

## Possibility of removing metals from acid mine drainage using industry waste processing agates as adsorbent

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**Abstract** A major challenge among researchers in recent years is the possibility of converting waste into products for primary use. The challenge is to change them, through simple and/or complex reactions, into useful raw material to be used in many technological applications. In return, it reduces environmental impact. The agate, an inorganic solid mineral founded in the crust, composed by silicon oxide and other oxides lesser extent, when extracted from nature, has about 65% success rate as feed-stock in the cutting process, and its waste is disposed in landfills. The sample used for this project was collected from one of these landfills. The collected material, when characterized by x-ray fluorescence and x-ray diffraction, showed in its composition above 98% of microcrystalline silica. The particle size was comminuted till passing through the sieve 200 mesh, Tyler series, and subsequently subjected to heat treatment. The microcrystalline silica subjected of the tests demonstrated satisfactory results when used as adsorbent to remove metals in Acid Mine Drainage (AMD). This microcrystalline silica revealed to be a satisfactory product by removing iron, copper, and aluminum, among other metals present in AMD.

**Key Words** microcrystalline silica, AMD, metals removal, adsorption.

### Introduction

About 60% of the silicon element present in Earth is in silicates form, which are one of the mineral types that occur naturally (Prado et al. 2005). Silica is one of inorganic material most used as substrates for a great number of applications, showing excellent adsorption properties. The microcrystalline silica can be found in the waste of agates rocks, reaching the amount around 98% of this waste, which are widely distributed in the crust. Brazil and northern Uruguay (PMSJ, 2009) is currently the world's most important source of agate. Brazil is leading producer of color gem and Rio Grande do Sul State has the highest production of agates, citrins and amethysts. The processing of these gems generates a large amount of waste, which are often improperly disposed. These wastes, when processed and characterized, presents possibility of reuse. Moreover, with increasing production costs and reduced availability of raw materials, combined with environmental constraints, it has increased the tendency to maximize many possible ways to incorporate by-products, generated in production processes, by the necessity of reducing environmental pollution. It is noteworthy also importance of this product, that can be useful by local economy. Based on the results obtained by adsorption in the removal of metals in AMD performed in laboratory, indicates positive characteristics for use. Detailed study is been developing. The regional waste generated shows to be value-added product, resulting in decreased exploration of nonrenewable resources. The microcrystalline silica was also used to check the possibilities for use as adsorbent in adsorption-desorption process for removing metals present in AMD, especially iron.

### Methods

Sampling procedure was performed on site as described by NBR 10007 (ABNT 2004). The sample used was provided by mineral beneficiation company from northern Rio Grande do Sul, Brazil. The granulometry analysis was accomplished by sieving, accordingly to NBR 6502 (ABNT 1995). For comminuting of the sample that did not pass the sieve 200, it was used a digital planetary mill, model Fritson, in a rotation of 370 rpm, for a period of 8 minutes, in order to the particle size acquires 0,075mm. After testing to determine the ideal time and temperature, it was shown that the ideal temperature for heat treatment is 700 °C, and the ideal period of stay in the furnace is one hour, for verifying adsorption property optimization of the microcrystalline silica. The raw material chemical composition was determined by X-ray fluorescence (XRF) and was quantified

through rational analysis. The main application of X-ray diffraction refers to the identification of crystalline compounds, whether organic or inorganic. The device used to determine BET (surface area) was the Quantachrome Nova-1200. The data were treated by providing specific surface area. In this work the objective analysis of the use of the zeta potential is checking if the microcrystalline silica is electronegative, reacting with ions or electropositive, reacting with anions. The determination of adsorption and removal of metals can be done by analysis of atomic absorption spectrophotometer. After separate out the solid (adsorbent) used for the removal of metals and the liquid portion containing the remainder of the AMD solution, which was then submitted to the new reading measuring the pH and investigation of metals in atomic absorption equipment.

**Results and Discussion**

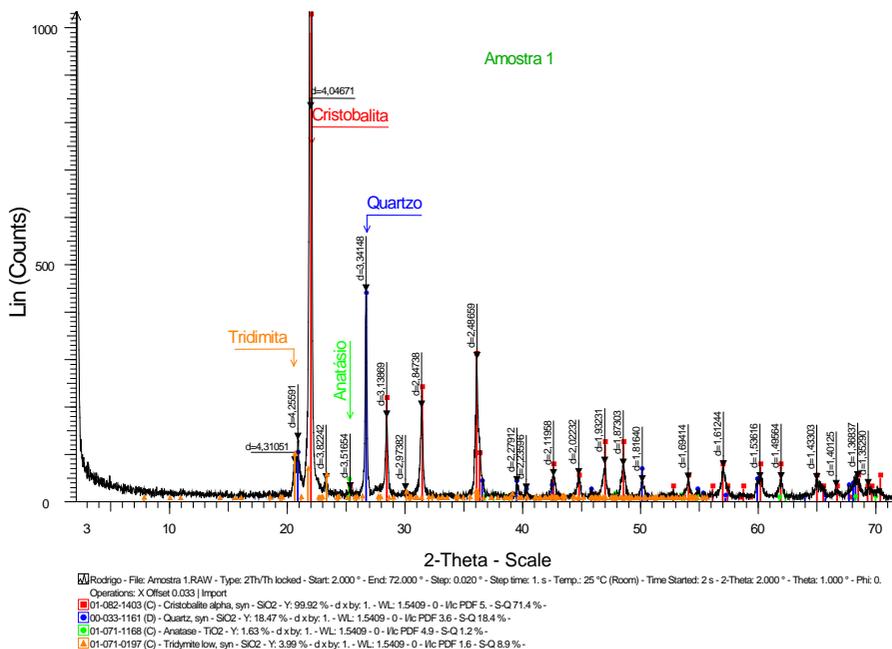
The collection of samples was performed according to NBR10007(ABNT 2004) and packed in plastic bags to preserve their chemical and physical characteristics. The result grind features the microcrystalline silica with the desired size after 8 minutes in a planetary mill. The results of X-ray fluorescence showed that the material is composed of more than 98% silicon oxide, about 1% aluminum oxide and iron and other compounds in smaller proportions.

By X-Ray Diffraction, one can observe that the silicon oxide, major compound, is divided into three distinct crystalline phases: cristobalite, tridymite and quartz. The results compared by X-ray diffraction peaks indicates a change in relation to its location on the graph, where before there were peaks of cristobalite, tridymite, anatase, after heat treatment left only the peak of quartz, with lesser intensity. This change can be seen in Figures 1 and 2.

Aiming to confirm the increased of porosity of the material, BET analysis was performed to visualize the surface of microcrystalline silica treated. Compared with a natural zeolite with a BET of 55m<sup>2</sup> / g (Oliveira, 2006), this studied silica has 4,91 m<sup>2</sup> / g. Anyway, adsorbent properties can be seen in Figure 3.

**Zeta Potential**

After proper characterization of the product and confirm that it has properties and affinity adsorbents for cations present in the Zeta potential negative character, the next step was to simulate the system under agitation for removal of dissolved metals present in the AMD. AMD in nature,



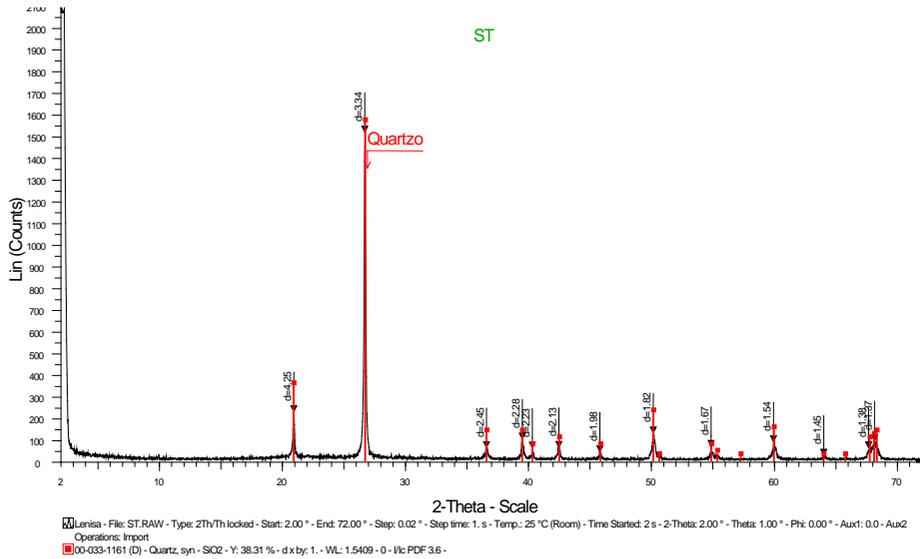


Figure 2 X-ray diffraction of heat treated microcrystalline silica

which initially had a pH of 3.7, was prepared after its reading of pH in Erlenmeyer flasks at a rate of 100 mL stipulated the ideal in this testing phase of this work. There were added various percentages of microcrystalline silica, containing varying characteristics of the fresh samples, only heat treated (calcined at 700 ° C for one hour), so that the simulation was a process under agitation to highlight the right amount for it to carry out the adsorption process and the optimal concentration.

**Determination of Adsorption**

In the system used for the metals adsorption, it was used a procedure that consisted of a system under stirring the mixture of the adsorbent with the solution until it reached equilibrium. After this stage, which was monitored every 30 minutes (till 8 hours of test) to determine the optimal time of reaction, was performed the separation of solid and liquid, to thereby calculate the amount of metals in solution was adsorbed by microcrystalline silica. These results were based on the reading equipment for atomic absorption determination of the initial concentration of the metals studied in solution and adsorbed in amount for the microcrystalline silica used as adsorbent. The

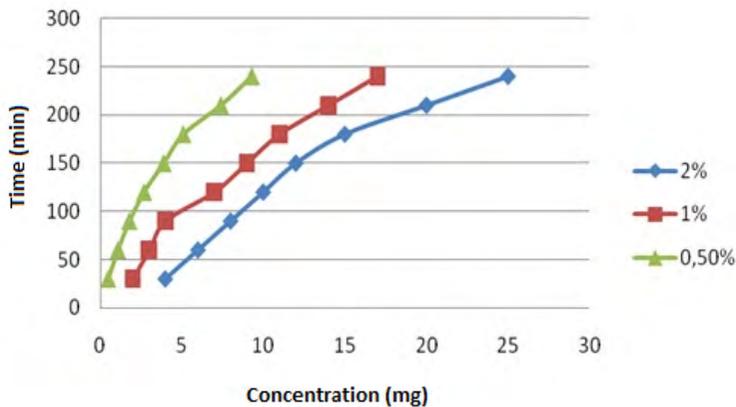


Figure 3 Blue methylene removal with calcinated silica at several temperatures in one hour time, using concentration adsorbent of 0.5%, 1% and 2%

microcrystalline silica tested was used in three ways for a satisfactory comparison and choice in the most appropriate use as adsorbent for removal of metals in AMD. These were: fresh as they were collected without any treatment and the product obtained from the collection by heat treatment. For each type of material under study, it was used different concentrations of the adsorbent in an amount determined in 100 mL of AMD and previously characterized by analysis of atomic absorption spectroscopy to verify the amount of metals present in the same investigation.

Microcrystalline silica was used in two ways and with different concentrations in solution, the two types were: no treatment and heat treatment. For each of the two types of silica used in the test were tested with concentrations of 500 mg, 800 mg, 1g, 2g, 4g and 5 g in flasks containing 100 ml of solution, the samples were placed under an agitation of 130 rpm for a specified period of four hours. After this period the samples were centrifuged and then subjected again to read the pH, to determine whether there was a change. The microcrystalline silica 2% only subjected to heat treatment showed to be ideal for presenting final pH of 6.8. The samples were then subjected to analysis by atomic absorption to verify the removal of metals in the AMD. The results were satisfactory using 2% microcrystalline silica removal which showed a decrease of 4,852 to 1,58% of iron (remotion of 32,57%) in the silica at 2% solution of AMD, a decrease of 0,1465 to 0% of aluminum (remotion of 100%) and a decrease from 0,105 to 0,038% copper (remotion of 36,19%). It was proved then that the ideal reaction time is 4 hours and a concentration of 2% for significant removal of metals such as iron, aluminum and copper. This time was ideal because after that the remotion rate was not significant.

### Conclusion

The tendency of the full use of waste is an increasing need due to serious environmental problems that have occurred worldwide. Because of its high percentage of silica, the residue of agate stones used as microcrystalline silica studied demonstrates a technological potential as feedstock for producing an adsorbent which can be used for various purposes. The tests showed the potential use of this waste, after heat treatment, removing the metals present in the AMD, thus reducing waste generation, treating an environmental problem at the moment using a drainage which means a serious environmental problem in beneficiary industries of coal and also bringing an economic return for companies. It was shown in this study that the optimum reaction time is 4 hours and a concentration of 2% for significant removal of metals such as iron, aluminum and copper. Further tests are being carried out following this study, aiming to confirm these data and their use in industrial scale. For that, intending to micronize the silica, diminishing its particle size, increasing its superficial area, improving its adsorbent properties.

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### References

- Associação Brasileira de Normas Técnicas. Rochas e solos- terminologia. NBR 6502, Rio de Janeiro, 1995.
- Associação Brasileira de Normas Técnicas. Amostragem de Resíduos Sólidos NBR 10007. Rio de Janeiro, 2004.
- Belmonte, E. P.; Espectrometria por fluorescência de Raios X por reflexão total: um estudo simulado utilizando o método de Monte Carlo; Dissertação (Mestrado em Engenharia- UFRJ); Rio de Janeiro, Brasil, março de 2005.
- Brunauer S.; Emmett P. H.; Teller E.; Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society* 60:309—19, 1938.
- Gomes, L. G. Estudo da caracterização física e da biodegradabilidade dos resíduos sólidos urbanos em aterros sanitários Dissertação de Mestrado – Escola de Engenharia de São Carlos – USP, 167p., 1989.
- Oliveira, C. R. Adsorção-remoção de íons sulfato e isopropilxantato em zeólita natural funcionalizada Dissertação – Mestrado de Mestrado – Escola de Engenharia– UFRGS, 135p., 2006.
- Prado, A.G.S; Maria E. A.; Padilha, M.P.; Aplicação e Modificação Química da Sílica Gel Obtida de Areia. *Química Nova* vol.3; pg. 544; 2005.
- Prefeitura Municipal Do Salto Do Jacuí (PMSJ), Salto do Jacuí: Capital Mundial das Pedras Águas, Salto do Jacuí, RS, acessado em 06/12/2009, disponível em, [www.rotadasterras.com.br/saltodojacui](http://www.rotadasterras.com.br/saltodojacui).