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Environmental Issues on the Industrial Processing of Raw Agate

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Abstract

Agate geodes are treated and stained for the production of handmade artifacts and jewelry, which greatly increases their aggregate value. Unit operations involve storage, sorting, cutting, crushing, dyeing, polishing, washing, and finishing. Substantial amounts of waste materials are produced, which include agate pieces, powders (with or without oils), and wastewaters from organic and inorganic staining procedures. The aim of this work was to quantify the amounts of these waste materials, their characteristics, and possibilities for reuse or recycling in other productivity sectors in the context of the second decade of the 21st century. A review of the theme was carried out and possibilities were analyzed in the light of classic and new technologies.

Keywords

Agate, Waste Materials, Environment

1. Introduction

Agates are fascinating minerals because of their wide spectrum of colors and forms. Agates are in general banded chalcedony with the chemical formula SiO_2, but in detail, they may represent a mixture of certain SiO_2 polymorphs and morphological quartz varieties [1]. They are found in sedimentary, metamorphic, and igneous environments, and can be present in every continent. More resistant to erosion than their surroundings, agates often survive long after their host rock weathers away [2].

Most agates originate as nodules in volcanic rocks or ancient lava, in former cavities produced by volatiles in the original molten mass, which were then filled, wholly or partially, by siliceous matter deposited in regular layers on the walls. Such agates, when cut transversely, exhibit a succession of parallel lines, often of extreme tenuity, that give a banded appearance to that section [3].

During the formation of an ordinary agate, it is possible that waters containing silica in solution—derived, perhaps, from the decomposition of some of the silicates in the lava itself—percolated through the rock and deposited a siliceous coating on the interior of the vesicles. Variations in the character of the solution or in the conditions of deposition may cause a corresponding variation in the successive layers, so that bands of chalcedony often align alternately with layers of crystalline quartz. Several vapor-vesicles may unite while the rock is still viscous, and thus form a large cavity [4].

The segregation of the silica polymorphs; with their different microstructural and compositional characteristics, create a distinctive concentric banding pattern observed in typical banded agates (**Figure 1**). The nomenclature and characteristics of SiO_2 minerals typically present in agate geodes are shown in **Table 1** [5].

The earliest evidence for working with agates comes from Mesopotamia, where ornaments and tools have been recovered. The best know is an axe head of agate with cuneiform writing on the side. It has been dated to the third millennium BCE [6]. The area of Idar-Oberstein in Germany may be the oldest gem-cutting center in the world. This region (then known as Hidera) supplied cut and polished agate to the Greeks and Romans and remained an important center for agate carving and polishing during the Middle Age and Modern Eras [7]. The knowledge developed in this site was brought to South America in the beginning of the twentieth century by a German artisan, which allowed for the development of the Southern Brazilian and Uruguay agate industry [8]. Currently, Brazil and Uruguay stand out in the international gemological market as major suppliers of raw agate and the stones are processed in hundreds of micro and

Figure 1. Transversally cut sample of raw agate.

Table 1. Nomenclature and characteristics of SiO_2 minerals typically present in agates (adapted from [5]).

Variety	Microstructure	"Crystal" size	Total water
Quartz	Crystalline	>20 µm	~0 wt.%
Fine-quartz	Granular	5 - 20 µm	<1 wt.%
Chalcedony	Parabolic fiber bundles	<100 µm length	1 - 2 wt.%
Crypto-crystalline	Poorly defined		1 - 10 wt.%

small enterprises worldwide [9] [10]. For example, the local productive arrangement of Rio Grande do Sul, Brazil, accounts for 300 companies and 1,500 direct and 3,000 indirect jobs.

Industrial uses of agate exploit its hardness, ability to retain a highly polished surface finish, resistance to chemical attack, as well as natural or post-staining beauty. Some uses are as follows:

- knife-edge bearings for laboratory balances and precision pendulums,
- mortars and pestles to crush and mix chemicals,
- balls for mills,
- jewelry,
- general handmade artifacts.

Processes involved in agate beneficiation produce waste materials that challenge the production sector for reduction, reuse, recycling, or the best form of discharge. Thus the aim of this work was to depict such waste materials by their characteristics and amounts, and analyze alternatives to improve environmental efficiency and, consequently, the sustainability of the sector.

2. Agate Beneficiation

The manufacturing process of agate is comprised of a sequence of operations that obtain, basically, plate-shaped, and pebble-shaped stones. The sequence of unit operations is summarized in **Figure 2**.

The agate geodes are sorted, shaped, dyed, washed, and prepared for sale. After geode selection, cutting is the first step in the processing of agates. It is carried out with diamond saws powered by electric motors. Diesel or naval oil are applied over the stones for the purpose of cooling and lubrication. The inside of the machines accumulate agate fragments resulting from the sawing process, most of them of very small particle size. Periodically, it is necessary to clean the machines, giving rise to an agate and oil sludge.

The agate plates are washed (first washing procedure) to remove the oil, which may adversely affect the subsequent dying procedure; special detergents and soda ash are normally utilized. The water from washing results in wastewater containing fine agate fragments, oil, and surfactants, which is treated in a water/oil separator container. It is also appropriate to submit the fresh plates to a sanding operation to remove the impregnated soil on surface pores, which could hinder the dyeing step that follows.

Dyeing is performed with inorganic or organic procedures, which are shown in **Table 2**, and samples of stained agate plates in different colors are shown in **Figure 3**. The classical inorganic procedures were developed in Idar-Oberstein, Germany [8]. The colors produced are: green (chromium oxide), red (iron oxide), blue (potassium cyanide), and black (burnt sugar) [11]-[14]. The dyeing of agates in exotic colors obtained with organic dyes has been gaining popularity, given its acceptance in foreign markets, mainly in the United States, Japan, and China, and given the fact that the production processes are simpler [12]. However, the effluents from the washing waters feature a high organic load and intense color due to the application of Brilliant green (green), Crystal violet (purple), and Rhodamine (pink) dyes. Old solutions and the water used to wash the stones are discharged as wastewater (second washing procedure).

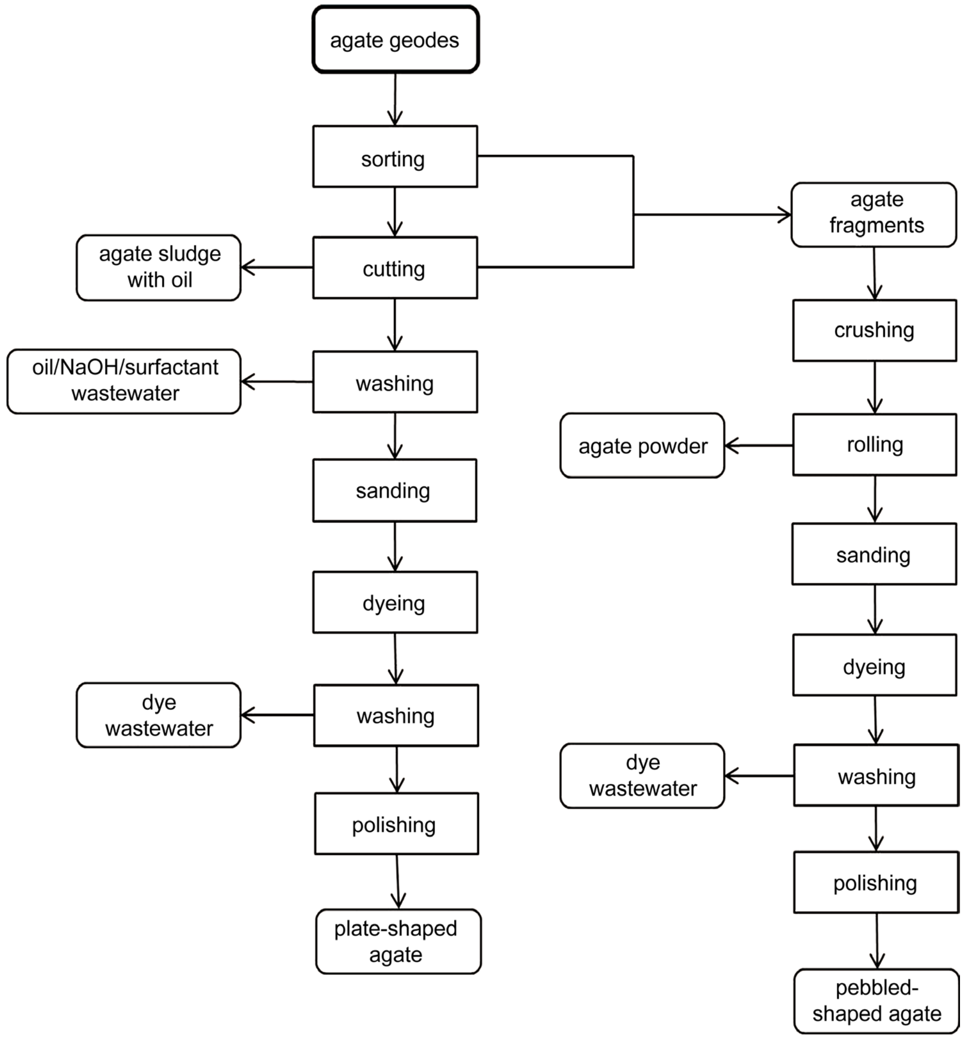

Figure 2. Basic fluxogram of agate beneficiation and the origin of waste materials.

Table 2. Agate dyeing processes.

	Color	Process
Classic Processes (Inorganic)	Green	Immersion in an aqueous solution of chromic acid and ammonium chloride. Then burn at temperatures of 150˚C - 300˚C.
	Red	Immersion in an aqueous solution of nitric acid, perchlorate, and iron scrap. Then burn at temperatures of 150˚C - 240˚C.
	Blue	Immersion in an aqueous solution containing potassium ferricyanide. Then immersion in a boiling sulfuric acid bath.
	Black	Immersion in heated sugar syrup. Then immersion on a commercial boiling sulfuric acid bath. Last, burn at temperatures between 150˚C and 200˚C.
Aniline Dyeing (Organic)	Green	Immersion in an alcoholic solution of Brilliant Green dye.
	Red	Immersion of agate in an alcoholic solution of a mixture of Rhodamine B and Basic Orange dyes.
	Pink	Immersion of agates in an alcoholic solution of the Rhodamine B dye.
	Purple	Immersion of agates in an alcoholic solution of Crystal Violet dye.

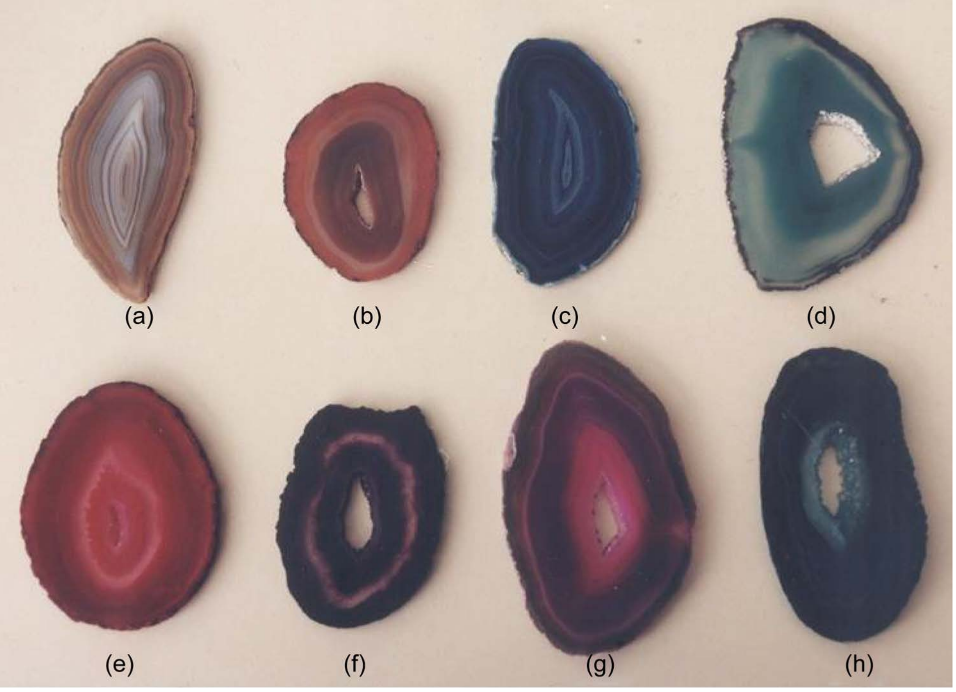

Figure 3. Agate plates: natural (a); colored by inorganic salts in red (b), blue (c) and green (d); and colored by organic dyes in red (e), purple (f), pink (g), and green (h).

Polishing and trimming are the final steps in the lapidating of agate plates. Larger pieces are polished in fixed grinding wheels and smaller pieces are polished in vibrators with abrasives.

Agate pieces not useful for plate conformation, such as the lateral extremities, are crushed and rolled to manufacture pebble-shaped stones. The pebbles are colored and finished by the same or similar procedures described for the plates generating dye-bearing wastewaters. However, in the pebble agates process line, the abrasion procedure in rolling drums produces an agate-powdered material, but in this case without oil.

It should be mentioned that some companies produce both plate and pebble stones, while other specialize in either plate or pebble production.

3. Waste Materials

The industrialization of gems produces different kinds of waste materials, such as agate fragments, agate sludge with oil, agate powder without oil, and wastewaters. Table 3 depicts some investigations in this area. Hereinafter, comments describe the characteristics and efforts for finding new uses for such wastes.

3.1. Agate Fragments

Agate pieces are composed of discharges in the sorting or cutting operations in the range of 5 - 30 cm (Figure 4). Theses fragments can exceed 50% - 60% of the raw geodes mass, and in the past they were almost entirely discharged in waste deposits. However, in recent years, some industries have specialized in producing agate pebbles from these fragments of agates. This material was used as a coarse aggregate for concrete production after crushing in different levels for the substitution of natural aggregates

Table 3. Studies regarding solid wastes and wastewaters from agate industry.

Waste Material	Uses or Treatment	Authors
Agate fragments	• Aggregates for concrete paving blocks and white concrete	• [15] [16]
	• New products through CNC machining	• [17]
Oil contaminated agate powder	• Oil separation by compression	• [18]
	• Oil removal using NaOH aqueous solutions	• [19]
	• Incorporation in red ceramic	• [20]
Agate powder	• Fine aggregate for mortar and concretes	• [21] [22] [23] [24]
	• Colored aggregate	• [25]
	• Material for ceramic tiles	• [26]
	• Adsorbent	• [27]
	• Support material for magnetic particles	• [28]
	• Soil fertilizer	• [29]
	• Soil stabilizer	• [30]
Dyeing wastewater	Treatment with:	•
	• NaClO	• [31]
	• NaClO	• [32]
	• UV/H_2O_2	• [33]
	• Fenton process	• [34]
	• Ozonization	• [35] [36]

Figure 4. Discharged agate fragments.

[15]. They concluded that the concrete produced with 50% substitution demonstrated good compressive strength. However, alkali-aggregate reaction, which causes expansion and cracking, was verified recently [16]. Some agate fragments can be conformed in a CNC machine, producing pieces of different shapes [17].

3.2. Agate Sludge with Oil

Oily sludge generation from cutting machines is around of 0.15 kg/kg of processed agate (**Figure 5**). Analysis indicated the following composition: 73% solids (agate powder and chips), 8% water, and 19% oil [18]. Some industries partially recover the oil by mixing water to the mud and stirring. The procedure forms two layers, a superior layer with oil and an inferior layer with a mixture of agate powder, water, and oil. By applying mechanical pressure, oil, and water can be removed from the solid. A pressure of 11.7 MPa produced a material with 95% solids, 3% oils and 4% water [18]. However, this residual amount of oil still hinders possible applications of the material as fine aggregates in cement pastes and concretes. Alkaline hot extraction procedures can reach oil removal efficiencies over 95% [19]; full oil removal can only be achieved by solvent extraction [18] [21].

Recycling by incorporation in red ceramics for the production of bricks was investigated [20]. The results showed that it is possible to incorporate agate sludge to compose up to 5% of the brick mass without significant changes to compressive strength, linear shrinkage, water absorption, and brick density. This procedure has the advantage of scale that red ceramic production can easily incorporate agate sludge production and that the ceramic industry is distributed worldwide.

3.3. Agate Powder without Oil

The generation of oil-free agate powder is estimated to be 0.08 kg of powder/kg of processed stone in sanding and polishing and 0.65 kg of powder/kg of processed stone in rolling (**Figure 6**). Generally, the agate powder is composed of approximately 98% finely fragmented SiO_2, with 95% of particles smaller than 74 μm. This material is currently used for padding landfills. However, it has proved to be suitable to be used as a fine aggregate for mortars and concretes [21]-[24]), including colored fine aggregates [25]. Stoneware tiles can also be produced using agate powder as a filler with a composition range of 15 - 45 wt.% [26]. Because of its high percentage of silica, agate powder was also suggested as adsorbent [27] and as a support material for micro and nano Fe_3O_4 magnetic particles [28]. In addition, the application of the material as a soil stabilizer has been also investigated [30].

3.4. Effluents

Effluent volume in agate processing is estimated to be 0.2 m^3 per kg of stained stones.

Figure 5. Agate sludge with oil from cutting machines.

Treatment of the inorganic effluents considers the reduction of Cr (VI) to Cr (III), cyanide oxidation, and metals settling as hydroxides at neutral pH. The metal sludge, considered as a dangerous waste, needs to be sent to industrial waste landfills [13].

Wastewaters containing organic dyes (**Figure 7**) are generally treated by oxidative processes. Discoloration with sodium hypochlorite (NaClO) is currently the most utilized process, mainly because of its easy implementation and low cost [31]. However, there is a risk that organochlorine molecules may form. These molecules have bio cumulative properties in living tissues, altering the functioning of the cells [32]. Ozonization [35] [36] and advanced oxidative processes (AOPs) [34] has been a focus of alternative treatment of such wastewaters. In particular, best results were achieved with AOPs, a process based on the generation of the hydroxyl radical (·OH), a species with a high oxidizing potential. This process has high efficiency in the oxidation of complex organic compounds, producing simpler molecules, more susceptible to biodegradation

Figure 6. Agate powder from pebble conformation in rotating drums.

Figure 7. Wastewater contaminated with the dye Rhodamine B.

or, in some cases, leading to the mineralization of organic compounds to CO_2, H_2O, and N_2. The Fenton reaction belongs to the advanced oxidative processes, and it has been used to treat the effluents of the agate industry, showing good results in terms of decolorization [34].

3.5. Operational Control, Energy and Environmental Management

Many of the above-mentioned problems could be minimized and processes could be improved. However, operational control procedures and environmental management systems are not practiced in South America, which is dominated by small factories, many of them working as a family business.

Process standardization can reduce energy and water consumption in the washing step that follows staining [37]. Concerning aniline coloring, it is possible, practically, to avoid wastewater generation by exchanging the water for ethyl alcohol in the washing step. Energy consumption is in the order of 15 m^3 of wood and 25 kWh of electric energy per 1 ton of raw agate. Since the heating process is not always necessary to provide the color there is an opportunity to save energy that is provided, in most of the cases, by firewood. Eliminating this operation will make it possible to reduce the costs associated with forest materials, avoid transport and storing, and air pollution.

Although legislation and inspection of environmental agencies has improved considerably in last few years, work security and environmental issues are still a problem that is not affordable to many companies considering the production scale. But it is also true that research and technological development in the sector by cooperation between industry, research institutions, universities, and governmental agencies is increasing.

4. Conclusion

Agate processing is an activity carried out worldwide by micro and small companies, providing useful and beautiful artifacts. However, there is a production of waste materials and wastewaters. Local arrangement demands for actions to minimize the production of wastes and actions to transform them into salable products. Especially challenging are agate sludges contaminated with oil and wastewaters containing organic dyes, such as Rhodamine B, Brilliant Green, and Crystal Violet. There are a range of actions that could improve the environmental efficiency of the production chain, providing cleaner production, better performance in energy consumption, and minimal waste generation. Central units for waste treatment and disposal that provide services for local industries, could facilitate the management of such materials, optimizing logistics and, probably, reduce costs.

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