سالانه کانسار کمپی ایران نعتى شاهرود - در ایران ۲۱ و ۱۷ بهمن ۹۸ (5-6 Feb 2020 یی جویی . اکتشاف . استخراج . فرآوری . بازاریابی Conference on Iraninan Gemstone Deposits Prospecting . Exploration . Mining . Processing . Marketing آگات های رضا آباد واقع در ایران مرکزی و

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ر نگ آمیز ی آنها

چکیده: در این مقاله آگات های واقع در 17 کیلومتری جنـوب غـرب روسـتای رضـا آباد که بخشی از زون ساختاری ایران مرکـزی می باشـد مـورد بررسـی قـرار می گیرد، یکی از ویژگی های بارز این آگات ها تنوع رنـگ آنهـا اسـت کـه شـامل رنـگ های سبز، زرد، سیاه، شیری، بی رنگ، دودی، زرد و قهوه ای می باشد. این مقاله سعی بر آن دارد که رنگ های مختلف آگات های رضا آباد را مورد بحث قرار داده و با استفاده از روش های شیمیایی آگات های بی رنگ و سـفید منطقـه را بـه رنـگ مهای زرد، صورتی، سیاه، آبی، سبز رنگ آمیزی کرد تا جـذابیت آنهـا بیشـتر شـده و بیشـتر مـورد پسـند واقـع شـوند، مـواد شـیمیایی اسـتفاده شـده شـامل پتاسـیم آهن و نیکل نیترات می باشند، رنگ های مورد نظر با ساخت محلول های اشباع از آهن و نیکل نیترات می باشند، رنگ های مورد نظر با ساخت محلول های اشباع از مرکدام از این مواد و غوطه ور کردن نمونـه هـا در آنهـا در مـدت زمـان مشخص بدست آمده است. در نهایت آگات های رنگ از نمونـه هـا در مـدت زمـان مشخص

کلمات کلیدی: آگات، رنگ آمیزی، محلول های شیمیایی، رضا آباد، ایران مرکزی

## **Reza Abad agates from Central Iran and their dyeing**

Abstract: The studied agates located in 17 km northwest of Reza Abad village are parts of the Central Iran structural zone and observe in volcanic rocks. A prominent feature of them is that they often reveal amazing patterns and beautiful distinct banding with a variety of colors including green, yellow, black, white, colorless, gray, red and brown. The present paper tries to discuss the different color agates from Reza Abad and a few chemical methods for dyeing the colorless and white agates into yellow, pink to lavender, black, blue and bluish green and make them more desirable and attractive. The used chemical materials are potassium chromate, cobalt chloride hexahydrate, sugar, concentrated sulfuric acid, potassium ferricyanide, ferrous sulfate and nickel nitrate hexahydrate. Desirable colors were obtained not only by making a saturated solution of them and immersing the samples for a given period of time but also in two and three temperatures. Consequently, the dyed agates were more attractive even more than the natural ones.



Keywords: Agate, dyeing, chemical materials, Rea Abad, central Iran

## 1. INTRODUCTION

Agate is typically untreated but can easily be dyed to enhance color since it is quite porous. Prices for agates are very affordable whether they have been dyed or not. Regardless, sellers should always disclose any and all treatments to the best of their knowledge. Lapidaries have used a wide variety of methods to change the color of stones for thousands of years. In Book 37 of Pliny's Natural History (Bostock, 1855) it was explained that how ancient lapidaries boiled gemstones in honey as part of the process of changing their color. Dyeing and many other methods such as heating and irradiation have been used to change the color of many types of stones.

The artificial coloring of gem materials to make them more desirable to the consumer is as ancient as greed and avarice. Unfortunately Iran's share in coloring and enhancement of gemstones in the world is about %0.02. This amount against the people's daily demand for desirable gems is really low (Khajeh-Bidokhti, 2010) The study area is located in the northern part of the Central Iran structural zone and in the south and south east of Shahrood city (Figure 1). In this paper the existent agates in the Reza Abad were colored into different colors by using different chemical materials in order to enhance and make them more attractive and desirable. Furthermore, there are some agate mines in Iran(e.g., Torud, Reza Abad) which most of their stones are white in color and have low price and seldom consumers, although they are banded and look very nice. Thus, the results of present paper can also be important and useful for them.



Figure 1. Simplified structural subdivision map of Iran and the locality of the study area (modified from Shahabpour, 1994).

## 2. GEOLOGICAL SETTING

Iran is located along the Tethyan suture between the Eurasia and Africa–Arabia plates and records the closure of at least two Tethyan oceans: Paleo-Tethys in the Paleozoic and Neo-Tethys in the Cenozoic (Sengör and Natal'in, 1996; Richards et al., 2006). The existence of these oceanic basins has been interpreted from the presence of dismembered ophiolitic sequences scattered throughout Iran (Stoneley, 1981; Hooper et al., 1994; Glennie, 2000). Iran has been divided into several structural units, each characterized by a relatively unique record of stratigraphy, magmatic activities, metamorphism, orogenic events, tectonics, and overall geological style. Systematic geological studies in Iran started in late 1960s with the establishment of the Geological Survey of Iran. Using mostly the NIOC (National Iranian Oil Company) database, Stocklin and Nabavi, 1973) published the first "Tectonic Map of Iran". The authors divided Iran into 10 structural zones (units). These structural divisions remained references for Iranian geologists for almost three decades.

The study area is a part of the magmatic belt of north Central Iran that the magmatic activities have been conducted from Eocene to late Miocene periods (Berberian, 1976). It is a part of Davarzan and Abrisham Rood 1:100,000 geological maps with geographic coordinates of 45° 81′ 00″ to 44° 46′ 00″E longitudes and 39° 88′ 45″ to 39° 63′ 00″N latitudes.

## **3. HOST ROCK PETROGRAPHY**

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Agates are most frequently found within a variety of fine-grained volcanic host rocks in the NW of Reza Abad which comprise mainly of basalt, andesite and agglomerates (Figure 2 a and b)...More than 300 samples of agates were collected from veins in the basaltic rocks and agglomerates with the thicknesses from <0.5cm up to more than 10 cm. About eight thin sections from the country rocks of agates were prepared for detailed petrographic studies.



Figure 2. a) A view of the basaltic rocks in the study area. b) Agglomerates, the coarse accumulations of large blocks of volcanic material, seen in the area.

As it is illustrated in figure 3a, the country rocks mainly comprise of basaltic rocks with different percentages of pyroxene, plagioclase, and olivine minerals. It shows glomoroporphyritic texture which is a common and often included plagioclase and pyroxenes (Figure 3b). This texture is formed by the settling of plagioclase in basic magma in which plagioclase crystals are less dense than the surrounding magma. Basalt also shows porphyritic texture in some thin sections which has a high percentage of crystals. Plagioclases are euhedral with continuous gradation in size with a seriate texture (Whitman Cross et al., 1906).



Figure 3. (a) The thin sections of basalt in the area with different percentages of plagioclase and pyroxene and (b) glomeroporphyritic texture of Reza Abad basalt.

#### **4. COLOR TREATMENT**

Reza Abad agates are observed in red, white, green, yellow, brown, black and gray. Although they look nice and suitable for manufacturers, most of them are white and colorless which are not desirable to the consumers. Morover, the high demand of color agates for making ring in Iran caused this paper tries to present a new metods for making them more desirable. Thus, in the following the dying and its various methods are going to be described for Reza Abad agates to increase their commercial value, manufacturer profits and the growth and economic development of the country.

The most important detail in the preparation of gemstone for chemical coloration was to keep it clean. Oil and grease must be removed entirely. We used a detergent solution (ordinary laundry detergent) to clean the samples. Moreover, the samples were placed into an ultrasonic to remove the dust and dirt particles even in holes. Further cleaning of the slabs consists of two additional washings in hot detergent suds, and thorough rinsing with clean water.

After the slabs (or other pieces) were thoroughly cleaned, they were dried via spreading out on metal trays and placed in the oven. We set the oven thermostat for about 60°C. The slabs were dried at this temperature for one or two day(s).

In this study the white and colorless agates were colored into different colors by using some chemical materials including ferrous sulfate, potassium chromate, potassium ferricyanide, nickel nitrate, cobalt chloride hexahydrate and thick liquid of the mixture of sugar and water and acid sulfuric. A saturated solution of any of these materials was made with various amounts depending on the type of each one.

#### 4.1. Sugar-concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)

The aim of using these materials is changing the white color of agates into black. This is a two-step process. First, 200 grams of sugar was dissolved into 0.5 liter of water, producing a thick liquid similar to honey. Then the slabs were immersed in the solution and left at room temperature for 2-3 weeks, adding water to the solution as it is lost from evaporation.

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After that the slabs were rinsed off and placed into a bath of concentrated sulfuric acid under a lab vacuum hood. Sulfuric acid is strong and must be handled with great caution. Thus, the slabs must be immersed in the acid very carefully, sliding them in one at a time. Then, the mixture was warmed slowly over a day until the slabs turning into black (Figure 4). Use a Pyrex glass vessel (not metal vessel as it reacts with acid) with a handle such as is used in making coffee to be able to pick up the vessel if the acid will be boiled. After cooling the acid, all of the acid had been poured off and the slabs slowly were washed cautiously by adding cold water to remove a little residual acid on the slabs.



Figure 4. The samples placed in the solution of Sugar for 2-3 weeks at 25°C and in concentrated sulfuric acid for one day on the hot plate. a) Before coloring. b) After coloring.

## 4.2. Cobalt chloride hexahydrate (CoCl<sub>2</sub>.6H<sub>2</sub>O)

This is a one-step process and caused the samples to turn into beautiful pink and lavender. An oversaturated solution of the cobalt chloride hexahydrate was prepared by adding 65 g of that into 65 ml of water at T=25°C. After obtaining the desired solution, the clean dried slabs were individually immersed in the solution. The glass container was put in the oven at 25 °C for two weeks. Then, the slabs were rinsed off, washed and dried in the open air. As a result, the samples which were colorless after coloring turned into pink (Figure 5b, f) and the sample which was white turned into lavender (Figure 5d). This experiment was also done with another solution to make sure about the effect of temperature. In this stage another solution of cobalt chloride hexahydrate was prepared with the exact same solution and the experiment was repeated at 50 °C. The color of the samples was changed into beautiful pink and lavender after about one week (Figure 5e, f).



Figure 5. The samples placed in the saturated solution of cobalt chloride hexahydrate. a,c,e) Before coloring. b,d,e) After coloring.

## 4.3. Nickel nitrate hexahydrate (Na (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O)

A saturated solution of nickel nitrate was prepared for this stage at 25 °C. Nickel nitrate is soluble; thus, 60 g of its crystals were added into 30 ml of water and the glass container was put on the heater. After the solution was stirred well, the saturated solution with a volume of 75 ml was ready and four of the clean and dried slabs were put in the solution. The prepared mixture was placed at a temperature of 25 °C. After about two weeks the color of the samples was obviously seen that were changed to green, thus the samples were rinsed off and dried to record (Figure 6).



Figure 6. The samples placed in the saturated solution of nickel nitrate for two weeks at 25°C. a) Before coloring. b) After coloring.

This experiment was also done at a temperature of 70 °C. Therefore, an under saturated solution of nickel nitrate hexahydrate was prepared by adding 70 g of the crystals into 35 ml of water (with the same proportion at the first time). Then, five samples were gently placed in this solution but this time the temperature of the oven was set at 70 °C. After two days we could obviously see the color changes of the samples. Thus, we rinsed off the samples in order to record their coloration. It was seen that compared to the previous step, the samples were colored in less time. The experiment was continued to determine the maximum color achieved at what time at this temperature. Subsequently, the coloration of the samples was also recorded after six and twelve days and there was not observed significant color change in the samples after two weeks (Figure7).



Figure 7. The samples placed in the solution of nickel nitrate at temperature of 70 °C.

## 4.4. Potassium chromate (K<sub>2</sub>CrO<sub>4</sub>)

Potassium chromate is used to evaluate the effect of yellow coloration on agates. Thus, 60 g of potassium chromate crystals were added to 60 ml of water (the solution volume after adding the crystals was about 75 ml) on the heater and was stirred it by using a magnet. In the next step, we carefully immersed the dried slabs into the desired chemical solution at temperature of 25 °C, 50°C and 70°C for a minimum of two weeks to determine the effect of temperature on the duration of the coloring.

At first step, we placed the prepared saturated solution at a constant temperature about  $25^{\circ}$ C (at room temperature) for two weeks and then we rinsed off the slabs and dried them in the oven at 60°C. After drying, the agates were changed into yellow color (Figure 8).

At second step, another solution of potassium chromate was prepared with the previous ratio. Two samples of the agates were put in the solution and then placed in the oven at a temperature of 50 °C. It was dramatically observed that the samples were changed to desired color (yellow) after one week (Figure 9).





Figure 9. The samples placed in the solution of potassium chromate for one week at a temperature of 50°C. a) Before coloring. b) After coloring.

# 4.5. Potassium ferricyanide (alias red prussiate of potash), K<sub>3</sub>Fe (CN)<sub>6</sub>- Ferrous sulfate (alias copperas, green vitriol, iron sulfate), FeSO<sub>4</sub>.7H<sub>2</sub>0

Since bright blue agates are very desirable, potassium ferricyanide and ferrous sulphate were used to color the stones. This is a two-step process. First, we dissolved 250 grams of potassium ferricyanide into one liter of lukewarm water. Then, we placed agates into this solution, kept at a temperature of 25 °C, for one to two week(s). After immersing, the slabs were washed and dried and their colors were changed to bright brown. Then, they were put into a solution of lukewarm ferrous sulphate for 10 days. For this purpose, 100 g of ferrous sulphate was dissolved into 100 ml of water and we made a solution of 165 ml. Consequently, it was seen the samples were colored into blue (Figure 10).

For the next stage, four new samples were prepared to be tested again but at a temperature condition of 50 °C and the experiment were followed as before. By increasing the temperature the samples were colored in less time as we could see the color changes after about one week of immersing the samples in the solution (Figure 11).

For the final stage, the temperature was set at 70  $^{\circ}$ C to reassure the effect of temperature on the duration of the coloring. Five new samples were placed in the solution of potassium ferricyanide until we achieved the maximum color intensity. The coloration was obviously seen after two days (Figure 13). The experiment was continued and the color changes were also recorded after six and twelve days. It seems that a significant coloration was not observed after two days of immersing the samples in the solution (Figure 12).

Finally, the agates, which we dyed here, are often similar to natural agates from the study area and people who are not familiar with tumbled stones will not recognize them. By the way, they are some tricks for distinguishing them from natural agates. (1) Dyed agates are darker in fractures and fissure. (2) In most cases a dyed agate has a darker colored surface, if the solution did not have enough time to penetrate deeply into the stone. (3) If agates comprise from several layers with different color, the layer boundary of nature agates are sharper than dye ones.



Figure 10. The samples placed in the solution of potassium ferricyanide- Ferrous sulfate for 10 days at room temperature. a) Before coloring. b) After coloring.



Figure 11: The samples placed in the solution of Potassium ferricyanide-ferrous sulfate at temperature of 50 °C. After about one week the samples were colored into desirable color.



Figure 12: The samples placed in the solution of Potassium ferricyanide-ferrous sulfate at temperature of 70 °C.

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## **5. CONCLUSION**

In this study the white and colorless agates, which form the most volume of Reza Abad mine, were colored by using chemical materials including thick liquid of the mixture of sugar and water and acid sulfuric, cobalt chloride hexahydrate, nickel nitrate hexahydrate, potassium chromate, potassium ferricyanide and ferrous sulphate. Desirable colors were obtained by making a saturated solution of any of these materials and immersing the samples in these solutions for given period of times. The effect of temperature on the duration of coloring was also studied by increasing the temperature conditions. As a result, we could found that by increasing the temperature conditions the coloring duration decreases. According to the investigations that we have done, it can be stated unequivocally that different chemical solutions can be used in order to dye and enhancement the agates. Even though synthetic and simulated gemstones are created in laboratories, they still possess beautiful attributes and make fashionable jewelry. Creative individuals enjoy buying loose gemstones to make their own jewelry or decorate their picture frames and other accessories. The benefits of synthetic and simulated gemstones are their beautiful qualities and affordable prices. The results of this study can be applicable for the other agate mines from Iran such as Torud, Galeh Zari and Cheshmehshoor.

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