DEVELOPMENT OF METHODS FOR PRODUCTION OF ARTIFICIAL COPPER PATINA

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Abstract

This work is focused on development of a method for production of artificial copper patina pigment based on brochantite. A suitable titration method for this type was chosen to add sodium hydroxide solution to cupric sulphate solution. Following parameters were studied: solutions concentrations, ferric ion addition, dosing rate of titration, stirring intensity. Produced pigment was studied by means of XRD (phase composition), spectrophotometry (colour) and SEM (morphology). In the first stage the suitability of this method was verified in small portions when the volume of cupric sulphate solution was less than 100 ml. In these experiments, the suitability of the method was confirmed both for pure copper sulphate and cupric sulphate solution with the addition of ferrous sulphate heptahydrate, which provide colour closer to natural patina. After successful confirmation of the suitability of this method, it was passed to the second stage when this procedure was tested at large doses, the volume of cupric sulphate being 5 liters. The results indicate that this procedure is applicable to a pure copper sulphate solution, but not to a mixture of copper sulphate and iron sulphate.

Keywords: Artificial copper patina, brochantite, spectrophotometry, XRD, SEM

1. INTRODUCTION

Nowadays, patina is among the common methods of surface treatment of copper sheets and copper products. The most commonly used method of patination is the application of solutions to the copper substrate and the subsequent reaction to form a patina. These patination procedures are described in some patents[1][2][3][4].

Brochantite ($Cu_4SO_4(OH)_6$ is one of the components of the patina that is formed in the urban environment during the reaction of copper with sulphur dioxide in the humid atmosphere. This patina component is very stable and resistant to dissolution and it is able to protect the base material very well. Brochantite can be formed in two ways: by exposure in the sulphur dioxide containing gaseous environment or by titration in the solution.

2. EXPERIMENTAL

To evaluate titration results, we used colorimetric methods to determine the color of the resulting pigment. We used a scanning electron microscope to determine the morphology, and Röentgen diffraction was used to determine the phase composition. At the beginning, we performed dynamic titration and continued the titration when we changed the volume and concentration of added NaOH and also the concentration and volume of the titrated solution $CuSO_4$. $5H_2O$. After these titrations, we went to the titrations to the solution $CuSO_4$. $5H_2O$ we added $FeSO_4$. $7H_2O$. Finally, we went into titration in large volumes when we titrated 5 liters of solution $CuSO_4$. $5H_2O$.

3. RESULTS AND DISCUSSION

3.1. Influence of dosing rate

To determine the consumption of sodium hydroxide for the perfect conversion of copper sulphate pentahydrate to Brochantite, the dynamic titration test was carried out, the volume of NaOH solution added ranging from 0.05 ml to 5 ml was 60 seconds. The resulting graph is shown in **Figure 1**.

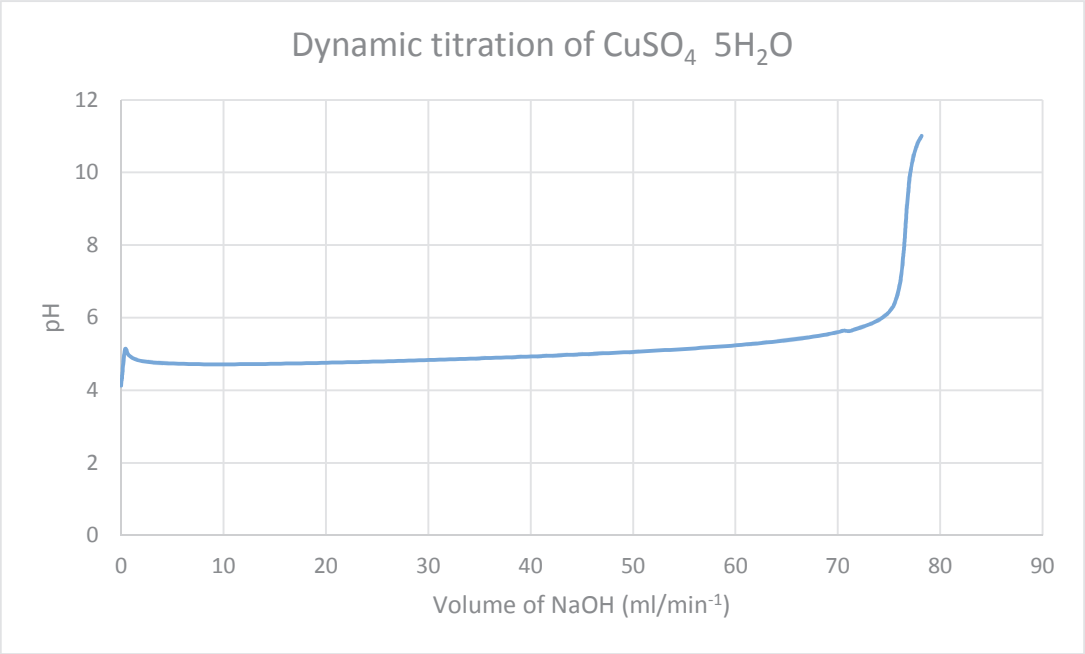


Figure 1 Dynamic titration of $CuSO_4 \cdot 5H_2O$ from which the necessary data were obtained to perform further titrations

3.2. Influence of concentration

After the dynamic titration was completed, we obtained accurate data according to which we proceeded to titrations when we changed the parameters as the rate and volume of NaOH added. In the next step, we changed the concentrations of both sodium hydroxide and $CuSO_4 \cdot 5H_2O$ solutions. Concentrations of the individual solutions are shown in **Table 1**. We started with the addition of 0.04 ml of NaOH for 60 seconds, gradually increasing to 0.8 ml with a time interval of 60 seconds. These changes were made to monitor changes in the kinetics of the reaction and the impact of the changes on the yield of the reaction. After evaluating the results of gravimetry, we found that the yield of the reaction was almost unchanged. The recovery rate at 0.04 ml/min^{-1} was about 42 % and at a rate of 0.8 ml/min^{-1} 45 %, but the difference was in the color of the samples as well as in the phase composition of the pigments formed.

Table 1 Concentrations and rates of addition of NaOH to $CuSO_4$ solution

Concentration of CuSO4 ($mol \cdot dm^{-3}$)	Concentracion of NaOH ($mol \cdot dm^{-3}$)	Rate of addition of NaOH ($ml \cdot min^{-1}$)
0.01	0.1	0.01; 0.04; 0.50
0.10	0.1	0.04; 0.80
0.60	1.0	0.80

3.3. Influence of Fe(III) addition

If we typed pure $CuSO_4 \cdot 5H_2O$ so produced a patch that was composed of Brochantite but the color was unsuitable for the final use, we decided to add to the $FeSO_4 \cdot 7H_2O$ solution, which ensured that the color of the resulting product was green and the resulting product was more suitable for the final use because the coloration was approaching the original patina. We titrated the $Cu(NO_3)_2 \cdot 3H_2O$ solution to confirm the assumption that neither the color nor the composition of the resulting pigment is in accordance with our requirements. Comparison of colour after adding $FeSO_4 \cdot 7H_2O$.

3.4. Large volume titrations

Large titrations were performed to test the usability of this method for large doses of $CuSO_4 \cdot 5H_2O$. For titrations without addition of $FeSO_4 \cdot 7H_2O$, a color pigment corresponding to the pigment formed in small amounts was formed. If we added $FeSO_4 \cdot 7H_2O$ color changed from green to black. This change is due to the alkaline environment in which this pigment was present for at least 30 minutes because we did not have the capacity to filter out five liters of the pigment solution.

3.5. X-ray diffraction

To determine the phase composition of the patina formed, we used X-ray diffraction. A powder pigment was used as the sample. The weight of the sample was approximately 0.3 g and was crushed and transported in plastic micro tubes. The PANanalytical X'Pert3 device was used for XRD measurements. Determination of the phase composition was performed after each titration in order to know the phase composition of the individual samples and accordingly adjust the titration procedure. The composition of some samples is shown in **Table 2**. Brochantite, Posnjakite ($Cu_4SO_4(OH)_6 \cdot H_2O$) and Tenorite (CuO) were found in the samples. These phases were in different proportions in the sample.

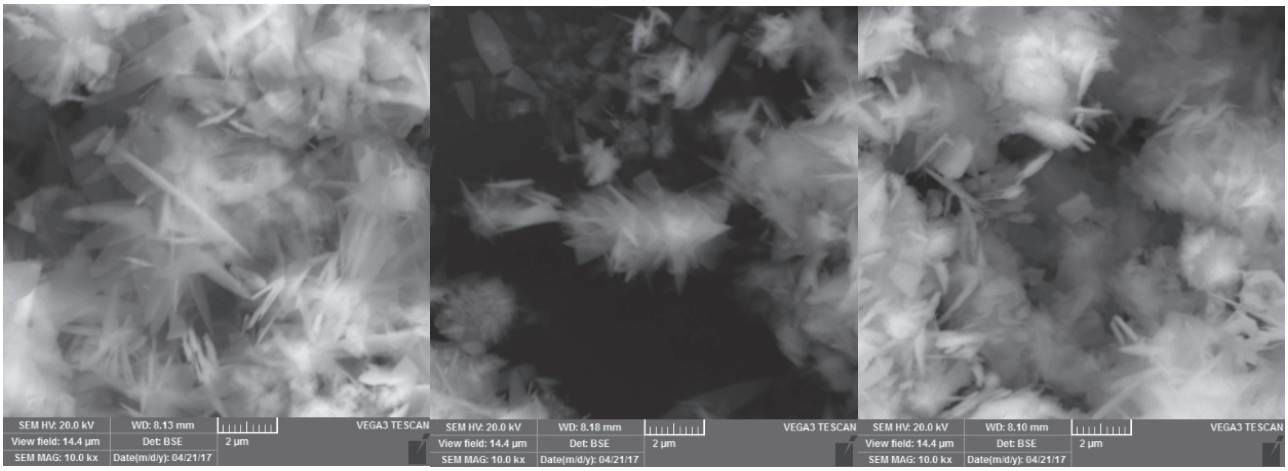
As shown in **Table 2**, the higher rate of addition of sodium hydroxide to the solution, the more phases were present in the resulting sample. To the sample labeled Brochantite with Fe^+ 4 was added to achieve the desired pigment color, but the resulting pigment composition did not affect this addition.

Table 2 Phase composition of individual pigments

Sample	Rate of addition of NaOH (ml min^{-1})	Component	Ratio %
Brochantite 1	0.01	Brochantite	73
		Posnjakite	27
Brochantite 2	0.04	Brochantite-	100
Brochantite 3	0.5	Posnjakite	85
		Brochantite-	8
		Tenorite	6
Brochantite with Fe^+ 4	0.04	Brochantite	100
Brochantite 5	0.8	Brochantite	98
		Posnjakite	2

3.6. Morphology of patina

The patina morphology was monitored by Tescan VEGA 3 scanning electron microscope (SEM). Samples with different phase composition were observed. Samples were lit at 100x, 1000x, and 10000x magnification. By visual analysis, the length and shape of the individual crystals were evaluated and, according to this analysis, the optimal rate of addition of NaOH to the $CuSO_4 \cdot 5H_2O$ solution was chosen. The morphology of most samples was needle-like with a needle length of 5 μm, which is suitable for practice. Only in one case they were of a grain-like nature, in a sample formed from a solution of $Cu(NO_3)_2 \cdot 3H_2O$. At the same time, this sample was only used at a magnification of 100x and 1000x as the grains were large enough for observation and image analysis at these magnifications. In **Figure 2** there are photos of three patches of $CuSO_4 \cdot 5H_2O$ solution. The photos show that although the patina was prepared by the same procedure, morphology is very similar. The reproducibility of the process is very high.



a) b) c)

Figure 2 Comparison of morphology of three samples prepared by the same titration procedure; a) Brochantite 1 b) Brochantite 2 c) Brochantite 3

3.7. Color

In order to evaluate the colorability of the samples, measurements of all samples were made and their coloring was compared with the sample of natural Brochantite, which was created on the roof of the University of Chemistry and Technology Prague. The Datacolor spectrophotometer was used to measure the color. We were looking at the individual components of the Lab color model, but for comparison we only observed a and b component. Only a few samples of pigments were selected for comparison in the graph, with respect to the transparency of the graph. Four separate graphs have been created. One sample was placed without addition of Fe^{+}, one sample with high amount of Fe^{+}, one sample with right amount of Fe^{+} and one sample which was dried in oven with high temperature.

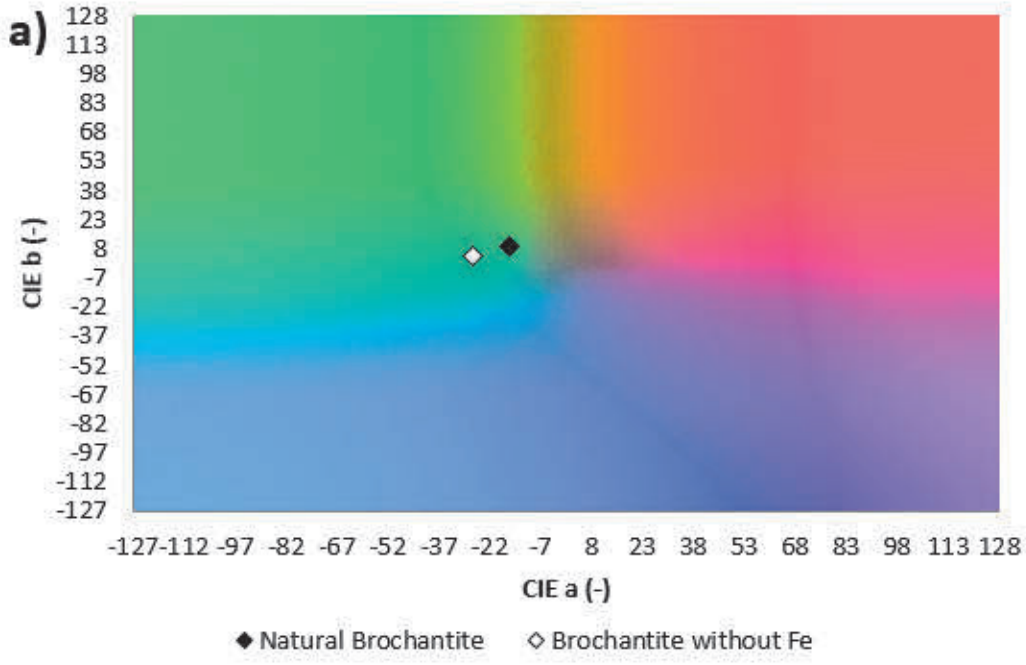
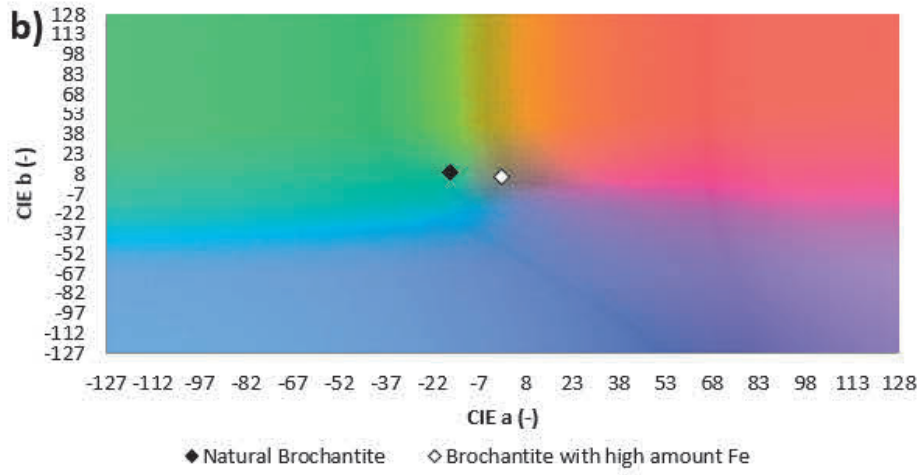
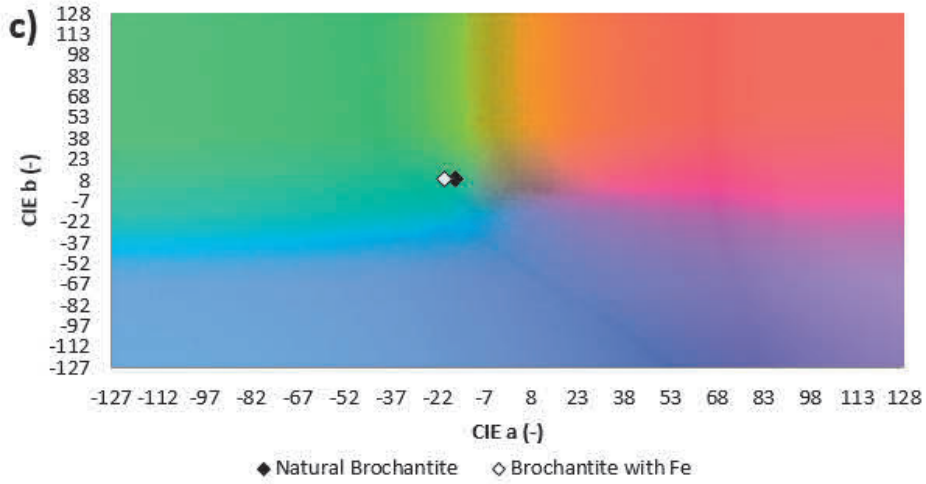


Figure 3/1 Comparison of some types of Brochantite; a) Brochantite without Fe





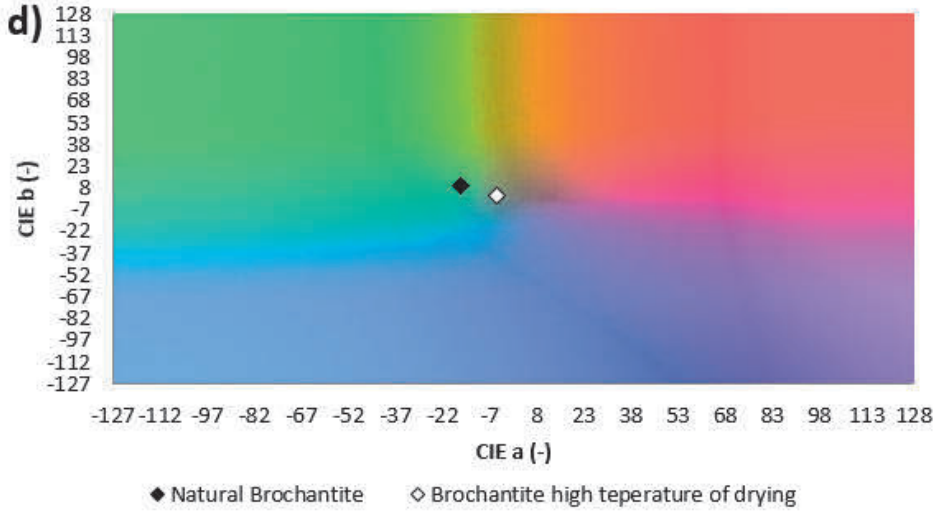


Figure 3/2 Comparison of some types of Brochantite; a) Brochantite without Fe; b) Brochantite with high amount of Fe; c) Brochantite with right amount of Fe; d) Brochantite drying in oven and high temperature

4. CONCLUSION

In this experiment, we performed several titrations to prove that this method of artificial shield creation is an appropriate and easily reproducible method. We have verified the suitability of Fe^{+} addition only in smaller quantities. This was confirmed by this method using x-ray diffraction because the resulting sample composition was in most cases pure Brochantite or only a small addition of other minerals. Using a scanning electron microscope, we confirmed the reproducibility of the size and shape of the patina grains. The suitability of the method for larger volumes was confirmed, but only in the case of Brochantite without the addition of Fe^{+} ions. In the case of addition of Fe^{+}, a suitable method of extracting the formed pigment from the alkaline medium has to be found where the alkaline environment degrades the color of the pigment. In the future, we will focus on accelerating the extraction of the pigment from the alkaline environment so that the color after the addition of Fe^{+} remains stable and does not change.

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REFERENCES

[1] GERVAIS, J. and LTEÉ, M. F. *Method for forming artificially and rapidly patina on copper, products thereof and solutions therefor.* Canada. United States patent, US005160381A. 1992 Nov 3rd.

[2] ATRENS, A. *Artificial patina,* Australia. International patent, WO 95/29207. 1995 Nov 2nd.

[3] HOKAZONO, T. and TANAKA, S. *Artificially patinated copper material,* Japan. United States patent, US006063480A. 2000 May 16th.

[4] HOVELING, S., RODE, D., PROTZER, H. and LUETIC, R. *Method for producing Brochantite patina on copper*. Germany. United States patent, US005714052A. 1998 Feb 3rd.