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Waste generation in Agate processing: use of SiO2 as a support matterial for Fe3O4

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Abstract — **Brazil is one of the main producers of colored gemstones, and Rio Grande do Sul is the state with the greatest production of agates, amethysts and citrines. This sector is preponderant in the economy of the regions of the Upper Uruguai and Middle Plateau, but it faces technological difficulties, among which we can highlight the large volume of gemstones exported in rough state, with low added value, and the low efficiency equipment. Another problem is the sheer volume of waste generated without the adequate treatment and appropriate place for disposal. The purpose of this study is to conduct a diagnosis of the processing of the gems, identify the types of waste generated and the importance of the implementation of environmental management for this industrial sector and propose an alternative of SiO2 use (a residue from the processing of Agates) as a support material for the compounds based on iron oxides.**

Keywords – **agates, residue, SiO2, Fe3O4, support material**

I. Introduction

Brazil stands out in the international gemological market as one of the biggest suppliers of colored gemstones. The state of Rio Grande do Sul is recognized for its production of agates, amethysts and citrines; in 2003, its exports in this sector reached US$ 47 million.

The local productive arrangement covers five regional municipalities: Ametista do Sul (where amethyst and citrine are produced), Salto do Jacuí (producer of agate) and Guaporé, Lajeado and Soledade, where the commercialization and export centers are located (Figure 1). There are about 300 micro and small companies operating in this sector in these cities [1].

The production of ornamental stone artifacts is mainly located in Soledade, Lajeado and Teutônia. Soledade is the center of industrialization and exportation of amethyst and agate products. About 95% of the production is exported, mainly to the USA, Germany and England.

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According to SINDIPEDRAS/RS, there are about 180 companies (micro, small, medium and large) producing artifacts of amethysts and agates in Soledade, and about 30 of these businesses are also exporters. The sector holds around 1,500 direct jobs and 3,000 indirect jobs, representing 31.5% of the GDP of the city economy. Exports of precious stones are responsible for 78.9% of the state mineral sector exports [2]. In Fig. 1 we have a map of South America and the region of Soledade, an important producer of precious stones.

Figure 1. Map showing the location of Soledade.

The manufacturing process is comprised basically of cutting and/or crushing operations, washing, trimming (pre-formation, drilling), dyeing, thermic treatment and polishing.

Cutting is the first step in the processing of agates. It is in this step that the pieces get their definitive form. The agate geode is trapped in a mobile vise perpendiculary to a diamond wheel powered by an electric motor, and the cooling of the resulting cut is made with fuel oil. This step presents great defficiency, because many times the equipment is built in-house without taking into account technical parameters for construction. The crushing is performed in a Jaw Crusher which aims at the fragmentation of agates [3, 4].

The first washing is performed to remove the oil from the cutting and other wastes which may adversely affect the uniform dyeing of pieces. Special detergents, soda solutions and washing powder are the products that are normally utilized. After a period of immersion the parts are rinsed under pressure and brushed piece by piece for a proper cleaning.

In trimming, the final shape of larger parts is given by wearing them with an abrasive in sandpaper; for smaller parts, the final form is obtained with vibrators. Also at this stage, some companies use more sophisticated equipment called copiers or grinding machines.

Dyeing is basically performed with inorganic colors, so called hot, which are: hot green (chromium oxide), hot red (iron oxide), blue (potassium cyanide) and black (burnt sugar); and with colors obtained by organic dyes, called cold, which are: cold green (bright green), pink (rhodamine B), purple (crystal violet) and red (mixture of rhodamine B and basic orange).

Polishing is the final step in the lapidation process and it can be separated into two types, depending on the size of the pieces. The larger pieces are polished in fixed grinding wheels and the smaller pieces are polished in vibrators with abrasives. The usual sequence of operations is demonstrated in the flowsheet representing the beneficiation of Agates, shown in Fig. 2.

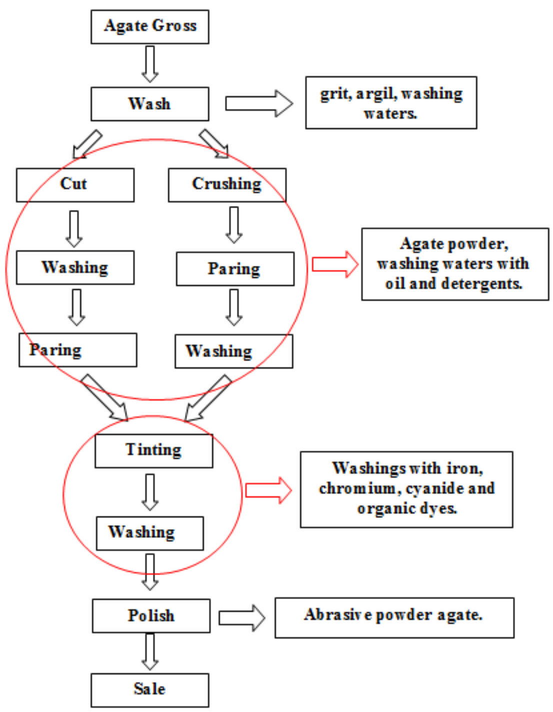

Figure 2. Basic fluxogram from Agate beneficiation.

The tailings from the beneficiation of Agates may be used as support material for particles in various sizes, including nanometre and the micrometric dimensions, supporting materials such as copper (Cu), Platinum (Pt), nickel (Ni) and iron compounds (FeO, Fe2O3). In particular, the obtention of iron compounds over the years has been achieved by various chemical practices, starting with metal precursors and resulting in colloidal systems supported in SiO2 and interacting with other noble metals, such as Platinum (Pt) and rhodium (Rh) [5-7], or supported in coal, used, for instance, in the oxidation of CO [8]. The use of nanoparticles (NPs) has generally been successfully applied in different processes, where it is possible to observe gains, not only in technology and inovation, but also in financial aspects, when compared to bulk materials. The obtention of nanostructured pigments supported in SiO2 can represent a milestone in this knowledge field, enabling applications beyond those which already exist with the use of microstructures, applied in cement mortar, cinder blocks and colored pavers, due to the modification of their optical, mechanical, electrical, magnetic and catalytic characteristics which are directly linked to changes in their electronic and structural properties.

A. *Generation of waste*

The industrialization of gems produces as waste cutting mud, metal ions, organic dyes in solution and washing waters from the different processes, which comprise buffing, polishing, dyeing and stoning. In an optimistic approach, it can be said that 65% of the weight of the rough agate is transformed into saleable product. Table 1 lists the residues with their origin in the production process [9].

TABLE I. COMPARISON OF PROCEDURES FOR PROCESSING AND TYPE OF RESIDUE GENERATED IN EACH.

Process	*Residue*	*Utilization of the residue/destination*
Selection: The agates are selected according to the "exportable" criteria;	Agates without quality to conventional processing;	What is not exported supplies the local industry;
Crushing (optional cut): production of agates fragments in a Jaw Crusher followed by a trommel classifier;	Agate fragments with diameter below 3cm and agate powder;	**Fragments:** used in the jewelry industry; **Agate powder:** landfill of land;
Cut: the cut is done with diamond wheels, chilled with naval oil during operation;	Cutting mud (mud containing agate powder and oil);	**Oil:** separated from dust and reused without due process; **Agate powder:** filling material in cement mortar;
Washing: the material is left immersed in the cleaning solution, then brushed and rinsed under pressure;	Alkaline effluent containing oil and detergents, powder of agate;	**No studies so far;**
Dyeing: dyeing operation consists in placing the pieces of agate immersed in one or two subsequent solutions, depending on the color;	Effluent highly contaminated with ions (iron, chrome and cyanide) and organic dyes (bright green, rhodamine B, crystal violet among others);	**Treatment and disposal in some companies;**
Thinning: For smaller parts it is utilized abrasive in the form of powder and drums (similar to a ball mill); to larger parts it is utilize abrasives in the form of sandpaper;	Agate with abrasive powder;	**Agate powder:** landfill of land;

Process	*Residue*	*Utilization of the residue/destination*
Polishing: For larger faceteded pieces it is used felt wheels with abrasive; for smaller parts it is used barrels similar to those used in thinning.	Agate powder, Tripoli.	**Agate powder:** landfill of land;

B. *Destination and residue treatment*

Fragments of agates: some industries specialize in producing ornaments and personal adornments with fragments of agates which are not featurered for artifacts making.

Agate powder without oil: generally speaking, the agate powder is composed of approximately 98% SiO2 thinly fragmented, with 95% of it with dimentions below 74 µm. This material is currently used for padding in landfills. According to Tramontina et al (1997) [10] agate powder residue can be used in the building industry as a filling material in cement, at a concentration of up to 1.25/5 of the cement-sand mass.

Agate powder with oil: in industries with an organized structure, the mud resulting from the cutting of agates is processed to be separeted from the oil. This process consists of mixing water to the mud and stiring, forming two phases, one in the superior level with oil and other in the bottom with agate powder. After that the oil is recovered and returns to the process, while the agate powder is used as an abrasive agent mixed with Tripoli dust. Then, the effluent is led to a separation box for treatment.

Effluents: effluents are treated by a physical-chemical process (pH adjustment, coagulation/floculation, decanting). Then the effluent is released in surface waters and the sludge generated in the treatment is sent to industrial waste landfills. Figure 3 presents a conventional scheme of treatment of effluents generated in the processing of gems.

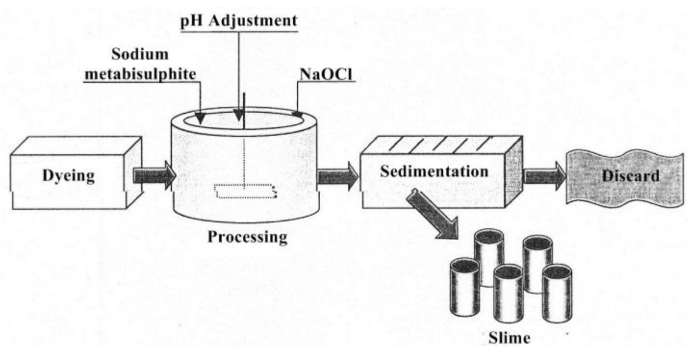

Figure 3. Conventional treatment process of wastewater generated in the process of processing of gems [11].

The dyeing of agates in exotic colors obtained with organic dyes has been gaining space, given its good acceptance in foreign markets, mainly in the U.S., Japan and China, and given the fact that its production processes are simpler. However, the effluents from the washing waters feature a high organic load and intense color due to the dyes.

Some methods have been developed in an attempt to reduce the impacts caused by these highly coloured effluents, which may include:

a) Photochemical Degradation: It uses solar radiation as an alternative source of energy; on the other hand, this method requires large areas, low flow and high time of detention. The addition of semiconductor as process catalysts has been studied with some success for textile industry effluents [12].

b) Oxidation with sodium hypochlorite: Discoloration with Sodium Hypochlorite (NaClO), is currently the most utilized process in industries, mainly because of its easy implementation and low cost. However, there is a risk that, during the oxidation of stained compounds, organochlorine molecules may form. These molecules have biocumulative properties in living tissues, altering the functioning of the cells. PCBs and DDTs, dioxins and furans, form the group of organochlorines, which are highly toxic [13].

c) Advanced Oxidative Processes: advanced oxidative processes (AOPs) are based on the generation of the radical hydroxyl (OH), a species with high oxidizing potential. This process has high-efficiency in the oxidation of complex organic compounds, producing simpler molecules, more susceptible to biodegradation, or in some cases, leading to the total mineralization with only CO_2 and H_2O being left. The Fenton reaction belongs to the advanced oxidative processes and it was used to treat the effluents of agate industry by Carissimi et al, (2006) [14], presenting good results in decontamination.

II. Experimental

A. *Sample synthesis*

One of the products of processing agates are the boulder which are obtained from the thinning of agate pieces with no aggregate commercial value. This material is placed in ball mills without grinding load, where the gems friction produces by itlself the thinning and generates a powder material with low particle size (passing 300 mesh), good adsorption characteristics and specific surface area. The adsorption capacity of this residue by the "methylene blue" technique presents a specific surface area of 80 m2.g-1 [15, 16]. The SiO2 resulting from this production process was used as a support for the iron oxide particles. The material is mainly composed of 98.9% of SiO2 and 1.1% of other oxides (FeO2, Al2O3, CaO, K2O, SO3 and TiO2). Containing SiO2 in Quartz and Cristobalite structures.

The iron oxide was synthesized via hidrometalurgic route, with pH and salt concentration according to literature [17]. After the preparation of the FeSO4 solution, 10g of SiO2 residue was added to the system under agitation for 3 hours. After this period the pH stabilized between 9 and 12. The system remained in turmoil for 24 hours, occurring the formation of magnetic material supported on the SiO2 resulting from the beneficiation process of Agates.

III. Results

A. Iron oxide supported on residue

The acquired SiO2 was placed into the solution containing particles of iron compounds. The following diffratogram, shown in Figure 4, has the crystalline plans refering to the SiO2 phase represented by the colour blue, and Magnetite phases represented in black, according to the ICSD database number 039830 (SiO2) and 064829 (Fe3O4). In this case the two phases appear, one provenient from the SiO2 “support material” and another from the particles absorbed in the support, containing Magnetite phase. This experiment promotes the recovery of waste from the processing of Agates as support, in this case acting as a kind of anchor to the structures containing iron oxides. This resulting material has a black color when in the dust stage, with adsorbents and reducing magnetic properties [18]. This material can be applied in various fields in science, especially in the paint industry, in the building industry and in the production of colored pavers and concrete blocks, aiming at the use of residue rather than conventional sand and contributing to an environment-friendly process and to wastewater treatment as adsorbents of toxic metals. In Fig. 4, next to the diffratogram we have the representation of the crystal structure in the form of clusters of the SiO2 support and of the Magnetite.

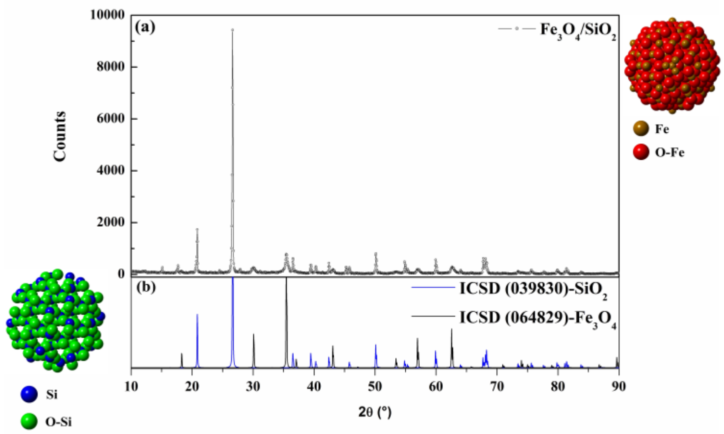

Figure 4. (a) Diffratogram of Fe_3O_4 particles supported on SiO_2. (b) indexation of crystalline plans corresponding to SiO_2 and Fe_3O_4, accompanied by the representation of the clusters for each structure.

IV. Discussion

The gemstone sector has a great influence on the economic development of the region. Due to the large number of small and informal enterprises, the environmental surveillance is impaired. In a general way, the gemstone sector, specifically around Soledade, demonstrates a disregard for the environment. The treatment of waste is performed by few companies, only about 2% of the total. Moreover, with the fall of the dollar exchange rate, in some big companies there was an outsourcing of the polluting production processes, aiming to reduce operating costs. The few companies which treat their effluents use the traditional method in which the goal is to transfer pollutants from a dispersed phase for another concentrated, without taking into account the advantages of new treatment processes. However, some companies are noting the importance of preserving the environment as a way of reaching new markets that prefer eco-friendly products.

However, currently the environmental situation has been aggravated due to the fall of the exchange rate, given that 95% of the production is exported. Aiming at reducing production costs, larger industries have outsourced some polluting production processes to small businesses, transferring the burden of treating the generated waste. These small industries, which are generally informal, dispose the industrial waste in the environment without pretreatment, generating an unprecedented environmental damage.

Yet, all environmental initiatives that have been implemented to remedy the environmental damage caused by processing industries of agates are not according to environmental trends, for it is still believed that the solution lies at the end of the process, or in the treatment of "end of pipe", and not on the application of the concepts "reduce, re-use and recycle". To achieve a substantial reduction in the environmental impacts, an assessment at each stage of the production process is required, reducing losses and increasing efficiency, therefore providing a reduction in waste generation.

An alternative of reduction and use of one of the stages of processing agates is using it as support for other materials, whether they are oxides or even metallic nanoparticles that can be used in the building industry, as well as in the paint industry.

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