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Marble waste as attenuator of acidic effluent

Resíduo de mármore como atenuador de efluente ácido

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Abstract

Dimension stones are worldwide used as building and finishing material, reason why the environmental problems inherent to this productive sector became relevant in various countries. One of these problems is the production of large amounts of wastes during the sawing of rocky blocks and polishing of plates. The waste generated by cutting marble with diamond wire consists of fine particles of calcium and magnesium carbonate dispersed in water. This mud has basic character, and it is destined to drying beds or open pit deposits. In parallel, many production processes generate hazardous acidic effluents, which disposal is a serious and global problem. The pH of these solutions must be neutralized or, at least, raised to levels that are considered safe by environmental regulations. In this work, a strong acid solution was treated with varying amounts of marble waste coming from the dimension stone industry. The treatment generated secondary solid and liquid phases that were analyzed to determine the feasibility of their disposal in landfills. The waste raised the pH of the acid solution from near 1.0 to values between 5.0 and 6.0, which are acceptable levels for non-dangerous effluents. Besides that, loss of up to 50% in mass occurred, diminishing the amount of the primary solid waste. By the other hand, the levels of total dissolved solids (TDS), Cu, chlorides and nitrates on the liquid phase of the effluent remained higher than that allowed by environmental legislation for discharge into water bodies. Nevertheless, their characteristics correspond to non-hazardous and non-inert wastes, which, after dried, can be discarded in ordinary waste landfills.

Keywords: Dimension stone; Acidic effluents; Waste treatment.

Resumo

As rochas ornamentais são utilizadas mundialmente como material de construção e acabamento, razão pela qual os problemas inerentes a esse setor produtivo se tornaram relevantes em vários países. Um desses problemas é a geração de grandes quantidades de resíduos durante a serragem de blocos rochosos e na etapa de polimento de chapas. O resíduo gerado pela serragem de mármores com tear de fio diamantado consiste de finas partículas de carbonato de cálcio e magnésio dispersas em água. Essa lama tem caráter básico e é destinada a lagoas de decantação ou depósitos a céu aberto. Paralelamente, muitos processos produtivos geram efluentes ácidos perigosos, cuja disposição constitui um sério problema mundial. O pH dessas soluções deve ser neutralizado ou, pelo menos, elevado a níveis considerados seguros pela regulamentação ambiental. Neste trabalho, uma solução ácida forte foi tratada com quantidades variáveis de resíduo de mármore proveniente da indústria de rochas ornamentais. O tratamento gerou fases secundárias sólida e líquida que foram analisadas para determinar a viabilidade de sua disposição em aterro. O resíduo aumentou o pH da solução ácida de próximo a 1,0 para valores entre 5,0 e 6,0, que são níveis aceitáveis para efluentes não perigosos, além de ter promovido a perda de massa em até 50%, diminuindo a quantidade de resíduo sólido primário. Em contrapartida, os níveis de sólidos totais dissolvidos, cobre, cloretos e nitratos na fase líquida do efluente permaneceram acima do permitido para lançamento em corpos d'água, contudo suas características correspondem a resíduos classificados como não perigosos e não inertes, que após secagem podem ser descartados em aterro comum de resíduos.

Palavras-chave: Rocha ornamental; Efluentes ácidos; Tratamento de resíduos.

INTRODUCTION

One of the main problems of the marble industry is the production of large quantities of very fine-grained wastes in the form of mud, generated when the stone blocks are sawed into plates to produce claddings. The waste produced by cutting marble with diamond wire is composed only by rock dust and water, which has a promising potential for application in other industrial sectors. The proportion of fine particles produced by cutting 1 m^3 of marble block is about 25% (Çelik and Sabah, 2008). In Brazil, the production of stone cutting waste tends to be higher and may comprise about 1/3 in dry weight or 2/3 in wet weight of the block (Braga et al., 2010). In addition to the large amounts, the pH of these wastes is generally high (pH-values between 9.1 and 11.2, according to Neves et al., 2013), in consequence of the lime used during sawing, which can represent environmental risks.

Various researchers have tested the use of dimension stone wastes for manufacturing ceramic products (Taguchi et al., 2014; Reis et al., 2015; Prado et al., 2012), concrete (Bacarji et al., 2013), vitreous material (Scarinci et al., 2000), and for treatment of acid mine drainage (Barros et al., 2009). Marble dust was also tested as corrective of natural soil acidity (Tozsin et al., 2014, 2015; Raymundo et al., 2013), in place of the lime (CaO) that is traditionally used for. The liming material reacts with carbon dioxide and water to yield HCO_3, which raises the pH of soils and removes the H^+ and Al^{3+} from the solution (Safari and Bidhendi, 2007). Other studies focused the use of marble waste in techniques for remediating contaminated areas (Zornoza et al., 2013; Kabas et al., 2012; Zanuzzi et al., 2009). In soils and sediments contaminated by mining, the use of marble dust effectively immobilized the free phases (Pérez-Sirvent et al., 2007), precipitating toxic metals such as Al, As, Cu, Pb, Zn and Cd (Fernández-Caliani and Barba-Brioso, 2010).

On the other hand, various industrial processes, and even some simple activities such as laboratorial analysis, generate acidic effluents that are dangerous due to their corrosivity. Some examples are the mining (Campaner et al., 2014) and fertilizer industry (Al-Harahsheh et al., 2014), which produce corrosive solutions highly concentrated in potentially toxic elements. Neutralization is a common practice for treating hazardous wastes, and, if they are corrosive, this is the primary step for the treatment (Goel et al., 2005).

Various works were conducted aiming to purpose or improve methods for treating acidic effluents. The techniques involve the use of bacteria and bioreactors (Nancucheo et al., 2017; Neculita et al., 2007), applying of chemical reagents (Peng et al., 2018; Jaiswal et al., 2015) or minerals such as zeolite (Motsi et al., 2009; Jimenez et al., 2004) and bentonite (Gitari, 2014). Some authors also described the natural attenuation as a strategy possible for managing these dangerous effluents (Torres et al., 2011; España et al., 2005).

Petruzzelli et al. (2009) tested the use of marble waste for neutralizing acidic wastewater from the glass industry containing hydrogen fluoride (HF). They confirmed that mass transfer phenomena control the neutralization rates, but concluded that the marble waste is not proper for neutralizing HF solutions due to the diffusional resistance for migration of ions in and out the stationary liquid-film around the particle. Their experiments showed that the increase of the solid-to-liquid exposed surface area, associated with the smaller particle size, is important to fast neutralization kinetics.

Barros et al. (2009) used marble wastes as chemical adjutant for the biologic treatment of acid mine drainage, using column experiments. Their results showed that these wastes provide adequate conditions for removing metals and sulphates from the acid mine drainage, generating water suitable for irrigation with low cost. According to these authors, when in contact with acidic solutions (pH of about 2.5), the marble dust reacts as it follows, in Equations 1 and 2:

$$CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2H_2O + 2CO_2 \qquad (1)$$

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2 \qquad (2)$$

When the pH is between 4.3 and 8.2, the reaction becomes as it is expressed in Equation 3:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (3)$$

The purpose of our study was to test the use of pure marble waste, without adjutants, to neutralize stronger acidic solutions with pH-values near 1.0, similar to the extremely acidic mine waters described by Nordstrom et al. (2000).

The rock wastes are, actually, an important environmental liability of the dimension stone industry. If properly managed and used, they can become a source of income, since the costs for reclaiming them are very low. The great advantage is to use waste to treat waste, minimizing the quantities of discarded material.

MATERIALS AND METHODS

The waste used in the experiment is marble dust supplied by a company located in the state of Espírito Santo, southeast Brazil, which cuts marble using looms with diamond wire. The composition of this kind of waste is practically identical to that of the sawn rock, once these looms generally use just water during the cutting of blocks. Then, the marble waste studied here is a very fine-grained dust, been 99.28% of its particles minor than 0.3 mm in diameter. About 5 kg of waste was collected and sifted through a 175 mesh sieve for subsequent de-agglomeration and quartering.

The solution commonly used for cleaning glassware in the laboratory, aqua regia, was used as the acid effluent to be treated. The solution was obtained by mixing nitric acid (HNO_3) 65% PA and hydrochloric acid (HCl) 36.46% PA, at the ratio of 1:3. The mixture was stored in an amber jar and allowed to rest at room temperature for at least 48 hours prior the tests. The experiments were performed as described below.

Experiments for pH attenuation of the effluent

A fixed volume of aqua regia (50 mL) and varying amounts (20, 24, 28, 32, and 44 g) of the marble waste (hereinafter referred as primary solid waste — PSW) were used in an initial test, aiming to define the mass of marble dust to be used, and the time necessary to stabilize the pH of the acidic solution. Two analytical blanks or control samples were prepared (called BLW), composed by marble waste (20 and 32 g) and deionized water, which was first boiled to eliminate the excess of carbon dioxide gas. All the experimental units were performed in triplicate.

The mixtures were magnetically stirred for 48 hours, and their pH was measured at 2-hour intervals to determine the minimum mass of waste needed to raise the pH of the solution and the average time elapsed to reach the pH stabilization.

After this first test, with the neutralization timing defined as 5 hours, further mixtures were prepared for the main test, consisting of 30, 38, 46, 54 and 62 g of marble waste, each with 50 mL of aqua regia. Two samples composed of 30 and 62 g of marble waste (the minimum and maximum amounts used in the treatments) and boiled deionized water were used as analytical blanks. After 5 hours of magnetic stirring, the pH was measured and the mixtures were passed through a 0.45 µm filter. These experimental units were also made in triplicate.

The solid fraction resulting from filtration was oven-dried at 60ºC for 6 hours and then weighed to determine the residual mass. The solid phase resulting from the reaction is called here the secondary solid waste (SSW), and the liquid phase obtained by filtration is called the secondary liquid waste (SLW). The same procedure was carried out with analytical blanks, thus obtaining the blank solid waste (BSW) and the blank liquid waste (BLW). The Figure 1 shows an outline of the experimental strategy explained above.

Compositional analysis of the materials

The chemical composition of the solid wastes (PSW, SSW and BSW) was determined by X-ray fluorescence (XRF). Samples were melted in a platinum crucible with lithium tetraborate to determine the main components of the rock: Si, Al, Mg, Na, Ca, Fe, Mn, K, P and Ti. Loss on ignition was determined by calcining the material in a muffle furnace at 1,075ºC. Trace elements were determined by induction-coupled plasma mass spectrometry (ICP-MS), and the samples were subjected to multi-acid digestion using nitric, hydrochloric, hydrofluoric and perchloric acids. The eluate thus obtained was diluted with ultrapure water for ICP-MS reading to determine the concentrations of Al, Ba, Co, Fe, K, Mg, Na, P, Se, Sr e Zn. The elements Ag, As, Be, Bi, Cd, Cr, Cu, La, Li, Mn, Mo, Ni, Pb, Sb, Sc, Sn, Th, Tl, U, V, W, Y and Zr were also analyzed, but they were below the detection limits of the mass spectrometer.

The secondary liquid phases (SLW and BLW) were also analyzed. The pH, electrical conductivity (EC), and total dissolved solids (TDS) were measured using benchtop meters, and the Al, Ca, Mg, Na, Fe, Mn, Cu, Pb and Zn concentrations were measured by ICP-MS.

The crystalline phases of the solid wastes (PSW, SSW, and BSW) were characterized by X-ray diffraction (XRD),

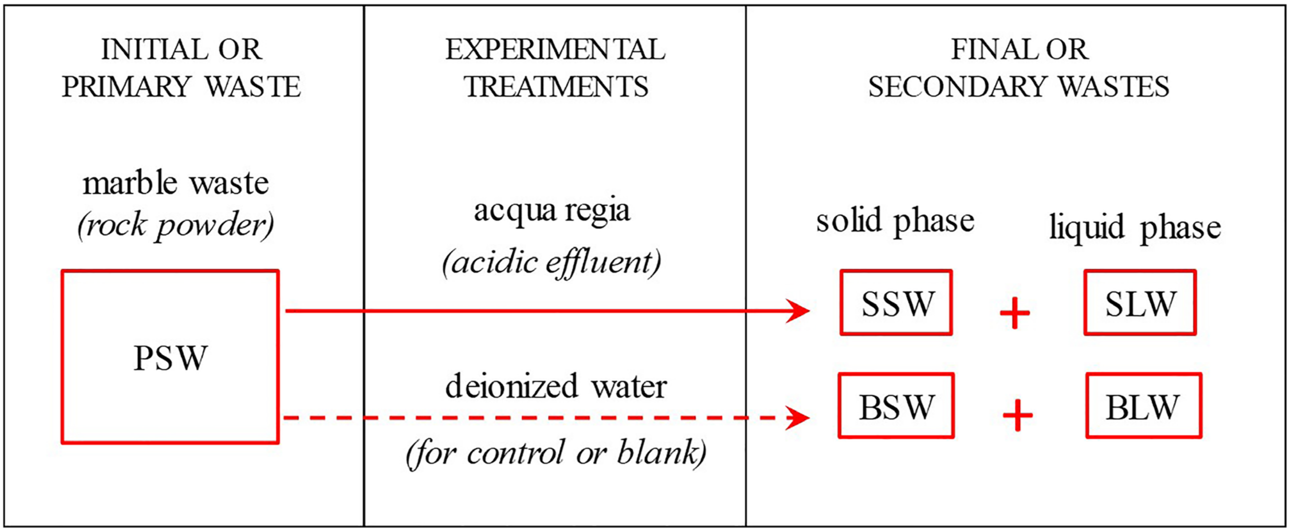

Figure 1. Outline of the experimental strategy adopted in this work (PSW = primary solid waste or marble dust; SSW = secondary solid waste; SLW = secondary liquid waste; BSW = solid phase of the analytical blank, and SLW = liquid phase of the analytical blank).

using CuKα radiation (l = 1.5418 Å) in the angular range of 2q = 4–90º, a scanning step of 0.02º, and a count time of 2 seconds. The crystalline phases were identified based on the Joint Committee on Powder Diffraction Standards (JCPDS) cards of the International Center for Diffraction Data.

RESULTS AND DISCUSSION

The addition of marble dust to the effluent caused effervescence of the liquid and changed its color, indicating that there was rapid reaction. The solution, which initially had a yellowish hue characteristic of aqua regia, became increasingly clear until it took on a milky white color similar to that of the marble dust.

Variation of pH, electrical conductivity, and residual mass

The acid solution had the initial pH of 1.0, which remained unchanged after the addition of 20 g of marble dust (Figures 2A and 2B). Increasing the marble dust mass to 24 g caused an exponential increase in the pH of the mixture, which stabilized at about 4.15 until the end of the experiment (48 hours). Exponential increase in pH also occurred in the experiments with 28, 32 and 44 g of marble dust. In the latter experiment, the pH behaved similarly to the experiment with 32 g. This indicates that the addition of larger quantities of marble dust would not improve the pH of the acidic solution to levels closer to neutral. In the experiment with 32 g of marble waste, for example, the pH went from 1.0 to 5.0 in 1 hour of reaction, achieved the value 5.17 in 4.5 hours, and stabilized at about 5.6 in the end of the experiment.

The analytical blank containing the smallest amount of waste (20 g) showed no significant variation in pH, starting from pH 8.0 to 8.4 in a few minutes, and remaining at a constant level throughout the experiment (Figures 2C and 2D). However, the blank containing 32 g of marble dust showed an increase in pH until it stabilized at 9.1.

The graph in Figure 3 was plotted from the first derivative of pH as a function of time. In all the experiments, the

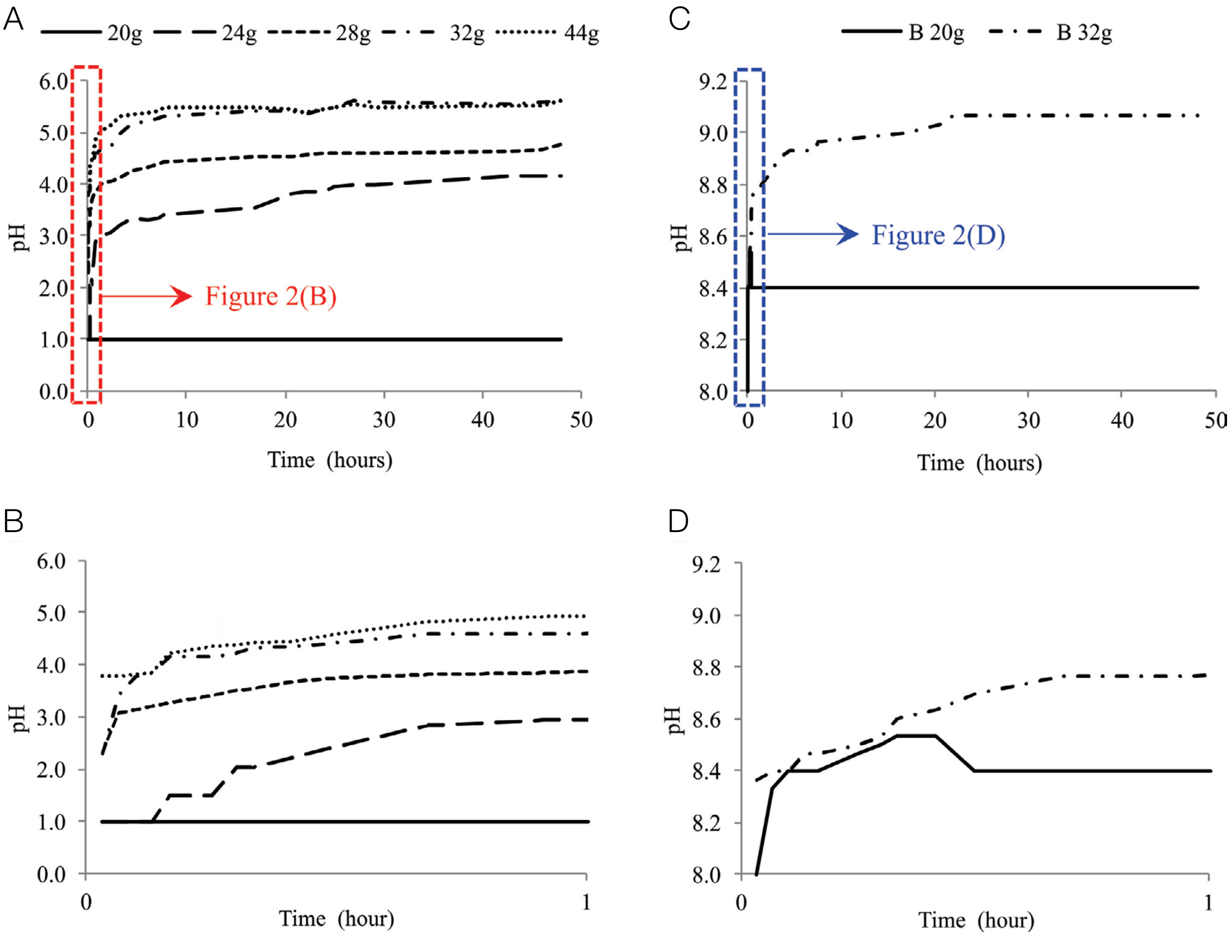

Figure 2. (A) Variation in pH-value of the acid effluent with increasing quantities of marble waste and (B) detail of the red dashed part, considering the first one hour of the experiment. (C) Variation in pH-value of the analytical blank using deionized water with marble waste and (D) detail of blue dashed part showing the blank experiment in the first one hour.

speed of reaction was found to decrease sharply during the first hour, exhibiting minor variations during the following 3 hours and tending to 0 after 5 hours. The second test was designed based on this information, using quantities of more than 30 g of waste in 5-hour experiments.

After magnetic stirring for 5 hours, the mixtures were filtered, resulting in a SLW and a SSW. Next, we described the variations of pH, EC, and TDS in the SLW, and mass in the SSW, according to the different quantities of marble waste used in the experiment.

The pH of the SLW showed values ranging from pH 5.5 ± 0.3 up to 5.9 ± 0.2 (Figure 4). Increasing the mass of waste to over 30 g did not lead to a significant increase in the solution pH, indicating that the reaction reached the equilibrium, possibly being buffered around the pH 5.5.

The discharge of effluents into rivers in Brazil is controlled by rules that classify the water bodies into the following categories: special class, whose levels are the most restrictive; and classes 1 to 4, with the highest number indicating the lowest degree of effluent discharge restrictions (Brasil, 2005). For Class 2 rivers, *i.e.*, water that can be used for drinking after conventional treatment, the acceptable range for effluent discharges is pH 6.0 to 9.0. Thus, the pH of the SLW from the treatment with 30 g of marble dust was very close to the acceptable range, although the use of a stabilization pond or a drying bed may be required to ensure the effluent complies with the discharge classification level (Class 2).

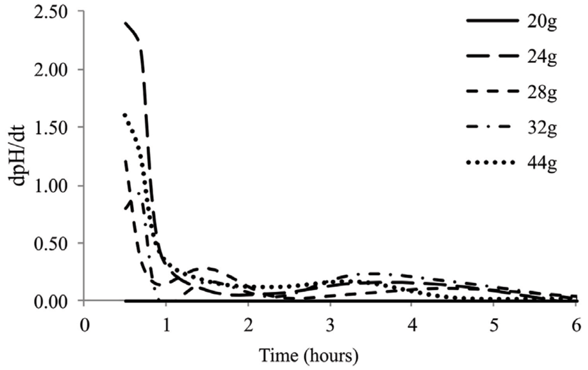

Figure 3. First derivative of the pH-value as a function of time (dpH/dt) in the experiment using acidic effluent and marble waste.

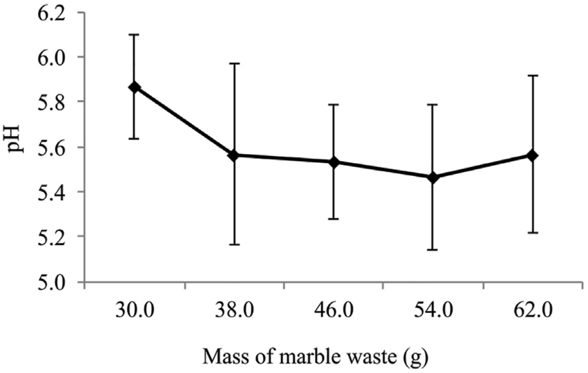

Figure 4. pH values measured in the SLW (Secondary Liquid Waste) resulting from each treatment of the acidic effluent with marble waste.

The graph in Figure 5 indicates that there are no significant differences in the values of EC of the SLW, regardless of the quantity of waste used in the experiment. The conductivity values ranged from 112.2 ± 7.1 mS cm^{-1} to 120.5 ± 9.7 mS cm^{-1}, indicating high contents of TDS in this effluent.

Mass loss occurred in all the treatments, *i.e.*, the weight of solid phase resulting from the reaction (SSW) was consistently lower than the waste's original weight (PSW). When 30 g of waste was used, the final weight was reduced by 55.7%, and, in the treatment with 62 g, the reduction was 14.2% (Figure 6).

Constitution of the solid phase

The marble dust used in the experiment (PSW) was rich in Ca (38.2%) and Mg (15.9%) carbonates, presenting high loss on ignition (42.81%) and small amount of Si (2.79%) (Table 1). Among the trace elements measured, only the Ba, Co, Se, Sr and Zn showed levels above the detection limit. In fact, marble is a metamorphic rock composed basically of calcite and/or dolomite [$CaCO_3$ and $CaMg(CO_3)_2$], and may contain secondary minerals such as quartz, amphibole, diopside, chlorite and pyrite (Winter, 2010). The wastes studied here, from processing of marbles extracted in the south of Espírito Santo state, southeastern Brazil, are of high purity, with dolomite and/or calcite as the main composition (Jordt-Evangelista and Viana, 2000). The metals that occur as trace elements are probably those present in the accessory minerals of these rocks. This is confirmed by the analytical blank (BSW), that shows values very close to those of the non-treated waste (Table 1).

The reaction between wastes yielded a highly hygroscopic solid phase (SSW), with the property of liquefaction when heated to 105ºC. This material was treated in a solubilization process, and after it was dried, it presented characteristics very similar to those of the original marble dust, except the concentration of Fe, that had a gentle increase (Table 1), probably provided by the acidic solution.

To prevent high metal concentrations in soil, the Brazilian rules establishes maximum levels of 72 mg/kg^{-1} of Pb, 300 mg/kg^{-1} of Zn, and 1.3 mg/kg^{-1} of Cd (Brasil, 2009). The waste under study do not have concentrations of these metals at levels that could represent environmental hazards. However, the level of prevention for Se recommended by the mentioned standard is only 5 mg/kg^{-1} and, as it can be seen in Table 1, the Se content of this waste exceeds the recommended level, which may lead to the release of this metal into the environment. In the case of Ba and Co, the values are below the maximum recommended level. The other metals analyzed here are not listed as guiding values of Brazilian rules or were below the limits of detection.

Figure 7 shows the X-ray diffractograms of the PSW, BSW and SSW samples. All the diffraction patterns reveal the presence of calcium and magnesium carbonate [$CaMg(CO_3)_2$], which are typically found in the marble and, consequently, in its waste. Most of the $CaCO_3$ peaks found in standard XRD chips are superimposed on the $CaMgCO_3$ peaks, making it difficult to confirm the presence of the $CaCO_3$. But the primary solid (PSW) has a Ca:Mg ratio of approximately 2:1, as shown in Table 1, indicating that in, addition to $CaMgCO_3$, the marble residue may also contain $CaCO_3$.

The presence of $CaCO_3$ in the SSW sample is related to the unreacted marble waste, that is, reaction excess. However, the peaks of the SSW appear slightly shifted to the right, possibly because the sample was hydrated, even after pre-drying at 300ºC, due to its hygroscopicity. The intensity of the SSW signal is lower than that of the other samples, indicating the possible formation of Ca and Mg chlorides and/or nitrates, which are soluble in water and went to the liquid phase.

Constitution of the liquid phase

The liquid phase resulting from the experiment (SLW) showed high levels of Ca and Mg in solution, originating from the dissolution of the marble dust, as well as

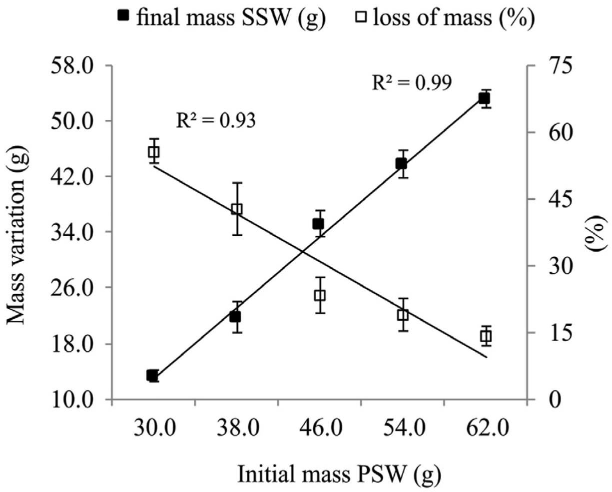

Figure 6. Mass loss of the secondary solid waste (SSW) relative to the mass of primary solid waste (PSW) used to attenuate the acid effluent.

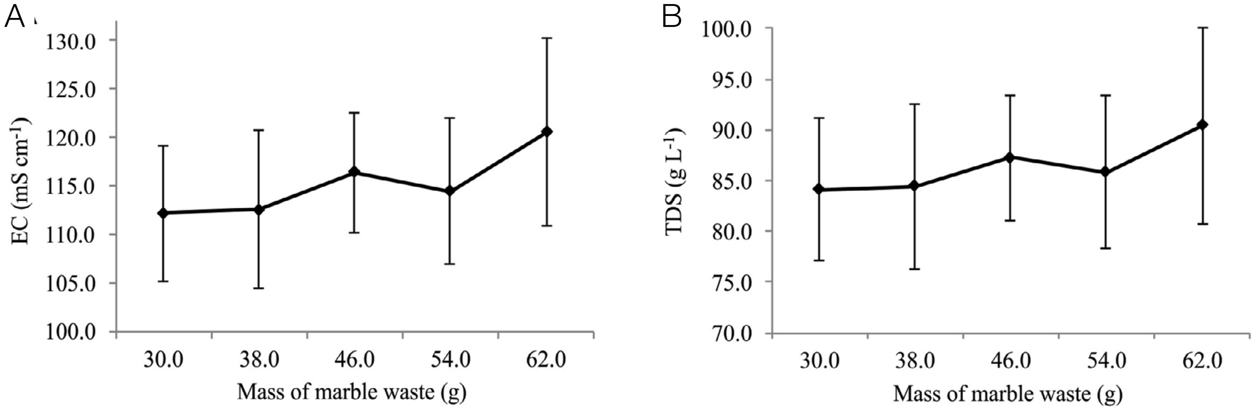

Figure 5. (A) Electrical conductivity (EC) and (B) estimated total dissolved solids (TDS) in the SLW obtained after 5 hours of reaction.

Table 1. Chemical composition of the marble waste used in the experiment (PSW), of the solid phase obtained after the reaction (SSW), and the solid phase of the analytical blank (BSW)

Sample	Si	Al	Fe	Mn	Ca	Mg	Na	K	Ti	P	LOI	Ba	Co	Se	Sr	Zn
						%								ppm		
PSW	2.79	0.07	0.02	< 0.01	38.2	15.9	0.02	0.02	0.01	0.05	42.81	56.0	19.0	44.0	92.0	6.0
SSW	2.80	0.08	0.12	< 0.01	34.8	17.4	0.02	0.03	< 0.01	0.07	42.32	55.0	13.0	< 20.0	67.0	9.0
BSW	2.70	0.06	0.02	< 0.01	37.7	15.8	0.02	0.02	0.02	0.04	42.76	52.0	19.0	28.0	89.0	7.0

PSW: primary solid waste or marble dust; SSW: secondary solid waste; BSW: solid phase of the analytical blank; LOI: loss of ignition.

chlorides and nitrates provided by the acid reaction as shown in the equations 4 to 7 and Table 2. Equations 4 to 7 show the formation of chlorides and nitrates resulting from the reaction between the acidic effluent and the marble dust.

$$CaCO_{3\,(s)} + 2HCl_{\,(l)} \rightarrow CaCl_{2\,(aq.)} + CO_{2\,(g)} + H_2O_{\,(l)} \quad (4)$$

$$CaCO_{3\,(s)} + 2HNO_{3\,(l)} \rightarrow Ca(NO_3)_{2\,(aq.)} + CO_{2\,(g)} + H_2O_{\,(l)} \quad (5)$$

$$MgCO_{3\,(s)} + 2HCl_{\,(l)} \rightarrow MgCl_{2\,(aq.)} + CO_{2\,(g)} + H_2O_{\,(l)} \quad (6)$$

$$MgCO_{3\,(s)} + 2HNO_{3\,(l)} \rightarrow Mg(NO_3)_{2\,(aq.)} + CO_{2\,(g)} + H_2O_{\,(l)} \quad (7)$$

The liquid phase of the analytical blank (SBW) do not present chlorides nor nitrates. Both SLW and BLW showed the Ca:Mg ratio of 3:1, as in Table 2, whereas PSW has 2:1 ratio, as in Table 1. This indicates that the Ca^{2+} was solubilized easier than the Mg^{2+}. The Na occurs in low concentrations and, as a highly soluble element, it was liberated probably providing from an accessory mineral of the marble. The source of Cu can be supposed as providing from the metallic leagues of the diamond wires used for sawing rocks.

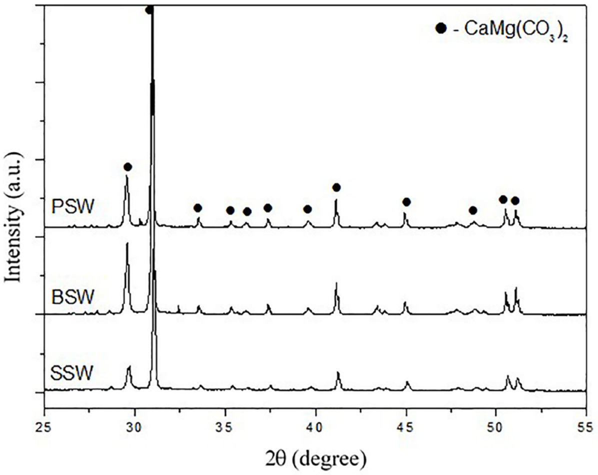

Figure 7. Mineralogical composition of the marble dust used in the experiment (PSW), the solid fraction of the analytical blank (BSW), and the solid phase obtained after treatment of the acidic solution (SSW).

Considering the discharge standard established by National Council for the Environment (Conselho Nacional do Meio Ambiente — CONAMA) (Brasil, 2005) for Class 2 rivers, the concentration of Cu, chlorides and nitrates in the secondary effluent exceed the permitted limits (0.009; 250 and 10 mg L^{-1}, respectively). This resolution does not include Ca nor Mg, but the hardness, which can be measured based on the sum of these elements (Hem, 1989), places the SLW in the high hardness category. High hardness can cause mineral buildup in pipes and limit the possibilities for water treatment and reuse. On the other hand, the abundance of chlorides and nitrates of Ca and Mg in the secondary waste could offer possibilities of using these substances in the pharmaceutical or fertilizer industry.

It is important to highlight that the original liquid waste (aqua regia) was hazardous due to its highly corrosive pH. The pH of the secondary liquid effluent generated after mixing the acid solution with marble dust was close to neutral and could be classified as non-hazardous and non-inert, according to the waste classification system of the Brazilian Association of Technical Standards (ABNT, 2004). Unlike the original acidic effluent, the secondary waste has pH levels that allow discarding it in an ordinary landfill.

CONCLUSIONS

Marble dust was employed successfully to attenuate the acid effluent (aqua regia) by raising the pH to levels very close to that allowed by Brazilian environmental legislation for discharge into Class 2 rivers, that is a relatively restrictive pattern. However, to ensure that pH levels are within legal limits, drying bed treatment or stabilization pond is indispensable, as defined by environmental rules.

Although the levels of TDS, Cu, chlorides and nitrates on the liquid phase of the secondary effluent (SLW) remained higher than that allowed for discharge into Class 2 rivers, their characteristics correspond to non-hazardous and non-inert wastes, which can be discarded in an ordinary landfill after it has been dried. Moreover, mixing marble dust into the acid effluent caused the mass of PSW to decrease by up to about 50% in one of the treatments.

Table 2. Constituents of the liquid phase of the secondary effluent (SLW) and the analytical blank (BLW) after the experiment

Sample	Al	Ca	Mg	Na	Fe	Mn	Cu	Chloride	Nitrate
SLW (mg L^{-1})	< 0.05	78,308	23,755	2.89	< 0.1	< 0.05	0.02	3,190.0	1,550.0
BLW (mg L^{-1})	< 0.05	16,687	5,167	2.08	< 0.1	< 0.05	0.02	0.0	0.0

SLW: secondary liquid waste; BLW: blank liquid waste.

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