APPLICATION OF THE CONSTRUCTION WASTE AS A REDUCING AGENT IN THE SOLUBILITY OF IRON TAILING METALS

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ABSTRACT
Iron ore tailings has acid pH and high content of metals, such as iron, aluminum and manganese. Regarding the environment, these metals poses a risk of contaminating the soil and underground water. Yet, construction residues usually have high pH and because of this, they can be used to neutralize soil acidity and to reduce metal availability in mining tailing piles. The objective of this study was to evaluate the applicability of CW to promote neutralization of the acidity in iron ore tailings aiming at decreasing the solubility and mobility of metal found in them. Thus, a sample of construction waste was collected and characterized which was later incorporated at different doses into a sample of iron mining tailing collected in the Iron Quadrangle (Minas Gerais – Brazil). The construction waste raised the pH of the tailing sample from 5.58 to 8.22. Moreover, the incorporation of the waste incorporation decreased the manganese solubility in at least 80%. Despite the lack of national legislations and policies on the use of construction waste for this purpose, the results show that it is a promising technological alternative.

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INTRODUCTION

Iron mining is the most important mining activity in Brazil, where iron is the most produced ore in the country, according to the Ministry of Mines and Energy (2019). Also, according to data from the U.S. Geological Survey (USGS, 2020), the country is in the second place in the international ranking of reserves and production, with 29 billion tons of iron ore in reserves and annual production of 460 million tons in 2018. The importance of the State of Minas Gerais in this scenario is unquestionable since the gross production of iron in the State of Minas Gerais in 2016 was approximately 3.9 million tons, which corresponds to 70% of all the Brazilian production, according to the National Department of Mineral Production (DNPM, 2017). This participation is mainly due to iron mining in the Iron Quadrangle (in Portuguese, Quadrilátero Ferrífero) region, which covers approximately 7,000 km² of the central area of Minas Gerais and where the largest iron ore deposit in the country is found (DNPM, 2017). Although there are no questions on the social and economic benefits arising from this activity, the environmental impacts generated by it must be considered by mining companies and inspection environmental agencies.

Among the environmental damage caused by mining, the generation of large volumes of mine tailings and the degradation of extensive areas stand out. Because of their characteristics, the tailings and the soil of areas degraded by iron mining usually have an acidic pH and a high content of metals, such as iron, manganese and aluminum. These metals have greater solubility and mobility in an acidic medium, therefore promoting the contamination of soils and groundwater.

Construction waste (CW) is a possible source of acidity correction agent for iron mining waste due to its physical and chemical characteristics and the amount that is generated. In Brazil, na amount of 183.5 thousand tons of solid urban waste are collected in Brazil on a daily basis, and according to PINTO (1999), the CW accounts for 54 to 70% of this total. Studies carried out by the National Secretariat for Environmental Sanitation (2010) estimate percentages higher than this range for the CW generated in Brazilian cities.

The use of CW to correct the soil pH in areas degraded by mining and the tailings from this activity can reduce the solubility and mobility of metals in the environment, bringing benefits both for the management of CW in cities - with a view to reducing their disposal in landfills or inappropriate locations - as for the management of this environmental liability by mining companies, allowing a safer final disposal of this tailings and reducing the expenses spent in the recovery of degraded areas.

Overall, the investigated studies that used CW to correct soil acidity and reduce metal solubility by increasing the pH obtained a satisfactory result. Ramalho and Pires (2009) obtained a raise in the pH of soils from 5.5 to 8.5 with the addition of different doses of CW in three samples denominated “ravine soils” by the authors. Melo et al. (2008), in a study carried out to evaluate the availability of cadmium, lead, copper and zinc with time and pH value, applied the described metals in the form of soluble salt in the doses of 20, 150, 100 and 150 mg/kg respectively in dystrophic Red- Yellow Clay soil, performing liming (pH increase from 4.3 to 6.5 – 7 range) with the addition of calcium carbonate in half of the samples. At the end of 210-day incubation period of the mixtures, the exchangeable concentration of metals found in them was evaluated, and the samples with calcium carbonate had lower levels, i.e., the raise in pH provided a reduction in their solubility in the soil.

In this context, the objective of this study was to evaluate the applicability of CW to promote the correction of the acidity of iron mining tailings, aiming at reducing the solubility and mobility of the metals iron, aluminum and manganese.

MATERIAL AND METHODS

The WC sample used in this study was collected in the Small Volume Receiving Unit, located in Contagem (Bela Vista neighborhood), metropolitan region of Belo Horizonte. The WC sample (approximately 10 kg) was collected and packed in a standard plastic bag, between January 15 2019 and January 30 2019, with the aid of the professional in charge for receiving these materials.
The sample was collected in batches in which the granulometry of the WC was smaller so to avoid the need for its physical breakdown.

It was observed, through visual inspection, that the residue is red and with a heterogeneous particle size, which can be associated with building bricks. Additionally, a large number of contaminants was not observed, as shown in Figure 1.

According to Matos (2015), the Relative Efficiency (RE) is directly related to the size of the particles, therefore, the particle size composition of the CW was necessary. Prior to the test, the WC was homogenized, and five samples of 200 g each were then collected. The particle size separation of the material was performed using ABNT sieves with a diameter of 20 cm, height of 5 cm and different mesh apertures.

The relative efficiency values corresponding to each granulometric fraction in which the sample was separated (RE₁, RE₂, RE₃ and RE₄) are shown in Table 1. The sieves were stirred for 5 minutes. Next, the retained mass (m₁, m₂, m₃ and m₄) was determined using an analytical balance (0.01-g precision).

Equation 1 was used for the calculation of the Material Relative Efficiency (REₘ):

\[
REₘ = \frac{m₁ + m₂ \times 20 + m₃ \times 60 + m₄ \times 100}{m_{total}}
\]  (1)

Where:
- \( m₁ \) = mass retained in the no.10-sieve;
- \( m₂ \) = mass retained in the no.20-sieve;
- \( m₃ \) = mass retained in the no.50-sieve;
- \( m₄ \) = mass in the tray; and
- \( m_{total} \) = total mass of the residue sample.

The value of the Neutralizing Power (NP) indicates the chemical capacity of the CW to neutralize the acidity of the materials mixed with it and calculated using Equation 2. For reaching such value, it was used 1 mol/L of hydrochloric acid – HCl and Sodium Hydroxide – NaOH solutions and a 1% w/v phenolphthalein indicator solution. A 250-mL titration flask was used in which it was added 1 g of WC with 100% RE (particle diameter <0.30 mm) and 25 mL of the standardized HCl solution. In another titration flask, 25 mL of HCl was added for the composition of the blank test. Afterwards, the titration flasks were heated for 5 minutes and the solution became less turbid and it was then left for cooling for 30 minutes, after which 20 drops of phenolphthalein were added. For titration, a standardized NaOH solution was added until a pinkish permanent color was observed in the suspension containing the CW and in the “blank”. The volume of NaOH required to make the solution pink was written down, and denominated \( Vₐ \) for the titration of the suspension containing the CW sample and \( V₏ \) for the “blank” titration; \( m \) refers to the mass of the residue used in the experiment (Equation 2).

### Table 1. Particle size distribution ranges and solid residue reactivity.

| Particle size fraction | ABNT sieve                  | Relative efficiency (%) |
|------------------------|------------------------------|-------------------------|
| > 2.00 mm              | Retained no. 10              | 0                       |
| 0.84 – 2.00 mm         | Passing no.10, retained in no. 20 | 20                      |
| 0.30 – 0.84 mm         | Passing no. 20, retained in no. 50 | 60                      |
| < 0.30 mm              | Passing no. 50               | 100                     |

Source: Matos (2015)

Figure 1. Visual Inspection of the sample
The test was carried out in triplicate. The Relative Power of the Total Neutralization (RPTN) of the material was calculated using Equation 3.

\[ RPTN(\%CaCO_2) = \frac{NP \times REM}{100} \]  

The iron ore tailings sample was collected at the tailings dam, denominated “Maravilhas I”, owned by Vale S.A., located in Mina do Pico, municipality of Itabirito, State of Minas Gerais. The access to this material was made possible through a partnership project between the Federal University of Minas Gerais and the company, for the characterization and classification of this waste in terms of its reactivity (inert and non-inert). Iron ore tailing is shown in Figure 2.

After the collection, six samples of 0.5L of tailings were separated into 1-L beakers, made up by the fraction of tailings containing a particle size smaller than 2 mm, that is, a fraction passing through the number-10 sieve.

Physical and chemical analyses of the iron mining tailings sample were carried out at the Soil, Plant Tissue and Fertilizer Analysis Laboratory of the Federal University of Viçosa, in November 2018. The tailings in the study showed a Sandy-Loam Textural Classification, with the following proportion of particles in Table 2:

| Particles   | Proportion (kg/kg) |
|-------------|--------------------|
| Coarse sand | 0.038              |
| Fine sand   | 0.533              |
| Silt        | 0.346              |
| Clay        | 0.083              |

The iron ore tailings passing through the no. 10 sieve was separated into six different 0.5-L samples. The fraction of CW passing through the No. 50 sieve, that is, the one with a RE equal to 100%, was incorporated into the six samples of the iron ore tailings material in the following quantities:

| Sample | Quantity of CW (g) | Proportion (kg/m³) |
|--------|--------------------|--------------------|
| 1      | 0                  | 0                  |
| 2      | 6.25               | 12.5               |
| 3      | 12.5               | 25                 |
| 4      | 25                 | 50                 |
| 5      | 50                 | 100                |
| 6      | 100                | 200                |

The materials were carefully mixed, in order to promote their homogenization (Figure 3). Distilled water was added to the mixtures in a volume of 125 ml and, homogenization was once more performed. Then, 10 mL of each sample was taken, mixed with 25 mL of distilled water and left to rest for 30 minutes to sediment the material (Figure 4). After this period, the samples had their (initial) pH measured.
After 21 days of incubation of the CW with the tailings, the pH was again measured to evaluate the occurrence of a change in the acidity of the mixture.

To assess the influence of CW on the solubility of iron, manganese and aluminum in the iron mining tailings, the samples were subjected to a solubilization test, following the procedures described by NBR 10006 (ABNT, 2004).

After the incubation of the tailings with different incorporated doses of CW, 250 g of each mixture was solubilized in 1 L of distilled water and placed in plastic capped-containers. The suspension was subjected to stirring for 5 minutes, promoted by the B.A.K. 250 D stirrer, under approximate rotation of 140 rpm. After stirring, the container was capped and left to rest for 7 days at room temperature. After the rest period, the samples were filtered through MilliporeTM membranes of 0.45 µm pore nitrocellulose, with the aid of a vacuum Prismatec 121 Pump, working under 600 mm Hg suction tension.

Considering that the concentration of the available metals is low in iron mining tailings, a concentration of solutions was necessary to increase the detection limit of the analysis, using the concentration factor of 20. Thus, 500 mL of each of the samples were concentrated to 25 mL, being firstly transferred to 2000 mL beakers with the aid of 500-mL tubes and heated to 80°C on an electric hot plate, until the volume was reduced to less than 100 mL. The remaining volume of each sample was transferred to 100-mL beakers and heated again on the electric plate, until it was reduced to less than 20 mL. Finally, each solution was transferred to 25 mL volumetric flasks and, with the aid of a Pasteur volumetric pipette (5 mL), the flasks were measured with distilled water.

After the concentration of the solutions, the samples were sent to the Department of Chemical Engineering at UFMG, to determine the concentration of metals in solution by means of atomic absorption spectrophotometry analyses.

RESULTS AND DISCUSSION

Table 4 shows the results obtained in the sieving tests.

The average of the measurements was performed for the calculation of the REm, as shown in Table 5.

| No. of the Test                  | 1st  | 2nd  | 3rd  | 4th  | 5th  |
|---------------------------------|------|------|------|------|------|
| Retained in no. 10 (g)          | 80.99| 79.52| 82.86| 67.11| 90.93|
| Passing no. 10, retained in no. 20 (g) | 34.66| 33.41| 31.69| 37.38| 33.69|
| Passing no. 20, retained in no. 50 (g) | 45.58| 48.18| 46.35| 54.29| 43.72|
| Passing no. 50 (g)              | 38.77| 38.89| 39.1 | 41.22| 31.66|

Table 5. Mass used for the calculation of the Relative Efficiency

| Particle size fraction | Mass (g) | Participation (%) | Relative Efficiency (%) |
|------------------------|----------|-------------------|-------------------------|
| > 2.00 mm              | 80.99    | 40                | 0                       |
| 0.84 – 2.00 mm         | 33.69    | 17                | 20                      |
| 0.30 – 0.84 mm         | 46.35    | 23                | 60                      |
| < 0.30 mm              | 38.89    | 19                | 100                     |
According to the results obtained and considering the sample used in this experiment, the particle size distribution of this CW would prevent its application as a soil acidity correction agent for agriculture, according to the Normative Instruction of the Secretariat of Agricultural Defense No. 35/2006. This instruction establishes that a soil acidity correction agent must have the following granulometric characteristics:

- 100% of the material should pass through no.10-sieve;
- At least 70% of the material should pass through no.20-sieve;
- At least 50% of the material should pass through no.50-sieve.

The value presented allowed to obtain the following REm:

\[ REm = \frac{38.99 \times 0.4 + 38.99 \times 0.2 + 46.35 \times 0.6 + 38.99 \times 1.0}{99.92} = 36.74\% \] (4)

The relative efficiency (REm) of the sampled CW was 36.74%, that is, only this portion would react with the tailings to correct its acidity in a short period of time. The calculated REm demonstrates that, in a situation where all the CW is mixed in the tailing sample to correct the acidity of the soil, no mass retained in sieve No. 10 would be effective for this purpose in the period of 3 months, only 20% of the mass retained in sieve No. 20 and 60% of the mass retained in sieve No. 50, the rest of the mass would only react with the tailings after a longer period of time. On the other hand, the mass passing through the no. 50 sieve would react completely with the tailings in a period of three months (EMPRAPA, 2004).

The volumes of NaOH used in the titrations of the suspensions prepared with the samples, in order to determine the Neutralizing Power (NP) of the CW, are shown in Table 6.

### Table 6. NaOH volume used in the titration of suspension prepared with CW samples

| Identification | Volume (mL) |
|----------------|-------------|
| Va1            | 17.1        |
| Va2            | 16.7        |
| Va3            | 16.9        |
| Vb             | 26.26       |

The use of Equation 2 resulted in the sample average NP, which was:

\[ NP_{average} = \frac{45.89 + 47.89 + 46.89}{3} = 46.8\% \]

It was observed in this test that the analyzed sample (1 g of RCC with 100% RE) has a neutralizing power equivalent to 46.8% of the neutralizing power of CaCO3, since, according to the principle of chemical equivalence, the amount of neutralized acid before the addition of NaOH is equivalent to the amount of neutralizing constituent in the sample. Based on the NP value found for the residue, the CW is expected to have a significant effect on the increase in the pH of the iron mining tailings.

From the Equation 3 and the values of the average NP and REm previously determined, the NPRT of the CW of the sample was calculated:

\[ NPRT = \frac{46.8\% \times 36.74\%}{100} = 17.7\% \] (6)

According to Normative Instruction No. 35/2006 of the Secretariat for Agricultural Defense and based on the calculated value of NPRT, the sampled CW is classified as a chemical corrective of low acid neutralizing value for agricultural purposes.

Both the NP and the NPRT of the CW did not meet the minimum standard expected for a soil acidity correction agent, as shown in Table 7. However, it must be considered that this is a waste with some usable acid neutralization power, but not equivalent to that of a chemical correction agent specifically prepared for this purpose. In addition, the NPRT value could be higher, if the sampled CW was crushed, so that most of its mass would reach fine granulometry (less than 2 mm), in order to allow greater reactivity with the soil acidity.

### Table 7. Comparison between the values obtained from the Neutralizing Power (PN) and Relative Power of Total Neutralization (RPTN) and constant values in the Agriculture Ministry

| Variable | Obtained value (%) | Value predicted in IN 35/2006 (%) |
|----------|--------------------|----------------------------------|
| NP       | 46.8               | 67                               |
| RPTN     | 17.7               | 45                               |
Table 8 shows the CW doses applied to the tailing sample as well as the pH values in the initial and final conditions (after 21 days) following the mixture.

**Table 8.** Values of pH in the initial and final conditions (after 21 days) of the incorporation of the different CW doses in the iron ore tailing samples

| Sample identification | CW dose (kg/m³) | pH Indicial | pH Final |
|-----------------------|----------------|------------|----------|
| 1                     | 0              | 5.54       | 5.58     |
| 2                     | 12.5           | 5.56       | 7.91     |
| 3                     | 25             | 5.56       | 8.05     |
| 4                     | 50             | 5.58       | 8.13     |
| 5                     | 100            | 5.58       | 8.18     |
| 6                     | 200            | 5.58       | 8.22     |

It can be seen in Figure 5 that small doses of the incorporated CW are already capable of significantly alter the pH value of the tailing, despite the low PNRT shown by the CW (17.7%). An alternative to provide an increase in the PRNT of the CW is the prior crushing of the material in order to increase its Relative Efficiency (REm) and to increment the interactivity of the material with the tailings, as a consequence. Thus, coarse CW materials would have their particle size reduced and could also be used. In addition, another observation is that, from the dose of 12.5 kg/m³, the increase in the applied CW dose generated little changes in the pH of the tailings.

The results achieved in this study shows that the application of the CW is efficient in neutralizing the acidity of the iron ore tailings. In addition, to increase the pH of this material up to 7, it would be necessary to apply 0.41 kg of CW for each m³ of iron mining waste.

Table 9 shows the results of the concentration of metals in the solubilized extract, obtained through analysis of atomic absorption spectrophotometry, considering the correction factor.

\[
pH = 0.2269 \ln(Dose_{volumétrica}) + 7.2
\]

**Figure 5.** Experimental data and adjusted mathematical equation that correlates the pH of the mixture (after 21 days) with the CW incorporated dose.
Table 9. Concentration of iron, manganese and aluminum in the solubilized extracts¹

| Sample identification | Iron  | Manganese | Aluminum |
|-----------------------|-------|-----------|----------|
|                       | mg/L  | mg/L      | mg/L     |
| 1                     <0.025 | 0.075    | <0.05    |
| 2                     <0.025 | <0.015   | <0.05    |
| 3                     <0.025 | <0.015   | <0.05    |
| 4                     <0.025 | <0.015   | <0.05    |
| 5                     <0.025 | <0.015   | <0.05    |
| 6                     <0.025 | <0.015   | <0.05    |

¹Result obtained after correction considering the concentration factor 20.

In all samples, the concentrations of iron and aluminum were lower than the minimum values detectable by the analysis method. However, the manganese concentration in the iron mining tailings sample, in which the CW was not incorporated, was 0.075 mg/L.

Based only on the concentration of iron, manganese and aluminum determined in the solubilized extract, the iron ore tailings are classified as inert waste (Class II-B), a low risk condition in relation to soil and groundwater contamination. It is observed that the initial concentration of Mn in the sample is as 5.3 times less than the maximum allowable (0.4 mg/L) for this metal in groundwater.

The remaining concentrated samples showed manganese concentration below the threshold detectable by the technique used in the study (0.015 mg/L), therefore indicating that the application and the mixing of a small dose of CW (12.5 kg of CW per m³ of tailings) was sufficient to reduce the solubility of manganese in the water. The mixture of the CW, with the consequent raise in the pH value to 7.91 generated a reduction of at least 80% of the concentration of soluble manganese in the iron ore tailings sample, thus, its concentration, which was already close to maximum admissible for classification of the waste as inert (0.1 mg/L), became considerably lower, that is, lower risk for the environment.

Regarding the other metals, the results are inconclusive in relation to the reduction of their concentrations provided by the incorporation of CW to the tailings. However, due to the similar behavior regarding the solubility of these metals in relation to pH, as presented in the bibliographic review, it is expected that the mixture of CW to the tailings has provided a similar reduction in solubility and, consequently, in the mobility of Fe and Al.

Currently, Brazil does not have any legislation neither policies on the use of CW as a correction agent for soil acidity and tailings found in areas degraded by mining. However, the results obtained in the experiment are an important indication that this is a technological possibility that deserves to be considered for the control of environmental pollution.

CONCLUSIONS

- In this study, the CW was efficient in neutralizing the acidity of the iron ore tailings.
- From the equation obtained by the mathematical adjustment of the experimental data, it is estimated that the application of 0.41 kg of CW per m³ of tailings is sufficient to correct its acidity (raising its pH to 7).
- Regarding the solubility of the metals in this study, it was observed that the raise in the pH resulting from the application of CW was sufficient to significantly reduce the soluble concentration of manganese in the samples. However, this was not observed in iron and aluminum, since the concentrations of these metals were lower than those detected by the quantification technique used in the experiment.

REFERENCES

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS – ABNT. NBR 10.004: Resíduos sólidos: Classificação. Rio de Janeiro, 71p. 2004.

______ . NBR 10.006: Procedimento para obtenção de extrato solubilizado de resíduos sólidos: Classificação. Rio de Janeiro, 3p. 2004.

DEPARTAMENTO NACIONAL DE PRODUÇÃO MINERAL – DNPM. Anuário Mineral Brasileiro – Principais Substâncias Metálicas. Brasil, 2017.
EMPRESA BRASILEIRA DE PESQUISA E AGROPECUÁRIA – EMBRAPA. Características de Corretivos Agrícolas. Brasil, 2004.

MATOS, A.T.de.; MATOS, M.P.de. Disposição de águas residuárias no solo e em sistemas alagados construídos. Viçosa: Universidade Federal de Viçosa, 2017.

MATOS, A.T.de. Manual de análise de resíduos sólidos e águas residuárias. Viçosa: Universidade Federal de Viçosa, 2015.

MELO, E.E.C.; NASCIMENTO, C.W.A.; SANTOS, A.C.Q.; SILVA, A.S. Disponibilidade e Fracionamento de Cd, Pb, Cu e Zn em função do pH e tempo de incubação com o solo. Revista Ciência e Agrotecnologia, v.32., n.3. p.776-784, 2008.

MINISTÉRIO DE MINAS E ENERGIA – MME. Boletim do Setor Mineral. Brasil, 2019.

PINTO, T. Metodologia para gestão diferenciada de resíduos sólidos da construção urbana. 1999. 189p. Tese de Doutorado, Escola Politécnica, Universidade São Paulo, São Paulo, 1999.

RAMALHO, A.M; PIRES, A.M.M. Viabilidade do uso Agrícola de Resíduos de Construção Civil e da Indústria Cerâmica: Atributos Químicos. Embrapa, São Paulo, 2009.

SECRETARIA DE DEFESA AGROPECUÁRIA – SDA. Instrução Normativa nº 35, de 4 de julho de 2006: Aprova as normas sobre especificações e garantias, tolerâncias, registro, embalagem e rotulagem dos corretivos de acidez, de alcalinidade e de sodicidade e dos condicionadores de solo, destinados à agricultura, na forma do Anexo a esta Instrução Normativa. Brasil: SDA, 2006.

SECRETARIA NACIONAL DE SANEAMENTO AMBIENTAL – SNSA. Panorama dos Resíduos de Construção e Demolição (RCD) no Brasil. Brasil, 2010.

UNITED STATES GEOLOGICAL SURVEY – USGS. Mineral Commodity Sumaries, 2020. United States of America, 2020.