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Color and Shade Parameters of Ultramarine Zeolitic Pigments Synthesized from Kaolin Waste

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Ultramarine pigments were successful synthesized from zeolite A obtained from kaolin waste. This waste has been used as an excellent source of silicon and aluminum for zeolite synthesis because of its high kaolinite concentrations and low contents of other accessory minerals. The cost is naturally less than the industrialized product. Color additives (Sulfur and Sodium Carbonate) were mixed with different proportions of zeolite A and further calcined for 5 h at 500 °C. They were characterized by XRD and XRF in addition to visual classification by color and shade. These products show colors from blue to green at different shades, both influenced by the amount of additives and cooling rate after calcination. Thus, a different quantity of the same additives in the same zeolitic matrix provides an increase in the color intensity. Cooling rate after calcination induces the color change which is substantially important in the pigments production.

Keywords: *kaolin waste, zeolite A, pigments*

1. Introduction

The state of Pará is home to three large plants that process kaolin for paper coatings and are responsible for 97% of the national production of that material[1]. The paper industry requires extremely fine white kaolin, which results in the accumulation of kaolinic material that does not meet the required specifications from the particle size separation and whitening stages[2,3]. This waste is composed predominantly of kaolinite, and its use as a source of silicon and aluminum in the synthesis of zeolites, including zeolite A, has become technologically feasible[4-6]. Zeolite A is a hydrated aluminum silicate composed of alkali metals and alkaline earths that has porous characteristics favorable to the production of ultramarine pigments[7-15]. The crystal structure of this zeolite allows for a cleaner production process because its sulfur gas emissions are almost zero. In contrast, the traditional process of producing this pigment uses kaolin and results in a great deal of pollution; therefore, it is being replaced by other processes[16,17].

To prepare ultramarine zeolite pigments, zeolite A is calcinated between 500 and 800 °C with different concentrations of sulfur and sodium carbonate. The reaction between the sulfur and sodium carbonate produces sodium polysulfides that diffuse through the pores and cavities of the zeolite A and act as chromophores[18,19]. The resulting color can vary from blue to green, depending on the chemical composition of the starting material, reagent concentrations, temperature and time of calcination, and other factors.

The sulfur radicals S_2^- and S_3^- present in zeolites, which are responsible for its yellow and blue colors, respectively, can also produce a green color when both radicals are present in certain proportions. According to Gobeltz et al.[20], the reaction between sulfur and sodium carbonate should follow Equation (1). Side reactions that are responsible for the formation of the previously described sulfur radicals are described by Equations (2), (3), and (4)[21-23].

$$3Na_2CO_3 + 10S \leftrightarrow 2Na_2S_4 + Na_2S_2O_3 + 3CO_2 \quad (1)$$

$$S_8 + 3O^{2-} \rightarrow S_2O_3^{2-} + S_2^{2-} + S_4^- \quad (2)$$

$$3S_4^{2-} \leftrightarrow 2S_3^{2-} + S_6^{2-} \quad (3)$$

$$S_6^{2-} \leftrightarrow S_3^- \quad (4)$$

The color of zeolite pigments is influenced by the constant S/zeolite (m/m) ratio and the varying S/Na_2CO_3 (m/m) ratio. Proportions of 20[24,25], 40[21,22], or 60 %[17] sulfur relative to the mass of zeolite are commonly used, and the S/Na_2CO_3 ratio is defined by considering that an excess of sodium carbonate favors the formation of S_3^- and an excess of sulfur favors the formation of S_2^-. Given this background on the subject, the objective of this study was to obtain ultramarine pigments from zeolite A derived from kaolin waste in the Amazon region and determine the influence of the reagent concentrations and cooling rates after calcination on the color and shade of the final product.

2. Experimental Procedure

Zeolites A derived from kaolin waste were obtained by hydrothermal synthesis, under reflux[4,6] as follows: 200 g of applied kaolin calcinated at 700 °C was mixed with 600 mL

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of 5 mol/L NaOH solution (Vetec) at 95 °C in a 1 L glass reactor with mechanical stirring for 2 h, after reaction, the samples were rinsed until pH approximately 7 with distilled water and was dried at 105 °C for 24h.

The methodology adopted for the synthesis of ultramarine zeolite pigments was that described by Kowalak and Jankowska[24], in which 1 g of zeolite A derived from kaolin waste was mixed with elemental sulfur (S, Synth) and sodium carbonate (Na_2CO_3 99%, Nuclear) in a porcelain crucible with additive (S/Na_2CO_3) to zeolite ratios varying from 10 to 50% m/m, without reductive agent. A molar ratio of 1 was maintained for the S/Na_2CO_3 additives. The mixture was homogenized and calcinated at 500 °C, in ambient pressure, for 5 hours, in porcelain crucibles closed. After calcination, the products were cooled, washed with distilled water, and dried at 105 °C for 24 hours.

Two cooling methods were evaluated: 1) cooling at room temperature in a desiccator and 2) cooling in an oven at a cooling rate of 1 °C/min. The products were weighed before and after washing and were characterized by XRD (X´Pert Pro MPD diffractometer) and XRF (Axios Minerals, sequential spectrometer), both of which from PANalytical. Visual classification of the products' colors and shades was performed based on the Munsell Color System. The PXX-AAA nomenclature was adopted as follows: "P" represented the product, "XX" the percentage of additives relative to the quantity of zeolite, and "AAA" the cooling method (RT - room temperature or OVE - oven).

3. Results and Discussion

3.1. *Kaolin waste and zeolite A*

Figure 1 shows a mineralogical analysis of the kaolin waste and zeolitic product. Kaolinite was the only phase detected in the waste, demonstrating that the material was composed of one mineral and that mineral impurities, if present, were below the limits of detection. The principal phase in the zeolitic product was zeolite A, for which the $d_{531} = 4.12$ Å (21.34° 2θ) determined the sodium type (zeolite 4A). The peaks marked with "+" in the figure indicate the presence of sodalite.

The chemical analysis of the kaolin waste (Table 1) confirmed the mineralogical analysis presented above. The waste material was essentially composed of kaolinite with a Si/Al ratio approximately equal to 1, which is typical of this clay mineral. The total concentration of Fe_2O_3 and TiO_2 was less than 1%. These results illustrated the potential use of this waste material as a source of silicon and aluminum for the synthesis of zeolite A. Table 1 also indicates that the values obtained for the zeolitic product confirmed the earlier analysis of the crystalline phase. The product was predominantly composed of sodium-type zeolite A and a small quantity of sodalite, which was also of the sodium type. The product showed an elevated percentage of sodium and a Si/Al ratio of approximately 1, which was typical of a zeolite with a low concentration of Si.

3.2. *Zeolitic pigments*

The colors and shades of the pigments (Table 2) were influenced by the quantity of additives utilized in the synthesis and the cooling method after calcination. The

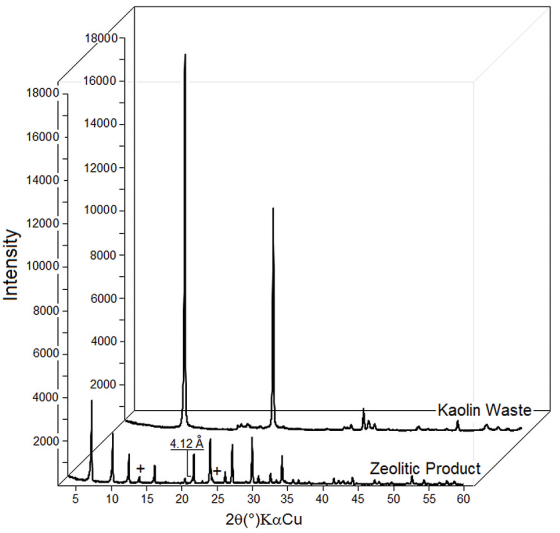

Figure 1. Diffraction patterns of kaolin waste and zeolitic product.

Table 1. Chemical analysis of kaolin waste and zeolitic product.

Components	Kaolin waste	Zeolitic product
SiO_2	46.13	33.30
Al_2O_3	38.97	27.65
Fe_2O_3	0.57	0.39
TiO_2	0.3	0.18
Na_2O	-	20.02
K_2O	<0.1	<0.1
P_2O_5	<0.1	-
LOI	13.99	18.43

- below the limits of detection; LOI (Loss On Ignition).

P10-RT and P10-OVE products maintained the same color as the reaction mixture. Neither the quantity of additives nor the cooling method resulted in any visible change due to the formation of an insufficient quantity of polysulfide chromophores or the formation of polysulfides that were not chromophores. A color gradient was first observed in the 20% additive product that increased in intensity as the proportion of additives increased. A color change was also observed that was related to the cooling method: the products that cooled more rapidly (RT) were green, and those that cooled more slowly (OVE) were blue.

In accordance with the results shown in Figure 2, it can be concluded that the initial LTA structure of the zeolite A was maintained after the pigments were produced and that the crystalline Na_2SO_4 phase (---- peaks) was formed in the process. Additionally, the products containing the same quantity of additives had identical diffraction patterns, even when subjected to different cooling methods. Thus, the following structural discussion is made for only one of the methods, OVE, although it is valid for both.

The decrease in the products' diffraction intensities relative to the starting zeolite was greater for increased quantities of additives. The $d_{622} = 3.70$ Å of the zeolite A showed different shifts for each quantity of additives within

the highlighted region from 23 to 25° 2θ: the P10-OVE and P20-OVE products displayed rightward shifts with a broadening of the peak's base, and the P30 to P50-OVE products displayed leftward shifts. The P30-OVE contained a double peak, highlighting a transition phase or a mixture of two phases, while the P40-OVE and P50-OVE had the most intense shades, and this shift was probably due to the greater incorporation of the polysulfide S_3^-, which was responsible for the blue color at this (these) site(s).

The chemical compositions of the products (Table 3) show the same Si/Al ratio as the starting material, which, together with the diffraction measurements, confirms the conservation of zeolite A and sodalite. There was a reduction in the concentration of sodium relative to the starting zeolite product due to the formation of sodium sulfate, which was removed by washing. The sulfur content in the pigments increased in proportion to the increase in the initial quantity of elemental sulfur used. The P40 and P50 products did not show differences in sulfur content such as those observed for the lower quantities of P10 to P30, which indicated a saturation limit. Therefore, the difference between the shades of P40 and P50 -RT and -OVE products, if one

Table 2. Color and shade of the zeolitics pigments synthetized. The products with 10% of additives exhibited the same color of the reactional mixture.

Sample	P10 RT	P20 RT	P30 RT	P40 RT	P50 RT	P10 OVE	P20 OVE	P30 OVE	P40 OVE	P50 OVE
Color	Beige	Light blue	Green	Olive Green	Olive Green	Beige	Light blue	Greenish	Bluish	Blue
Munsell Classification	10Y 9/2	5B 8/2	7.5GY 4/4	5Y 4/8	5Y 3/8	10Y 9/2	10G 8/2	7.5G 6/4	2.5BG 3/20	5BG 4/6

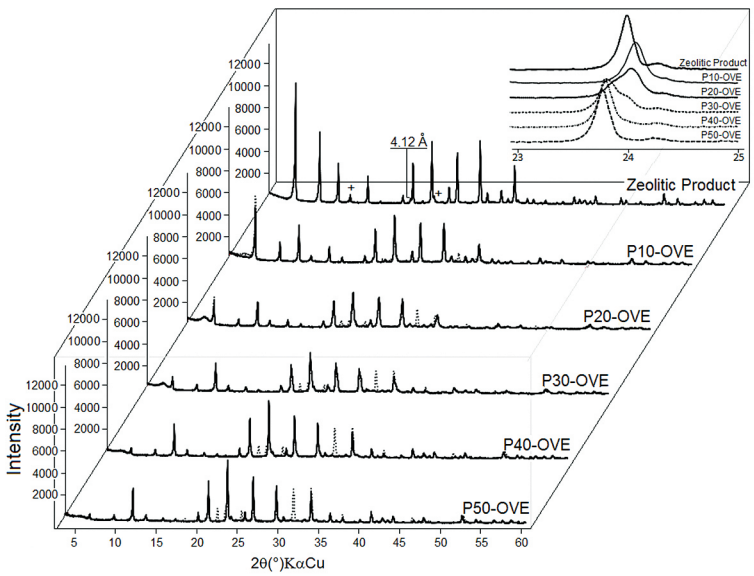

Figure 2. Diffraction patterns of zeolitic product and OVE series pigments.

Table 3. Chemical analysis of zeolitic pigments.

Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	SO_3	K_2O	CaO	LOI
P10-RT	30.89	25.50	0.37	0.21	16.83	6.62	<0.1	<0.1	19.56
P20-RT	28.98	23.92	0.37	0.21	17.40	11.24	<0.1	<0.1	17.82
P30-RT	25.23	21.10	0.31	0.15	18.99	18.95	<0.1	<0.1	15.22
P40-RT	24.31	20.31	0.27	0.12	19.09	22.07	<0.1	<0.1	13.80
P50-RT	23.87	20.09	0.26	0.12	19.53	23.36	<0.1	<0.1	12.70
P10-OVE	30.70	25.32	0.41	0.18	16.88	6.66	<0.1	<0.1	19.61
P20-OVE	27.71	23.26	0.33	0.20	18.18	13.28	<0.1	<0.1	16.98
P30-OVE	25.60	21.60	0.30	0.16	19.06	18.00	<0.1	<0.1	15.18
P40-OVE	24.14	20.33	0.28	0.15	19.47	22.03	<0.1	<0.1	13.51
P50-OVE	23.43	19.95	0.30	0.16	19.75	23.50	<0.1	<0.1	12.81

LOI: Loss on ignition at 1000 °C.

Table 4. Loss of mass during calcination and product washing.

(%)	P10 RT	P20 RT	P30 RT	P40 RT	P50 RT	P10 OVE	P20 OVE	P30 OVE	P40 OVE	P50 OVE
Δm_1	4.6	10	15	19	21	5	11	15	19	21
Δm_2	17	19	18	23	25	21	18	22	23	26
Δm_T	21.6	29	33	42	46	26	29	37	42	47

Δm1 (after calcinations), Δm2 (after washing), ΔmT (total).

existed, was almost imperceptible compared to the shades present in the P20, P30, and P40 -RT and -OVE products.

The loss of mass after calcination and washing is shown in Table 4. It was observed that the loss of mass increased with increasing quantities of additives, and the loss during calcination from the liberation of CO_2 gas was caused by heating Na_2CO_3[20] and by the dehydration of the zeolite A and sodalite[4]. The loss of mass during washing was due to the leaching of sodium sulfate and the remaining soluble reagents.

The most significant factors in the formation of polysulfide are related to the following factors: reactional mixture, temperature and reaction time. The manipulation of such factors causes the melting of sulfur and consecutive homolytic dissociation reactions with further chromophores formation. For the yellow chromophores (S_3^-), the homolytic dissociation will induce the formation of blue chromophores (S_6^{2-}) only if an appropriate reaction time is adopted, otherwise it may cause partial formation of blue species, which will impart a green color to the material due to the mixture of the two chromophores[17].

Since the equilibrium with ambient temperature was faster for AMB samples, the reaction was stopped quickly and therefore did not favor the formation of S_3^-. This was the reason why the blue color was not observed in these samples. It is also possible that S_3^- chromophores have been partly formed and that part of the S_6^{2-} chromophores were not dissociated, giving rise to the typical green color for these samples. On the other hand, for the MUF samples the cooling rate was lower, and therefore, the reaction conditions favor the formation of S_3^- chromophores.

4. Conclusion

This study indicated that it was possible to obtain ultramarine pigments from zeolite A derived from kaolin waste successfully, even with quantities of S/Na_2CO_3 below those generally reported in the literature. It is important to note that different quantities of the same additives in the same zeolite matrix cause an increase in color intensity and that the cooling rate after calcination causes a change in color, both of which are important in the production of pigments. This study will also be of benefit to those seeking another use for kaolin waste.

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