

# Physicochemical Study of Hematite Rock from the Kyzyltash Deposit for the Production of Ceramic Pigments

Z.R. Kadyrova<sup>1,\*</sup>, A.A. Eminov<sup>1</sup>, H.L. Usmonov<sup>1</sup>, Zh.A. Khonimkulov<sup>1</sup>, and S.S. Tairov<sup>1</sup>

<sup>1</sup>*Chemistry and Chemical Technology of Silicates” Institute of general and inorganic chemistry, Academy of sciences of the Republic of Uzbekistan*

**Abstract:** The results of a study of the chemical and mineralogical composition of hematite rock from the Kyzyltash deposit for the production of a reddish ceramic pigment that is thermally and chemically stable at high temperatures are presented. The changes in the color characteristics of the synthesized pigment depending on the firing temperature in the range of 1000-1100°C are studied. It has been established that this domestic raw material can be used to produce ceramic pigments for coloring ceramic, porcelain, earthenware, and glass products for household, construction, and technical purposes.

**Keywords:** Ceramic pigment, Hematite, Spectral analysis, Maghemite, Mineralogical, Amorphous silica.

## INTRODUCTION

Concepts for the synthesis and classification of ceramic pigments are evolving. One pressing issue is the development of a new approach to raw materials. The current trend is not only toward using cheaper materials but also toward developing new formulations of inclusive ceramic pigments based on industrial waste and locally available natural minerals.

It is well known that many natural and synthetic pigments are of great practical importance in the industrial production of ceramic products as colorants for glass, enamel, and unglazed products. Currently, numerous inorganic ceramic pigments are produced, which have a wide range of applications and, in particular, are essential components for the production of traditional glazed and unglazed tiles.

The use of inorganic pigments for colored ceramic products requires certain conditions [1-3], specifically, the pigment must be thermally stable at combustion temperatures [4]. Among the synthetic inorganic ceramic pigments used in the ceramic industry, there is a limited selection of red-pink and orange pigments (Cr-Sn-Ca-Si, Pb-Sb-Sn-Fe, Mn-Al systems). These pigments are generally easy to handle when handling bottles, but they can be sensitive to atmospheric conditions and high temperatures.

In recent years, interest in inclusion pigments has grown. The main reason for this is that they make dyes resistant to thermal and chemical conditions in industry by incorporating the dyes into a stable glassy or crystalline matrix (heteromorphic pigments) [4-6].

Much research has been conducted on iron(III) oxide. Iron(III) oxide ( $\text{Fe}_2\text{O}_3$ ) has four polymorphic forms:  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\beta\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$ , and  $\epsilon\text{-Fe}_2\text{O}_3$  [6]. Of particular importance are the  $\alpha\text{-Fe}_2\text{O}_3$  (hematite) and  $\gamma\text{-Fe}_2\text{O}_3$  (maghemite) forms. Hematite occurs naturally as a crystalline mineral composed of iron(III) oxide. It was also used by humans as a color pigment (red ochre) in laurels dating back to the Upper Paleolithic, approximately 14,000 years ago.[7-9] Often referred to as ochre's, they have been used to discuss the antiquity of human symbolic behavior and for artistic purposes [10-15]. It is found in sandstone, granite, quartzite, and various metamorphic rocks. It is red in powder form as a pigment, but can have a variety of colors when found in nature (Figure 1).

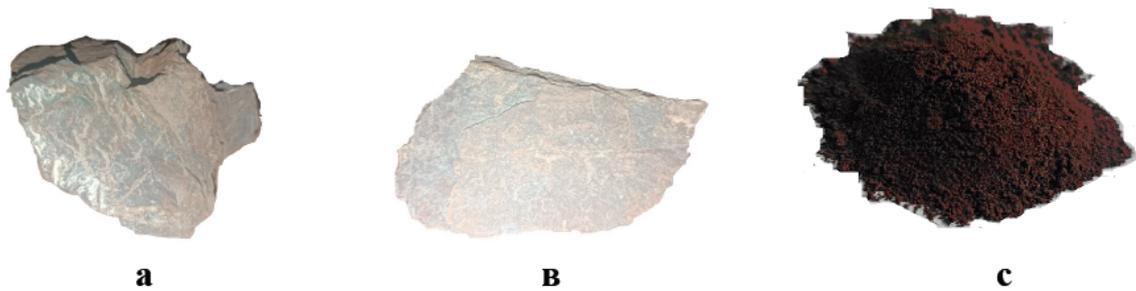
Hematite is a low-cost and less energy-intensive material for producing pigments. In industry, large pieces are primarily used for steel production. It is also used to produce pigment powder. X-ray diffraction data from Kyzyltash hematite samples showed that the Jizzakh region has large sources of high-quality hematite, and research into establishing and improving the use of this material is urgently needed. One possible improvement is to increase the use of this material by establishing pigment production, which is associated with the higher demand for ceramic pigments and their relatively high cost.

Mining existing raw hematite-containing ores in the Jizzakh region offers potential for pigment production. In addition, the hematite rock of the Kyzyltash deposit in its chemical and mineralogical composition contains a sufficient amount of iron oxides within the range of about 60 wt.%, after enrichment its amount reaches up to 96 wt.% The chemical composition of the ore is presented in Table 1.

## MATERIALS AND RESEARCH METHODS

The starting materials include hematite rock from the Kyzyltash deposit, limestone ( $\text{CaCO}_3$ ), microsilica

\*Address correspondence to this author at the Chemistry and Chemical Technology of Silicates” Institute of general and inorganic chemistry, Academy of sciences of the Republic of Uzbekistan; E-mail: kad.zulayho@mail.ru



**Figure 1:** Samples of natural Kyzyltash hematite (a and b) and powder state (c).

**Table 1: Chemical Composition of Hematite Mineral Samples from the Kyzyltash Deposit**

Oxide content, wt. %	Synthesized Samples			
	GM-1	GM-2	GM-3	GM- average
Fe <sub>2</sub> O <sub>3</sub>	60,80	57,70	55,20	57,90
SiO <sub>2</sub>	25,40	24,60	26,55	25,5167
CaO	7,30	8,40	9,00	8,233
MgO	2,79	3,90	4,10	3,597
Al <sub>2</sub> O <sub>3</sub>	2,60	3,57	3,4	3,19
Cl	0,0133	0,0115	0,0140	0,0129
P <sub>2</sub> O <sub>5</sub>	0,374	0,227	0,450	0,350
SO <sub>3</sub>	0,0797	0,0568	0,0858	0,0741
V <sub>2</sub> O <sub>5</sub>	0,0600	0,0670	0,0710	0,066
Cr <sub>2</sub> O <sub>3</sub>	0,0215	0,0200	0,0250	0,0221
MnO	0,0963	0,1100	0,0890	0,0984
ZnO	0,0042	0,0050	0,0033	0,0038
CuO	0,133	0,227	0,125	0,1616
As <sub>2</sub> O <sub>3</sub>	0,0046	0,0035	0,0052	0,0041
SrO	0,0103	0,0200	0,0102	0,0134
Y <sub>2</sub> O <sub>3</sub>	0,0032	0,0032	0,0025	0,0027
ZrO <sub>2</sub>	0,240	0,230	0,220	0,230
Ag <sub>2</sub> O	0,0017	0,0015	0,0065	0,00323
SnO <sub>2</sub>	0,0048	0,0058	0,0085	0,0053
TeO <sub>2</sub>	0,0031	0,0036	0,0016	0,0027
П.П.П, мас. %	0,0603	0,8093	0,8304	0,5667

(SiO<sub>2</sub>), a waste product of the Uzmetkombinat, as well as the chemical reagents SiO<sub>2</sub>\*nH<sub>2</sub>O and boron oxide (B<sub>2</sub>O<sub>3</sub>).

Raw rock samples were obtained using high-performance energy-dispersive X-ray fluorescence spectrometry on a Japanese-made Rigaku NEX CG EDXRF Analyzer with Polarization in Set spectrometer. The mineralogical composition was determined using powder X-ray diffraction analysis on a Japanese-made Shimadzu LABX XRD-6100 X-ray diffractometer using CuK $\alpha$  radiation. Identification of the detected mineral phases in the X-ray diffraction patterns and the obtained analytical results were

performed using standard reference books and the generally accepted ICDD PDF-2 database.

## RESULTS AND DISCUSSION

When studying the physicochemical properties of the mineral raw materials in this area using X-ray diffraction and spectral analysis, it can be seen that they are saturated with iron(III) oxide to a sufficient degree to produce a red ceramic pigment.

Chemical analysis results indicate that the main rock-forming elements of Kyzyltash hematite are iron oxides and, to some extent, silicon oxide. The rock is slightly carbonated, leading to the presence of

Table 2: Elemental Composition of Hematite Rock Samples from Kyzyltash

Elemental content	Synthesized Samples			
	GM-1	GM-2	GM-3	GM- average
Fe	57,70	56,55	54,20	56,15
Si	14,90	13,79	15,55	14,746
Ca	6,940	7,110	8,450	7,50
Mg	2,090	3,228	4,33	3,216
Al	1,720	2,57	2,4	2,23
Cl	0,0166	0,0157	0,0169	0,0164
P	0,182	0,177	0,192	0,2755
S	0,0402	0,0322	0,0495	0,0406
V	0,0450	0,0550	0,0610	0,05366
Cr	0,0194	0,0199	0,0201	0,0198
Mn	0,100	0,1100	0,0990	0,103
Zn	0,0046	0,0058	0,0043	0,0049
Cu	0,144	0,287	0,215	0,2153
As	0,0048	0,0035	0,0052	0,0045
Sr	0,0118	0,0220	0,0122	0,0154
Y	0,0034	0,0035	0,0028	0,00323
Zr	0,259	0,220	0,210	0,230
Ag	0,0023	0,0021	0,0069	0,00373
Sn	0,0054	0,0062	0,0088	0,0068
Te	0,0036	0,0041	0,0021	0,00326

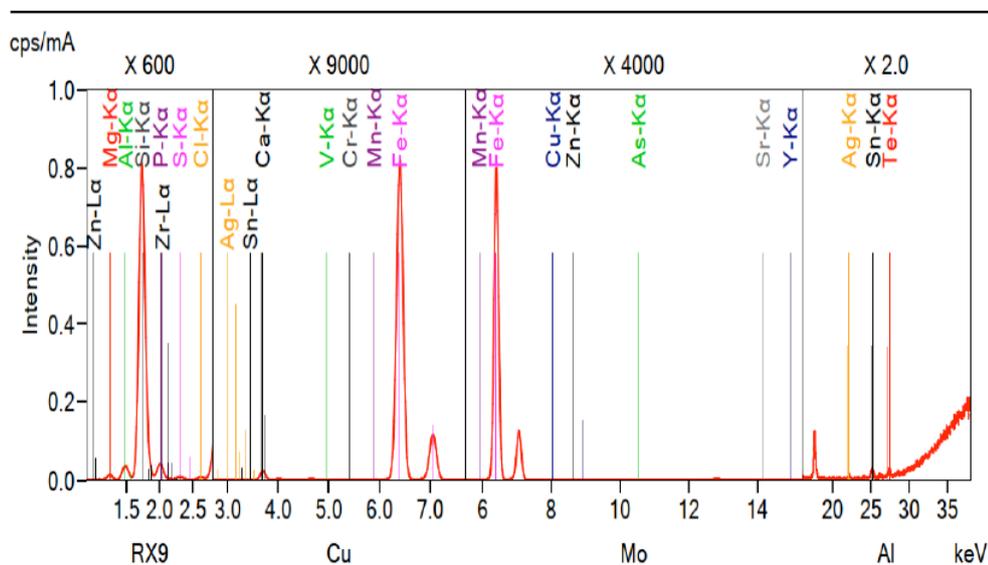


Figure 2: Spectral analysis of the hematite mineral from the Kyzyltash deposit.

magnesium and calcium oxides. After enrichment of this hematite rock, the content of these secondary oxides decreases, resulting in an increase in the iron oxide content of the original Kyzyltash hematite.

The elemental composition of the hematite samples

from the red stone deposit was also studied, and the results are presented in Table 3.

The results of determining the physicochemical and color characteristics of a hematite sample from the Kyzyltash deposit are presented in Table 2.

**Table 3: Physicochemical and Color Characteristics of a Hematite Sample from the Kyzyltash Deposit**

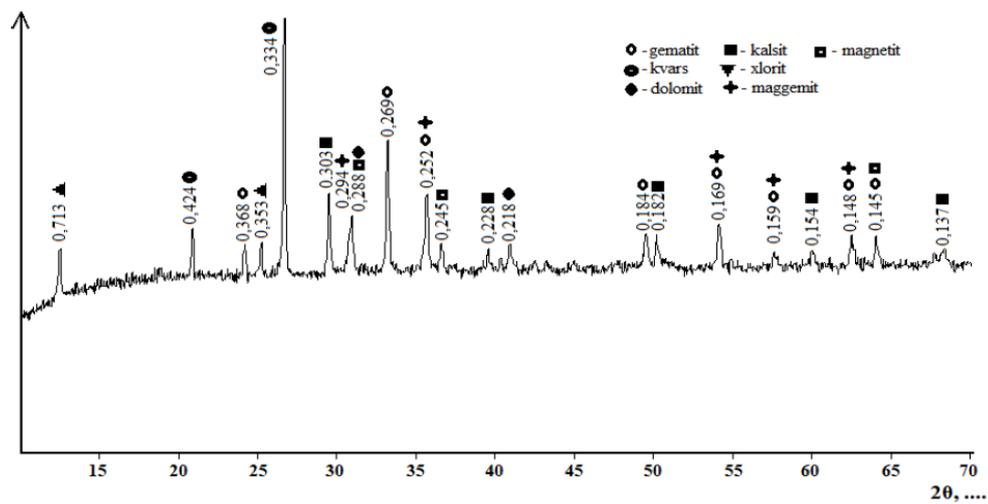
Indicator	Characteristic of sample
Sample Color	Silvery-gray to brownish-black
Minor Minerals	Carbonates, chlorites, quartz
Lustre	Matte
Mohs Hardness	5-6
Density, kg/m <sup>3</sup>	5000 – 5300
Degradability	Highly soluble in hydrochloric acid
Syngony (structure)	Trigonal

### SAMPLE PREPARATION

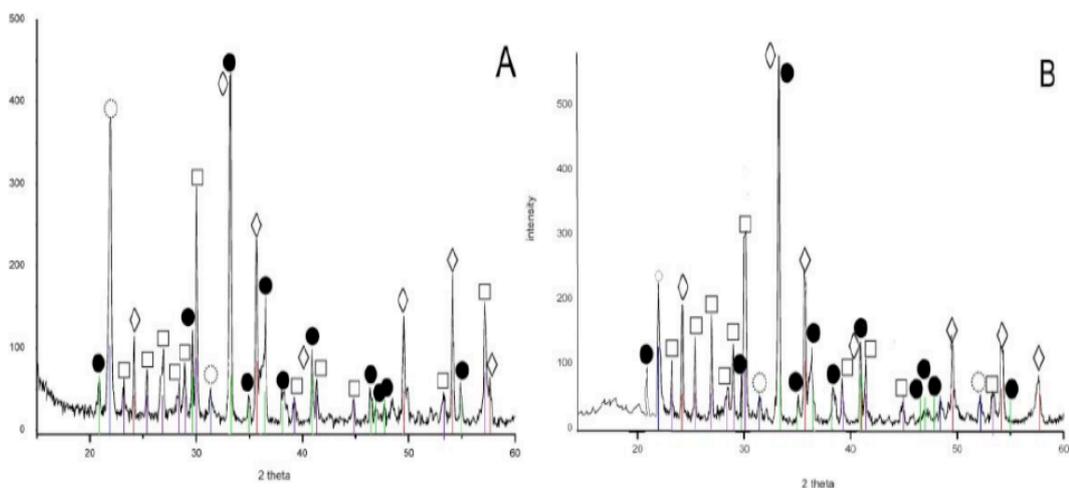
The mineral hematite was ground in a ball mill to a size of 0.1 mm. Limestone,  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , and amorphous silicon (II) oxides were obtained by

crushing in a separate, isolated state. The components were weighed in appropriate proportions, and the samples were prepared in an electric oven at 900-1300 °C for 240 minutes using the traditional preparation method (heating and cooling rate of 20 °C/min). It should be noted that the optimal temperatures for color formation and phase transition are 1000-1000°C. Two different silicon sources ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  and amorphous silicon (II) oxide) were used to accelerate the reaction and increase its surface area. To reduce the temperature,  $\text{B}_2\text{O}_3$  was added in an amount of 2% by weight. The temperature was systematically increased and decreased proportionally. При этом следует

To determine the crystalline phases present in green and mature samples, X-ray diffraction maxima were obtained using a conventional powder diffraction method.



**Figure 3:** X-ray diffraction pattern of the hematite mineral from the Kyzyltash deposit.



**Figure 4:** X-ray diffraction patterns of fired samples at temperatures of 1000°C (A) and 1100°C (B). ● - Andradite  $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ , □ - Wollastonite  $\text{CaSiO}_3$ , ◇ - Hematite  $\text{Fe}_2\text{O}_3$ , ○ - Cristobalite  $\text{SiO}_2$ .

The X-ray diffraction pattern of the redstone hematite mineral shows the presence of oxides of Si, Fe, Al, Ca, and Mg, in sufficient quantities to synthesize pigment. Samples prepared at different temperatures, based on the X-ray diffraction maxima, reveal the formation of mineral phases such as andradite, vallostanite, and cristobalite, which impart the pigment's color.

## CONCLUSION

Based on physicochemical studies, it was established that the chemical and mineralogical compositions of hematite rock samples from the Kyzyltash deposit are sufficiently rich in the rock-forming element iron(III).

The results of X-ray phase analysis of the mineralogical composition of hematite rock from the Kyzyltash deposit revealed the presence of crystalline structures associated with hematite itself, some quartz, calcite, and minor amounts of dolomite, chlorite, and other impurity minerals.

Thus, it was established that the obtained results of determining the physicochemical and color characteristics of the hematite sample from the Kyzyltash deposit demonstrated its suitability for producing ceramic pigments, in particular for producing red to brown colors after firing at various temperatures. Ceramic pigments based on this hematite rock can be used in glazes and engobes for glazing fired silicate and refractory materials for various purposes.

The analysis results showed that the synthesized pigments exhibit good chemical and thermal stability at high temperatures. Therefore, the resulting ceramic pigments based on this hematite rock can be used in glazes and engobes for glazing fired silicate and refractory materials for various applications.

## CONFLICTS OF INTEREST

The authors of this article have no conflict with each other.

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