Neutralization Potential (NP) of a Porcelainate Production Alkaline Waste in the Prevention of AMD Generation

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Abstract—In the Coal Minning Region of Santa Catarina is located the largest pole producing ceramic floors in Brazil. Considering the large volume of alkali feldspar rich waste that is generated during the porcelain polishing step. The ceramic industry is great generator of solid waste, usually deposited in landfills, being responsible for the pollution of extensive areas. There is a great availability of this alkaline material that can potentially be used as a neutralizing agent to prevent the generation of AMD in the coal minning. In this work the characterization of the potential of the generation of DAM through static and kinetic tests of a coal waste obtained in a beneficiation plant of the coal minning region, was characterized chemically the waste originated during the step of polishing in the production of porcelain tiles and determined the neutralization potential of the alkali feldspar waste. The results indicate that the coal mining waste presents a high potential of acidity (AP), the waste of the production of porcelanates presents as a major component of its composition silicon oxide and aluminum oxide, but also other oxides such as of potassium and has a moderate neutralization potential (NP). The results indicate a moderate potential of use as an alkaline additive in the prevention of AMD generation. However other uses are recommended, such as the production of soil-cement with this waste.

Keywords—Porcelain, Wastes, AMD, Prevention.

I. INTRODUCTION

Acid Mine Drainage (DAM) comes from the natural oxidation of sulfide minerals when in contact with air and water. DAM is associated with coal mining and polymetallic sulphides, especially in the presence of iron sulphide (pyrite or marcassite - FeS2). These sources remain active for decades and even centuries after their production [1, 2, 3, 4].

The Carboniferous Region of Criciúma, in Santa Catarina, is highly affected, being considered one of the 14 most polluted areas in Brazil. The improper management of these wastes, practiced in the past, and in certain cases even in the current activities, resulted in the formation of an AMD contaminating soil and water with low pH and a high concentration of sulfate, iron (II and III), aluminum, zinc and manganese [5].

It is estimated that, in the Carboniferous Basin of Southern Santa Catarina, there are about 786 km of rivers affected by DAM in the Araranguá, Tubarão and Urussanga Rivers basins. The contamination of water resources is due to 134 areas mined in the open air amounting to 2,924 ha, 115 areas with waste deposits to 2,734 ha, 77 acidic lagoons amounting to 58 ha, as well as hundreds of underground mines [5, 6, 7].

II. PREDICTION OF THE ACID DRAINAGE GENERATION

The pressure from environmental agencies, public ministry, the community at large and awareness of the Carboniferous are promoting a major joint effort to minimize the environmental problem. An important tool in this context is the need to forecast the generation of DAM by the materials handled in the mining activities and mainly by the tailings of the beneficiation. The DAM prediction through static and kinetic tests has been applied worldwide for decision-making in mining enterprises [2, 8, 9]. However, these methods have not been applied in the Carboniferous Region of Criciúma.
The static tests have the purpose of evaluating the potential of generation of AMD by a certain material. They are easy and fast and allow the application of specific criteria that allow the classification of the samples according to their potential for acid generation. Afterwards, the materials are subjected to a series of kinetic tests that will determine the acid generation behavior over time, as well as the expected quality of drainage [8].

The usual kinetic tests are performed on Soxhlet reactors, agitated flask techniques, humidity cells and column leaching tests. Although there is no standardized method, the most popular laboratory kinetic assay is that of moisture cells [10]. In-situ tests on stacks are also employed. Kinetic tests require a long time, ranging from weeks, months or even years. Based on the results of the static and kinetic tests, appropriate mathematical models can be applied in order to extrapolate the results over a period of years, decades or even centuries.

AMD is due to an autocatalytic reaction. Thus, the best method of control is not to generate it. The use of alkaline additives in mixture with pyrite wastes is a technique recognized as a preventive method for the generation of DAM and little (or none) has been applied in the coal region of southern Brazil.

Sintered porcelain ceramics, known as porcelain tiles, are a class of ceramic products used for coatings. The porcelain stoneware is the ceramic for coatings that presents the best technical and aesthetic characteristics when compared with the others found in the market. Due to its properties this material has increased its participation in the market of ceramic material. The ceramic mass of porcelain tiles requires a proportion of feldspar up to 50% of the ceramic mass.

III. METHODS
The methodology of the work within the context of the prediction of DAM was initially restricted to the static test of determination of the ABA Neutralization Potential by the SOBEK and modified SOBEK method, to the kinetic test with moist cells.

3.1 Samples of coal tailings
The materials studied were collected directly from coal beneficiation plants of the Carboniferous Region of Santa Catarina. Samples of coal generated in beneficiation operations were sampled. The samples were conditioned, transported and prepared for the static and kinetic tests.

3.2 Samples of alkaline residues
The alkali feldspar rich were supplied by Cerâmica Eliane S/A. Only this company produces approximately 1000 tons of this waste per month, and is currently destined for grounding. The samples were conditioned, transported and prepared for the static and kinetic tests.

3.3 Static Tests - "Acid Basic-Accounting (ABA)"
The static tests to be implemented were the acid and base accounting procedure developed by Sobek [9]. It is an essay that aims to determine the balance between acidity production and acidity consumption (neutralization) by the mineral components of a sample. The test involves calculating the sample's acidity potential (AP) from measurements of sulfur concentration and the measurement of neutralization potential (NP) [8]. From this data will be calculated:

- net neutralization potential (NNP) = NP - AP
- neutralization potential ratio (NPR) = NP / AP

where AP, NP and NNP are generally expressed in kg CaCO3 / t sample.

The procedure for the determination of the acidity potential (AP) will be from the total sulfur content (Sobek) or pyritic FeS2 (Model Sobek). Stoichiometrically, one mole of CaCO3 is required per mole of S:

AP (kg CaCO3 / t sample) = (1000/32) x weight% S

The Neutralization Potential Determination was performed by attacking the sample with acid heated at 90°C to consume the neutralizing minerals and titration with NaOH to pH 7.0.

NP (kg CaCO3 / t sample) = (HCl cons., G / g sample) x (50/36.5) x 1000

The ABA criteria for identifying the acidity potential of the materials are (NNP and NPR):

NNP values less than -20 will form acid
NNP values above +20 will not form acid
NNP values between -20 and +20 are difficult to verify potential.

NPR values less than 1:1 indicate the likely generation of AMD
NPR values between 1:1 and 2:1 indicate the possible generation of AMD
NPR values between 2:1 and 4:1 indicate that AMD is not expected.
NPR values greater than 4: 1 indicate that DAM was not generated.

3.4 Characterization and Neutralization of a Acid Mine Drainage (AMD)

The treatment of a sample of acid mine drainage (DAM) was carried out by the addition of porcelanate powder under mechanical agitation in jar test equipment. The DAM used in the tests was collected at the same mine that provided the coal mining tailings for the experiments.

To characterize the acid mine drainage sample, the pH and concentration of iron, manganese, zinc, aluminum and sulfate were analyzed. The metals were analyzed in an Agilent brand AA-240 atomic absorption spectrometer, while the sulfate was determined by the turbidimetric method using a Hach turbidimeter. These analyzes were carried out at the Environmental Studies Laboratory for Metallurgy and followed the procedures of the Standard Methods for Water and Wastewater Analysis [11].

IV. RESULTS AND DISCUSSION

The following results were presented in the characterization tests of the materials, coal mining tailings and porcelain powder. As well as the neutralization potential (NP) of the porcelanate powder residue, aiming to evaluate its applicability in the treatment of AMD or in the prevention of its generation. It was also evaluated the potential of generation of AMD by the mining tailings used in the work.

4.1 Mineralogical Characterization of Materials

Initially the characterization of the materials used in this work, mining tailings and porcelain powder was carried out. For mineralogical characterization, the X-ray diffraction technique was used. The analyzes were performed on a Siemens D5000 X-ray diffractometer. The following are the diffractograms (Fig. 1).

The results obtained show the presence of silicon and aluminum oxides, but also a large amount of pyrite. This indicates that the material has the potential to generate acidity.

4.2 Determination of Net Neutralization Potential

Table 1 presents the results obtained in the tests to determine the neutralization potential of the material originating from the porcelain tile production. Performed according to the ABA methodology.

<table>
<thead>
<tr>
<th>Static Test</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>In Paste pH</td>
<td>8,57</td>
</tr>
<tr>
<td>Total Sulfur (%)</td>
<td>0</td>
</tr>
<tr>
<td>AP (kg CaCO3/t)</td>
<td>0</td>
</tr>
<tr>
<td>NP (kg CaCO3/t)</td>
<td>30,70</td>
</tr>
<tr>
<td>ABA</td>
<td></td>
</tr>
<tr>
<td>NNP</td>
<td>30,70</td>
</tr>
<tr>
<td>NPR</td>
<td>30,70</td>
</tr>
<tr>
<td>AMD formation</td>
<td>No</td>
</tr>
</tbody>
</table>

The results obtained in the step of determining the neutralization potential of the analyzed samples, demonstrates that the material has a relative capacity of neutralization. Featuring reasonable potential for use with the alkaline agent in preventing the generation of AMD.
Also, the tailings produced during the process of concentrating the coal from the Barro Branco layer of the State of Santa Catarina were analyzed. The results obtained are shown in Table 2.

**Table 2: Results of coal wastes characterization analyzes**

<table>
<thead>
<tr>
<th>Parâmetros analisados</th>
<th>Rejeito de carvão antes do processo de lixiviação</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash (%)</td>
<td>80,4</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>12,4</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>7,2</td>
</tr>
<tr>
<td>S total (%)</td>
<td>9,7</td>
</tr>
<tr>
<td>S pyritic (%)</td>
<td>9,6</td>
</tr>
<tr>
<td>S sulphatic (%)</td>
<td>0,1</td>
</tr>
<tr>
<td>S organic (%)</td>
<td>ND</td>
</tr>
<tr>
<td>Pyrite (%)</td>
<td>23,0</td>
</tr>
<tr>
<td>AP (kg CaCO₃ t⁻¹)</td>
<td>304</td>
</tr>
<tr>
<td>NP (kg CaCO₃ t⁻¹)</td>
<td>0</td>
</tr>
<tr>
<td>NNP (kg CaCO₃ t⁻¹)</td>
<td>-304</td>
</tr>
<tr>
<td>C (%)</td>
<td>5,3</td>
</tr>
<tr>
<td>H (%)</td>
<td>1,0</td>
</tr>
<tr>
<td>N (%)</td>
<td>0,1</td>
</tr>
</tbody>
</table>

The results obtained demonstrate that the material has a very high acidity potential. This indicates potential for generation of AMD. The NNP value is equal to -304, which according to the ABA criteria indicates potential for the generation of AMD.

### 4.3 Kinetic Generation Assays of AMD

Kinetic prediction of the generation of AMD was carried out using the materials used in this work. From the results obtained in the analyzes of the Liquid Neutralization Potential (NNP) of the porcelain powder and the Acid Generation Potential (AP), the mass mixing ratios were determined. The ratio obtained between the porcelain dust mass and the coal tail is approximately 10 times, then static tests were performed with the raw material, with a mixture of 10 parts of porcelain powder and one part of coal tailings, were also 15 parts of porcelain tile powder and one part of coal mining tailings were used. The results indicate what the results of the static tests pointed out, that is, if the coal mining tailings are inadequately deposited in the environment, acidity will occur. And we can classify this waste as high-power generating AMD.

Assays with one part of tailings from coal mining added to 10 parts of porcelain powder indicate that it greatly reduces the potential for acidity generation. Even so there is release of acidity by the material, which indicates that this mass ratio still produces acidity. When a higher proportion of porcelain powder material was used, the potential for acidity generation was greatly diminished, even though in a few weeks the pH became slightly acid. The obtained results indicate that this mass mixing ratio can be used to avoid the generation of AMD.

### V. CONCLUSION

From the results obtained in the present work, it can be concluded that:

Coal mining in Brazil generates millions of tons of coal tailings, rich in pyrite, that generate DAM with great environmental impact. To solve this problem, companies have invested in effluent treatment plants, with high operating costs. However, an alternative to this operational procedure is the adoption of the practice of alkaline additives in coal mining tailings, thus preventing the generation of this serious environmental problem.

The porcelain power was efficient in preventing the generation of DAM, however the ratio of porcelain powder / coal waste mass is quite high.

Also the porcelain powder can be used as a source of alkalinity in the treatment of acid effluent (DAM), however the dosages should be studied aiming at a lower generation of sludge in the treatment process of AMD.

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### REFERENCES


