15th International Conference on Environmental Science and Technology

Rhodes, Greece, 31 August to 2 September 2017

Application of Thermal Plasma for Inertization of Metals in Acid Mine Drainage Treatment

Cubas A.L.V.[1*], Machado M.M. [1,3] , Andrade P.R. [2], Gelsleichter J.M.K. [1] And Moecke E.H.S. [1]

[1]Environmental Engineering Department, University of Southern Santa Catarina State (Unisul), Av. Pedra Branca, n° 25, CEP 800137-270, Palhoça, SC, Brazil.

[2]Eletrical Engineering Department, University of Southern Santa Catarina State (Unisul), Av. Pedra Branca, n° 25, CEP 800137-270, Palhoça, SC, Brazil.

[3] Environmental Engineering Department, Federal University of Santa Catarina State (UFSC), Campus Rector João David Ferreira Lima, CEP 88040-900, Florianópolis, SC, Brazil.

*corresponding author:

e-mail: anelisecubas@gmail.com

Abstract: Acid mine drainage (AMD) is a strongly acidic aqueous solution containing high levels of sulfate and toxic metals. In this study, the treatment of mine-impacted water (MIW) aimed at its safer disposal was investigated. Firstly, shrimp-shell and mussel farming waste were used as metal biosorbents and alkalinizing agents and thermal plasma technology was then applied for the inertization of metals contained in the substrate. The substrates employed for the MIW remediation were raw shrimp shell (SS) and mussel byssus filaments (MB). SS contains chitin in its composition, a metal-sorbent biopolymer, and calcium carbonate, an acidity removal agent. SS and MB saturated with metals from MIW were submitted to pyrolysis in a direct current thermal plasma reactor. Scanning electron microscopy (SEM/EDS) and flame atomic absorption spectroscopy (FAAS) were carried out in order to verify the metal inertization. The vitrification the inertization of the metals present in the samples analyzed was shown to be efficient, reaching to 99.8 to 100%. It was noted that the pyrolysis of the filter material impregnated by metals through thermal plasma allows the total inertization of these metals, and they can return to the environment or be stored in an environmentally safe way.

Keywords: Acid Mine Drainage, shrimp-shell, mussel byssus, toxic metals, thermal plasma.

1. Introduction

Mining practices have generated serious environmental changes since the last century and made it virtually impossible to maintain aquatic life in affected water bodies. Mines are associated with important environmental problems, like hindered plant growth and the siltation of rivers close to the mining activity, all around the world (Sarmiento *et al*. 2016; Trujillo 2016; Valente *et al*. 2015; Strosnider *et al*. 2014; Tempelhoff *et al*. 2014).

Coal extraction processes, processing and use generate highly toxicity effluents due to the degree of acidity (pH < 4.0), significant metal ion concentrations (Fe, Al, Mn, Cu, Zn, Pb and others) and high sulfate levels. These effluents, known as acid mine drainage (AMD), pollute natural surface or ground water bodies resulting in mine-impacted water (MIW), causing serious environmental problems that can damage ecosystems and human health (Fávere *et al*. 2004).

In general, the remediation of MIW involves three different processes: the addition of a neutralizing agent; a decrease in SO_4^{2-} concentrations; and the removal of other dissolved and/or particulate contaminants (metals and/or metalloids). Traditional treatment of MIW involves chemical processes. Due to the very high cost of this type of treatment, alternative and low-tech approaches have been investigated. These include the use of natural biopolymers like chitin. Crustacean shells (such as shrimp shells) are composed of a complex solid matrix of chitin (poly-N-acetylglucosamine), protein, and $CaCO_3$. In an aqueous medium, they provide the slow release source C, N and alkalinity, and they can be used to remove dissolved metals due to the sorbent characteristics of the chitin (Núñez-Gomez *et al*. 2016).

The aim of the research study reported herein was to find an alternative and low-cost solution to the acid mine drainage problem using Crustacean shells (such as shrimp shells), by producing a pH neutral and metal-free effluent with. The specific objective was to recover inert metals by plasma technology in such a way that they can be disposed of in an industrial dumping site without environmental risk. Lastly, the heavy metal ions remaining in the plasma waste could be recycled for the supply of metals and to obtain added value.

2. Methodology

2.1 Mine Impacted Water (MIW)

The MIW used in all experiments was collected from a closed mine within the coalfield area of the Santa Catarina State in southern Brazil. Samples were taken in non-sterile polypropylene containers and capped with minimal headspace. All material samples and containers had been pre-washed with detergent and deionized water followed by acid rinsing. The samples were transported and stored in a refrigerator at approximately 4°C (AWWA 2012) and used within a week of sampling.

2.2 Metal concentrations

The concentration of the metals, including Fe, Al and Mn, in the MIW was determined using inductively coupled plasma-mass spectrometry (ICP-MS) (Perkin Elmer Nexlon 300D) applying the EPA Method 3005 A (Table 1). Liquid samples were filtered through a 0.22 µm membrane filter (Sartorius Company) to remove the solids and acidified with concentrated HNO_3 solution to avoid precipitation of the metals due to changes in the pH (USEPA 1992). A digital pH meter was used to monitor the solution pH during the tests.

2.3 Substrate (shrimp-shell and mussel byssus)

The substrates used for the MIW remediation in this study were raw shrimp-shell (SS) (without the head) as an acidity and metal removal agent and raw mussel byssus filaments (MB). The SS and MB were washed with water meticulously to eliminate the remains of organic matter and other coarse materials. Subsequently, the shells were dried in an oven for 72 h (at 100°C for the first 48 h and at 50°C for the last 24 h). After this process, the SS was pulverized in a blender and sieved to promote greater homogeneity and obtain a larger contact surface. To prevent moisture absorption, the substrates were kept in a glass desiccator until use (Núñez-Gómez 2014; Núñez-Gómez *et al*. 2016). After the treatment, the substrates were dried in an oven for 24 h at 50°C and then used in the plasma experiments.

2.4 Microcosm test setup

Microcosm tests were prepared in a 10 L beaker with 152 g of substrate (80.2 g of SS and 71.66 g of MB) and 7 L of MIW. A control experiment (without the biopolymers) was carried out. The microcosm was sealed with Teflon-lined stoppers, manually shaken to mix the contents and incubated at room temperature (24 ± 3°C) for 72 h. After the incubation period, the sample was analyzed to determine the pH (<0.16 h) and filtered (0.45 µm and 0.20 µm) prior to the analysis to determine the dissolved metals. Dissolved metal concentrations were measured by atomic absorption spectrometry (AAS) at the Department of Environmental Engineering at the Federal University of Santa Catarina (Brazil), according to the procedure described in the USEPA method (3010 A).

2.5 Inertization of the mining sludge through thermal plasma technology

The saturated SS and MB substrates were pyrolyzed in a direct current plasma reactor. In the next step, 114 g of the pyrolyzed material was mixed with quartzite sand in three different proportions (1:2, 1:3, 1:4) to aid the vitrification. The contents used were: Sample A1 - 38 g of filter medium with 96 g of sand (1:2.5); Sample A2 - 38 g of filter medium and 114 g of sand (1:3); and Sample A3 - 38 g of filter medium and 152 g of sand (1:4). Another two samples, considered as blanks, were also prepared: Sample A0 – 100 g of sand and Sample A4 – 8.87 g of filter medium impregnated with mining residues, according to Figure 1. The conditions for the reactor were optimized (5 min per sample, current 300 A and plasmogenic gas (argon) flow rate 9 L/min.

Pyrolysis was carried out in a plasma reactor with a transferred-arc plasma torch. The reactor is comprised of a cathode and a graphite anode and a node used as a support for the sample. The whole system is located inside an oven with an opening to collect the gases, as shown in Figure 2. The argon, the gas used in the plasma formation, has the function of refrigerating the cathode. A source of direct current, used commercially for welding using the TIG (tungsten inert gas) process (ELETROMEG, model RG 550), was used to provide the high current (~ 200 A and 12 V, equivalent to 2.4 kW) required for the gas ionization.

Figure 2 shows a schematic drawing of the plasma reactor used for the inertization of metals.

2.6 Analysis by SEM/EDS

Scanning electronic microscopy (SEM) analysis using a JEOL microscope model JSM-6390LV was carried out on the raw samples and after pyrolysis in the Central Laboratory of Microscopy at Federal University of Santa Catarina (UFSC). Electron beams with nominal resolutions of 20, 50 and 100 µm adjusted for a voltage of 15 kV were used as the analytical conditions. Magnifications of 200, 500 and 1000 times were applied for each sample and vacuum metallization with gold (Au) 10-5 bar. The energy dispersive X-ray spectroscopy (EDS) system (Philips XL 30) coupled to the SEM enabled the qualitative and semi-qualitative determination of the composition of the samples. The appliance operated with electron beams adjustable to a voltage of 10 kV. SEM analysis allows the chemical compositions of samples to be determined, as well as visualization of crystal surfaces and an evaluation of the homogeneity of the vitreous matrix.

2.7 Leaching test

The efficiency of the inertization of the material was verified by subjecting the pyrolyzed material to a leaching test carried out according to the standard NBR 10005/2004. The samples were placed in a 50 mL beaker, followed by the addition of 20 mL distilled water. The pH of the leaching test must be 5 and thus a small quantity of 0.5 N acetic acid was added in order to correct the pH. The resulting solution was maintained under agitation (30 rpm) in a bench shaker for 24 h, followed by filtration. The solid residue was separated and the metals were determined by scanning electronic microscopy (SEM) to verify the incorporation in the solid material. The liquid sample from the leaching tests were analyzed by flame atomic absorption spectrometry (FAAS) for the determination of solubilized metals.

2.8 Analysis by flame atomic absorption spectrometry

The metal concentrations of the samples were determined on a Perkin Elmer atomic absorption spectrometer (model PinAAcle 900T) with hollow cathode lamps. Standard solutions containing 0-54 mg.L^{-1} of Al, 0-2.5 mg.L^{-1} of Mn and 0-2.5 mg.L^{-1} of Fe were used. The optimized conditions for the FAAS were obtained at wavelengths of 309.27 nm (for Al), 279.48 nm (for Mn) and 248.3 nm (for Fe). The hollow cathode lamp current was 15 mA (for Al), 10 mA (for Mn) and 30 mA (for Fe) and the gas mixture used was acetylene-nitrous oxide (7.5 and 6 L.min^{-1} for Al), air-acetylene (10 and 2.5 L.min^{-1} for Mn), air-acetylene (10 and 2.5 L.min^{-1} for Fe).

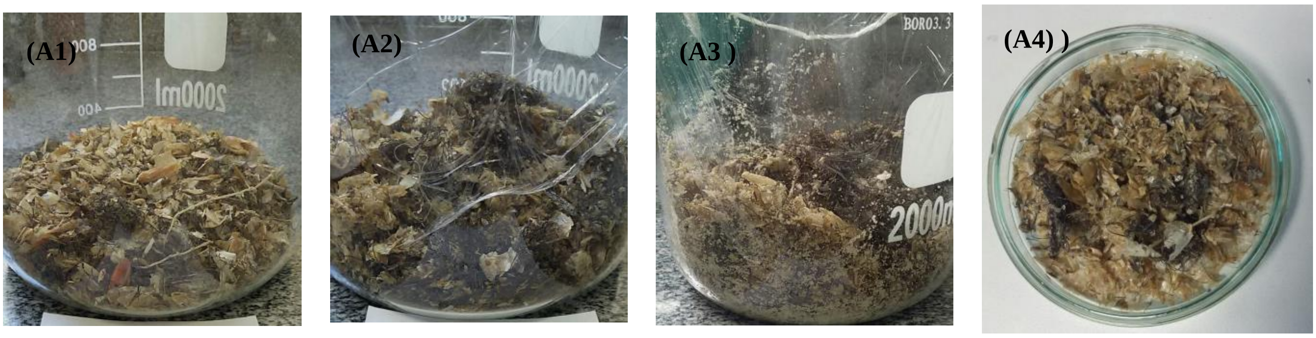

Fig. 1 Saturated SS and MB with and added in three different proportions. (A1) 38g of filter medium with 96g of sand (1:2.5); (A2) 38g of filter medium with 114g of sand (1:3); (A3) 38g of filter medium and 152g of sand (1:4); (A4) 8.87g of filter medium impregnated with mining residues

Figure

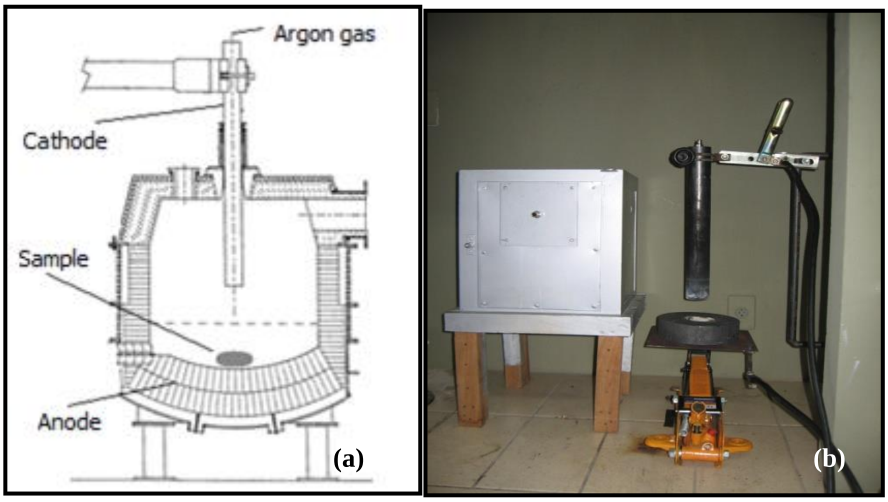

Figura 2: (a) Transferred-arc plasma torch furnace; (b) Plasma furnace and electrodes (placed next to the furnace for better viewing).

3. Results

3.1 Water sources and microcosm test

The mine-impacted water (MIW) samples were initially characterized according to the parameters shown in Table 1.

Table 1 Characteristics of MIW before and after treatment

Parameter	MIW before treatment (mg L^{-1})	MIW after treatment (mg L^{-1})
pH	3.49	8.7
Fe	83.24	6.00
Al	25.00	0
Mn	14.70	10.7
SO_4^{2-}	3630,80	3529.43
Cl^-	226,99	224.73
PO_4^{3-}	51.36	51.34

It can be observed in this table that the sample had high acidity and significant concentrations of metals, particularly Fe. With regard to the environmental problems related to coal mining, the most severe is the pollution of water sources in regions close to the deposits with a high quantity of Fe. The high acidity of the MIW sample is mainly due to the oxidation of pyrite (FeS_2), a very common sulfite mineral in Brazilian coals. Pyrite is oxidized faster and dissociates when exposed to water, releasing Fe2+ in solution (2 FeS2 (s) + 7 O2 (g) + 6 H2O (l) ↔ 2 Fe2+ + 4 SO4 2- + 4 H3O+), which can be oxidized faster to Fe3+ and precipitate as hydroxides (4 Fe2+ + 18 H2O (l) + O2(g) ↔ 4 Fe (OH)3(s) + 8 H3O+). After the first reaction has started, a cycle is initiated where Fe 2+ is oxidized to Fe 3+ (4 Fe 2+ + ½ O2(g) + 2 H3O+ ↔ 4 Fe 3+ + 3 H2O(l)) and, subsequently reduced by pyrite (FeS2 (s) + 14 Fe 3+ + 24H2O(l) ↔ 15 Fe 2+ + 2 SO42- + 16 H3O+), releasing Fe 2+ and additional acidity (ORTIZ, L. *et al*. 2002).

A very rapid pH increase was observed with the applied treatment and around neutral pH was achieved after only two days. The pH continued to increase until it reached a plateau at around pH 8.7 after three days. In the control microcosm, the pH remained unchanged throughout the experiment. Aluminum was completely removed and iron, with an initial concentration of 83.24 mg L-1 in the raw MIW, had a final concentration of 6.0 mg L^{-1}. However, the manganese concentration showed only a slight decrease (10.7 mg L^{-1}), possibly due to the influence of hydroxide precipitation (around pH 8-9). Under the test conditions, the system showed inefficiency in relation to the removal of anions. In this regard, complementary tests need to be carried out.

3.2. Inertization of mining sludge by plasma corona download

The saturated SS and MB samples were submitted to pyrolysis in a thermal plasma reactor. In the plasma process the sample fuses with the sand. During this stage several physicochemical reactions occur, such as the transformation of silica into the liquid phase followed by solidification, forming silicates in the form of a black vitreous material with a high hardness value, with inert and reusable byproducts.

After the pyrolysis, the solid samples were analyzed by SEM/EDS, with image magnifications of 100, 200, 500 and 1000 times. The chemical composition was determined and all of the metals from the mining effluent were retained in the filtered material following the pyrolysis.

A blank sample (A0) comprised only of sand, was analyzed in order to verify the chemical composition of the sand added to the filter medium samples. Table 3 shows the chemical compositions of samples A0, A1 (1:2.5), A2 (1:3), A3 (1:4) and A4 (filter medium only) obtained from the SEM/EDS analysis.

Table 3: SEM/EDS results for the elemental analysis of samples A0 (sand only), A1 (1:2.5), A2 (1:3), A3 (1:4) and A4 (filter medium only) after pyrolysis in the plasma reactor

Elemento	A0 (%)	A1 (%)	A2 (%)	A3 (%)	A4 (%)
C	**14,45**	**15,48**	**20,55**	**13,02**	**49,54**
N	**0,00**	**6,14**	**5,47**	**0,00**	**12,64**
Mg	**0,00**	**0,00**	**0,00**	**0,27**	**0,49**
O	**18,49**	**18,29**	**22,19**	**29,14**	**20,22**
Al	**0,41**	**0,15**	**0,13**	**0,30**	**0,32**
P	**0,00**	**0,00**	**0,00**	**0,00**	**1,77**
Si	**21,57**	**19,16**	**17,91**	**19,58**	**0,00**
Ca	**6,71**	**3,61**	**3,72**	**7,04**	**8,77**
Mn	**0,00**	**0,04**	**0,08**	**0,11**	**0,00**
Fe	**0,00**	**0,53**	**0,40**	**0,28**	**1,11**
Cu	**0,00**	**0,00**	**0,41**	**0,00**	**0,00**
Na	**0,00**	**0,00**	**0,00**	**0,00**	**0,18**
K	**0,00**	**0,00**	**0,00**	**0,00**	**0,20**

The increase in the percentages observed for the elements N, O and Mg could have resulted from the contact of the sample with atmospheric air, interference from the aluminum plates during the analysis, or even from the sand used.

3.3 Determination of leached metals by FAAS

The pyrolyzed samples were submitted to a leaching test (NBR 10005/2004) to verify the inertization efficiency of the plasma. The leached metals were determined by flame atomic absorption spectroscopy as described in the methods section. The concentrations of the metals Fe, Al and Mn, obtained in the leaching tests carried out on the samples after the pyrolysis process, obtained by FAAS are given in Table 4.

Table 4: Metals present in extract of pyrolyzed samples obtained in leaching tests

	Samples					
	A1		A2		A3	
	($mg.L^{-1}$)	efficience (%)	($mg.L^{-1}$)	efficienc (%)	($mg.L^{-1}$)	efficience (%)
Fe	0,13	99,84	0,15	99,82	ND	100
Al	ND	100	ND	100	ND	100
Mn	ND	100	ND	100	ND	100

ND – no detected

The inertization efficiency can be confirmed for aluminum and manganese, since neither of these metals was not detected in the extract, indicating an inertization and incorporation efficiency in the vitreous matrix of 100%. A small quantity Fe was presented in the extract; however, the levels are well below national and international standards of water quantity with concentrations of 0.13 $mg.L^{-1}$ for the sample A1 (99.84% efficiency) and 0.15 $mg.L^{-1}$ for the sample A2 (99.82% efficiency). In the case of the sample with the highest quantity of sand (A3) Fe was not present in the extraction liquid, which confirms that the addition of a greater amount of silica enhances the vitrification of the samples and thus the incorporation of metals.

Therefore, the results obtained verify that thermal plasma inertizes inorganic material and metals are encapsulated in the vitreous matrix.

4. Conclusions

The efficiency of SS and MS in reducing the metal pollution load of effluents, and their neutralization, is significant, although the metals only pass from the liquid to the solid state (adsorption). Based on the results obtained in this study it is possible to verify that the process used for the inertization of the metals present in the samples analyzed was efficient, reaching to 99.8 to 100%. The pyrolysis of biomaterials saturated with metals by thermal plasma leads to the inertization of these metals, allowing them to be returned to the environment in an environmentally safe condition.

References

AWWA – American Water Works Association.Standard Methods for theExaminationofWaterandWastewater. 22 Edition. 2012.

SARMIENTO, A. M., NIETO, J. M., CÁNOVAS, C. R., & OLÍAS, M. La contaminación minera de los ríos Tinto y Odiel. Geología de la provincia de Huelva, 173, 183. 2016.

TRUJILLO, Max Clive Alcántara. Recuperación de suelos de relaves mineros para convertirlos en áreas verdes en la planta piloto metalúrgica de yauris-uncp. Convicciones, v. 2, n. 1, p. 36-43, 2016.

VALENTE, T., GRANDE, J. A., de la TORRE, M. L., GOMES, P., SANTISTEBAN, M., BORREGO, J., & BRAGA, M. S. Mineralogy and geochemistry of a cloggedminingreservoiraffectedbyhistoricalacid mine drainage in anabandonedminingarea. JournalofGeochemicalExploration, 157, 66-76. 2015.

STROSNIDER, W. H., LLANOS, F. S., MARCILLO, C. E., CALLAPA, R. R., & NAIRN, R. W. Impacto en afluentes del río Pilcomayo por contaminantes adicionales de drenaje ácido de minas desde cerro rico, Potosí - Bolivia. Avances en Ciencias e Ingeniería, 5(3) 2014.

TEMPELHOFF, J. W. N., GINSTER, M., MOTLOUNG, S., GOUWS, C. M., & STRAUSS, J. S. The 2012 acid mine drainage (AMD) crisis in Carolina's municipal watersupply. AfricanHistoricalReview, 46(2), 77-107. 2014.

FÁVERE, V. T.; LAUS, R.; LARANJEIRA, M. C.; MARTINS, A. O.; PEDROSA, R. C. Use ofchitosanmicrospheres as remedial material for acidityandiron (III) contentsofcoal mining wastewaters. Environmental Technology, v. 25, 2004.

NÚÑEZ-GÓMEZ, D. Potencial da casca de camarão para remediação de águas contaminadas com drenagem ácida mineral visando seu reuso secundário não potável. Dissertação mestrado. Universidade Federal de Santa Catarina. Florianópolis. 2014.

NÚÑEZ-GÓMEZ, D., NAGEL-HASSEMER, M. E., LAPOLLI, F. & LOBO-RECIO, M. A. Potencial dos resíduos do processamento de camarão para remediação de águas contaminadas com drenagem ácida mineral. Polímeros, 2016. https://dx.doi.org/10.1590/0104-1428.1757.

USEPA – UnitedStatesEnvironmentalProtection Agency. Method 3010A: Aciddigestionofaqueoussamplesandextracts for total metals for analysisby FLAA or ICP spectroscopy. 1992. https://www.epa.gov/sites/production/files/2015-12/documents/3010a.pdf

USEPA – UnitedStatesEnvironmentalProtection Agency. Method 3005A: Aciddigestion of watersforrecoverableordissolvedmetalsforanalysisby FLAA or ICP spectroscopy. 1992. https://www.epa.gov/sites/production/files/2015-12/documents/3005a.pdf.