## Comissão 3.5 - Poluição, remediação do solo e recuperação de áreas degradadas

# USE OF STEEL SLAG TO NEUTRALIZE ACID MINE DRAINAGE (AMD) IN SULFIDIC MATERIAL FROM A URANIUM MINE<sup>(1)</sup>

Camila Marcon de Carvalho Leite<sup>(2)</sup>, Luisa Poyares Cardoso<sup>(3)</sup> & Jaime Wilson Vargas de Mello<sup>(4)</sup>

#### **SUMMARY**

Acid Mine Drainage (AMD) is one of the main environmental impacts caused by mining. Thus, innovative mitigation strategies should be exploited, to neutralize acidity and prevent mobilization of trace elements in AMD. The use of industrial byproducts has been considered an economically and environmentally effective alternative to remediate acid mine drainage. Therefore, the objective of this study was to evaluate the use of steel slag to mitigate acid mine drainage in a sulfidic material from a uranium mine, as an alternative to the use of limestone. Thus, increasing doses of two neutralizing agents were applied to a sulfidic material from the uranium mine Osamu Utsumi in Caldas, Minas Gerais State. A steel slag from the company Arcelor Mittal Tubarão and a commercial limestone were used as neutralizing agents. The experiment was conducted in leaching columns, arranged in a completely randomized, [(2 x 3) + 1] factorial design, consisting of two neutralizing agents, three doses and one control, in three replications, totaling 21 experimental units. Electrical conductivity (EC), pH and the concentrations of Al, As, Ca, Cd, Cu, Fe, Mn, Ni, S, Se, and Zn were evaluated in the leached solutions. The trace element concentration was evaluated by ICP-OES. Furthermore, the CO<sub>2</sub> emission was measured at the top of the leaching columns by capturing in NaOH solution and titration with HCI, in the presence of BaCI<sub>2</sub>. An increase in the pH of the leachate was observed for both neutralizing agents, with slightly higher values for steel slag. The EC was lower at the higher lime dose at an early stage of the experiment, and CO<sub>2</sub> emission was greater with the use of limestone compared to steel slag. A decrease in trace element mobilization in the presence of both neutralizing agents was also observed. Therefore, the results showed that the use of steel slag is a suitable alternative to mitigate AMD, with the advantage of reducing CO<sub>2</sub> emissions to the atmosphere compared to limestone.

Index terms: acid mine waters, trace element mobilization, waste reuse, global warming.

<sup>(1)</sup> Undergraduate research thesis section, required by Environmental Engineering Bachelor's degree. Received for publication on May 23, 2012 and approved on March 7, 2013.

<sup>(2)</sup> Environmental Engineering, Universidade Federal de Viçosa - UFV. E-mail: camilamcleite@gmail.com

<sup>(3)</sup> Environmental Engineering, Universidade Federal de Viçosa - UFV. E-mail: luisa.cardoso@ufv.br

<sup>(4)</sup> Soil Science Department professor, Universidade Federal de Viçosa - UFV. E-mail: jwvmello@ufv.br

### RESUMO: USO DE ESCÓRIA SIDERÚRGICA COMO CORRETIVO DE DRENAGEMÁCIDA DE MINA (DAM) EM MATERIAL SULFETADO DE UMA MINERAÇÃO DE URÂNIO

A Drenagem Ácida de Mina (DAM) destaca-se entre os impactos ambientais decorrentes das atividades mineradoras, sendo necessária a avaliação e inovação de métodos para sua mitigação, via neutralização das águas ácidas e imobilização de metais pesados. O uso de coprodutos industriais na correção de acidez tem se evidenciado alternativa viável e eficaz no âmbito econômico-ambiental. Assim sendo, o objetivo deste trabalho foi avaliar o uso de uma escória de siderurgia como agente neutralizante de drenagem ácida em material de uma mineração de Urânio, em relação a um calcário comercial. Para tanto, aplicaram-se doses crescentes dos dois corretivos em material estéril sulfetado, proveniente de mineração de Urânio da Mina Osamu Utsumi (Caldas, MG). Como corretivos utilizaram-se uma escória siderúrgica da Cia. ArcelorMittal Tubarão e um calcário comercial. O experimento foi conduzido em colunas de lixiviação, dispostas em delineamento inteiramente casualizado, fatorial [(2 x 3) + 1], sendo dois corretivos, três doses e um tratamento testemunha com três repetições, totalizando 21 unidades experimentais. Foram avaliados o pH, a condutividade elétrica (CE) e a concentração de AI, As, Ca, Cd, Cu, Fe, Mn, Ni, S, Se, Zn nas águas lixiviadas. As concentrações dos elementos nos lixiviados foram determinadas por ICP-OES. Além disso, avaliou-se a evolução de CO2 acumulado no topo das colunas de lixiviação, por captura em solução de NaOH e titulometria com HCI, na presença de BaCI2. Verificou-se o aumento do pH dos lixiviados para ambos os corretivos, com valores ligeiramente superiores para a escória. A condutividade elétrica foi tanto menor quanto maior a dose de corretivo aplicada, nos primeiros dias do período experimental; e a evolução de CO2 foi maior nos tratamentos com calcário. A mobilização dos elementos-traco também foi menor com o uso dos corretivos. Portanto, os resultados sugerem que o uso da escória é alternativa ambientalmente viável para a correção da DAM, com a vantagem de promover menor evolução de CO₂ para a atmosfera em relação ao calcário.

Termos de indexação: águas ácidas de mina, mobilização de elementos-traço, reutilização de resíduos, aquecimento global.

#### INTRODUCTION

Mining plays an important role in the social and economic context in Brazil, particularly in the state of Minas Gerais. In spite of generating jobs and income, this activity is associated to several types of environmental impacts, including: noise generation, water contamination and atmospheric pollution.

Acid mine drainage (AMD) is a result of the inevitable wastewater production of the mining industry. It is characterized by strong acidity and significant levels of metal and other ions in the water, especially iron and sulfate (Pérez-López et al., 2010). This is a common problem in mining operations associated to sulfide minerals, particularly pyrite (FeS<sub>2</sub>), which, upon exposure to water and oxygen, oxidizes, generating acidic products that are dissolved in drainage waters. Decreases in pH promote the solubilization of heavy metals and metalloids that contaminate water. AMD can be remediated with active or passive techniques (Kalin et al., 2006), of which the passive treatment is more common. Most AMD treatment systems involve the use of neutralizing agents to increase pH and promote metal precipitation (Younger et al., 2003). The most common methods to ensure an economically viable neutralization are based on the use of limestone and precipitation under oxidizing conditions (Matlock et al., 2002). Despite the relevance of this subject, little research has been done on its environmental impact.

The use of limestone to remediate acid drainage is based on the neutralizing effect of Ca or Mg carbonates. In addition to its effect, calcium carbonate can interfere in the kinetics of pyrite oxidation, and even inhibit this oxidation (Caruccio & Geidel, 1996). Evangelou (1995) demonstrated that iron hydroxides may precipitate on the surface of pyrite crystals, decreasing the oxidation kinetics. In Brazil, Soares et al. (2006) evaluated the effect of carbonates on acid drainage, reporting neutralization and decreased metal mobilization in AMD from coal mine overburden.

Despite the high efficiency of limestone in AMD remediation, its use on a large scale implies high economic and environmental costs, since it is considered a "resource" rather than a "residue" (Pérez-López et al., 2010). Moreover, the use of limestone is associated to  $\rm CO_2$  emission to the atmosphere. Most of the world's carbon (C) source is stored in limestone basins (Teixeira et al., 2009). In the last decades, greenhouse gas emissions have dramatically increased, inducing an intensified search for alternative neutralizing agents and other methods of AMD mitigation that reduce  $\rm CO_2$  emissions to the atmosphere.

The steel industry produces great amounts of slag (Geyer, 2001), which is a byproduct resulting from several eliminated chemicals whose presence in steel is undesirable. After cooling, processing and quality control of the siderurgical residue, the steel slag is classified and can be used in soil remediation and fertilization (CCA Brasil, 2010). Some constituents of the slag, e.g.,  ${\rm SiO_3}^{2-}$  and CaO, can neutralize acidity (Alcarde & Rodella, 2003), of which silicic acid is environmentally less harmful than carbonic acid. Consequently, steel slag can be a suitable alternative to the neutralizing agent limestone for the neutralization of acid mine drainage.

According to *Instituto Aço Brasil* (2013), the crude steel production in Brazil was approximately 35.1 million tons in 2011, generating 19.2 million tons of byproducts. Of these, 60 % are slags, according to data published in the *Relatório de Sustentabilidade* de 2012 do *Instituto Aço Brasil* (2012). The reuse of this byproduct to mitigate AMD may be a successful alternative and a proper way of disposal, reducing the need for storage of this huge amount of slag.

Therefore, the objective of this study was to evaluate steel slag as an alternative neutralizing agent of acid mine drainage from a sulfidic sterile from a uranium mine in comparison with a commercial limestone.

#### MATERIAL AND METHODS

Samples of waste material from a uranium mine were collected from a waste pile (Bota-Fora 4) of the Osamu Utsumi mine, in the city of Caldas, at Planalto de Poços de Caldas, Minas Gerais. The neutralizing potential (NP) and acidification potential (AP) were analyzed according to the method described by Lawrence & Wang (1997) and by O'Shay et al. (1990), respectively. The capacity of generating acid drainage from the waste material was calculated by the acid-base balance (ABB = AP - NP). The chemical characterization of the waste material is shown in table 1, according to analyses performed by Abrahão (2002).

A slag sample from the company ArcelorMittal Tubarão, in Vitória, State of Espírito Santo, and a commercial limestone were both used as neutralizing materials. The neutralizing potential (NP) by the method described by Lawrence & Wang (1997) and the relative efficiency (RE) according to Embrapa (1999) were assessed for both slag and limestone. Based on NP and RE values, the total relative neutralizing potential (TRNP) was calculated to assess the quality of the neutralizing agents. Also, the CaO and MgO contents in the limestone were determined. The chemical analysis of slag (Table 2) was performed as described by Corrêa (2006).

The experiment was conducted in PVC leaching columns (diameter 0.0254 m, length 0.35 m) arranged

in a completely randomized design, in a factorial scheme  $[(2 \times 3) + 1]$ , with two neutralizing agents, three doses and one control, in three replications, with a total of 21 experimental units.

Of the waste material from mining, 74 g were filled in the leaching columns and mixed with three doses of the neutralizing agents, corresponding to 40, 80 and 120 % of the dose required to neutralize acid drainage, considering the ABB of the waste material, named C-40; C-80 and C-120 for limestone and E-40; E-80 and E-120 for steel slag. Moreover, a control column, named T-0, containing only waste material, without neutralizing agent, was used.

The columns were sealed and distilled water was periodically added (during the leaching cycle), simulating the annual average rainfall (1,695.5 mm) in the region of Poços de Caldas (MG), according to ANA (2009). The total amount of water applied to the columns was twice the average annual rainfall.

The leached solutions were collected from the bottom of the columns, and an aliquot from each leachate sample was used for chemical analysis of EC and pH. Another aliquot of the leachate was acidified with HNO $_3$  50 % (v/v) and stored for analysis of AI, As, Ca, Cd, Cu, Fe, Mn, Ni, S, Se, Zn by ICP-OES (Perkin Elmer, Optima 3300 DV). The amounts of CO $_2$ emitted from the columns were assessed by capturing the gas in NaOH solution, followed by titration with HCI solution in the presence of BaCI $_2$ , according to the modified method of Curl & Rodriguez-Kabana (1972) and Stotzky (1965). The flasks containing NaOH to capture CO $_2$  were fixed in the top of the columns, which were sealed after each leaching.

The experiment was conducted for 262 days, at controlled temperature ( $24\pm1\,^{\circ}$ C). Analysis of variance for accumulated CO<sub>2</sub> emissions was performed using Statistica 7.0 software. The EC values, pH and trace element concentrarion were expressed as average values of the different treatments with their standard errors.

#### **RESULTS AND DISCUSSIONS**

The values of neutralizing potential (NP), acidification potential (AP) and acid-base balance (ABB) indicated that the waste material from uranium mining is a potential AMD generator (Table 3).

Both neutralizing agents were found to be suitable for AMD remediation (Table 4). The NP values are within the limits for commercialization of liming materials, according to the current legislation. The relative efficiency (RE) of both neutralizing agents was also high, suggesting a relatively fast reaction when in contact with acid water.

Statistical analysis suggested that the CO<sub>2</sub> emissions accumulated in the experimental period

Table 1. Chemical characterization of the waste material from a uranium mine

pH <sup>(1)</sup>	S - p <sup>(2)</sup>	S - s <sup>(3)</sup>	C <sup>(4)</sup>	P.F. <sup>(5)</sup>	Si	ΑI	Fe <sub>total</sub>	FeIII	Ca	Mg
					_ dag kg <sup>-1</sup> _					
3.72	1.13	1.95	0.06	3.45	26.15	11.69	2.10	1.92	0.03	0.05
Na	K	Ti	Mn	Cu	Zn	Ni	Pb	As	Cd	S + m <sup>(6)</sup>
				m(	g kg <del>-1</del>					– dag kg <sup>-1</sup>
0.10	11.40	0.30	0.00	34.68	45.00	58.77	50.00	19.03	4.99	1.67
SiO <sub>2</sub>	$Al_2O_3$	$Fe_2O_3$	FeO	CaO	MgO	$TiO_2$	MnO	$CO_2$	Na <sub>2</sub> O	$K_2O$
					– dag kg <sup>-1</sup>					
56.04	22.08	2.74	0.23	0.05	0.08	0.5	0.01	0.23	0.13	13.74

<sup>&</sup>lt;sup>(1)</sup>pH measured in waste material of an uranium mine (substrate:water ratio 1:25, volume); <sup>(2)</sup>S - pyrite: S inferred by the production of titratable acidity. Digestion with  $H_2O_2$  30 % (O'Shay et al., 1990); <sup>(3)</sup>S - sulfide: S determined by concentrated aqua regia digestion (Corrêa, 2000); <sup>(4)</sup> C determined after melting at 1000 °C - LECO; <sup>(5)</sup> Loss by ignition; <sup>(6)</sup>S + metals. Source: Abrahão (2002).

Table 2. Chemical analyses of steel slag sample from the company Arcelor Mittal

			Continu	uous casting p	orocess			
CaO	MgO	Fe	Mn	Cr	Ni	Zn	Cu	Cd
	———dag	kg <sup>-1</sup>				— mg kg <sup>-1</sup> —		
42.19	8.09	14.12	1.20	327.59	12.05	32.12	20.20	n.d.

Source: Corrêa (2006).

Table 3. Neutralization potential (NP), acidification potential (AP) and acid-base balance (ABB) of the waste material from uranium mine

NP	AP	ABB
mmol g <sup>-1</sup> OH <sup>-</sup>	——— mmol g	<sup>-1</sup> H <sup>+</sup>
0.04	0.84	0.80

were influenced by the use of the neutralizing agents. The differences between the neutralizing agents and interaction between doses and neutralizing agents were significant at 95 % probability (Table 5). It was observed that the use of steel slag reduces  $CO_2$  emission compared to limestone (Figure 1). This was probably a result of the decomposition of the bicarbonate formed as a product of acidity neutralization from calcium carbonate. On the other hand, in the steel slag treatment, neutralization occurs by the use of silicates, so the accumulated  $CO_2$  values were lower.

In general, the emission of  $CO_2$  was more pronounced during the first 50 days in all treatments, but the rate of  $C-CO_2$  emission was lower in treatments with slag throughout the experimental period (Figure 2). This lower  $CO_2$  emission from the slag treatment must not necessarily be ascribed to toxic effects on living organisms, since the slag was classified as non-dangerous Class II waste, according to ABNT NBR 10.004 (Corrêa, 2006). Therefore, the

toxic effect of waste material from uranium mining on microorganisms can be disregarded, since the emission of  $CO_2$  in the control treatment was slightly higher than in the steel slag treatment and lower than in the limestone treatment.

The electrical conductivity (EC) values in the leachates decreased over time, reaching a minimum value of around 0.5 mS cm<sup>-1</sup> for all samples (Figure 3). On average, the higher the doses of the neutralizing agent, the lower the electrical conductivity, at the early stages of the experiment. This can be caused by the marked increase in pH (Figure 4) in this same time interval, which lowers the solubility and, consequently, the ion mobility, particularly in metals. These results indicate that the use of both neutralizing agents decreased ion leaching, promoting a satisfactory control of acid drainage and contamination of water resources. A similar behavior was reported by Pérez-López et al. (2010), in a study where alkaline waste from a paper mill was used as AMD neutralizer. According to the authors, EC values decreased from 8.0 to 2.2 and 3.6 mS cm<sup>-1</sup>, in treatments with slurry of calcium and calcite powder, respectively, contributing to the quality of drainage water, later confirmed by a reduced sulfate concentration in the solution.

The pH in the leachate increased for both neutralizing agents, particularly in the first 12 days of the experiment, ranging from 2.8 to 4.1 in the control, from 4.2 to 9.0 in the slag and from 4.1 to 7.9

Table 4. Neutralization Potential (NP), Relative Efficiency (RE) and Total Relative Neutralization Potential (TRNP) of limestone and steel slag

	NP	RE	TRNP	CaO	MgO	Ca	Mg	Classification
		%		-	——— dag k	.g-1 ———		
Limestone	82.5	98.3	81.1	30.9	9.5	22.1	5.7	Magnesian
Slag	58.2	93.1	54.6	-	-	-	-	-

Classification according to CFSEMG - 5th Approximation. (1999, p.58)

Table 5. Analysis of variance of C-CO<sub>2</sub> emission from waste material treated with limestone or steel slag, accumulated in 262 days

Source of variance	Degree of freedom	Mean square	p-Value
Neutralizing agent	1	2817.4	0
Dose	3	16.16	0.563876
Neutralizing agent x Dose	3	388.74	0.000032
Residual error	16	22.99	
CV (%)	43		

p-Value: critical value of F (significant > 0.05) and CV: Coefficient of variation.

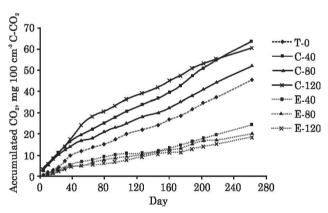


Figure 1. Accumulated  $CO_2$  emission from columns treated with increasing doses of limestone and steel slag for 262 days.

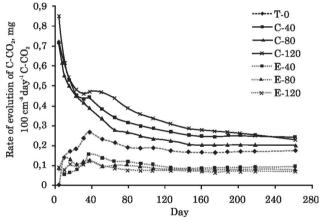


Figure 2. Rate of  $CO_2$  emission, from columns treated with increasing doses of limestone and steel slag, during 262 days.

in the limestone treatment (Figure 4). The values obtained in the control treatment corroborated the results of Castro et al. (2006), who evaluated the concentration of ions dissolved in acid drainage from the same waste pile (BF4) of the Osamu Utsumi mine. According to these authors, the pH of the drainage water is approximately 3.5; a repetition of this value in the leachate analysis may suggest a stabilization of the drainage acidity. In this study, the pH was lower at the beginning of the experimental period, with increasing differences between the control and the other treatments. This can be explained by the acidity released by the waste material, which exceeded the alkalinity released by alkaline additives in the beginning of the experiment.

The concentrations of Ca, Fe, S, Al and Mn in the leachates were higher than of other elements (Table 6). The mobility of Ca increased with the limestone doses, which was expected, as this element is a major constituent of the neutralizing agents applied to the columns. On the other hand, there was no significant increase in Ca mobility as the slag doses increased. The mobility of Fe and S can be ascribed to the oxidation of pyrite and our results clearly showed the effect of increasing pH on Fe mobility. High levels of sulfur (S) were detected in the leachates from the control columns, reflecting the sulfide oxidation in the waste material. Apparently, the use of limestone stimulates sulfide oxidation at the lower applied dose, whereas no relation was observed between limestone

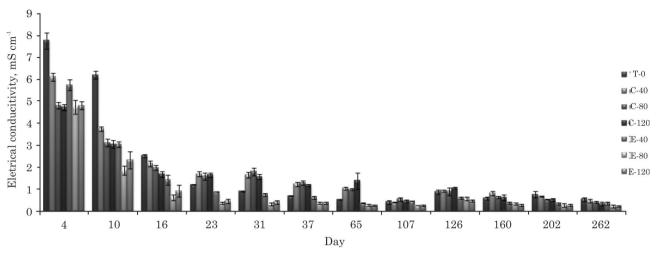


Figure 3. Average values and their respective standard errors of Electrical Conductivity of leachates from leaching columns treated with increasing limestone and steel slag doses, for 262 days.

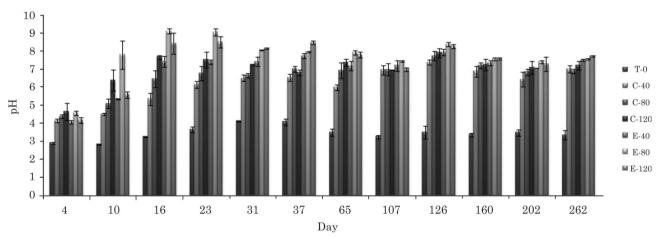


Figure 4. Average values with the respective standard errors of pH of leachates from leaching columns treated with increasing doses of limestone and steel slag doses for 262 days.

doses and sulfate leaching. On the other hand, higher slag doses decreased the movement of S, suggesting that in this case, increasing the pH was sufficient to directly affect the oxidation process. These results can be ascribed to the formation of geochemical barriers due to the precipitation of iron hydroxides on the surface of the sulfides in the sterile. This hypothesis is reinforced by the fact that the Fe movement was more limited by increasing doses of steel slag than of limestone. The mobility of Fe was increasingly limited with increasing doses of both neutralizing agents, indicating the precipitation of this metal in the columns. According to Castro et al. (2006), the hydrogeochemistry of AMD is usually characterized by high iron and sulfate concentrations, induced by pyrite oxidation and the dissolution of the existing minerals. Matlock et al. (2002) also reported high Fe contents in water samples collected from coal mine drainage. High sulfate concentrations have also been reported in AMD studies, and according to Younger (1997), soluble sulfate can be used to assess the duration of acid drainage.

Aluminum (Al) mobilization from leaching columns was also high, except at the highest doses of neutralizing agents. This result can be ascribed to the geological nature of the waste material, since the local geology of the uranium mine is dominated by alkaline volcanic rocks, therefore subsaturated in silica and rich in Al. Both neutralizing agents proved to be effective in precipitating Al in the column, controlling its mobility at doses with ABB of more than 80 %.

The use of both neutralizing agents also decreased Mn, Zn and Cu concentrations in the leaching solutions. The contents of copper were generally lower than the detection limit in the columns treated with limestone or steel slag. This is in agreement with several studies on mobility and availability of Cu in soils of Sodré et al. (2001). Copper has been considered the least mobile micronutrient in soil and its

Table 6. Average contents of AI, As, Ca, Cd, Cu, Fe, Mn, Ni, S, Se and Zn leached in 262 days, from columns treated with increasing doses of limestone or steel slag, followed by their respective standard errors

Material	AI	As	Ca	Cd	Cu	Fe
			mg/co	olumn ————		
T-0	10.00 ± (1.18)	$0.04 \pm (0.007)$	12.26 ± (1.47)	< 0.002 <sup>(1)</sup>	$0.043 \pm (0.001)$	17.66 ± (0.96)
C-40	$3.47 \pm (0,.67)$	0.07 ± (0.055)	39.99 ± (2.92)	< 0.002	< 0.004	8.93 ± (1.89)
C-80	$2.18 \pm (0.71)$	$0.03 \pm (0.025)$	41.15 ± (1.28)	$0.003 \pm (0.002)$	$0.004 \pm (0.003)$	$7.04 \pm (0.19)$
C-120	$0.86 \pm (0.19)$	< 0.02	44.62 ± (4.93)	< 0.002	< 0.004	$4.29 \pm (0.71)$
E-40	$2.71 \pm (0.37)$	$0.03 \pm (0.010)$	23.17 ± (2.02)	< 0.002	$0.007 \pm (0.003)$	12.64 ± (3.67)
E-80	$2.38 \pm (0.49)$	$0.03 \pm (0.013)$	13.14 ± (1.93)	< 0.002	< 0.004	$5.10 \pm (0.70)$
E-120	$0.84 \pm (0.15)$	< 0.02	16.92 ± (1.58)	< 0.002	< 0.004	1.26 ± (0.27)
	Mn	Ni	S	Se	Zn	
			— mg/column —			-
T-0	$4.74 \pm (0.27)$	$0.006 \pm (0.001)$	14.86 ± (1.08)	$0.287 \pm (0.026)$	$0.85 \pm (0.033)$	
C-40	$3.55 \pm (0.52)$	$0.011 \pm (0.005)$	20.91 ± (1.30)	$0.242 \pm (0.009)$	$0.41 \pm (0.075)$	
C-80	$3.19 \pm (0.49)$	$0.014 \pm (0.010)$	17.68 ± (0.71)	$0.316 \pm (0.077)$	$0.32 \pm (0.053)$	
C-120	2.11 ± (0.02)	$0.013 \pm (0.006)$	18.86 ± (1.85)	$0.303 \pm (0.037)$	$0.16 \pm (0.028)$	
E-40	$2.44 \pm (0.62)$	$0.013 \pm (0.001)$	14.18 ± (2.98)	$0.171 \pm (0.035)$	$0.40 \pm (0.118)$	
E-80	1.16 ± (0.19)	< 0.005	$5.82 \pm (0.45)$	$0.153 \pm (0.020)$	$0.17 \pm (0.021)$	
E-120	$0.86 \pm (0.32)$	< 0.005	$5.52 \pm (0.52)$	$0.142 \pm (0.011)$	$0.06 \pm (0.026)$	

<sup>(1)</sup> Values after < refer to the quantitation limit.

availability decreases as the pH increases. Copper is likely to form hydroxides that precipitate when pH is above 7.0 and its mobility is also controlled by organic and inorganic ligands (Kabata-Pendias & Pendias, 1992). Manganese (Mn) and zinc (Zn) mobility in the leaching solutions were also controlled by limestone and slag, but in these cases, only the highest slag dose was effective to minimize their mobilization.

Although the concentrations of selenium (Se) in the leachates were not very high, the use of steel slag as only neutralizing agent was effective to control the mobility of this element. Studies by Soares et. al. (2001) indicated that high doses of calcium silicates decrease Zn levels below the critical toxicity values in nutrient solution. Cunha et al. (2008) observed that the use of calcium silicate favored the immobilization of Zn and Cd in soil contaminated by these elements, decreasing their availability to plants. However, the use of calcium carbonate confirmed that increasing the pH decreases the mobility of this metal, as already known for the chemical solubility equilibria involving metals in general (Lindsay, 1979).

Arsenic (As) mobility was not affected by the use of limestone or steel slag. The same behavior was observed for nickel (Ni), but the concentration of this element was below the detection limit of the ICP-OES spectrometer at the highest slag rates. According to Abrahão (2002), the levels of As detected in the samples of waste material from uranium mining are below the critical values of toxicity, but the soluble concentrations found in the leaching solutions can be considered high, except in the treatments with the highest doses of limestone and steel slag.

#### CONCLUSIONS

- 1. The use of both, limestone and steel slag, mixed with a waste material from uranium mine, effectively neutralized acid mine drainage. However, the  $\rm CO_2$  emissions from limestone-treated materials were greater than in the steel slag treatments.
- 2. The electrical conductivity of the leaching solutions decreased over time and with increasing doses of neutralizing agents, suggesting an effective control of ion mobility in the drainage.
- 3. Lower mobility of potentially toxic elements in leaching columns was observed after the use of neutralizing agents.
- 4. The use of steel slag is a suitable alternative to the use of limestone to mitigate AMD, with the advantage of reducing  $\mathrm{CO}_2$  emission to the atmosphere. Moreover, steel slag is efficient in the formation of a geochemical barrier, observed by the reduced mobility of Fe, S and trace elements in the leachates.

#### LITERATURE CITED

AGÊNCIA NACIONAL DAS ÁGUAS - ANA. Hidroweb, dados hidrológicos. Available at <a href="http://hidroweb.ana.gov.br/">http://hidroweb.ana.gov.br/</a>. Accessed: 01 Feb. 2009.

ABRAHÃO, W.A.P. Aspectos químicos e mineralógicos relacionados à geração experimental de drenagem ácida em geomateriais sulfetados. Viçosa, MG, Universidade Federal de Viçosa, 2002. 125p. (Tese de Doutorado)

- ALCARDE, J.C. & RODELLA, A.A. Qualidade e legislação de fertilizantes e corretivos. In: CURI, N.; MARQUES, J.J.; GUILHERME, L.R.G.; LIMA, J.M.; LOPES, A. S. & ALVAREZ V., V.H., eds. Tópicos em ciência do solo. Viçosa, MG, Sociedade Brasileira de Ciência do Solo, 2003. v.3, p.291-334.
- CARUCCIO, F.T. & GEIDEL, G. Acid mine drainage, DTHE laboratory and Fields settings. Knoxville, American Society for Surface Mining and Reclamation, 1996. 58p.
- CASTRO, E.; LOUREIRO, C.& VETTORI, L. Comportamento da concentração de espécies dissolvidas em drenagem ácida. In: CONGRESSO BRASILEIRO DE ÁGUAS SUBTERRÂNEAS, 14., São Paulo, 2006. Anais... São Paulo, Associação Brasileira de Águas Subterrâneas, 2006.
- CENTRO DE COPRODUTOS AÇO BRASIL CCA Brasil. Available at: <a href="http://www.ccabrasil.org.br/">http://www.ccabrasil.org.br/</a> Coproduto\_Coprodutos.asp>. Accessed: 21 Jan. 2013.
- CORRÊA, M.L.T. Utilização de escória de aciaria como corretivo da acidez de solos para cultivos de soja e cana-de-açúcar e avaliação da contaminação ambiental. Viçosa, MG, Universidade Federal de Viçosa, 2006. 165 p. (Tese de Doutorado)
- CUNHA, K.P.V.; NASCIMENTO, C.W.A.N.; PIMENTEL, R.M.M.; ACCIOLY, M.A. & SILVA, A.J. Disponibilidade, acúmulo e toxidez de cádmio e zinco em milho cultivado em solo contaminado. R. Bras. Ci. Solo, 32:1319-1328, 2008.
- CURL, E.A. & RODRIGUEZ-KABANA, R. Microbial interactions. In: WILKINSON, R.E., ed. Research methods in weed science. Atlanta, Southern Weed Science Society, 1972. p.162-194.
- EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA EMBRAPA. Centro Nacional de Pesquisa de Solos. Sistema brasileiro de classificação de solos. Brasília, SPI/CNPS, 1999. 412p.
- EVANGELOU, V.P. Pyrite oxidation and its control. Boca Raton, CRC Press, 1995. 293p.
- GEYER, R.M.T. Estudo sobre a potencialidade de uso das escórias de aciaria como adição ao concreto. Porto Alegre, PPGEM/UFRGS, 2001. 190 p. (Tese de Doutorado)
- INSTITUTO AÇO BRASIL Números de Mercado Estatísticas. Available at: <a href="http://www.acobrasil.org.br/site/portugues/numeros/estatisticas.asp">http://www.acobrasil.org.br/site/portugues/numeros/estatisticas.asp</a>>. Accessed: 21 Jan. 2013.
- INSTITUTO AÇO BRASIL Relatório de Sustentabilidade de 2012. Available at: <a href="http://www.acobrasil.org.br/site/">http://www.acobrasil.org.br/site/</a>
  portugues/sustentabilidade\_2012.pdf>. Accessed: 21 Jan. 2013.
- KABATA-PENDIAS, A. & PENDIAS, H. Trace elements in soils and plants. 2.ed. Boca Raton, CRC Press, 1992. 365p.

- KALIN, M.; FYSON, A. & WHEELER, W.N. The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage. Sci. Total Environ., 366:395-408, 2006.
- LAWRENCE, R.W. & WANG, Y. Determination of neutralization potential in the prediction of acid rock drainage. In: INTERNATION CONFERENCE ACID ROCK DRAINAGE, 4., Ottawa, 1997. Procedings... Ottawa, MEND Natural Resources Canada, 1997. p.451-464
- LINDSAY, W.L. Chemical equilibria in soils. New York: Wiley-Interscience, 1979. 449p.
- MATLOCK, M.M.; HOWERTON, B.S. & ATWOOD, D.A. Chemical precipitation of heavy metals from acid mine drainage. Water Res., 36:4757-4764, 2002.
- O'SHAY, T.; HOSSNER, L.R. & DIXON, J.B. A modified hydrogen peroxide oxidation method for determination of potential acidity in pyritic overburden. J. Environ. Qual., 19:778, 1990.
- PÉREZ-LÓPEZ, R.; CASTILLO, J.; QUISPE, D. & MIGUEL, J.N. Neutralization of acid mine drainage using the final product from CO<sub>2</sub> emissions capture with alkaline paper mill waste. J. Hazard. Mat., 117:762-772, 2010.
- SODRÉ, F.F.; LENZI, E. & COSTA, A.C. Utilização de modelos físico-químicos de adsorção no estudo do comportamento do cobre em solos argilosos. Quím. Nova, 24:324-330, 2001.
- SOARES, C.R.F.S.; GRAZZIOTTI, P.H.; SIQUEIRA, J.O.; CARVALHO, J.G. & MOREIRA, F.M.S. Toxidez no crescimento e nutrição de *Eucalyptus maculata* e *Eucalyptus urophylla* em solução nutritiva. Pesq. Agropec. Bras., 36:339-348, 2001.
- SOARES, E.R.; MELLO, J.W.V.; SCHAEFER, C.E.G.R. & COSTA, L.M. Cinza e carbonato de cálcio na mitigação de drenagem ácida de mineração de carvão. R. Bras. Ci. Solo, 30:171-181, 2006.
- STOTZKY, G. Microbial respiration. In: BLACK, C.A., ed. Methods of soil analysis. Madison, American Society of Agronomy, 1965. p.1551-1572.
- TEIXEIRA, W.; TAIOLI, F. & FAIRCHILD, T. Decifrando a Terra. 2.ed. São Paulo, 2009. 623p.
- YOUNGER, P.L. The longevity of minewater pollution: A basis for decision-making. Sci. Total Environ., 194/195: 451-466, 1997.
- YOUNGER, P.L.; JAYAWEERA, A.; ELLIOT, A.; WOOD, R.; AMOS, P.; DAUGHERTY, A.J.; MARTIN, A.; BOWDEN, L.; APLIN, A.C. & JOHNSON, D.B. Passive treatment of acidic mine waters in subsurface flow systems: Exploring RAPS and permeable reactive barriers. Land Contam. Reclam., 11:127-135, 2003.