrial Organizations

IBRAM – Brazilian Minig Institute.

ABM – Brazilian Association of Metallurgy, Materials and Minig.

IBS – Aço Brasil Institute.

FIEMG – Industrial Federation of Minas Gerais.

AMIG – Association of the Mining Municipalities of Minas Gerais.

Governmental Agencies

SECTES/MG – State Secretariat of Science, Technology and High Education of Minas Gerais.

SEDE/MG – State Secretariat of Economic Development of Minas Gerais.

SEMAD/MG – State Secretariat of Environment and Sustainable Development of Minas Gerais.

ABDI – Brazilian Agency of Industrial Development

MME – Ministry of Mining and Energy – Secretariat of Geology, Mining and Mineral Transformation.

MCT – Ministry of Science and Technology.

Major Events

3rd Workshop Quadrilátero Ferrífero 2050. June 8-10, Ouro Preto - MG. *Renato Ciminelli, Issamu Endo and Paulo de Tarso Castro (chairs). Mineral and Metallurgic Pole of Excellence and Universidade Federal de Ouro Preto*

ABM Annual Congress 2009. July 13-17, 2009. Belo Horizonte – MG. *Renato Ciminelli (chair). Organizer: ABM – Brazilian Association of Metallurgy, Materials and Mining*

Workshop: How the Mineral Sector can Challenge the Crisis. Belo Horizonte: April 15, 2009. *Organizers: Mineral and Metallurgic Pole of Excellence and Brazil Mineral Magazine*

Secretaria de Estado de Ciência, Tecnologia e Ensino Superior





Estado de Minas Gerais



education (© and outreach activities

Environmental education will be directed to communities in the mining areas. An ambitious plan is being carried out aimed at introducing the concepts of INCT-Acqua in environmental education programs, enhancing and supporting particularly those already existing. Videos, printed material, interactive games and other educational tools will contribute towards the construction of a new ethical perspective of sustainability. The Water School (Escola da Água), created by the International Institute of Ecology and Environmental Management (IIE) and established in the Nova Lima city with the support of Pole of Excellence in Water Resources/ SECTES (the State Secretariat for Science, Technology and Higher Education of the State of Minas), will be a partner in building of the Institute's strategies in environmental education in mining areas.

Capacity Building

Post-Graduate Degree in Watershed Management – *ICB/UFMG*. F, Barbosa (chair). Participants: Arnola C. Rietzler, Francisco A. R. Barbosa, Júlio César J. Silva, Magda K. B. Greco, Paulina M. M. Barbosa, Virgínia S. T. Ciminelli.

Graduate Program in Metallurgical and Mines Engineering "Geochemistry of Acid Mine Drainage and Transport of Contaminants throughout Porous Media" 60 hours. Dina Lopez, Ohio University–USA. April–July, 2010.

Graduate Program in Metallurgical and Mines Engineering *"Hydrometallurgy"*, 30 h. K. Osseo-Asare, Pennsylvania State University – USA. October, 2009

Graduate Degree in Mineral Processing Engineering for the Mining Industry (UFOP). "Hydrometallurgy Processes". Invited lecturers: Virginia S. T. Ciminelli, Cláudia L. Caldeira, Marcelo B. Mansur, Carlos A. Morais, Ana Cláudia Q. Ladeira e Flávio M. Vasconcelos. October 3–November 21, 2009.

Short Courses – "Density Functional Theory: Methods and Applications". Hélio A. Duarte XVII Chemical Week of the Institute of Chemistry – UFRJ. March 30–April 2, 2009. Rio de Janeiro – RJ, Brazil (10 h).

Short Courses – "*Guide of Acid Rock Drainage GARD*", Dr. Terrence Chatwin, EUA – INAP, Dr. Flávio Vasconcelos, Brasil – AECOM/ INCT, Dr. Rens Verburg – Golder Associates, EUA. – offers at II Symposium on Mining and Underground Water Resources – ABAS – MG. May 30–June 2, 2010.

Short Courses – "Arsenic Removal Technologies", Virginia S. T. Ciminelli. October 12-13, 2009. Montevideo, Uruguay.

Knowledge Transfer to Communities, Elementary and Secondary Schools

Escola da Água – School of Water. Nova Lima – MG, Brazil. The partnership with the School of Water established in Nova Lima (by means of an initiative IIE/SECTES-MG) aims at introducing information related to the use of water in mining and metallurgical processes to children from schools located in areas where the economy is based on these industrial activities. (P. Barbosa and collaborators).

OSCIP Verde Novo. Nova Lima, MG, Brazil. The partnership INCT-Acqua/VerdeNovo aims at preparing elementary and secondary school teachers in regions where mining and metallurgical activities are predominant. INCT-Acqua will provide technical information on these industrial activities within the framework of sustainability as well as the relationship of the technical content with the traditional curricula. (R. P. de Carvalho; P. Barbosa and others).

Cycle of lectures for teachers of the elementary and secondary schools; mining companies and local community – "Mining activities and Nova Lima's community", October, 2010 – Organizing: INCT-Acqua; School of Water – Nova Lima, Verde Novo and Anglo Gold Ashanti, (R. P. de Carvalho; P. Barbosa and others).

Workshop Open Dialog – Kinross and Paracatu Community. August, 2010. Virginia S. T. Ciminelli and Jaime Melo (keynote speakers), Massimo Gasparon and Graziele Duarte (participants). **Conferences for the municipality of São Carlos.** Sven E. Jorgensen, Copenhagen University. Organization of IIE – May, 2009. **INCT-Acqua Stand during 6**th **Technology Innovation exhibition**. September 8-10, 2010. Expominas/ Minas Gerais.



Workshop Open Dialog (Aug. 2010) - aiming at consolidating KINROSS interaction with Paracatu Community.

Products and Educational Materials

Digital Games and Installations Computational Environmental Art Installations	Game <i>"Waste Recycling"</i> Installation / game <i>"Piracema"</i> Installation / Game <i>"Rain Dance"</i> Game <i>"Oil Spill"</i> Game <i>"lumber"</i> <i>"Human Nature"</i> <i>"Interactive Ecology"</i>
Guide	São Paulo Municipality - Guide for Watershead Management, 2009.134 p. (Tundisi et al.).
Videos	Four (4) technical videos produced and presented at 6 th INOVATEC - set 2010.
Brochure	Freire, M. L. (Org.); Barbosa, P. M. M. (Org.); BARBOSA, F. A. R. (Org.) <i>Water: Source of Life (Primer).</i> Belo Horizonte: Editora e Gráfica Silveira, 2009. Vol. 1. 24 p.
Website	http://acqua-inct.org/
Institutional folders, logo and catalog were created	acqua recursos minerais bio diversidade
News for Radio Broadcast and Magazines	Interview Radio CBN, 30/8/2010 – <i>"Water situation in Minas Gerais"</i> by Francisco A. Barbosa. Interview Radio CBN, 2/9/2010 – <i>"Mining and Sustentability"</i> by Virginia S.T. Ciminelli. Veja Magazine 11/8/2010, Ed 2177, 43, nº32 – Comment about <i>"New Forest Code"</i> by José Galizia Tundisi. Radio UFMG Interview. October 20-21, 2010 – <i>"Conservation of Biodiversity and Mining"</i> by Virginia S.T. Ciminelli. News UFMG, website 21/10/2010 – <i>"The impact of mining on water resources will be the topic of this sixth lecture"</i> by Virginia S.T. Ciminelli.

Escola da Água – The "School of Water" project

 T.H.P. Correa, V.C.R.O. Genovez, J.G. Tundisi International Institute of Ecology (IIE), São Carlos, SP, Brasil
 *Corresponding author: mailto:thais@iie.com.br – Instituto Internacional de Ecologia;
 R. Bento Carlos, 750 CEP 13560-000, São Carlos SP, Brazil; Tel.: +055 016 – 3362-5400 Key-words: Environmental education, Sustainability, Environmental management.

The project "School of Water" aims to promote community through actions that show how water and environmental issues, with the help of science and technology, can help improve the quality of life and human health. This project was sponsored by SECTES-Secretary of State for Science, Technology and Higher Education of Minas Gerais, with the support of OSCIP, Verde Novo Rio das Velhas, and the Municipality of Nova Lima, MG and part – INCT Acqua as an effort to inform, educate and transfer knowledge to society. It is "a recognition that we have entities in a new era of responsibility" (Obama, 2010), so the "School of Water" is an initiative that considers science as a method for social transformation (Tundisi, 2010).

This report describes working experiences in Environmental Education in small and medium cities, starting from the assumption that high rates of urbanization, growing environmental problems and the reduced capacity of the municipalities to deal with these problems, suggest the need to generate tools for environmental management. These tools will aid to build a sustainable society, which will be able to adapt themselves in their own local environment. This research aims to contribute to the discussion on the assessment of sustainable development strategy, and propose policies, plans, programs and environmental projects in the city through a systemic approach, and issues of transparency, participation and social engagement.

The aim is to deepen the concepts developed on sustainable development and environmental education and increase the actions to reach all parts of the population and mobilize the entire set and segments of society. Through programs of Environmental Education, we seek to promote a significant change in the process of municipal management, integrating environmental, social and economical issues within the concept of sustainability, enabling the ability to protect and restore the capacity of the city to interfere in environmental processes, enlarging the ability to intervene positively in the municipal economy. Within this context, it is obvious that humankind needs to make changes of behavior as regards to nature, with sustainable and conservation practices, with positive effects for the quality of life for all.

The School of Water has been established in the city of Bocaina (SP) since 2005. The project was extended to Nova Lima (MG) in November 2009. It is a place where interactive activities are designed around the water-environment, thus resulting in a network of projects and ideas that are taken to the local schools to encourage and to support a new way of learning, involving teachers and students in order to explore possibilities of reintegrating and integrating school and community. The projectbased learning is a teaching strategy that allows students to take responsibility for their learning, to make decisions and create solutions to problems that concern them. By inserting the population in the matters of the community, they are able to develop a perception of sense of common place to all and there is a great chance that they will learn and start taking care of the environment, knowing that it will be a benefit not only for nature, but also for themselves and, therefore, for the whole city.

Local school students are guided by teachers and are encouraged to have a more active role in learning, so we can say that the project seeks to teach students and the entire community to take care of water through participatory-action projects.

High school teachers can teach students subjects related to the physical and chemical composition of water and then visit the School of Water where the subject water is discussed through lectures and analysis of microscopic aquatic organisms. They can also visit the streams of the county for collecting water and measuring important physical-chemical properties like pH, oxygen concentration, temperature and conductivity. Afterwards, the importance of such analyzed properties is explained in order to differentiate unpolluted from polluted water. Elementary school students may also visit the area, take field trips to the streams and then plant trees along the streams. Another simple action, but important for the perception of elementary school students, is the relation and interaction of the physical and biological environment and the water through the construction of the eco terrarium. Each student makes his terrarium with plants, stones, earth, coal and bottles and, at the same time, studies the hydrological cycle, global warming and greenhouse effects.

All students are advised to preserve and conserve water not only in school but also the water in their own homes, through a software program that explains how to save water. Students take their water bills to the School of Water and through this tool they determine how much water is spent and how much water could be saved. Simple actions such as: (i) distribution of a cup and a toothbrush to the students not to waste water when brushing their teeth, (ii) guiding the population not to waste water washing sidewalks with treated water, (iii) reusing water from the washing machine, (iv) closing the tap while brushing their teeth and while doing the dishes, and (v) reducing time to take showers, for instance, are discussed on the everyday basis of the child's activities. In fact, children play the role of disseminator, acting as agents of water preservation, so all will thrive when schools and communities work together. With the assistance from the "School of Water", local schools have developed projects that help students to improve their community and community education, identifying the needs in order to help people to improve their daily living. Therefore, the development of projects at each school promotes a network of relationships that help the community to improve education, identifying key environmental, water quality and quality issues, and human health related problems.

Activities Developed in Nova Lima – MG

(i) Periodic visits to monitor and to develop the project from November 2009 to October 2010; (ii) Training of monitors, (iii) Monitoring of activities in the School of Water.

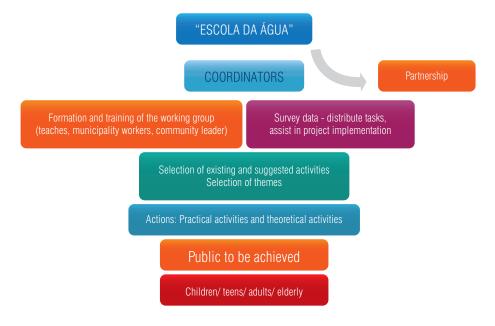
• First Cycle Activities (March–April, 2010)

Lecture: The 10 commandments to save water.

- 1. Calculation of daily water use in households and individual students.
- 2. Development of "Let's take care of the Planet".
- 3. Walk with the students in the Seedling Nursery.
- 4. Water filtration and water treatment.
- 5. Letter to the Lodgers.
- 6. Tree of Knowledge.
- Activity book of crosswords, unscramble words and connecting the dots puzzles.
- 8. Playing with words and "Take a drop happy".
- We worked on the lyrics of the song "Heirs of the Future" by Toquinho (a song about the Environment).
- 10. Presentation on Collection and Recycling.

• Time Reading with Students – Second Cycle of Activities (May–June, 2010)

Other activities were developed such as (i) Environment Week, (ii) Mini plant nursery, and (iii) Production of boxes made of recycled paper.





Water filtration and water treatment.

Environmental Actions

In April and July 2010, meetings were held between the coordinators of monitors, professors from UFMG and OSCIP Verdenovo to prepare a free series of lectures for the municipal and school teachers of Nova Lima. The first series of lectures was held on October 28, 2010 in CVT-Nova Lima and it addressed the interdisciplinary theme: Mining, Water and Society. High school teachers, last-year students from elementary school and representatives from mining companies and social organizations from the region of Nova Lima attended lectures on:

(i) The Process of Mining (Prof.: Regina Pinto de Carvalho); (ii) Biodiversity and Mining (Prof.: Paulina Maia). This activity aims to provide professional education to build critical knowledge, skills and values that contribute to achieving a qualified citizenship, thus empowering the population and improving their knowledge.

Conclusions

The "School of Water" aims to create a network where information exchange occurs between the municipalities and the Center, in order to expand the perception of citizens to the problems of other cities. Through the project firstly implemented in Bocaina (SP) we observed that the best way to deal with environmental issues is with through the participation of all concerned citizens at various levels: informing, listening and deciding are tasks related to public participation in the process. It reverberates into law in Brazil: Federal law no. 10,650 from April 2003 provides for the right to environmental information. However, in addition to being informed and having the right to participate in decisions, the citizen must be instructed to create an awareness of preserving the site as well

Planting seedling mini-nurseries.

as making citizens feel inserted and integrated in the environmental issue, making it part of a whole to become co-responsible for the process and, thereby, assume a portion of care at the local level, contributing to improve quality of life and their region.

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science highlights

research topic 1

Evaluation of water/environmental quality and aquatic biodiversity, aiming at the proposition of restoration and conservation strategies for mining areas

- 26 S.Francisco river studies: limnological and ecological characteristics and the river hydrodynamics; water quality, sediment toxicity; aquatic biota diversity and responses to toxicity
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- 42 Phytoremediation of acid mine drainage by aquatic floating macrophytes

S. Francisco River studies: limnological and ecological characteristics and the river hydrodynamics; water quality, sediment toxicity; aquatic biota diversity and responses to toxicity

José Galizia Tundisi¹*, Takako Matsumura Tundisi¹, José Eduardo M. Tundisi¹, Donato S. Abe¹, Corina S. Galli¹, André Peret¹, Valéria Teixeira da Silva¹, Jorge Rodrigues¹, Deyves Elias Grimberg¹, Fernando Soares Souza¹, Ricardo Milanetti Degani¹, Carlos Rogério Lopes Faria¹, Edson Silverio¹, Aline Formentão¹, Karyna Pereira¹, Guilherme R. Medeiros¹, Débora Fernandes Almeida², João Eudes Pereira²

¹International Institute of Ecology and Environmental Management (IIEGA, São Carlos, Brazil)

²Votorantim Metais Zinco S.A – Três Marias Plant – Minas Gerais
 *Corresponding author: thais@iie.com.br, Instituto Internacional de Ecologia, Rua Bento Carlos, 750, CEP 13560-000, São Carlos SP, Brazil

Key-words: river studies, hydrodynamics, aquatic biota, toxicity, sediments, metals, contamination, remediation.

Scope of the Project and Region of Study

The studies on the S. Francisco River are developed in a region downstream Três Marias reservoir (Lat 180° 12' 262S Long 45° 15' 321 S0) in a site contaminated by the discharges of a zinc processing industrial plant. This is a 40 Km stretch of the river sampled intensively during the last 5 years with studies of sediment quality and distribution of contaminants, limnological and hydrodynamic features of the river, toxicity of water and sediments and responses of aquatic biotal fishes and macro invertebrates) to toxicants. The aim of this research work, besides understanding the distribution of toxic metals in the sediment and water, is to evaluate the impact in the biotic community and to study the dynamic interaction between the sediment, the water, the aquatic biota and the hydro fluvial characteristics of the river in this region. This study will provide a basis to promote the recovery of the river at this region based on the knowledge of the limnology, hydro chemical and biota aquatic responses.

Limnological Characteristics and Water Quality

Sampling is performed in 30 stations located at different sections along the river. The stations cover the 40 Km of the river downstream Três Marias reservoir, physical, chemical and biological conditions were measured during dry season (July/August) and wet season (January/February). Physical and chemical characteristics of the river (measured with multiparametric sensors) are not favorable to the dissolution of metals to sediment to the water. pH and dissolved oxygen conditions prevent solubility of Zn and other metals (Pb) (Cd) in the water. Higher concentration of Calcium in the water prevent toxicity of Zn and Cu. Nictemeral variations studied during a 24-hour sampling, showed small fluctuations of temperature, pH, conductivity, dissolved oxygen and redox potential in the water, demonstrating that stable limnological conditions prevail in the dry and wet season, in the water column.

Hydrodynamic Characteristics of the River

In order to understand the hydro chemical dynamics of the river, measurements of the intensity and direction of sediments were performed in the 40 Km stretch. The sampling strategy and design were based on the factors that influence the discharge of the São Francisco river in the stretch studied: discharge of the Três Marias reservoir, discharge of the main tributaries and discharge of the effluents of the Zn processing industrial plant. This study was fundamental for the understanding of the metal distribution (Pb, Cd, Zn) in the sediment and the identification of metal hot-spots, as well as to provide a basis for the management and recovery of the river sediments.

Distribution, Responses of the Aquatic Biota and Toxicity Studies

To understand the response of the aquatic biota to sediment and water contamination, sampling of macro invertebrates was performed. Indexes of the benthic macro invertebrate responses were developed based on the BMWP indexes, as well as species richness and species diversity. Responses of fishes to toxicants were studied by determining the P450 liver enzyme response and the methalothionein content of fish muscle. Responses to the toxicology of interstitial water were determined by using international standards ecotoxicological tests with *Ceriodarphnia-dubia*, *Daphnia similis* and *Danio rerio*.

Trace Metals Tolerance Bioassays Using São Francisco River Organisms

One of the main research issues that are being conducted this year is the species tolerance to metals from processing industry effluent, which is responsible for São Francisco River sediment contamination, see Peret et al. 2010 this report.

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Metal contaminated sediment assessment in São Francisco River

Taurai Bere¹, Andre Peret¹, Valéria Teixeira da Silva¹, Jorge L. Rodrigues Filho¹, Deyves Elias Grimberg¹, Fernando de Paula Blanco¹, Fernando Soares Souza¹, Ricardo Milanetti Degani¹, Carlos Rogério Lopes Faria¹, Donato S. Abe¹, Corina Sidagis¹, José Galizia Tundisi¹*, Takako Matsumura Tundisi¹, Débora Fernandes Almeida²

¹International Institute of Ecology and Environmental Management – IIEGA, São Carlos, SP, Brazil ²Votorantim Metais Zinco S.A-Unidade – Três Marias Plant, MG, Brasil *Corresponding author: thais@iie.com.br, Instituto Internacional de Ecologia, Rua Bento Carlos, 750, CEP 13560-000, São Carlos SP, Brazil

Key-words: river studies, hydrodynamics, aquatic biota, toxicity, sediments, metals, contamination, remediation.

The São Francisco River has its fountain head in the state of Minas Gerais in the Canastra mountain range and flows for 2,863km through the states of Bahia and Pernambuco until its mouth in the Atlantic ocean between the states of Alagoas and Sergipe (ANA, 2009). In its middle region (Figure 1), there are diverse antropogenics activities; such as discharge of industrial effluents form zinc manufacturing industry, which potentially have an impact on the ecosystem.

In this way, the sediments in this stretch of the river have high metal concentrations, particularly cadmium, lead and zinc. These components, besides having great potential of bioaccumulation, are highly toxic. It has already been established that zinc, for example, can have short term effects, such as organism mortality, and long term effects, such as compromised development, reproduction and growth of various species (Gómez, et al., 1998; Schimitt et al., 2007; PAN Pesticides Database, 2010). One important approach to evaluate sediment quality is through triad, which integrates the results of benthic community structure, toxicological evaluation and chemical analysis of sediment. Ecotoxicological assays that evaluate the effects of contaminated matrices on biota have been frequently used worldwide as a form of biological monitoring of ecosystem quality. However, in Brazil, only a few organisms have been standardized for such assays. The organism commonly used for monitoring sediments is the crustacean Hyalella azteca, but a lot of criticism has been raised about its utilization, among which, is the discovery that this organism does not

interacts closely with the sediment under natural conditions and that under stress conditions, this interaction is sporadic (Chapmann, 2002; Wang, 2005). To evaluate the quality of San Francisco river sediments, one sampling was done in July 2010. At the international institute of ecology laboratory, the sediment matrices collected were used in ecotoxicology assays using the deptera Chironomus xanthus, as indicator organism of the chronic toxic effects of the sediments on the biota. For this reason, clutches of Chironomus xanthus were obtained from the benthic organism laboratory of the Federal University of São Carlos, cultured according to Fonseca e Rocha (2004). The ecotoxicological assays were realized based on modified regulations established by Guidelines of OECD (Organization for Economic Cooperation and Development) for assays with Chironomus riparius. The assays consisted of exposure of lavas with up to 24hr of age to 100g of sediments from the São Francisco River and 300ml of reconstituted water (ABNT, 2009). The system, which consisted of a recipient of glass and trap tissue and PVC (Figure 2), was maintained at constant aeration until the end of the experiment. The rate of emergence, that is, the rate of conversion of lavers to adults, was used to obtain the results. The sampling points were compared to the control with artificial sediments (Arrate, et al. 2004).

The results showed a good sensitivity of the organisms, since all sampling points, except point SF1, located before the influence of the zinc processing industry, showed lower rates of emergency when compared to control by Dunnett statistical

test (Figure 3). It should be emphasized that it was not possible to perform the toxicity test for point 4 due to limited availability of sediment in this stretch of São Francisco River.

In assessing the influence of sediment on the benthic community, sediment samples of the sampling sites from the São Francisco River were collected and fixed with 4% formaldehyde until they got to the laboratory, where they were observed under an optical microscope. The relative abundances of families of organisms found were calculated with the application of the BMWP index (Biological Monitoring Working Party), which aims to establish the sediment quality, awarding points to the presence of families of benthic organisms more sensitive or more resistant to contamination (Tables 1 and 2).

Figure 4 summarizes the results of this analysis and shows that all sampling sites ranged from very contaminated to strongly contaminated sediments, including the first point, under direct influence of the Três Marias hydroelectric dam.

As previously indicated, in addition to the evaluation of the composition of benthic organism communities and biological tests, chemical tests were performed to assess the metal content aiming to completely describe the quality of the sediments.

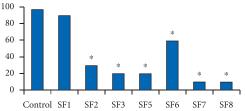


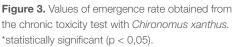
Figure 1. Satellite image of selected stretch of São Francisco River showing the sampled sites sampled in this study.



Figure 2. Traps for the ecotoxicology assays with *Chironomus xanthus.*







Metal analyses were obtained by sediment digestion following USEPA 91996 and were analyzed by atomic absorption spectrometry. The results show values that exceed the maximum suggested by CONAMA Resolution 344/2004, particularly for zinc, as described in Table 3.

In general, it is observed that the Sao Francisco River in the stretch focused of this study is contaminated by zinc in almost the entire length assessed. Still, even if the levels reported of other metals were below the guide values at points distant from the location of the industry in question, there is toxicity in the sediments of these points, which may be due to the synergistic effect of contaminants from various sources and nonpoint sources along river.

Future Prospects

The INCT ACQUA – IIEGA will continue with the studies to correlate the contamination in the different compartments of the river with potential changes in biota and subsequent influences on ecological diversity of the São Francisco River. To achieve this objective, some specific goals will have to be accomplished, that will culminate in the relationship between biodiversity and tolerance of organisms to the effluent of the metal industry. Among these goals are:

- Analyses of metals, pesticides and toxic sediments during the rainy season;
- Performing analyses of metals (especially cadmium, lead and zinc) in fish, plankton and benthic organisms representing different trophic levels;
- Analysis and comparison of the diversity of communities of phytoplankton, zooplankton, benthic organisms and fish fauna between points where discrepancies occur in the levels of chemicals (especially cadmium, lead and zinc) along the São Francisco River; and
- Tests for tolerance of representatives of various taxa to the effluent of the zinc industry.

Table 1. Score used for the application of the index BMWP.

Family	Score
Anomalopsychidae, Atriplectididae, Blepharoceridae, Calamoceratidae, Ptilodactylidae, Chordodidae, Gomphidae, Hydridae, Lampyridae, Lymnessiidae, Odontoceridae, Oligoneuriidae, Perlidae, Polythoridae, Psephenidae	10
Ampullariidae, Dytiscidae, Ephemeridae, Euthyplociidae, Gyrinidae, Hydraenidae, Hydrobiosidae, Leptophlebiidae, Philopotamidae, Polycentropodidae, Polymitarcydae, Xiphocentronidae	9
Gerridae, Hebridae, Helicopsychidae, Hydrobiidae, Leptoceridae, Lestidae, Palaemonidae, Pleidae, Pseudothelpusidae, Saldidae, Simuliidae, Veliidae	8
Baetidae, Caenidae, Calopterygidae, Coenagrionidae, Corixidae, Dixidae, Dryopidae, Glossossomatidae, Hyalellidae, Hydroptilidae, Hydropsychidae, Leptohyphidae, Naucoridae, Notonectidae, Planariidae, Psychodidae, Scirtidae.	7
Aeshnidae, Ancylidae, Corydalidae, Elmidae, Libellulidae, Limnichidae, Lutrochidae, Megapodagrionidae, Sialidae, Staphylinidae.	6
Belostomatidae, Gelastocoridae, Mesoveliidae, Nepidae, Planorbiidae, Pyralidae, Tabanidae, Thiaridae.	5
Chrysomelidae, Stratiomyidae, Haliplidae, Empididae, Dolichopodidae, Sphaeridae, Lymnaeidae, Hydrometridae, Noteridae.w	4
Ceratopogonidae, Glossiphoniidae, Cyclobdellidae, Hydrophilidae, Physidae, Tipulidae.	3
Culicidae, Chironomidae, Muscidae, Sciomyzidae, Syrphidae	2
Tubificidae	1

Source: Roldan (2003).

Table 2. Classification used for the application of the index BMWP.

Class	Quality	BMWP	Meaning	Color
Ι	Good	>105, 101-120	Very clean to clean	Blue
	Acceptable	61-100	Slightly contaminated	Green
	Doubtful	36-60	Moderately contaminated	Yellow
IV	Critical	16-35	Very contaminated	Orange
V	Very Critical	<15	Strongly contaminated	Red

Source: Roldan (2003).

Table 3. Levels of metals in sediments of the São Francisco River.

Sample spot	Cr (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	As (µg/kg)	Hg (µg/kg)
SF1	16,23	<ld< td=""><td><ld< td=""><td>39,78</td><td>34,17</td><td>654,89</td><td>8,76</td></ld<></td></ld<>	<ld< td=""><td>39,78</td><td>34,17</td><td>654,89</td><td>8,76</td></ld<>	39,78	34,17	654,89	8,76
SF2	11,4	<ld< td=""><td><ld< td=""><td>28,74</td><td>117,34</td><td>954,19</td><td>14,32</td></ld<></td></ld<>	<ld< td=""><td>28,74</td><td>117,34</td><td>954,19</td><td>14,32</td></ld<>	28,74	117,34	954,19	14,32
SF3	10,19	<ld< td=""><td><ld< td=""><td>44,1</td><td>48,9</td><td>1254</td><td>22,09</td></ld<></td></ld<>	<ld< td=""><td>44,1</td><td>48,9</td><td>1254</td><td>22,09</td></ld<>	44,1	48,9	1254	22,09
SF4	16,4	<ld< td=""><td>5,48</td><td>98,76</td><td>1732,08</td><td>1134,03</td><td>9,87</td></ld<>	5,48	98,76	1732,08	1134,03	9,87
SF5	20,51	<ld< td=""><td>2,32</td><td>79,65</td><td>854,48</td><td>765,38</td><td>34,23</td></ld<>	2,32	79,65	854,48	765,38	34,23
SF6	11,54	<ld< td=""><td>45,89</td><td>44,01</td><td>765,23</td><td>1786,4</td><td>19,38</td></ld<>	45,89	44,01	765,23	1786,4	19,38
SF7	17,21	<ld< td=""><td>22,17</td><td>32,3</td><td>284,04</td><td>453,03</td><td>5,54</td></ld<>	22,17	32,3	284,04	453,03	5,54
SF8	19,17	<ld< td=""><td>43,74</td><td>41,09</td><td>238,9</td><td>716</td><td>48,04</td></ld<>	43,74	41,09	238,9	716	48,04
EDI	7,7	6,48	0,28	15,86	5,35	0,08	0,12
OV	90	35,9	3,5	91,3	315	17000	486

*EDL = experimental detection limit, OV = orientation levels (CONAMA 344/2004).

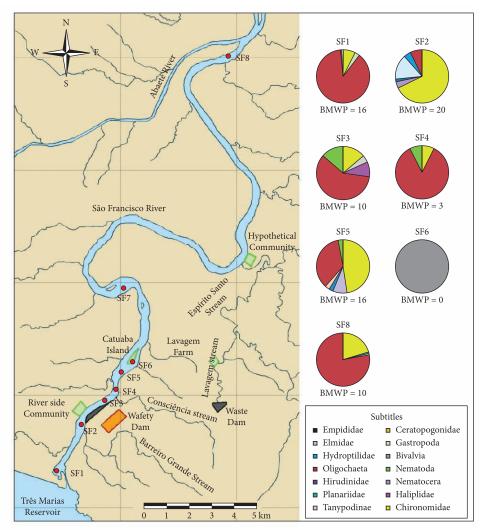


Figure 4. Results of relative abundance of benthic organisms and BMWP index at the sampling points analyzed.

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3

Contribution of the Biotic Ligand Model (BLM) for copper water quality criteria in the Carajás region of Brazil – acute toxicity

Flávio D. Café de Castro^{1*}, Virgínia S. T. Ciminelli², Flávio de Morais Vasconcelos³, Karel De Schamphelaere⁴

¹Vale/Department Nickel Projects
 ²Federal University of Minas Gerais/DEMET
 ³AECOM Environment/Brazil
 ⁴Ghent University, Belgium
 *Corresponding author: flavio.cafe@vale.com, Vale/Nickel Projects, Av. Getúlio Vargas, 1300/20° andar, Bairro Funcionários, CEP 30112-021, Belo Horizonte, MG, Brazil

Key-words: copper, toxicity, water quality criteria.

The *Biotic Ligand Model* (*BLM*), whose development started in the beginning of the 80's and continues even today, is based on conceptual models and experimental work. It is a computer tool based on the hypothesis that toxicity is not related simply to the total concentration of the metal in an aqueous medium, but rather to its bioavailability. This bioavailability depends on the speciation of the metal, which itself is related to the physico-chemical characteristics of the water.

The schematic representation of BLM is illustrated in Figure 1.

The method used in this work consists of various steps:

i) Two field survey to collect water in the areas of the Sossego Mine and the Salobo Project, with three samples collected per campaign per area; (ii)Physico-chemical characterization of the samples; (iii) Toxicological assays carried out on the *Ceriodaphnia dubia* organism, according to ABNT and USEPA methodologies; (iv) Application of the *BLM*; (v) Comparison between the average toxicity results found in a laboratory and those predicted by the method, as well as the calculation of the *Water Quality Criteria* – *WQC (USEPA, 1985)*, using the *BLM, June* 2007 version – Biotic Ligand Model Windows Interface, Version 2.2.3 (HydroQual, 2007); (vi) Interpretation of the results.

As regards the results from the physicochemical analyses, the main observations are as follows:

- i) The values of many parameters in the Sossego Mine area were always greater than those in the Salobo Project area, indicating that the mining activity brought about a greater solubilization of ions and anions for the region's watercourse.
- ii) The main exceptions for this situation occur at point SS2, which is located in the Igarapé Sossego region, the remaining area of the mine, and can be considered as a reference point for the area, due to its geographic situation, which tends to be less vulnerable to the mining impacts.

- iii) As regards seasonability, it can be observed that the parameters of alkalinity and Mg generally present higher levels in campaigns during the dry season as compared to the rainy season, thus supporting the chemical dilution principle in these cases;
- iv) By contrast, the parameters of Na, K, Mn, Fe, Al, total solids, and dissolved organic carbon generally present higher values in campaigns during the rainy season as compared to the dry season, which may well be explained by a greater solubilization of ions, anions, and organic material in this season.

On any account, this interpretation of seasonable influences on the results is made even more difficult by the low values of the parameters, by the relative proximity of the results, in some cases, and by the lack of data.

Figure 2 presents the acute toxicity results obtained in a laboratory for the first and second campaigns (EC-50 – concentration which caused an adverse effect on 50% of the organisms). Figure 3 shows the correlation between the toxicity results predicted by the BLM and those obtained in the acute toxicity assays (laboratory) in the first and second field survey. The continuous line expresses the perfect correlation, while the dotted lines mark the limits of the acceptance range of the point dispersion, corresponding to approximately 2 times.

From the analysis of the previous figures, one can observe a greater solubilization of ions and anions for the watercourses in the Sossego Mine contributed significantly to the attenuation of the adverse effect of copper and the reduction in

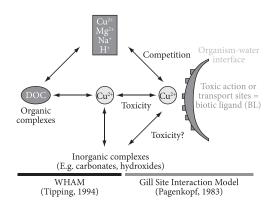


Figure 1. Schematic representation of BLM (JANSEN et al., 2003).

toxicity. Negative impacts from mining activities can be attenuated by the same activity, so long as the solubilization of determined elements is not increased to such an extent that it casues adverse effects. Physico-chemical parameters demonstrated a good correlation with acute toxicity, resulting in a reduction in toxicity when the values of these parameters increased (protector effect for the aquatic biota). Nearly all the points could be identified within the acceptance range of the correlation graph of measured and predicted results, and the model proved to be robust as it was able to predict the toxicity of copper quite accurately. The correlation between the physico-chemical parameters and the toxicity showed that the theoretical and experimental foundations of the model were applicable to this study, insofar as the attenuation factors of toxicity truly contributed to the increase in the EC50 index.

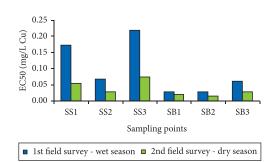


Figure 2. EC50 results (laboratory).

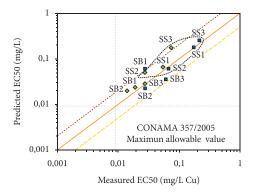


Figure 3. Relation between the predicted (BLM) and measured results for acute ecotoxicity Ceriodaphnia dubia.- EC50 - in the first (■) and second (◆) field campaigns in the areas of the Sossego Mine (SS) and the Salobo Project (SB), expressed as dissolved copper.

Concerning the regulatory context, three indexes of water quality for copper were compared:

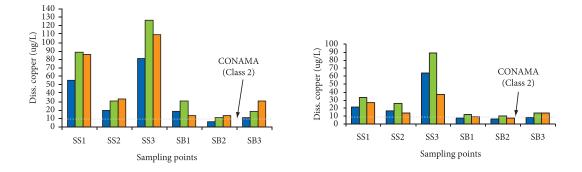
- *WQC* calculated directly by the model;
- CE50/2* (acute); CE50/FACR** (chronic) predicted by the model;
- CE50/2* (acute); CE50/FACR** (chronic) measured in a laboratory.

* divided by two to protect the more sensitive species, as done in the "direct WQC" calculation; ** divided by the *Final Acute to Chronic Ratio*

Figures 4 and 5 illustrate these results for both field survey.

From the regulatory viewpoint, despite the low number of samples collected in each area, as

well as the restricted number of field survey, it can be said that the maximum value permitted for copper in Class 2 waters (0.009 mg/L), according to Brazilian regulations, proved to be consistent enough to protect the aquatic communities in the Salobo Project area, but was considered relatively conservative in the Sossego Mine area. To establish protection criteria for the aquatic communities in a more consistent and safe manner, the collection of a larger number of samples in a larger number of campaigns and in different hydrographic basins/ sub-basins, with a posterior use of the BLM, is recommended.



Figures 4 and 5. Comparison between the copper water quality criteria (WQC): i-calculated by BLM (■), ii-EC50 values predicted by the model (■), and iii-EC50 values measured in a laboratory (■) (both EC50 divided by two) versus the maximum value allowed for copper, according to the CONAMA357/2005 Resolution (9 µg/L), for water samples collected in the first and second field campaigns in the Sossego Mine (SS) and the Salobo Project (SB).

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Characterization of the environmental liabilities from a degraded mineral area due to uranium mining activities

Ana C.Q. Ladeira^{1*}, Carlos A. Carvalho Filho¹, Carolina B. Abreu³, Dina L. Lopez², Otavio E. A. Branco¹, Paulo C. H. Rodrigues¹, Peter M. Fleming¹, Vinícius V. M. Ferreira¹, Virgílio L. Bomtempo¹

¹Nuclear Technology Development Center (CDTN), www.cdtn.br; Belo Horizonte, Brazil ²Department of Geological Science, Ohio University, Ohio, USA

³Department of Metallurgical and Materials Engineering, Fed. University of Minas Gerais, Belo Horizonte, Brazil *Corresponding author: ana.ladeira@cdtn.br, Centro de Desenvolvimento da Tecnologia Nuclear, Av. Antonio Carlos, 6627, CEP 31270-901, Belo Horizonte, MG, Brazil

Key-words: water and sediment quality, hidrogeochemistry, water balance, uranium, manganese, acid mine drainage, manganese oxide, waste rock pile.

The uranium mine named Osamu Utsumi is located in the municipality of Caldas (Minas Gerais State), and belongs to INB – Brazilian Nuclear Industries. The operation of the complex started in 1982, but the mining activities ceased in 1997 and the site is under the process of decommissioning. It was the first Brazilian uranium mining industrial facility and its closure has to fulfill the legal demands of CNEN (National Commission of Nuclear Energy) and IBAMA (Brazilian Institute of the Environment and Renewable Natural Resources).

For the decommissioning of the uranium mine, specifically in the aspects associated to the environmental quality, the activities are divided in 4 items:

- 1. Hydrogeochemical characterization of a uranium waste rock pile
- Water, residues and sediment quality assessment in order to estimate the potential pollution;
- 3. Residues characterization and acid water treatment;
- 4. Geoprocessing of the available and new collected data.

1. Hydrogeochemical Characterization of a Uranium Waste Rock Pile (Bota-Fora 4)

The target area is shown in Figure 1 and the main objectives are related to:

- a) Determination of the chemical and physical processes occurring inside the waste rock pile as well as the inputs and outputs of water, solutes, and energy to and from the pile.
- b) Determination of the best option for the waste rock remediation: the decrease of the acid mine drainage and/or the acceleration or control of the oxidation processes to extract the remaining uranium and other valuable products.

The CDTN and partners have been working in the following activities:

- Characterization of source term: physical, chemical and geochemical processes, determination of gases (oxygen, carbon dioxide, radon that exhale from the rock pile), and temperature in deep wells;
- A water balance evaluation: rainfall determination (Figure 2, runoff and infiltration rates and evaluation of evaporation/evapotranspiration;
- The hydrogeochemical modeling (conceptual model, simulation codes, calibration and validation of the models).

2. Water and Sediment Quality Assessment in Order to Estimate the Potential Pollution

The assessment of the water stream quality and bottom sediments is important to determine if there is contamination coming from the uranium mine, specifically from the mine pit, the waste rock pile (Bota-Fora 4) and tailing dam. The following activities were proposed for the assessment: (i) to calculate the indexes of water quality according to approved Brazilian protocols; (ii) to propose a new index of water quality, specifically for metal mining areas and specially for uranium mining areas; (iii) to calculate the indicators indexes of sediments quality; (iv) to propose a new quality index for sediments, specific for metallic mining areas and specially for uranium mining areas;(v) to identify the existence of potentially contaminated areas, and to propose a general implementation plan for the Preliminary Evaluation and for the Confirmatory Investigation of areas that have a potential for contamination; (vi) to propose emergency measures to minimize the environmental contamination, in case of being present.

The area comprises the Taquari stream basin and was divided into 3 sub-basins according to Figure 3.

In terms of water quality, the analytical parameters were selected to allow the determination of the quality indexes adopted by the Institute of Water Management in the State of Minas Gerais-IGAM (SEMAD, 2005), the National Sanitation Foundation (NSF) and by the Canadian Council of Ministers of Environment, CCME (CCME, 2001). For the determination and classification of the sediments contamination, the same criteria established by CONAMA Resolution 344/04 (CONAMA, 2004), by the Canadian Council of Minister of the Environment and by Florida Department of Environment Protection.

3. Residues Characterization and Acid Water Treatment

a) Residues Characterization

In Caldas mining area, tons of waste containing sulfides produce acid mine water at pH 2.7, which contains significant concentrations of uranium and other metals. The acid water is treated by precipitation of the elements using lime to comply with the permissible limits. The precipitation has been used for more than 15 years and generates a sludge which is disposed into the open pit that is flooded with acid water (Figure 4).

This study consisted in the characterization of different samples of the sludge and their classification according to leaching standard procedures in order to assess the dissolution of the contaminants and their migration to the environment. The sludges were classified as fresh, old and intermediate, according to its age. The intermediate sludge is in contact with acidic water. The results showed that despite being classified as non toxic, the samples are not inert, which means that a specific site is required for their disposal instead of the open pit mine.

Fluoride and sulfate are responsible for the chemical instability of the samples (6). Other elements, like Fe, Zn, Mn, U and Al, are present in significant concentrations.

The main crystalline phases of the samples, according to X-ray diffraction, are ettringite



Figure 1. View of open pit mine and waste pile area (points in red are boreholes).

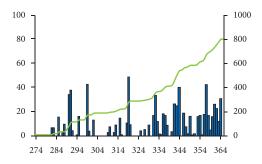


Figure 2. Rainfall in 2009 (Preliminary information: daily and accumulated data; mm;period: October – December; time scale: Julian day).

 $Ca_6Al_2(SO_4)_3(OH)_{12}$, 26H₂O, gypsum (CaSO₄,H₂O) and calcite (CaCO₃) and minor constituents are fluorite (CaF₂), and Portlandite Ca(OH)₂. The fresh and old sludges are similar in the prevalence of ettringite in its composition.

This was not observed for the Intermediate sludge because the contact with the acidic water favors the dissolution of ettringite and, consequently, the formation of gypsum and gibbsite. The formation of gibbsite in the Intermediate sludge was confirmed by the X-Rays diffraction. Uranium was mainly determined in the labile portion which demonstrates that the uranium in the samples is easily exchangeable or highly mobile. In addition, the Intermediate sludge is the one that presents the highest content of uranium in the soluble form which is a matter of concern.

b) Acid Water Treatment

Besides other metals that are present in the acid water of Caldas, manganese is particularly above the permissible discharging levels. Manganese removal is notoriously difficult due to its high solubility over a wide range of pH. While most of the metals precipitate at a pH below neutrality, the pH necessary for manganese precipitation is very high, above 10. Most systems that effectively remove this element from mine waters use the oxidation

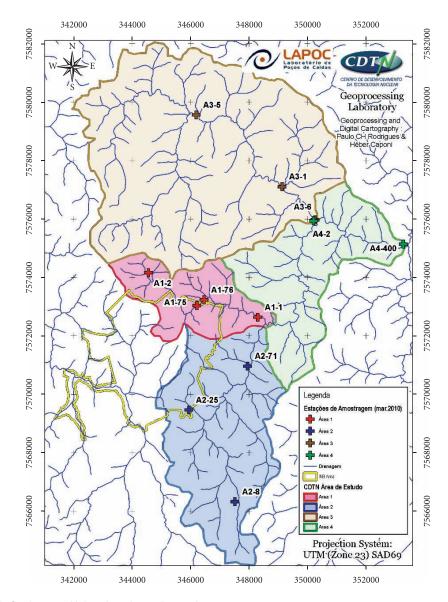


Figure 3. Study area with location of sampling stations.

of Mn (II) followed by precipitation at an elevated pH. Precipitation consumes a great amount of lime, which implies in a high operational cost and a large amount of sludge containing metals that has to be disposed. The objective of this study is to optimize the removal of manganese in order to achieve the Mn permitted level for discharging (<1mg/L) and to reduce the amount of sludge generated. The precipitation process has been studied using lime, limestone and a non-conventional adsorbent (MnO₂ residue). The results showed that both lime and limestone are effective in the removal of Mn but the pH must be higher than 10. However, there is a slight difference between the two reagents and lime shows a better performance. Figure 5 shows that the use of the non-conventional material made the removal of almost 100% of the Mn possible as the concentration of manganese was reduced from 140mg/L to <1mg/L at a pH near neutrality (6.8 to 7.2). The addition of MnO₂ increased Mn removal and the final solution complies with the legal requirement for Mn concentration in liquid effluents.

4. Geoprocessing of the Available and New Data

The procedures in GIS comprises the processing of the available data from INB (followed by their format conversion), the achievement of primary data from other institutions (IBGE, NASA, METI/ERSDAC, DER-MG, Google Earth, Umiacs, and MDGeo) as wells as the development of the database for CDTN. The activities have been carried out in three scales:



Figure 4. Open pit flooded with acid water and used as temporary site for the sludge disposal.

Regional Scale

- Generation of the altimetric map (5m contours) and theoretical drainage network based on the elevation data from the SRTM (Topography Radar Topography Mission, downloaded from the NASA Web site) with the data grid of 90 x 90m, interpolated to 25m;
- Loading of the ArcGis bases (in shape format) of the drainage maps from IBGE, scale 1:50,000;
- Download of the Landsat 7 image from 20.ago.2000 with the RGB-IHS-RGB transform, rising the original resolution from 30 to 15m;
- Generation of altimetric map (5m contours), shaded relief and theoretical drainage network based on the elevation data from the ASTER (Advanced Spaceborne Thermal Emission and Reflection, NASA, and METI-ERSDAC/Japan) with rid data from 30 x 30m, interpolated to 25m with further delineation of sub-basins areas;Generation of different 3D diagrams.

Medium Scale

- Acquisition by the LAPOC's team of the georeferenced color image of the Spot satellite (resolution 2.5 m) Figure 6;
- Delineation, by altimetry and sub-basins, of the 4 areas concerning the detailed studies by CDTN;
- Scanning and georeferencing by the LAPOC's team of geological and radiometric maps of the INB plant region and its vicinity;

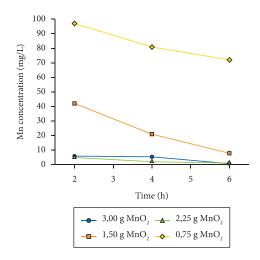


Figure 5. Influence of MnO_2 in the removal of Mn, pH adjusted with lime (6.8-7.2), use of aeration and T= 25°C. (7)

- Plotting of the sampling points of the field survey carried out in October 2009 and March 2010;
- Plotting of the current and future monitoring sites for the CDTN studies;
- Generation of 3D diagrams for the INB area based on altimetric data supplied by INB and converted by the LAPOC's team;
- Scanning and mosaicking of aerial photographs of the 80's, photocopied from the DER's collection;
- Acquisition of aerial photographs from 1997 of the INB plant region. in digital format.

Small Scale

- Generation of original (pre-mining period) altimetric and hydrographic maps of the Bota-Fora 4 obtained from the data available (1);
- Plotting of water wells and spring points data (52 records) from the MDGeo Company (Figure 7);
- Detailed plotting of some special place features inside the influence zone of the Bota-Fora 4.
- Generation of interpolated thematic maps for Eh, pH, electrical conductivity and temperature, including their isolines in the Bota-Fora 4;

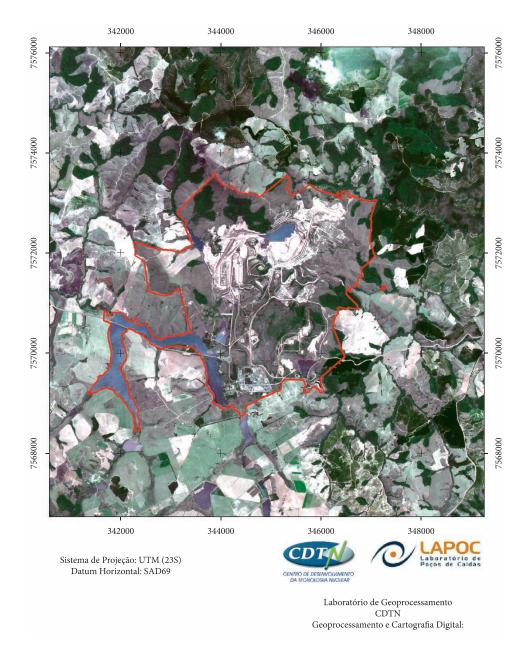


Figure 6. Spot image of the INB plant and surrounding area.

• Conversion of some INB geodata from the CAD format (dwg) to ArcGIS format (shape) by the LAPOC's and CDTN's teams;

of INB (1:2,500) for the periods before and after the mining activities for the Bota-Fora 4 (Figure 8);

- Generation of 3D diagrams for the Bota-Fora 4.
- Generation of the TIN (Triangulated Irregular Network) model based on altimetric maps

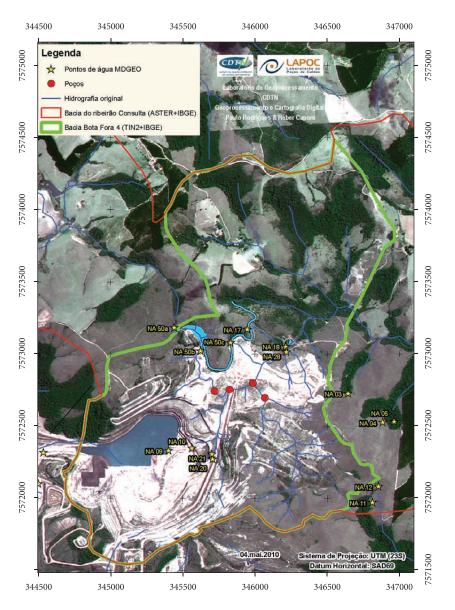


Figure 7. Spot image zoomed in the mine pit and Bota-Fora 4 showing water wells and springs.

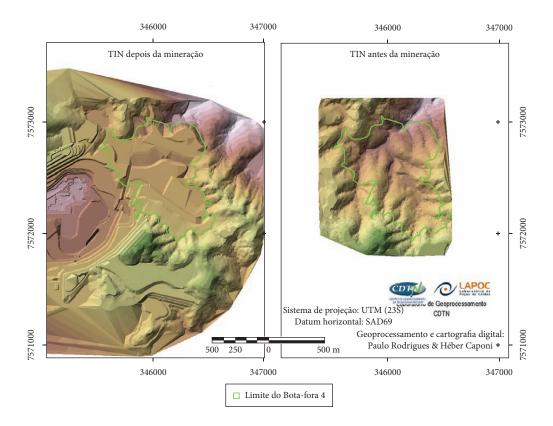


Figure 8. TIN models before (right) and after (left) mining activities.

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Phytoremediation of acid mine drainage by aquatic floating macrophytes

Michelle B. da Cruz^{1*}, Rosane Aguiar¹, Jaime W. Vargas de Mello¹

 ¹Research Group on Acid and Geochemical As Drainage, Soil Department, Federal University at Viçosa – UFV, CEP 36570-000, Viçosa, MG, Brasil
 *Corresponding author: michellebcruz@gmail.com, Departmento de Biologia Vegetal, Universidade Federal de Viçosa, Av. P.H. Rolfs, s/n, CEP 36570-000, Viçosa MG, Brasil

Key-words: water contamination, reclamation, arsenic, phytoremediation.

Mining activities may generate environmental impacts in surrounding areas and even far from its origin. Tails and refuse piles containing sulphidic minerals, such as arsenopyrite (FeAsS), are among the main contamination sources in mining industry. When exposed to atmospheric water and oxygen, sulphidic minerals can be oxidized releasing potentially toxic elements to the environment through acid mine drainage (AMD). Elements such as S, Fe, Mn and As are commonly associated to AMD, being the last one highly toxic even at low concentrations¹. AMD can affect aquatic systems and impact the biological community structure by eliminating species in the food chain. In this scenario, phytoremediation is an *in situ* low cost option to the reclamation of contaminated environments². Phytoextraction and phytofiltration are the more used phytoremediation and well known techniques. Free floating macrophytes are among the plant species used to phytoremediation due to their high growing rate, high capacity to accumulate heavy metals and metalloids, survival under adverse conditions and tolerance to high concentrations of toxic elements^{3,4}.

Phytoremediation studies are still limited to some selected plant species and focused on few metals, typically one to three metals^{5,6}. So, there is a lack of information on simultaneous absorption of several contaminants. Due to the inherent capacity of *Eichhornia crassipes, Pistia* *stratiotes* and *Spirodela polyrhiza* species to absorb several different elements; in a certain extent, they could be able to simultaneously accumulate heavy metals and toxic metalloids from AMD, with no damage to the plant growing. Preliminary results showed that *Pistia stratiotes* and *Spirodela polyrhiza* are susceptible to low pH in the aquatic medium, main characteristic of the AMD. On the other hand, *E. crassipes* was more tolerant to acidic environment (Figure 1).

The effects of AMD on plants includes a decrease in the chlorophyll content, mainly to the species *P. stratiotes* and *S. polyrhiza*, due to the necrosis on the leaves (Figure 2).

The *E. crassipes* plants accumulated part of the soluble arsenic from AMD in different tissues, but the roots presented higher concentrations (Figure 3). Absence of data for *P. stratiotes* and *S. polyrhiza* in figure 3 is due to the death of the plants exposed to AMD.

Simultaneous absorption of other heavy metals by aquatic macrophytes and their interactions are still being evaluated. Further studies on the effects of AMD at anatomical level also are also in course.

Acknowledgement

We would like to thank CNPq, Fapemig, CAPES and the INCT – Water, Mineral Resources and Biodiversity.

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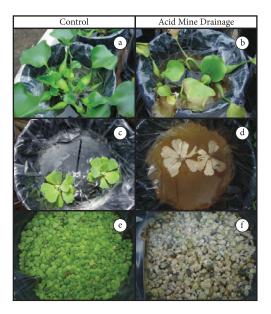


Figure 1. Phytotoxic effects of acid mine drainage in aquatic floating macrophytes. (a, b - E. *crassipes*; c, d - P. *stratiotes*; e, f - S. *polyrhiza*).

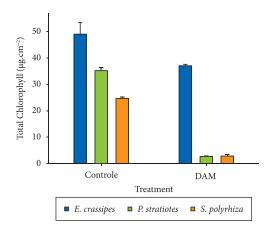


Figure 2. Total chlorophyll contents in *E. crassipes, P. stratiotes* e *S. polyrhiza* plants exposed to acid mine drainage.

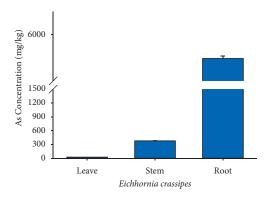


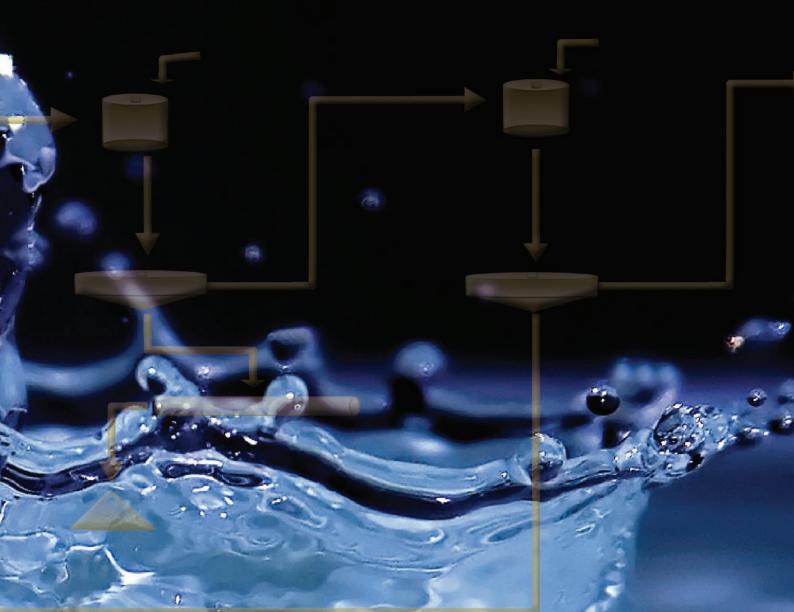
Figure 3. As accumulated in different tissues of *E. crassipes* plants exposed to acid mine drainage.

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science highlights



research topic 2

Modeling and simulation of hydrometallurgical processes, optimized to achieve a better environmental performance

- 46 Investigation of new routes for uranium concentrate production from the Caetité ore, State of Bahia
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- 51 Simulating acid mine drainage (AMD) in columns

Investigation of new routes for uranium concentrate production from the Caetité ore, State of Bahia

Carlos A. Morais^{1*}, Luiz A. Gomiero²

¹Department of Mineral Technology, Hydrometallurgy Sector, Development Center for Mineral Technology-CDTN/CNEN, CEP 31-270-901, Belo Horizonte, MG, Brazil

²Productiion Department, Nuclear Industries - Brazil – INB, Caetité Plant, CEP 46400-000, Caetité, BA, Brasil *Corresponding author: hduarte@ufmg.br, Department of Chemistry, Universidade Federal de Minas Gerais, Av. Antonio Carlos, 6627, CEP 30270-091, Belo Horizonte MG, Brazil

Key-words: uranium concentration, uranium leaching, uranium production.

The uranium concentrate production in Brazil is responsibility of Indústrias Nucleares do Brasil S/A - INB, a federally owned company. Presently, there is only one uranium mining and milling facility in operation, which is the Uranium Concentrate Plant - UCP, located at the municipality of Caetité, State of Bahia. The Caetité-Brazil uranium facility produces about 400 t/y of U₃O₈ from a 0.29 U₃O₈ wt% averaging ore. This production is sufficient to supply the two operating nuclear power plants in the country. As the Brazilian government has recently confirmed its plan to build other nuclear plants from 2009, the uranium production will have to expand its capacity in the next two years. With the reopening of the new nuclear program by the Brazilian government in 2007, now inserted in the Growth Acceleration Program 2007 - 2010 (Programa de Aceleração do Crescimento - PAC 2007-2010)¹, the completion of the construction of the Angra 3 nuclear power plant as well as the construction of 4 to 8 new other plants are considered to have been concluded by the end of the 2030's¹. Therefore, the demand for uranium concentrate, which is now around 400 tons per year, will increase up to 2,000 tons per year. This increase in demand will lead to the opening of new uranium pits and also to prospect other areas. Nowadays Brazil is believed to have the sixth largest uranium reserve in the world, having 177,500 t of U_3O_8 when inferred and measured reserves are considered, which corresponds to

resources reasonably assured. The inferred reserve is estimated to be 309,370 t of U_3O_8 (additional resources estimated according to the National Agency of Atom Energy guidelines AEIA)^{2,3}.

The process steps currently adopted by INB-Caetité uranium facility consist in: ore crushing, heap leaching with sulfuric acid, uranium separation and purification by solvent extraction with a tertiary amine followed by stripping with a sodium chloride solution and its precipitation as ammonium diuranate. This process is similar to that successfully used for 10 years in Caldas -MG. The main difference is the water. Caetité is located in a region of severe water shortage, which requires that all liquid effluent - including the rafinate - be recycled to the leaching step after treatment with lime and solid-liquid separation. As chloride ion is not removed in this treatment, its concentration in the pregnant solution has increased causing a drop in the uranium extraction efficiency as shown by Morais et al.4,5. CDTN together with INB have been studying some alternative routes in order to increase the production as well as the uranium recovery. At first, it was investigated the replacement of the sodium chloride in the stripping step of the solvent extraction process. The studies were carried out using sulfuric acid and ammonium sulfate4, 5. Another problem in the Caetité mills is that, as the open-pit mine becomes deeper, the uranium recovery in the heap leaching process has began to decrease due to the increasing presence of primary uranium

minerals inside rock grains. The uranium content in the leached ore became too concentrated, reaching values higher than 600 μ g/g U₃O₈⁶. In other to increase the uranium recovery in the leaching step, some studies with the Caetité Ore using Dynamic leaching have been done. At last, it was investigated a new route for the uranium concentrate production aiming the replacement of the solvent extraction process in the uranium productive chain. The following steps were investigated: (i) dynamic leaching of the ground ore with sulfuric acid; (ii) sulfuric liquor pre-neutralization until pH 3.7; (iii) uranium peroxide precipitation. The study was carried out in batches and continuous circuits. In the dynamic leaching of the assayed ground ore in agitated tanks, the uranium content in the leached

ore may be as low as 100 µg/g U_3O_8 , depending on grinding size. In the pre-neutralization step, the iron content in the liquor is decreased by 99 wt.%, decreasing from 3.62 g/L to 0.030 g/L. The sulfate content in the liquor is reduced from 46 g/L to 22 g/L. A calcinated final product assaying of 99.7wt.% U_3O_8 was obtained. The full process recovery was over 94%⁶⁻⁸.

The INB/Caetité mining and milling facility is presented in Figure 1. Figures 2 and 3 shows the circuits used in the studies described in this work.

Acknowledgments

Sincere thanks to CNPq, FAPEMIG, CAPES and the INCT of Water, Mineral Resources and Biodiversity.



Figure 1. The INB/Caetité mining and milling facility view.

Figure 2. Solvent extraction circuit.

Figure 3. Leaching and precipitation circuit.

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Hydrometallurgical recovery of industrial wastes

Raquel Annoni¹, Daniela A. Lázaro¹, Marcos V. Cantarino¹, Marcelo B. Mansur^{1*}

¹Department of Metallurgical and Materials Engineering, Federal University of Minas Gerais – UFMG, Belo Horizonte, MG, Brazil *Corresponding author: marcelo.mansur@demet.ufmg.br

Key-words: environmental, leaching, adsorption, BOF sludges, metallurgical residues.

The amount of wastes produced worldwide is significant. While adequate disposal of residues in landfills meets environmental requirements, it results in the loss of valuable metals, recyclable species, energy resources and money. Therefore, recycling is essential to assure sustainability. Technologies that allow both metals and water recoveries from toxic residues are urgently needed to help industry cost-effectively meet new environmental requirements. Treatment of the following residues are considered here: 1) Recovery of Al and Ti from welding flux slags by selective leaching, 2) Adsorption of basic dyes from textile effluents and/or metals from acid mine drainage using carbons made of residues from the biodiesel industry, and 3) Removal of Zn and alkalis from BOF (Basic Oxygen Furnace) sludges.

Removal of Al and Ti from Welding Flux Slag

Nearly 10.5 ton/year of welding flux slags are generated in Brazil. Such residue is commonly disposed in sanitary landfills, so its metal content (see typical composition on Table 1) is fully lost. In order to reuse it, a palliative solution would be the incorporation of this residue in the manufacture of ceramic materials, cement and concrete blocks (Morete et al., 2006; Viana et al., 2008). However, despite of environmental advantages, metal content is still lost.

Therefore, aiming to recover Al and Ti from welding flux slags, a hydrometallurgical route

based on sequential leaching steps is under investigation: firstly, the residue is leached with NaOH solution in order to recover Al; then, the remaining solid is leached with HCl or H_2SO_4 to solubilize all metal content but Ti which remains in the solid phase. The study is being undertaken in cooperation with Technique University of Kosice, in Slovakia.

	Table	1.	Chemical	composition	of a	typical	slag.
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able 1. Chemical comp	Usition of a typical slag.
Components	Composition (%)
Al_2O_3	25.748
MnO	23.255
SiO ₂	11.020
TiO ₂	10.993
Fe ₂ O ₃	9.883
CaO	6.292
Na ₂ O	2.456
ZrO ₂	2.227
MgO	2.036
V ₂ O ₅	1.619
K ₂ O	0.720
Other	3.753

Removal of Contaminants from Effluents by Adsorption onto Carbons Made of Residues from the Biodiesel Industry

The performance of the cold-pressed cake from *Raphanus sativus* (*L. Var.*) oilseeds activated carbon, a solid residue from biodiesel production, was evaluated as an adsorbent for basic dyes like methylene blue (MB) from dilute aqueous solutions. The study comprised two main steps (Lázaro et al., 2008).

In the first step, adsorption tests focusing on the evaluation of equilibrium, kinetics and effects of main operational parameters (particle size, contact time, adsorbent dosage and pH) were conducted. Adsorption kinetics was determined by data fitting to first and second-order kinetic models, with the latter providing best description for MB adsorption. The adsorption process can be described by a two-stage kinetic behavior, with a rapid initial adsorption for the first 6 hours followed by a much slower rate afterwards. Equilibrium was attained after 12 hours for an initial dye concentration of 100 mg/L. Adsorption data after 72 hours were fitted to Langmuir and Freundlich adsorption models, with the former one providing the best fit (see Figure 1). Langmuir based maximum MB uptake capacity was 19.8 mg/g, higher than several other adsorbents employing similar types of residues such as sunflower oil cake, coffee seeds press cake and date pits.

The second part of the study comprised the characterization of the carbon, including morphology, textural properties (surface area, total volume and average pore diameter) and structural variation of the carbon before and after MB adsorption. BET, BJH, Scanning

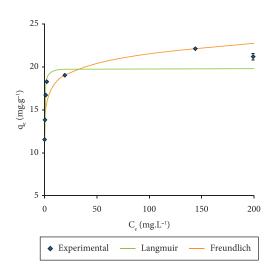


Figure 1. Adsorption isotherm of MB (pH = 5; adsorbent dosage = 10 g/L; adsorbent particle size ≤ 0.425 mm; T = 25 °C; t = 72 h).

Electron Microscopy, X-ray Energy Dispersive Spectrometry and Raman spectroscopy were used. The latter was found to be a potential method to analyze physical properties of porous carbons and a tool to evaluate adsorption mechanisms. It was concluded that MB adsorption occurs predominantly at the surface of the adsorbent (surface area = 236.3 m²/g, pore volume = 0.06 cm³/g; pore size = 1.4 nm) and probably by MB bonding of monomer species through central nitrogen atom. This carbon is being investigated now to remove metal species from effluents generated by acid mine drainage.

Removal of Zn and Alkalis from BOF Sludges

Basic oxygen furnace (BOF) sludges are residues generated in steelmaking process, more specific in dedusting systems of LD converters. Such residues, normally classified as fine and coarse sludge, are potential materials to be recycled in the sinter process of steel due to the high iron content, nearby 50-60%w/w. But, to be reused, it is necessary to reduce their contents of Zn and alkalis because they affect refractory materials, increase thermal loses and increase coke consumption in the blast furnace. An alternative method would include alkaline leaching in order to selectively separate zinc from iron.

BOF sludge samples were analyzed to assess their chemical and mineralogical compositions. The total content of zinc in the fine sludge was 4-5%w/w and that in the coarse sludge was inferior to 1%w/w. However, X-Ray diffraction analysis revealed that zinc exists predominantly as ZnO and ZnO.F₂O₃ (franklinite), so it is necessary to decompose franklinite into soluble ZnO by fusion before the leaching step.

Figure 2 shows the fusion results of BOF using different materials like ladle slag, HR scales, $Ca(OH)_2$ and NaOH (Cantarino et al., 2009). After fusion, samples were leached 3 times with 5 M NaOH, solid:liquid ratio 1:20 p/v, for 6 hours. Solely 15.8% and 6.6% of zinc was recovered when ladle slag and HR scale were used, respectively; this recovery was even lower than that obtained when the original sludge was leached without any fusion treatment, thus revealing that such materials favor the formation of franklinite. Around 75% of zinc

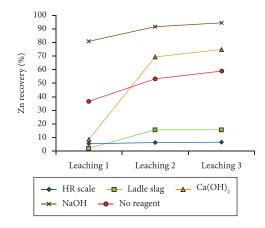


Figure 2. Zinc recovery using different reagents to decompose franklinite in BOF sludge.

was recovered with $Ca(OH)_2$ but filtration of pulp was rather difficult. The use of NaOH showed satisfactory results as 95% of zinc was recovered with high selectivity to iron as iron, concentration in the leach solutions were inferior to 3.4 ppm.

The evaluation of alkaline fusion and NaOH leaching steps is being investigated in order to find more favorable conditions to treat BOF sludges.

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Simulating acid mine drainage (AMD) in columns

Cláudio Marcelo Bernardes de Souza¹, Marcelo Borges Mansur^{1*}

¹Department of Metallurgical and Materials Engineering, Universidade Federal de Minas Gerais – UFMG, Belo Horizonte, MG, Brazil

*Corresponding author: marcelo.mansur@demet.ufmg.br

Key-words: AMD modeling, columns, environmental.

Pyrite oxidation in mining wastes can be a source of significant groundwater contamination due to the generation of acid mine drainage (AMD). In fact, AMD is recognized as one of the most important problems facing the mining industry because it can cause serious chemical degradation of the aqueous environments. Such effluents are generated by chemical and microbiological reactions which might occur when pyritic materials are exposed to oxygen and humidity. The prediction of water quality at mine sites is quite complex due to its technical complication and inherent uncertainties such as weather, soil characteristics, mineralogy, heap disposition, etc. Actually, factors that complicate drainage quality prediction range in scale from small to large, so the use of a phased approach to data collection and interpretation is necessary in order to (Mend Report, 2009):

• Focus on the materials and issues of greatest concern;

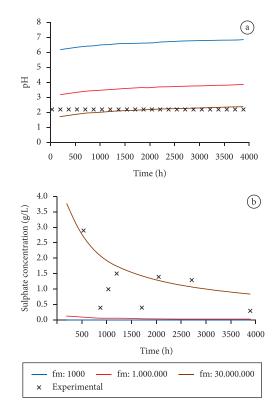


Figure 1. Effect of microorganisms on AMD generation for the coal mine waste of São Roque: a) transient pH, b) transient sulfate concentration on the acid solution.

- Minimize work on materials with no significant uncertainty;
- Use the most appropriate test materials and procedures, and
- Make timely refinements in response to unforeseen conditions.

In this context, a simple conceptual model to simulate pyrite oxidation and acid mine drainage

in laboratory columns was developed in order to gain insight on how AMD is affected by some parameters such as microbiological effect, oxygen diffusive coefficient, average particle radius and pyrite content (Souza, 2010).

In order to describe AMD in columns it is necessary to consider two main aspects: 1) water infiltration patterns in the column, and 2) chemical

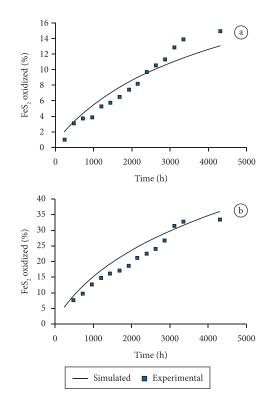


Figure 2. Comparison between experimental and simulated oxidation of pyrite with time: a) waste of São Roque, b) waste of Volta Redonda.

processes mainly related with pyrite oxidation including oxygen diffusion through spherical particles weighted by microbiological interaction. The water flow through the column was calculated using the analytical solution of the Richard's equation given by Prevedello et al. (2009). The pyrite oxidation incorporating oxygen diffusion, according to the shrinking core model and microbiological effect on the generation of AMD, was done by transient material balances, which were solved numerically. No neutralizing or competing metal reactions were considered. Pyrite oxidation was considered to occur according to the following global reaction:

 $\mathrm{FeS}_{2} + 1/2 \ \mathrm{H_{2}O} + 15/4 \ \mathrm{O_{2}} \rightarrow \mathrm{Fe^{3+}} + 2 \ \mathrm{SO_{4}^{2-}} + \mathrm{H^{+}}$

The model was used to simulate drainage quality for the coal mine wastes from São Roque and Volta Redonda (Santa Catarina state, Brazil). Column experiments were carried out by Guevara (2007).

Figure 1a exhibits the simulation results for the pH on the exit of the column at changing values of microbiological factor (f_m) for the waste of São Roque coal mine. According to the model, the increase on f_m resulted in lower pH values, thus indicating that microorganisms affect significantly in order to increase the generation of acid drainage from pyrite oxidation processes. A quite high value of $f_m \approx 3 \times 10^7$ was obtained by data fitting (deviation error around 5%), thus indicating that microorganisms might increase reactions rate in

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many orders of magnitude (10^5 up to 10^8 times) if compared to purely chemical oxidation rates corroborating previous studies (McBride, 1994). Consequently, the increase in f_m reflects on the higher concentration of sulfate on the aqueous drainage, as shown in Figure 1b for the waste of São Roque. In fact, both behaviors are due to the consumption of pyrite in the column, which decreased from 0.4 to 0.1 g/day.

Calculated oxidation rate decreased from 180 to 40 $g_{02}/(m^3 day)$ in six months. Total oxidation of pyrite is shown in Figure 2a. The same trends were

obtained by data fitting using the Volta Redonda mine's waste ($f_m \approx 2.5 \times 107$ with average deviation on pH of 5%) as it can be seen in Figure 2b for the total oxidation of pyrite with time.

Therefore, the model developed was found to be able to reproduce experimental behavior from leaching tests on columns using two different wastes from coal mines located in Santa Catarina state, Brazil. The model reproduced satisfactorily the effect of other parameters such as the oxygen diffusive coefficient, average particle radius and pyrite content (Souza, 2010).

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science highlights

research topic 3

Design and application of natural and synthetic materials for separation, fixation or encapsulation of chemical species

- 56 Evidences of the mechanism for As(III) immobilization on gibbsite by combining EXAFS and theoretical calculation
- 60 Development of porous materials based on pillared clays for environmental application
- 63 Soil materials, laterite and limestone filters for arsenic removal from acid drainage water
- 65 The role of Al-goethites on arsenate mobility

Evidences of the mechanism for As(III) immobilization on gibbsite by combining EXAFS and theoretical calculation

Graziele Duarte¹, Maria S. S. Dantas¹, Hélio A. Duarte², Igor F. Vasconcelos³, Augusto F. Oliveira⁴, Kwadwo Osseo-Asare⁵, Virginia S. T. Ciminelli¹

¹Metallurgic and Materials Engineering Department, Federal University of Minas Gerais (UFMG), CEP 31270-901, Belo Horizonte, MG, Brazil

²Chemistry Department, Federal University of Minas Gerais (UFMG), Belo Horizonte, MG, Brazil
³Metallurgic and Materials Engineering Department, Federal University of Ceará (UFC), Campus do Pici, Bloco 714 – 60455-760, Fortaleza, CE, Brazil

 ⁴Physical Chemistry, Technische Universität Dresden, Bergstr., 66B, 01062, Dresden, Germany
 ⁵Department of Materials Science and Engineering and Department of Energy and Mineral Engineering, The Pennsylvania State University (PSU),16802, University Park, United States of America

Key-words: arsenite, gibbsite, DFT, EXAFS, sorption mechanism.

It is well known that arsenic mobility in the environment is often associated to its interactions with Fe and Al compounds present in soils (Smedley and Kinniburgh, 2002; Ladeira and Ciminelli, 2004). Most of the studies regarding arsenic sorption have focused on the As(V) species, allowing a conclusive understanding about its interactions with many oxide minerals (Ladeira et al., 2001; Sherman and Randal, 2003). In view of its higher toxicity and mobility in soils when compared to As(V) species, there is a great environmental concern on As(III). Nevertheless, only limited studies concerned on As(III) sorption mechanisms have been reported (Ona-Nguema et al., 2005; Morín et al., 2009). Since As(III) is the most common As species under reducing environments, which is the typical condition in groundwaters and deeper regions in tailings dams, a better understanding of its behavior will contribute to control As mobility in aqueous environments.

A particularly important mineral commonly found in soils and usually associated to arsenic natural attenuation in the environment is gibbsite, a aluminum oxy-hydroxide α -Al(OH)₂ (Mello et al. 2006). Hence, a better understanding of the mechanisms whereby As(III) interacts with gibbsite surface will greatly advance the prediction and control of its distribution in aqueous environments (Ladeira et al, 2001; Arai et al., 2001). In this context, the present work combines DFT calculations and EXAFS analyses to elucidate the structural environment of As(III) surface complexes on gibbsite, aiming at predicting their stability in aqueous environments and, consequently, its potential for remobilization. Various adsorption modes for As(III) linkage on the gibbsite surface were investigated by means of theoretical calculations. The most energetically favorable adsorption sites were used as a model to fit the EXAFS spectra. The EXAFS data were collected for As(III) immobilized on gibbsite surface at different pH values (5.0, 7.0 and 9.0) and different coverage levels.

Theoretical calculations have found the binuclear-bidentate/acid-base adsorption (bb/ab) as the most stable complex for As(III) adsorption on gibbsite surface with As-Al and As-O distances of 3.24 and 1.75 Å, respectively. Table 1 shows the theoretical modeling results.

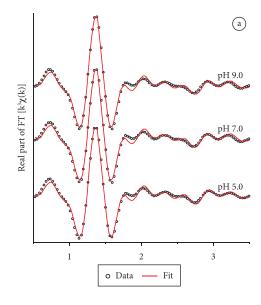
To investigate the local structure of arsenic on gibbsite, the Fourier-transformed EXAFS spectrum was fitted using As-O and As-Al scattering paths derived from the structures of sodium meta- arsenite (NaAsO₂), mansfieldite (AlAsO₄.2H₂O) and Al-substituted tooeleite $(Al_6(AsO_3)_4SO_4(OH)_4.4H_2O)$. These paths were obtained from FEFF 6.0 code built-in the Artemis software (Ravel and Newville, 2005). The three datasets assessed were fit simultaneously (R range from 1.0 to 3.5 Å with a single ΔE_0 value. Fig.1 shows the real part of the Fourier-transformed EXAFS region of the As K-edge XAFS spectra for the gibbsite loaded with As(III) at different pH values, together with the best fitting curve for each sample. The individual contributions of the As-O,

and As-Al scattering paths to the fits of the sample at pH 7.0 are shown in Figure 2(b). The other two samples (pH 5 and pH 9) were fitted using the same scattering paths shown for pH 7. The best fits to the data are shown in Table 2.

Figure 1. Real part of the Fourier-transformed As K-edge EXAFS data for (a) As(III) on gibbsite at different pH values – scatter and line curves represent data and fit, respectively; and (b) individual contributions of scattering paths used to the fits.

Results shown in Table 2 indicate that at pH 7.0 the arsenic atom is coordinated by 3.3 ± 0.2 oxygen atoms at a distance of 1.77 ± 0.01 Å in the first shell. Regarding the second shell, firstly only the As-Al₁ path contribution to the fitting was considered, with amplitude set at 1.0 or 2. At pH 7.0, the fitting has returned an As-Al₁ distance of 3.21 ± 0.03 Å

Adsorption complex	E (kcal.mol ⁻¹)	As-Al distance (Å)	As-O distance (Å)
bb/ab	0.0	3.24	1.75
mm/ab	11.2	3.29	1.85
mm/nd	33.3	3.38	1.80
bb/nd	51.0	3.12	1.82
mb/ab	90.5	3.47	1.80



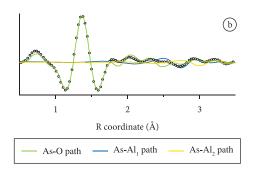


Figure 1. Real part of the Fourier-transformed As K-edge EXAFS data for (a) As(III) on gibbsite at different pH values – scatter and line curves represent data and fit, respectively; and (b) individual contributions of scattering paths used to the fits.

Table 2. Results of fits to EXAFS data.							
Samples	l (pl	H 5)	ll (pl	H 7)	III (pl	H 9)	
Shell	As	-0	As-O		As-O		
Ν	3.3 =	± 0.3	3.3 ± 0.2		3.3 ± 0.2		
R (Å)	1.77 =	± 0.01	1.77 ±	± 0.01	1.77 ± 0.01		
σ^2 (Å ²)	0.004 =	± 0.002	0.004 ±	± 0.001	0.004 ±	- 0.001	
Shell	As-Al,		As-Al,		As-Al ₁		
Ν	1*	2*	1*	2*	1*	2*	
R (Å)	3.19 ± 0.06	3.22 ± 0.05	3.17 ± 0.04	3.21 ± 0.03	3.17 ± 0.03	3.21 ± 0.03	
σ^2 (Å ²)	0.005 ± 0.009	0.011 ± 0.007	0.004 ± 0.005	0.011 ± 0.005	0.004 ± 0.004	0.011 ± 0.004	
Shell	As-	Al ₂ **	As-/	4l ₂ **	As-A	Al_**	
Ν	1*	2*	1*	2*	1*	2*	
R (Å)	3.5 ± 0.1	3.49 ± 0.09	3.48 ± 0.06	3.48 ± 0.06	3.48 ± 0.05	3.48 ± 0.05	
σ^2 (Å ²)	0.01 ± 0.02	0.02 ± 0.01	0.007±0.009	0.02 ± 0.01	0.007 ± 0.007	0.02 ± 0.01	
$\Delta E_{_{0}}(eV)$	10.9 ± 0.8	10.9 ± 0.7	10.9 ± 0.8	10.9 ± 0.7	10.9 ± 0.8	10.9 ± 0.7	

R = Interatomic distance; N = Coordination number; σ^2 = Debye–Waller factor; ΔE_0 = difference between the user-defined and the experimentally determined threshold energy; * Fixed parameter; ** Considering N AsAl₁ = 2; *** All samples were fitted using the same ΔE_0 for each fitting condition.

for N = 2, and an As-Al₁ distance of 3.17 ± 0.04 for N = 1. Thus, it is reasonable to say that the As-Al distances are very similar, independently on the amplitude considered in the fitting. This observation gives the confidence that the As-Al distance in the second shell is in fact around 3.2 Å, which is a typical interatomic distance for an inner-sphere bidentate-binuclear complexation of arsenic on Al and Fe oxy-hydroxides (Ladeira et al., 2001; Arai et al., 2001; Sherman and Randal, 2003).

Regarding the pH effects on the As(III) complexation on gibbsite, the As-O and As-Al interatomic distances remained virtually unchanged regardless the value of pH evaluated (Table 2). This suggests that, although the As(III) loading increases with increasing pH from 5 to 9, its sorption mechanism on gibbsite is not significantly dependent on the pH, under the conditions of the present investigation.

Regarding the practical implications of the results obtained in the present work, one may consider the often-stated argument that the As(III) mobility in the environment is higher than the As(V) mobility due to the neutral character of the arsenite molecule in a wide pH range (< 9.2) as too simplistic. Like As(V) (Ladeira et al., 2001), As(III) was also suggested to preferably form inner-sphere complexes on gibbsite's surface in a pH interval (pH 5 to 9) where the neutral H₃AsO₃ predominates. In order to understand such higher mobility of the As(III) it is important to notice that the first pKa

of the H_3AsO_3 is about 9.2, and the point of zero charge (pzc) of gibbsite and other aluminum oxides is in the pH range of 8-10 (Ladeira and Ciminelli, 2004; Arai et al., 2001). It means that the the As(III) sorbed complex has similar ability to be protonated as the gibbsite surface.

Summarizing, the formation of inner-sphere complexes of As(III) on gibbsite, in a pH range of 5-9, has been demonstrated by combining theoretical calculations and experimental measurements. Based on these results, it is proposed that the high As(III) mobility in the environment is related to the feasibility of protonation of the bidentate-binuclear As(III) complex, besides the protonation of the Al oxy-hydroxides surfaces, rather to the formation of outer-sphere complexes. Such protonation would restore the neutral H_3AsO_3 molecule, which could be released from the mineral surface.

The authors are grateful to the Brazilian agencies: CNPq, CAPES and Fapemig; and to the INCT of Water, Mineral Resources and Biodiversity. The authors also thanks to Dr. Johannes Frenzel, at the Ruhr-Universität Bochum-Germany, for generating the SCC-DFTB parameter files used to calculate the interatomic interactions of arsenic with Al, O and H; and to Dr. Jaime Mello and Dr. Juscimar Silva, at the Universidade Federal de Viçosa-Brazil, for supplying the synthetic gibbsite. Thanks are extended to the National Synchrotron Light Laboratory (LNLS) in Campinas, Brazil.

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2

Development of porous materials based on pillared clays for environmental application

Ângela de Mello Ferreira Guimarães1*, Wolfgang. H. Höll1, Virgínia S. T. Ciminelli1

¹Materials Research Group, Department of Materials, Federal Center for technological Education of Minas Gerais – CEFET/MG, Av. Amazonas, 5253, CEP 30480-000, Belo Horizonte, MG, Brazil *Corresponding author: angelamello@des.cefetmg.br

Key-words: pillared clay, porous materials, adsorbent, catalyst.

Clays are low cost and readily available materials functioning as excellent cation exchangers, and have often been used in adsorption and catalysis. One important class of clay derivatives is pillared clays (PILCs) obtained from the insertion of metal oxide species into the clay (Kloprogge, 1998, Schoonheydt, 1999). Pillared clay is a promising material to be used as adsorbent and catalyst due to its large specific surface area. This work is a result of bilateral cooperation in education and research Brazil-Germany. The research activities were carried out at KIT- Karlsruhe Institute of Technology at its Institute of Functional Interfaces. The first phase of this work is regarding to the synthesis of pillared clays for subsequent modification with functional groups aiming selective materials for water treatment. This report presents the preparation process of pillared using one natural smectite, named Volclay, as well as some characterization results. Therefore pillared montmorillonite (Ti-ILCs, Al-PILCs, and Zr-PILCs) have been produced at different routes and calcination temperatures. The influence of the nature of the pillars and its thermal stability on the porosity will be investigated. Further experiments will be performed in order to test the performance of these materials as catalysts and adsorbents. BET analysis was applied in order to calculate porosity and specific surface area of the

modified clays. The samples were investigated also using XRD data, CEC determination. Changes in morphology were evaluated by SEM. Further investigation using XRF data and FT-IR spectroscopy will be carried out. The PILCs were prepared according to the method showed at Figure 1 scheme.

A suspension containing layered clay is mixed with a solution containing a polyoxocation. The reaction between the polycation and the clay, consisting of the substitution of the exchangeable cations in the interlayer space of the clay by the inorganic polyoxocations, is usually known as cationic exchange reaction or intercalation. After the reaction, the resulting suspension is separated and washed, giving rise to the intercalated clay. Its calcination at high temperature stabilizes the polymeric cation, thus reventing the collapse of the interlayer space and generating a stable porous structure. An increase of basal spacing as well as the specific surface area and pore volume was obtained for all pillared samples. Results obtained from N₂ adsorption analysis (Table 1) show that SSA are in the range of 200-300 m²/g and indicate a successful pillaring process. All PILCs exhibit both micro and mesoporosity, Figure 2. For Ti-PILC and Zr-PILC, the mesoporosity is more accentuated. All samples show higher surface areas and porosity than the raw material Volclay. The

Zr-PILC and Ti-PILC at 60°C are very interesting, because both have around the same SSA and pore volume, but the distrubution is quite different; Ti-PILC has more mesopores whereas Zr-PILC more micropores. Al-PILC presents pore volume mostly in the micropore range and its pore volume is about the same as for Ti-and Zn-Pilc (60°C). It suggests that the particle size of the Al-PILC is smaller than the others, maybe a more pronounced delamination. The cation exchange capacity CEC of PILCs was determined with coppertriethylenetetramine, in order to see the influence of the pillaring process as well as the calcination temperature effect. The calcination step converts the different polyoxycation precursors into their oxides pillars. This heating process has a great influence on the obtained porosity and stability (Kloprogge,1998).

For all samples the pillarization led to the decrease of the CEC. Moreover, this feature is different as a function of the pillar species (Tab.1). At low temperature (60 °C) the CEC compared with that of the starting clay was reduced to about 50 %. After heat treatment at 500 °C the reduction of 76 % in CEC was obtained for Ti-PILC sample. This suggests the irreversibility of cationic exchange; the intercalated polycations were hardly exchanged. Thus, CEC represents only the exchange of the residual interlayer cations mostly Na+, K+, Ca2+, and Mg²⁺. The decrease of CEC with increasing calcination temperature is also related to the dehydration of titanium pillars

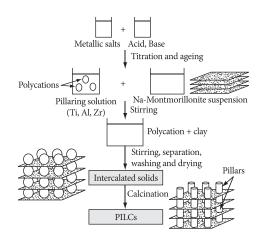
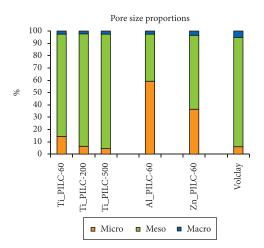
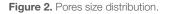


Figure 1. General preparation procedure of pillared clay (BACHIR et al. 2009).

at 60-500 °C. In this range, the water content decreases with increasing heat treatment. During calcination, dehydration and dehydroxylation reactions of the charged pillar precursor occur to give neutral oxide particles.

Figure 3 shows the morphology of the starting material Volclay, which is typical layered morphology of the smectite particles. After pillaring process the morphogy changes strongly. The pillared clay particles seem to be more compact. The sorption and catalytic properties of PILCs will be tested further.





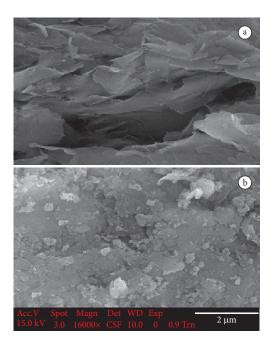


Figure 3. SEM – 16000× picture of a) Volclay *in nature* and b) Ti-PILC-500 °C.

Table 1. Results of the BET N	l ₂ -gas-sorption,	basal spacing and	Cátion Exchange	Capacity - CEC.
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	20 1 /	0 1	5
Sample	SSA m ² g ⁻¹	CEC (meq/100g)	d _{001 (Å)}
Volcaly	48,8	84	12,49
Ti-PILC -60	207,2	44	30,59
Ti-PILC-200	310,7	41	28.30
Ti-PILC-500	310,8	21	25,63
AI-PILC-60	281,7	41	18,31
Zr-PILC-60	219,9	49	17,37

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Soil materials, laterite and limestone filters for arsenic removal from acid drainage water

Renato W. Veloso1*, Jaime W. V. de Mello1, Luiz E. Dias1, Walter A. P. Abrahão1

¹Research Group on Acid Drainage and Geochemistry of As, Soils Department,

Federal University at Viçosa – UFV, CEP 36570-000, Viçosa, MG, Brazil

*Corresponding author: hduarte@ufmg.br, Department of Chemistry, Universidade Federal de Minas Gerais, Av. Antonio Carlos, 6627, CEP 30270-091, Belo Horizonte, MG, Brazil

Key-words: acid water treatment, adsorption, arsenate.

Sulfides exposition to atmosphere promotes its oxidation resulting in acid drainage and mobilization of heavy metals and metalloids in water. Arsenic (As) mobilization can be a serious problem due to anthropogenic activities in the presence of sulfide minerals such as arsenopyrite (FeAsS). The use of limestone gravel is a common practice to neutralize the acid drainage. In this process, mobilization of metals and metaloids is decreased by precipitation, co-precipitation or adsorption onto recently precipitated Fe oxides.

In this work, the efficiency of limestone filters for As remotion from water and neutralization of acid drainage was evaluated under field conditions. Arsenic stability in sediments next to a gold exploitation area was evaluated by sequential extraction chemical analyses. The efficiency of horizontal filters prototypes, containing soil materials combined with limestone, for acidity neutralization and As remotion from acid solutions, was also evaluated in laboratory. Water and sediment samples were collected from creeks in area close to a gold mineralization. Water samples were collected during wet and dry seasons, while sediments were collected only during the wet season. Measurements of pH, Eh, electric conductivity (EC), dissolved oxygen and temperature were registered immediately after water sampling and As concentrations were determined in laboratory. In sediment samples, it was determined texture, particle density, remaining As, organic carbon (OC); As, Al, Ca, Mg and P contents extracted by Mehlich-3, pH in water, potential acidity, As sequential extractions and total contents of As and Fe. In order to evaluate the prototypes in laboratory, acid solutions with approximately 58 mg L⁻¹ As were applied throughout PVC modules (Figure 1) filled with Laterite (LAT), an Oxisoil (SOLO), a 3:1 mixture of SOLO and organic waste (SOLO+RO), and with limestone gravel (BRITA). Twelve filtration cycles, totalizing applications of 6.2, 67.21, 99.74, 20.22, 10.13 g As, Fe, S, Mg and Ca per filter, respectively, were performed. The residence time of the solution in the filters, as well as pH, CE, acidity and As, Fe, S, Mg and Ca contents in the input and output solutions were monitored.

In the field, contents of As in water samples were low except in two points, which presented values above 100 ug L⁻¹. There was not a consistent behavior for As in water samples respective to the collection time, but it could be observed a trend to decrease As concentrations during dry season. In general, As content in sediments was related to the organic matter content. It was observed that sediments and limestone filters play an important role in As mobility in water streams affected by acid drainage. Arsenic was mainly associated to stable fractions of the sediments, with a mean of 58% of the As linked to Fe oxides and residual fractions, which present practically null mobility (Figure 2).

In the laboratory, prototypes of limestone gravel filters removed approximately 26 and 23% of the As and Fe applied, respectively. There was no significant sulfate removing or pH alteration in the filtered solutions for all prototypes. However, significant levels of the total acidity neutralization were observed, directly related to the residence time. Prototypes with SOLO+RO presented the highest residence times. The use of soil containing filters associated to limestone filters removed 2.6 and 2.45 times the As and Fe, respectively, than removed by the limestone filter (Figure 3). The prototype LAT/BRITA/SOLO presented the highest As removal capacity, around 70% of the applied As, and the highest As removal rate, by 1.2 mg min⁻¹, among soil containing filters. However, the residence time was higher to the filters containing soil materials than to the limestone filters. This can be a disadvantage to the use of soil filters. Notwithstanding, the use of soil materials combined with limestone can be

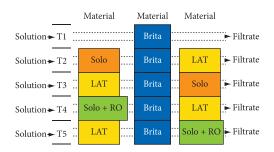


Figure 1. Sketch of the horizontal filters prototypes. Arrows indicate direction of the acid solution flow.

an important strategy to increase the safety of the systems for As removal and acid drainage neutralization during rainy season.

We would like to thank CNPq, Fapemig, CAPES and the INCT – Water, Mineral Resources and Biodiversity.

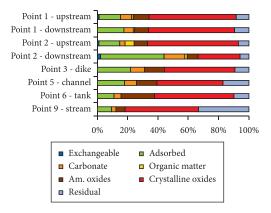


Figure 2. Arsenic percentage in different fractions of the sediments.

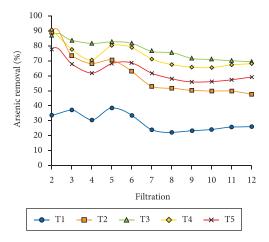


Figure 3. Arsenic removal capacity of the filter prototypes.

The role of Al-goethites on arsenate mobility

Juscimar Silva^{1*}, Jaime W.V. de Mello¹, Massimo Gasparon², Walter A.P. Abrahão¹, Virginia S.T. Ciminelli³, Tony Jong²

¹Research Group on Acid Drainage and Geochemistry of As, Soils Department, Federal University at Viçosa – UFV, CEP 36570-000, Viçosa, MG, Brazil

²University of Queensland

³Federal University of Minas Gerais

*Corresponding author: juscimarsolos@yahoo.com.br, Department of Soil, Universidade Federal de Viçosa, Av. P.H. Rolfs s/n, CEP 36570-000, Viçosa, MG, Brazil

Key-words: water contamination, remediation, biological reduction.

The geochemical fates of Fe and As are so closely correlated that methods of As removal from contaminated water are in general based on the high affinity of this metalloid for Fe (hydr) oxides. Dissimilatory Fe reducing bacteria, however, play a fundamental role in catalysing the redox transformations that ultimately control the mobility of As in anoxic environments. The potential of Al-goethites in adsorbing As(V) compared with hematite, goethite, ferrihydrite, and gibbsite, and the stability of As-rich sludge under anoxic conditions were investigated in this study.

Arsenate adsorption maxima and its isotherm adsorption at different pH were measured following Fe (hydr)oxides synthesis. Arsenic loaded samples were anaerobically incubated in the presence of Shewanella putrefaciens cells, and the solution was periodically sampled to evaluate the contents of soluble As and Fe. The As(V) adsorption maxima decreased in the following order: $Fh > AlGt_{13} > AlGt_{20} >$ $AlGt_{23} > Gb > Hm > Gt$ (Table 1). In terms of surface area, Gb, Gt, and Hm showed higher As(V) loading capacity than Fh (Figure 1), suggesting that available reactive sites were not fully occupied by arsenate on Fh and Al-goethites. The presence of Al enhanced considerably As uptake capacity of the goethites. Thereby, the Algoethites showed good potential as adsorbents to remove As from water.

S. putrefaciens cells were able to utilise non- and crystalline Fe (hydr)oxides as electron acceptors, releasing As into solution. The iron reduction ratio was restrained, however, by presence of adsorbed As relative to the non-Asloaded samples (Figure 2).; Arsenic mobilization decreased as structural Al increased (Figure 2).

Two different mechanisms for As mobilization were observed (Figure 3): first, As mobilization from Gt and Hm was delayed in relation to Fe reduction; and secondly, a congruent release of As with Fe reduction from Fh and Al-goethites. These results suggest preferential mobilisation of Fe not associated with

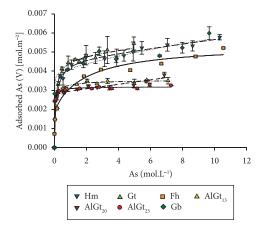


Figure 1. As(V) adsorbed onto different AI and Fe (hydr)oxides normalized by surface area. Error bars not visible are smaller than symbol (N = 3).

adsorbed As at the initial stages of the reductive dissolution of well crystallized minerals. On the other hand, Fe dissolution from Fh gave rise to a prompt As mobilisation, which increased up to approximately 100 mmol L^{-1} during roughly 400 h of incubation time. This behaviour is possibly associated with higher surface area and As adsorption capacity for Fh compared with Hm and Gt. Al-goethites exhibited an intermediate pattern between well and poorly crystalline Fe (hydr)oxides.

Summarizing, it has been demonstrated that Al – Fe association in Al-substituted goethites is beneficial both to arsenic uptake and fixation, the latter even under reducing conditions (e.g. in the presence of *S. putrefaciens*). The results are particularly relevant in tailing dams and wetlands, where, therefore, Fe (hydr)oxides may become chemically unstable and release the adsorbed As into the water. Further information about this work can be seen on Silva et al. (2010).

Table 1. Adsorption maxima (b), binding constant (K), and correlation coefficient (r2) of the linear form of the Langmuir Isotherm for As(V) onto different Fe and Al compounds. Hm = hematite; Fh = ferrihydrite; Gt = goethite; Gb = gibbsite. AlGt₁₃, AlGt₂₀, and AlGt₂₃ are Al-Goethites with Al:Fe molar ratio of 13, 20, and 23 respectively.

Adsorbent	b			k	r ²
	mmol g ⁻¹	mmol m ⁻²	mmol mol ⁻¹ Fe	L mmol ⁻¹	- 1
Hm	0.193	0.0055	16.409	2.562	0.9949
Gb	0.228	0.0050	18.415 ^{a/}	7.116	0.9964
Gt	0.101	0.0049	9.806	10.188	0.9988
AlGt ₁₃	0.417	0.0035	51.010	22.301	0.9988
AIGt ₂₀	0.395	0.0032	54.462	35.401	0.9996
AIGt ₂₃	0.365	0.0032	53.519	13.634	0.9975
Fh	1.258	0.0047	132.896	2.041	0.9932

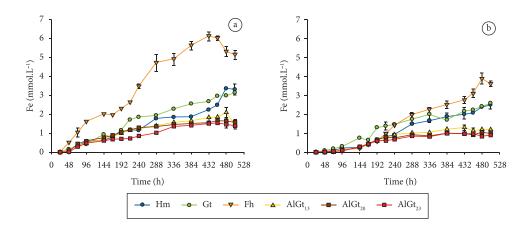


Figure 2. Fe(III) reduction from different Fe (hydr)oxides incubated with *S. putrefaciens* in samples without (a) and with (b) sorbed As. Data are represented as means \pm standard error (N = 3); bars not visible are smaller than symbol.

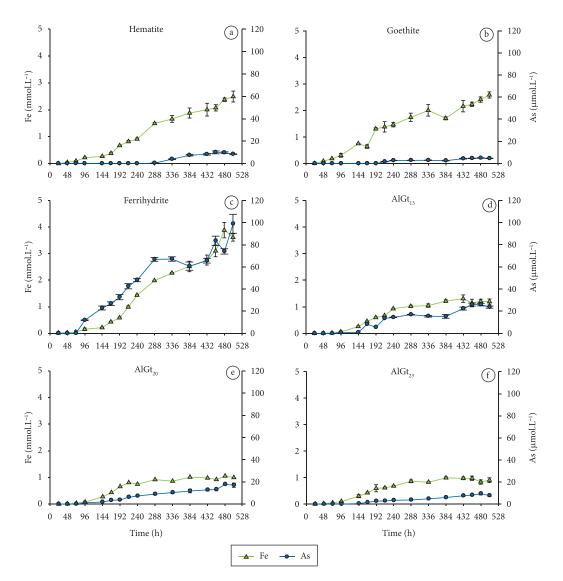


Figure 3. Iron reduction and As mobilisation from different Fe (hydr)oxides incubated with S. putrefaciens. Data are represented as means \pm standard error (N = 3); bars not visible are smaller than symbol.

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science highlights

research topic 4

Metal sulfide oxidation applied to metal extraction and control of acid mine drainage

- 70 Surface relaxation of the chalcopyrite surface
- 72 The role of carbonate ions in pyrite oxidation in aqueous systems
- 75 Galvanic interaction between chalcopyrite and pyrite: beneficial effect on chalcopyrite dissolution under practical conditions

Surface relaxation of the chalcopyrite surface

Guilherme F. de Lima¹, Cláudio de Oliveira¹, Heitor A. de Abreu¹, Hélio A. Duarte^{1*}

 ¹Research Group on Theoretical Inorganic Chemistry – Department of Chemistry, Federal University of Minas Gerais (UFMG), 31-270-901 – Belo Horizonte, Brazil
 *Corresponding author: duarteh@ufmg.br, Department of Chemistry, Universidade Federal de Minas Gerais, Av. Antonio Carlos, 6627, CEP 30270-091, Belo Horizonte, MG, Brazil

Key-words: Chalcopyrite, DFT, surface reconstruction.

Sulphide minerals are involved in the extraction of many metals of economic importance and also in some phenomena observed in degraded areas such as acid mine drainage. The oxidation and leaching mechanism of the sulphide minerals is still a matter of debate. Chalcopyrite (figure 1) is an important sulphide mineral which is the main source of copper. Its composition is $CuFeS_2$ and its electronic structure is still not completely understood.

The hydrometallurgical extraction of copper ores often involves the leaching of chalcopyrite. This process has received much attention due to the increasing need to treat chalcopyrite ores through hydrometallurgical processes.

Traditionally, copper is extracted through a pyrometallurgical processe in which chalcopyrite is heated in the presence of oxygen, as shown in Equation 1.

$$2CuFeS_2 + 5O_2 \rightarrow 2Cu + 2FeO + 4SO_2 \qquad (1)$$

The pyrometallurgical process is efficient to treat high grade ores, which respond well to concentration by flotation. However, it is not efficient to treat complex and low grade ores.

Considering the limitations of the pyrometallurgical route and its environmental impact, the hydrometallurgical process emerges as a promising way to obtain cooper from chalcopyrite¹. Plenty of treatments can extract the cooper, however, the reaction of chalcopyrite with $\text{Fe}_2(\text{SO}_4)_{3(\text{aq})}$ at low temperature is drawn as economically viable and environmentally secure. Equations 2 and 3 show the reactions of chalcopyrite and Fe(III).

$$CuFeS_{2} + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^{0}$$

$$CuFeS_{2} + 16Fe^{3+} + 8H_{2} O \rightarrow$$

$$\rightarrow Cu^{2+} + 17Fe^{2+} + 2SO_{4}^{2-} + 16H^{+}$$
(3)

Experimental studies of the reaction between chalcopyrite and Fe(III) indicate a decrease of the reaction kinetics related to surface passivation.¹ The formation of elemental sulphur and jarosites in the chalcopyrite surface is pointed as a possible passivation candidates. However, many experimental studies are still ambiguous and not in fully agreement with each other.

Our work consists in investigating the chemical properties of the chalcopyrite surfaces. This is the first step for understanding the oxidation mechanism and the surface passivation. The surface reconstruction, geometry and electronic structure have been investigated.

Calculations have been made using the Density Functional Theory (DFT) considering the plane waves formalism. The chalcopyrite unit cell is presented in Figure 2.

The sulfur and metal terminated chalcopyrite (001) surface reconstruction has been investigated. The chalcopyrite surface undergoes important reconstruction leading to the formation of disulphides and change in the oxidation number of the metal surface atoms.

The S²⁻ ions on the surface migrate to form disulfide bond, S_2^{2-} , undergoing oxidation. The oxidation (from -2 to -1) is accompanied by the reduction of the Fe, which was with the oxidation number +3 and reduced to +2. The Electron Localization Function (ELF) of the

optimized structure, figure 3, was evaluated. The S-S bond is well characterized with the electron pairs on each sulphur atom. This theoretical result is in agreement with experimental XPS studies reported by Harmer et al.^{2,3}.

The electrons released by the oxidation process migrate to Fe(III) ion converting it to Fe(II), according to Equation (4).

 $Bulk - 2Fe(III) - 2S^{2-} \rightarrow Bulk - 2Fe(II) - S^{2-}_{2} \quad (4)$

The metal (001) chalcopyrite surface also undergoes important reconstruction leading to the sulphur-metal complexes. Other chalcopyrite surfaces are being investigated. The formation of intermediates involving oxygen and sulphur has been detected with the TOF-SIMS experiments and a modeling of the surface will contribute to interpret such results.

Other chalcopyrite surfaces are being investigated. Preliminary results show the formation of disulphides and the formation of metal-metal bonds. The final aim of this project is to understand, at a molecular level, the mechanism of the oxidation of the chalcopyrite surface and the influence of the water and other chemical species such as sulphates and Fe(III) ions. The understanding of the reaction mechanism will permit us to envisage innovative approaches to enhance chalcopyrite leaching.



Figure 1. Picture of chalcopyrite.

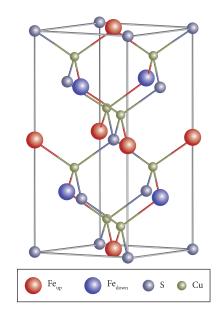


Figure 2. Chalcopyrite unit cell.

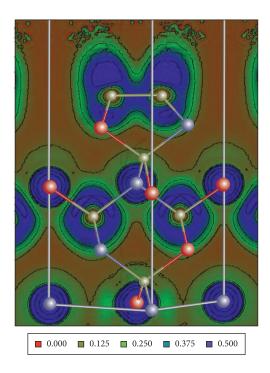


Figure 3. Electron Localization Function of the optimized sulfur terminated Chalcopyrite (001) surface.

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2

The role of carbonate ions in pyrite oxidation in aqueous systems

Claudia L. Caldeira^{1,3}, Virginia S. T. Ciminelli^{1,3*} and Kwadwo Osseo-Asare^{2,3}

 ¹Novas Group. Dept. of Metallurgical and Materials Engineering – UFMG, Av. Antonio Carlos, 6627, Engineering School, Bl2, s/2233, CEP 31270-901, Campus Pampulha, Belo Horizonte, MG, Brazil
 ²Dept. of Materials Science and Engineering and Dept. of Energy and Mineral Engineering, The Pennsylvania State University, University Park, PA 16802, USA
 ³National Institute of Science and Technology: INCT-Acqua

*Corresponding autor: ciminelli@demet.ufmg.br

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The kinetics and mechanism of pyrite oxidation have received much attention for many decades, especially in acidic solutions (Bailey and Peters, 1976; Mishra and Osseo-Asare, 1988; Wei and Osseo-Asare, 1997; Holmes and Crundwell, 2000), in order to understand and control pyrite oxidation and associated reactions in mineral processing, metal extraction, acid mine drainage (AMD) and other related systems. Pyrite oxidation is usually described by an electrochemical mechanism, thus implying that the overall reaction can be written in terms of half-cell reactions. The anodic oxidation of pyrite produces ferrous and sulfate ions and the oxidant (e.g. molecular oxygen or ferric ion) is reduced in the corresponding cathodic reaction. A main difference between pyrite oxidation under acidic and alkaline conditions is the hydrolysis and precipitation of ferrous/ferric ions as pH increases.

With the help of information derived from reaction kinetics, thermodynamic modeling, and diffuse reflectance infrared spectroscopy (DRIFTS), the present work aims to further contribute to our understanding of the reaction between pyrite and molecular oxygen in NaOH and Na₂CO₃ solutions.

The results indicate that the beneficial effect of carbonate on the rate of pyrite oxidation is restricted to moderately basic solutions. The observed variation in the rates of pyrite oxidation in sodium carbonate/sodium hydroxide systems can not be attributed to the higher ionic strength of the former. The conditions that favor the predominance of iron carbonate complexes, according to the thermodynamic modeling, are consistent with those where the greater effect of carbonate ions on the rate of pyrite oxidation is observed (i.e. pH 10-12) (Table 1) and with the increase in the soluble iron concentration. The highest soluble iron concentrations were obtained at pH values where the largest differences in the initial oxidation rates were observed (Table 1). Thus, iron remains soluble at higher carbonate/ bicarbonate concentrations, due to the formation of iron complexes in the pH range 8.5 to 10. In pH 12.5, the soluble iron concentrations are very small. These findings clearly indicate the formation of soluble iron-carbonate complexes. Eh measurements (0.1 < Eh < 0.4 V) suggest the predominance of Fe(III) complexes in the aqueous phase.

In addition to the results noted above, another evidence of carbonate complexes formation is the presence of surface-bound carbonate compounds among the products formed during pyrite oxidation, which was observed with the use of diffuse reflectance infrared spectroscopy.

The multiple of carbonate bands suggests the presence of more than one carbonate complex

on pyrite surface. Nonsplitting of the carbonate band (at 1430 cm⁻¹) indicates the formation of weak carbonate complexes on pyrite and iron oxides surface or the formation of a carbonate compound. The peaks at 1350 cm⁻¹ and 1530 cm⁻¹ were assigned to the v_3 symmetric stretching vibration (v_s) of C-O bond and to the C-O asymmetric stretching vibration (v_{as}), respectively. The magnitude of this splitting indicates the formation of monodentate binuclear inner sphere carbonate complexes on the pyrite surface or on iron oxyhydroxides.

The Role of Carbonate in Pyrite Oxidation

The results presented above showed that soluble Fe(II)/Fe(III) carbonate complexes can form during pyrite oxidation. It is proposed here that these complexes may be responsible for the relatively fast reaction rate in bicarbonate and carbonate media. The observed carbonate effect may be rationalized by considering a combination of three factors: (a) the effect of Fe(II)-CO₃ complexes on the Fe(II)-O₂ oxidation reaction, (b) the buffering effect of carbonate complexation on Fe(III) solubility.

In absence of carbonate, the oxidation of Fe(II) to the Fe(III) is slow in strong acidic solutions and independent of the hydroxyl ion concentration, but it increases rapidly with pH above pH 4, which is ascribed to the hydrolysis of iron species. The similar behavior of pyrite oxidation, changing from zero order (pH<4) to pH dependent at about 4, supports the hypothesis that the surface mineral oxidation is controlled by the rate of oxidation of Fe(II) and hydrolysis of iron. The Fe(CO₃)₂²⁻ and Fe(CO₃)(OH)⁻ species are expected to be the main species involved in Fe(II) oxidation in carbonate/

bicarbonate solutions as showed in Eh-pH diagram (Caldeira et al., 2010).

The rate of Fe(II) to Fe(III) oxidation is the rate determining step of pyrite oxidation in acidic and circumneutral pH (Singer and Stumm,1970; Moses et al., 1987). Therefore, it is proposed that the formation of soluble Fe(II)-CO₃ complexes favors the oxidation of Fe(II) to Fe(III) by dissolved oxygen, which in turn increases the overall rate of pyrite oxidation, even under alkaline conditions.

A second factor to affect the reaction rate is the buffering effect of carbonate, which minimizes the variation of pH at the reaction interface, thus maintaining more favorable conditions for pyrite oxidation. The increase in carbonate concentration keeps the pH constant during the experiments.

An additional possible factor enhancing pyrite oxidation in carbonate solutions is related to the fact that the complexation with bicarbonate/ carbonate ions provides a more effective Fe(III)/ Fe(II) redox couple by increasing iron solubility. The increased availability of total iron concentration strengthens its role as pyrite oxidant.

A schematic diagram illustrating the proposed model for pyrite oxidation in carbonate solutions is shown in Figure 1. It will be assumed here that in oxygenated systems containing carbonate ions the electron acceptors are iron (III) carbonate complexes adsorbed on the pyrite sites. Adsorbed Fe(II)-CO₃ is oxidized by dissolved oxygen to Fe(III)-CO₃ at pyrite surface (or in solution). The Fe(III)-CO₃ is reduced to Fe(II)-CO₃ at the cathodic sites, by receiving electrons from the conduction band of pyrite (anodic site). Thus, the cycle of the Fe(II)/Fe(III) redox couple is formed, mediating the electron transfer from the sulfur atoms to dissolved oxygen. At the anodic site, the

Table 1. Initial reaction rates (k) of pyrite oxidation in carbonate/bicarbonate and hydroxide systems at different pH conditions.

рН	$k \times 10^2 (h^{-1})$	
	NaOH	Na ₂ CO ₃ /NaHCO ₃
10.1	1.2	2.2
10.7	1.3	2.3
11.4	2.3	2.8
12.0	2.8	3.0
12.4	3.6	4.0

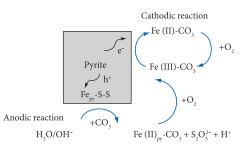


Figure 1. Schematic representation of the mechanism of pyrite oxidation in carbonate solutions.

adsorption of hydroxyl or water occurs at ironpyrite sites; the presence of holes at the iron sites strengthens the adsorption of the OH⁻ species and is followed by the transfer of the OH radical to the sulfur sites (Mishra and Osseo-Asare, 1988; Wei and Osseo-Asare; 1997). Further hydroxylation takes place at the sulfur sites until thiosulfate is formed and eventually released to solution with the Fe(II) from pyrite.

Following the Singer-Stumm model for pyrite oxidation in acidic solutions, it is assumed

that Fe(III) is the preferred pyrite oxidant under alkaline conditions. We propose that carbonate ions facilitate the electron transfer from soluble iron(II)-carbonate to O_2 , increase the iron solubility, and provide buffered, favorable alkaline conditions at the reaction front, which in turn favors the overall kinetics of pyrite oxidation. Therefore, the electron transfer from sulfur atoms to O_2 is facilitated by the formation of the cycle of Fe(II)-pyrite/Fe(III)-carbonate redox couple at the pyrite surface.

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Galvanic interaction between chalcopyrite and pyrite: beneficial effect on chalcopyrite dissolution under practical conditions

Daniel Majuste¹, K. Osseo Asare², Virginia S.T. Ciminelli^{1*}

¹Department of Metallurgic and Materials Engineering, Federal University of Minas Gerais (UFMG), CEP 31270-901, Belo Horizonte, MG, Brazil

²Department of Materials Science and Engineering, Pennsylvania State University (PSU), 16802, University Park, United States of America

*Corresponding author: ciminelli@demet.ufmg.br, Departamento de Engenharia Metalúrgica e de Materiais, Universidade Federal de Minas Gerais, Av. Antonio Carlos, 6627, CEP 31270-901, Belo Horizonte, MG, Brazil

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Chalcopyrite (CuFeS₂) is the most abundant copper mineral and accounts for about 70% of the world's known copper (Cu) deposits (Wang, 2005). For the porphyry Cu deposits, the most extensive ones, this sulfide is commonly associated with pyrite (FeS₂) and with minor sphalerite (ZnS) and molybdenite (MoS₂) content (Habashi, 1978). Currently, copper production from pyrometallurgy is about 82% and about 80% of this value comes from chalcopyrite concentrates (Bravo, 2006), which do not dissolve easily in aqueous solutions. The pyrometallurgical treatment of high-grade sulfide ores has dominated the copper industry since the 1800's, but this scene is being slowly modified (Dreisinger, 2006). The limitations of this alternative involve the treatment of low-grade and complex ores; capital costs of the smelter and refinery plants; and generation of large amounts of solid waste and atmospheric emissions (Prasad and Pandey, 1998; Davenport et al., 2002). Thus, in the last decades, the hydrometallurgical processing of Cu sulfides has been widely studied aimed at treating chalcopyrite - commercially and environmentally important copper mineral.

Chalcopyrite does not significantly dissolve under the heap leaching conditions (*i.e.*, sulfuric acid as the leaching solution and atmospheric conditions) with mesophiles bacteria. Processing at high pressure and high temperature conditions is economically attractive to high-grade ores.

Chalcopyrite leaching rate in acidic solutions and under low temperatures is known to be very slow and usually tends to decline with time (Dreisinger, 2006; Córdoba et al., 2008; Klauber, 2008). Most of the studies ascribe the slow leaching kinetics to the formation of insoluble non-porous layer, which prevents further mineral dissolution. In function of the slow leaching rate, which in turn results in long residence times and deficient Cu extraction, many efforts have been made to increase the reactivity of chalcopyrite in solution, overcoming the so-called hindered dissolution effect. Addition of catalysts as pyrite, chloride ion and silver ion affects both the leaching rate and the dissolution mechanisms. It is well established that galvanic interaction increases the dissolution rate of one or both the minerals that constitute a galvanic couple. The enhancement of CuFeS, leaching rate, when in contact with pyrite (FeS₂) (Berry et al., 1978; Mehta and Murr, 1983; Nowak et al., 1984; Abraitis et al., 2004; You et al., 2007; Miller et al., 2008; Littlejohn and Dixon, 2008) has been attributed to galvanic effect. It has been described that FeS₂ - the mineral with higher OCP (i.e., the open circuit potential) - acts as the cathodic site for oxygen and ferric ion reduction reactions (Equations 1 and 2, respectively), while CuFeS, - the mineral with lower OCP - acts as the anode and, therefore, is preferentially dissolved (Equation 3) (Berry et al., 1978; Mehta and Murr,

1983; You et al., 2007). Figure 1 illustrates this galvanic couple.

 $O_{2(q)} + 4H^{+}_{(aq)} + 4e^{-} = 2H_2O$ (1)

$$Fe^{3+}_{(aq)} + e^{-} = Fe^{2+}_{(aq)}$$
 (2)

$$CuFeS_{2} = Cu^{2+}_{(aq)} + Fe^{2+}_{(aq)} + 2S + 4e^{-}$$
(3)

Since pyrite is a mineral phase commonly found in Cu sulfide deposits, its interaction with CuFeS, has very important implications on leaching systems. In heap leaching, for example, treatment of FeS₂-bearing chalcopyrite concentrates might contribute to increase the chalcopyrite dissolution rate, since in this leaching method, the contact between these minerals naturally occurs. Hence, in this context, the purpose of this work is to investigate the role of naturally associated pyrite micro-crystallites on the electrochemical behavior of CuFeS, electrodes in sulfuric acid (H₂SO₄) solutions and in the presence of ferric ion and dissolved oxygen. Potentiometric and voltammetric studies were conducted in order to evaluate the effect of pyrite crystallites, Fe3+ ion and O2(g) on fundamental properties of chalcopyrite electrodes such as the mixed potential (E_{M}) and the exchange current density (i_{0}) .

Prior to these experiments, all the electrodes were analyzed by scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS); optical microscopy; and Raman spectroscopy. Particularly for the mixed electrodes – chalcopyrite electrodes containing pyrite micro-crystallites –, the Standard Test ASTM E562 (2008) was employed for estimating the fraction of pyrite on the surface by a systematic manual point count. Figure 2 presents typical micrograph of (a) a pure CuFeS₂ electrode and (b) a mixed electrode. The electrode matrix, larger impurity and massive dark points correspond to chalcopyrite, pyrite and diopside (CaMgSi,O₆), respectively, as indicated

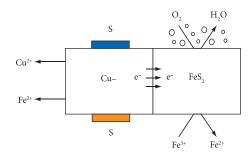


Figure 1. Galvanic interaction between chalcopyrite and pyrite in acidic media.

by SEM/EDS and Raman spectroscopy. The dark points can also be cavities. Using the method described by ASTM E562 (2008), electrodes containing about 0% of FeS₂ (CE), 14% of FeS₂ (ME 1), 31% of FeS₂ (ME 2) and 42% of FeS₂ (ME 3) on the surface (1 cm²) were selected and then submitted to potentiometric and voltammetric experiments.

In the absence and in the presence of oxidants, the increase of pyrite fraction on the surface of $CuFeS_2$ electrodes caused a positive shift in both the mixed potential (E_M) and exchange current density (i_0), as indicated in Figure 3. In addition, it must be noticed that the E_M and i_0 values of both the CE and ME electrodes increased significantly in the presence of the Fe³⁺ ion, an effect more pronounced than that observed in the presence of oxygen. This result is possibly due to the faster kinetics of the Fe³⁺ ion reduction on the electrode surface.

As also indicated in Figure 3, the positive effect of combined Fe³⁺ ion and dissolved oxygen on E_M and i_0 values was magnified on the ME electrodes. The mixed potential increased around 250 mV *vs* Standard Hydrogen Electrode (SHE) in the presence of both Fe³⁺ ion and O_{2(g)}, on CE electrodes and about 350 mV SHE in the presence of Fe³⁺ ion, O_{2(g)} on pyrite (42%) – CE electrodes. The exchange current density increased about

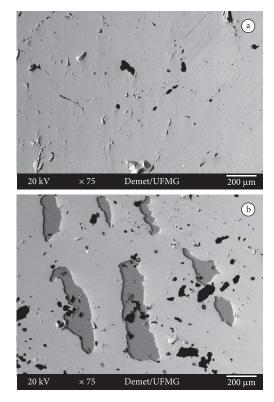


Figure 2. Back-scattered electron micrographs of (a) pure chalcopyrite electrode and (b) mixed electrode (Magnification: 75x).

55× in the presence of both Fe^{3+} ion and $O_{2(g)}$, and around 79x in the presence of Fe^{3+} ion, $O_{2(p)}$ using pyrite (42%) - CE electrodes. A faster oxidation of Fe²⁺ to Fe³⁺ ion in solution and the resulting increase of oxidant concentration possibly explain such effect. Electrochemical models explain that the mixed potentials and the exchange current densities depend on the oxidant concentration and on the rate constants of anodic and cathodic half-cell reactions involved in the galvanic process. When galvanically-coupled to chalcopyrite, pyrite possibly provides a more favorable site for the reduction reactions. The H⁺ ion, Fe³⁺ ion and $O_{2(q)}$ reductions would occur with lower overpotential - difference between the applied potential and the mixed potential - on the pyrite surface than on the chalcopyrite surface. By the mixed potential theory, it may be demonstrated that this coupling causes a positive shift of the E_M to the galvanic potential (E_c), resulting in increase of the anodic current and the cathodic current.

Summarizing, electrodes prepared with mineral samples with a natural variation in $\text{FeS}_2\text{-CuFeS}_2$ composition were used in electrochemical investigations of chalcopyrite oxidation in acidic solutions, atmospheric conditions. The results demonstrated the positive effect of combining Fe³⁺ ion and O_{2(g)}, on CuFeS₂ oxidation, and that this effect is magnified by FeS₂-CuFeS₂ galvanic interactions. These findings can be used to improve Cu extraction from chalcopyrite, low grade ores.

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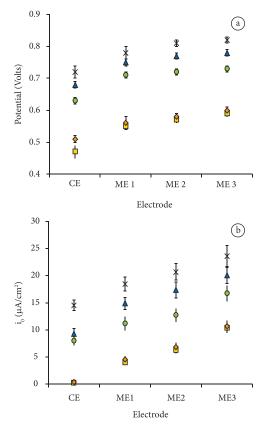


Figure 3. Effect of pyrite and oxidants on the (a) E_M and (b) i_0 for CE and ME electrodes in 0.1 mol/L H_2SO_4 solution, at 25°C: £ Absence of oxidants; ⁻ 0.20 L O_2 /min; 0.01 mol/L Fe³⁺; r 0.05 mol/L Fe³⁺; and \hat{I} 0.20 L O_2 /min + 0.05 mol/L Fe³⁺.

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e-mails

INCT-ACQUA MANAGEMENT COMMITTEE

Virginia S. T. Ciminelli – DEMET-UFMG, *chair* José Galizia Tundisi – IIEGA-SP, *co-chair* Francisco A. R. Barbosa – ICB-UFMG, *co-chair* Ângela Mello Guimarães – CEFET

Ana Claudia Q. Ladeira – CDTN

Jaime W. V. Mello – UFV

Hélio Anderson Duarte - DQ-UFMG

EXECUTIVE OFFICE

Dr. Claudia L. Caldeira – DEMET/UFMG Assistant Manager claudia@demet.ufmg.br

Christina Salvador – INCT-ACQUA Secretary inct.acqua@demet.ufmg.br

FUNDEP – Fundação de Desenvolvimento da Pesquisa

Patricia Rodrigues Accacio Project Analyst patriciaaccacio@fundep.ufmg.br

INSTITUTIONS AND CONTACTS

• UFMG – Universidade Federal de Minas Gerais

Prof. Virginia S.T. Ciminelli – DEMET ciminelli@demet.ufmg.br

Prof. Wander Luiz Vasconcelos – DEMET Research Module Coordination wlv@demet.ufmg.br

Prof. Marcelo Borges Mansur – DEMET Research Module Coordination marcelo.mansur@demet.ufmg.br

Dr. Flavio M. Vasconcelos Invited Researcher flavio.Vasconcelos@aecom.com Prof. Regina Pinto de Carvalho Invited Researcher reginapc@fisica.ufmg.br

Prof. Hélio Anderson Duarte – ICEx/DQ duarteh@ufmg.br

Prof. José Domingos Fabris – ICEx/DQ jdfabris@ufmg.br

Prof. Francisco A. R. Barbosa – ICB/DBG barbosa@icb.ufmg.br

Prof. Andréa M. Amaral Nascimento – ICB/DBG amaral@ufmg.br

Prof. Arnola Cecília Rietzler – ICB/DBG rietzler@icb.ufmg.br

Prof. Edmar Chartone de Souza – ICB/DBG echartone@yahoo.com.br

Prof. Paulina Maria Maia Barbosa – ICB/DBG Research Module Coordination maia@icb.ufmg.br

Prof. Francisco Marinho – Escola Belas Artes chicomar.francisco@gmail.com

 IIEGA – Associação Instituto Internacional de Ecologia

Prof. José Galizia Tundisi jgt.iie@iie.com.br

Prof. Takako Matsumura-Tundisi takako@iie.com.br

Dr. Donato Seiji Abe donatoabe@iie.com.br

CDTN/CNEN – Centro de Desenvolvimento de Teopologia Nuclear

Tecnologia Nuclear

Prof. Ana Cláudia Queiroz Ladeira ana.ladeira@cdtn.br

Prof. Carlos Antônio de Morais Research Module Coordination cmorais@cdtn.br

• UFV – Universidade Federal de Viçosa

Prof. Jaime W. V. de Mello – Depto. de Solos jwvmello@ufv.br

• CEFET-MG – Centro Federal de Educação Tecnológica de Minas Gerais

Prof. Ângela de Mello Ferreira Guimarães angelamello@des.cefetmg.br

Prof. Sidney Nicodemos da Silva sidney@des.cefetmg.br

• UFCE – Universidade Federal do Ceará

Prof. Igor Frota de Vasconcelos ifvasco@ufc.br

• UFJF – Universidade Federal de Juiz de Fora

Prof. Júlio José da Silva silvajcj@yahoo.com.br

SECTES – State Secretariat of Science, Technology and Superior Education

• The Mineral and Metallurgic Pole of Excellence

Renato Ciminelli renato.ciminelli@tecnologia.mg.gov.br

• The Water Resources Pole of Excellence

Dr. Magda Karla Barcelos Greco magda.greco@tecnologia.mg.gov.br

Dr. Maria Margarida Marques mmarques@icb.ufmg.br

INTERNATIONAL COLLABORATION

Prof. Wolfgang Höell Chemistry Institute of Karlsruhe, Germany (in memorian)

Prof. Dina L. Lopez Ohio University, USA lopezd@ohio.edu

Prof. K. Osseo-Asare The Pensylvania State University, USA ako1@psu.edu

Prof. Marta Litter CNEA-Argentina marta.litter@gmail.com

Prof. Massimo Gasparon University of Queensland, Australia m.gasparon@uq.edu.au

Prof. Paulo Vasconcelos University of Queensland, Australia paulo@earth.uq.edu.au

Prof. Gotthard Seifert *TU-Dresden, Germany* Gotthard.Seifert@chemie.tu-dresden.de

Prof. Thomas Heine Jacobs University, Germany t.heine@jacobs-university.de



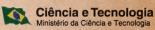




Headquarters	Universidade Federal de Minas Gerais – UFMG	
	Escola de Engenharia – Bloco II	
	Depto. de Engenharia Metalúrgica e de Materiais	
	Av. Antonio Carlos, 6627 – 31270 - 901	
	Belo Horizonte – MG, Brazil	
Telephone	+55 (31) 3409-1825 / 1810	
E-mail	inct.acqua@demet.ufmg.br	
Home Page	www.acqua-inct.org	



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