# DAMAGE INDUCED BY MOISTURE IN BITUMINOUS MIXTURES FABRICATED WITH RED MUD AND STONE DUST AS FILLER: METHODOLOGY FOR ENVIRONMENTAL ANALYSIS

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## ABSTRACT

The usage of solid wastes composing bituminous mixtures is a growing practice and a worldwide trend. Among the several industrial solids studied there is the red mud, a residue generated during the processing of bauxite into aluminum. Like many other materials, the red mud possesses properties capable to promote water contamination when applied on road pavements. However, although there are researches that analyse the leaching of residues from bituminous mixtures, there are no recognized standards that allow a careful and coherent analysis to verify the feasibility of their usage. Thus, this study aims to use the damage induced by moisture test as methodology of environmental analysis for bituminous mixtures composed by two different fillers: red mud and stone dust. For this, four types of mixtures with 7% of filler were manufactured, however, the amount of red mud and stone dust were varied. The water from the test was analysed with a photocolorimeter to verify the residue leaching. The water analysed showed a minimum quantity of red mud leached.

**Keywords**: Red mud. Bituminous mixtures. Damage induced by moisture.

## 1. INTRODUCTION

The red mud is a solid waste originated in the beneficiation of bauxite into aluminum. The process is named as 'Bayer process' and it has four main steps: digestion, clarification, precipitation and calcination [1, 2, 3]. Digestion consists on granulometry reduction of bauxite. At clarification stage, the bauxite is immersed in a sodium hydroxide solution to separate the alumina and impurities (red mud). Precipitation allows taking out the alumina and introducing it to the calcination, when it is exposed to temperatures higher than 960°C [2]. The next stage is the reduction process (Hall-Hérout), where the alumina is transformed into aluminium through electrolytic procedures [3].

Because of the sodium hydroxide, the red mud has alkalinity properties and some heavy metals in the constitution [4, 5]. This characteristic made most part of the researchers classify the red mud as a hazardous waste for the environment. However, there are some studies that classify the red mud as a non-inert waste [6, 7, 8].

There are studies that prove the feasibility of using this residue for construction materials [4, 9, 10, 11, 12], compounding roofs, tiles, bricks, road sublayers, cement and bituminous mixtures.

As the red mud there are a lot of other solid wastes being applied in road layer, however there are no standards that help to evaluate leaching or polluting capacity of the residue inserted in bituminous mixtures.

In this context, this work aims to evaluate the water quality from the damage induced by moisture test and use it as an environmental analysis methodology for mixtures composed with by-products.

## 2. MATERIALS AND METHODS

In this study, were made four types of bituminous mixtures with 7% filler. However, two types of filler were used (red mud and stone dust), as shown below:

- Mixture 1 : 7% stone dust (reference mixture)
- Mixture 2 : 3% red mud + 4% stone dust
- Mixture 3 : 5% red mud + 2% stone dust
- Mixture 4 : 7% red mud

It is important highlight, under Brazilian legislation filler corresponds to a material with 65% or more passing the 0.075 mm sieve.

All the mixtures were made with granite aggregates and bitumen (50/70), compacted using Servopac gyratory compactor. The number of design turns (N) used to establish compaction efforts during the dosage process was 125, corresponding to a high volume traffic.

All mixtures adopted a theoretical grading curve corresponding to the range "C" average, according to the National Department of Brazilian Transport Infrastructure (DNIT) rules.

Prior to carrying out the tests, red mud was evaluated using X-ray diffraction (XRD) and laser granulometry. With bitumen were made softening point, penetration and apparent viscosity test.

### 2.1 Red Mud

The red mud used in this work it is from a company located in the north of Brazil.

The mineralogical analysis of the red mud was performed using X-ray diffractometer RIGAKU, model Miniflex II with copper Ka radiation from the tube and wavelength of 1.540562, parafocal geometry endowed with Bragg-Brentano system.

The test was performed between 2θ angles of 5° to 90°, with step of 0.05 and 1 second. The phases were identified using a database of the International Center for Diffraction Data - Powder Diffraction File (ICDD-PDF) and Crystallography Open Database (COD).

The particle size of the red mud was observed in laser particle analyser Microtrac, model S3500, with a detection range of 0.02 to 2,800 micrometers (μm) using Microtrac Flex software version 10.5.4. This methodology was chosen for convenience and precision of results compared to other forms of particle size measurement.

With the particle size was possible to calculate the specific surface area of the red mud. The same was done for the stone dust filler used at the reference mixture.

The red mud has some agglomeration issues, thus prior to the tests, the residue was dried at 100 °C and crushed in a mortar, which afforded granulometry regularity.

### 2.2 Bitumen

The bitumen used was CAP-50/70, provided by CBB Bitumen Company, based in Brazilian south region.

The bitumen characterization was performed using softening point test, defined by DNIT ME 131/10 [13] standard. Also penetration point, according DNIT ME 155/10 [14], and apparent viscosity made with Brookfield viscometer. The results are presented in Table 1:

**TABLE 1 Bitumen characterization**

| Test | CAP-50/70 |
|---|---|
| Softening Point (°C) | 49,5 |
| Penetration (0,1 mm) | 64 |
| Viscosity (cP) 135°C, SP 21, 50 rpm | 308,67 |

The appropriate mixing temperature for unmodified binders according SUPERPAVE methodology is when the binder has a viscosity corresponding to 170 ± 20 cP, and for compaction, temperature corresponds to a viscosity around 280 ± 30 cP. These values are traditionally applied to bituminous mixtures dosed using the Marshall methodology with pure binders, and have also been used with Gyratory compactions. According to the DNER ME 043/95 [15], binder temperature in both procedures should not be less than 107 ° C or exceed 177 ° C.

With the viscosity results could be set temperatures 148° C and 137° C for mixing and compaction procedures, respectively. The heating temperature of aggregates was 15° C above the mixing temperature of the bitumen, which is 160° C.

## 2.3 Dosage

The dosage mixtures followed AASHTO M 323 and AASHTO R 35 [16, 17] recommendations.

Prior to the compaction process, the bitumen mixtures were conditioned for 2 hours in an oven at a temperature of 137 ° C (compaction temperature), in order to simulate the aging of the bitumen [18]. Compaction was performed in Servopac gyratory compactor, using 1.25° ± 0.02 rotation angle, 30 revolutions per minute rate and 600 kPa vertical stress. The content design adopted for the mixtures with red mud (RM) and stone dust (SD) it is shown at Table 2:

**TABLE 2 Mixtures content design**

| Mixture | Content (% wt) |
|---|---|
| 7% SP | 4,7 |
| 3% RM + 4% SD | 4,6 |
| 5% RM + 2% SD | 4,5 |
| 7% RM | 4,4 |

## 2.4 Damage Induced by Moisture (DIM)

This test is used to analyze the bituminous mixtures resistance to humidity. In Brazil, the standard is prescript by NBR 15617/2011 [19].

To realize this test it was necessary producing 6 samples for each mixture, with 100 mm diameter, compacted with 7±1% voids.

The samples were divided in two groups. Three samples were submitted into a tensile strength test without any conditioning process (A). The other three samples were submitted into a conditioning process (B), where the samples are saturated with 55 – 80% of water, afterward, frozen into a -18°C temperature for 16 hours and then allocated inside a container with water at 60°C for 24 hours.

After conditioning, it is made a tensile strength test with the samples. The results between both groups are compared. This process can be seen in Figure 1:

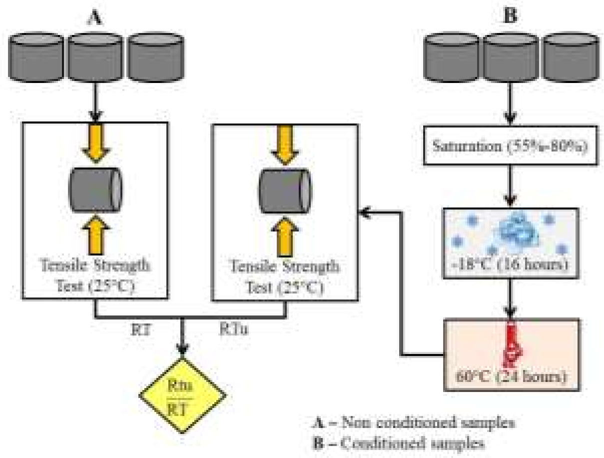


**FIGURE 1 Schematic representation for DIM**

## 2.5 Water quality analysis

In this work, the water analysis from damage induced by moisture test has preliminary character, and aims to exam the possibility to use this method as an environmental parameter to predict leaching from surface road layers.

The samples conditioning at 60°C were made in 60 liters container, equipped with resistances to maintain the temperature, and some conduits which maintain the water circulating inside.

The analyze was made with the water before conditioning (reference sample) and after conditioning samples. The samples with 0% and 3% red mud were conditioned together in first place, then the conditioning process was made with 5% and 7% red mud samples, also together. Thus, 6 samples were put in the container each time, 3 for each mixture. The quantity of water collected was 500 ml.

The water analysis was made using photocolorimeter, equipment that determines concentration according the wavelength emitted by the solution.

As iron and aluminum are representative elements in red mud, they were the chosen substances to be analyzed. Phosphorus and zinc were also evaluated. Other substances could not be evaluated due to the restriction of reagents available. Alkalinity was also evaluated.

Each sample had 5 ml. Were made 3 samples for each analysis (pH, Aluminum, Iron, Phosphorus and Zinc).

The pH analysis was made using a visual comparison with color chart.

# 3. RESULTS AND DISCUSSION

## 3.1 Red mud caracterization

The X-ray diffraction detected phase of hematite ($Fe_2O_3$), anatase ($TiO_2$), quartz ($SiO_2$), karelianita ($V_2O_3$), gibbsite ($Al(OH)_3$) and sodalite ($Na_8Mg_3Si_9O_{24}(OH)_2$), formed during the Bayer process.

Hematite, the anatase, quartz, gibbsite and sodalite are substances that do not pose health risks, except as noted in concentrations higher than those allowed by standard (Appendix 'G') NBR 10.004 / 2004 [20].

The karelianita ($V_2O_3$), or vanadium trioxide in the presence of moisture can come to oxidize and turn into vanadium pentoxide ($V_2O_5$), in the list of 'substances which give hazardous waste', on Annex 'C' of NBR 10.004 / 2004.

Despite the red mud pH was 10,25 ± 0,05, because of the $V_2O_5$ presence the residue can be classified as Class I – Dangerous according Brazilian standards.

At laser granulometric test can be seen that the red mud is a fine grained material with 100% of the particles smaller than 290 µm, 80% than 50 µm in diameter and 40% than 5 micrometers.

The particle size of the red mud is an important factor to be considered when it is used compound bituminous mixtures, since particles bigger than 40 µm tend to fill the voids of the aggregates and particles smaller than 20 µm are mixed to the bitumen, modifying the viscosity, softening point and thermal susceptibility [21, 22, 23, 24].

Therefore, since about 70% of the grains that make up the red mud have a particle size less than 20 µm, it is possible that part of the residue used in the composition of bitumen mixtures is incorporated into the CAP, changing its rheological properties.

The specific surface found for the red mud was 119.003 $m^2$ / kg, and for stone powder was 132.287 $m^2$ / kg.

### 3.2 Environmental Analysis

All the samples used in the damage induced by moisture test obeyed the voids range (6% - 8%) stablished by the standard.

After samples conditioning, parameters as Aluminum, Iron, Phosphorus, Zinc and pH were analyzed using photocolorimeter. It is important mentioning, before each test the water container was cleaned to avoid contamination and discrepancy results.

The results were compared with reference water collected before conditioning samples, as shown in Table 3:

**TABLE 2 Water analysis after conditioning samples**

| Analyzed Parameter | Reference water | Water from 0%-3% red mud mixtures conditioning | Water from 5%-7% red mud mixtures conditioning | Accepted ranges |
|---|---|---|---|---|
| Aluminum ($mgL^{-1}$) | **0,42** | **0,98** | **1,44** | 0,10 |
| Iron ($mgL^{-1}$) | 0,09 | **0,41** | 0,29 | 0,30 |
| Phosphorus ($mgL^{-1}$) | **0,61** | **0,81** | **0,47** | 0,025 |
| Zinc ($mgL^{-1}$) | 0,03 | 0,05 | 0,06 | 0,18 |
| pH | 7 | 8 | 8 | 6 – 9 |

According to CONAMA Nº357/2005[25] Brazilian resolution, the accepted ranges presented in the Table 3 correspond to domestic water consumption, able to normal utilization (except drinking).

The Aluminum and Zinc concentration increase according to the red mud percentage in the samples tested. This indicates a relative leaching from the bituminous mixtures. All water samples analyzed had higher aluminum concentration than the maximum limit allowed by Brazilian standards, which means neither the public water supply could be accepted.

As aluminum, iron is not considered to be toxic. However, it brings several problems to the public water supply, giving color and flavor to the water. For these reasons, it is stablished 0.3 mg/L the iron limit concentration.

Despite Iron being one element present in the red mud, the higher quantity of Iron found in water from 0%-3% red mud mixtures conditioning suggests this variation can be caused by the quality of the water, and not necessarily by the leaching of the residue.

As Phosphorus and Zinc are not common elements found in the red mud, the different values suggest a variation in the water pattern from public supply. Neither of the samples respected the maximum Phosphorus limit. The zinc variation suggests there were no influence from the samples in the water concentration.

The alkalinity measured in the water samples it is other evidence about red mud leaching, once the residue has a pH around 10 and the reference water has a pH = 7. In this case, the red mud could be the cause for the increasing alkalinity.

## 4. CONCLUSION

The granitic rocks used in this work have electronegativity and hydrophilicity characteristics, which may have been responsible for the reduction of adhesiveness to the asphalt binder in the presence of water.

Although the red mud has some electronegative substances in its composition, it is possible the residue might be able to improve adhesiveness between binder-aggregates by the existence of electropositive elements, such as calcium and sodium present in its composition.

The red mud is composed by hydrophobic and hydrophilic substances, which characterizes it as an amphiphilic material. Which means it is capable of being dissolved in polar and nonpolar solvents. Thus, at the same time as the residue is surrounded by the binder, when in contact with water, part of its components tend to be dissolved, favoring the release of the non-encapsulated red mud.

The water evaluation carried out in this work is preliminary and therefore it cannot be said that the use of red mud in asphalt mixtures is capable of causing contamination to the environment.

The water analysis from damage induced by moisture test can be used as an environmental methodology evaluation, especially to identify any hazardous leaching from bitumen mixtures. However, it is necessary do more precise and deep evaluations regarding the polluting substances capable to affect underground water channels.

Therefore it would be necessary using more reagents or other equipment specialized in water analysis. It is important check local regulations regarding the maximum limits per element in the water.

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