Verification of the Utilization of Fly Ash Generated by Municipal Sewage Sludge Incineration as A Pigment in Mural Painting

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Summary

The objective of the research was to verify the possibilities of utilizing fly ash generated by municipal sewage sludge incineration, following an adjustment of the grain size, as a pigment and its comparison with an industrial pigment used in mural painting.
The testing of the sample under examination included its grinding, application in the restoration of a mural painting on a test panel, simulation of the aging process in a climatic chamber and a comparison with an industrial pigment commonly used in practice by means of a microscopic analysis, infrared and Raman spectrometry.

Keywords: waste utilisation, pigments, mural painting, municipal sevage sludge incineration, test panel

Characteristics of the waste material

The selected waste material was the fly ash generated by the incineration of sewage sludge from a wastewater treatment plant in Krakow, Poland. At the plant, the waste is incinerated in fluid boilers. A chemical analysis of the composition showed a high content of SiO_2 (43.20%), CaO (22.29%), P_2O_5 (22.19%), Al_2O_3 (4.96%) and Fe_2O_3 (2.17%). An analysis of metals in the fly ash showed a dominating content of Zn and Cu. [2] The colour of the sample was light brown.

Industrial pigment

The comparative industrial lime pigment S 079, KEIM Farben, was selected on the basis of the following criteria – a colour similar to the sample under examination, its quality and frequency of usage in practice.

Grinding

To obtain the finest material, the fly ash sample was ground using two types of grinding machines. In the first case, in which the sample had been ground using the LAMOW–C–5×2 rotational vibrating mill at the AGH laboratory in Krakow, a relatively fine-grained material was obtained. Based on a laser analysis of particle sizes, 50% of the grains represented in the sample had a grain size of less than approx. 3 μm. The grinding process resulted in changes to the colour of the material. The colour of the fly ash sample (K.O.Krakow) changed from light brown to dark ochre (natural Italian sienna). Other grinding tests were performed using the Pulverisette 7 planetary mill at Precheza Přerov, a. s. at 300 rev/min for a period of one hour. In addition to the fly ash sample under examination (K.O.Krakow), the selected industrial pigment (having a similar colour) S 079, KEIM Farben (S079 Keim) was also ground. [1]

Application in mural painting, Simulation of the aging process of a mural painting in a climatic chamber and **Microscopic analysis** are the same as presented in article Verification of the Utilization of Pigments Obtained from Sewage Sludge With Fe Content in Mural Painting by L. Černotová, L. Zamrazilová, L. Mišková and B.Tora (Journal of the Polish Engineering Society, January - June 2014, p. 235 - 248).

The sample from polished section 1 contained the S079 Keim industrial pigment, bound by a natural binder – an egg yolk emulsion. Place on the panel from which the sample was taken – 4. The observation took place in VIS and in UV light (see Figures 5, 6).

The sample from polished section 2 contained the pigment under examination, K.O.Krakow, bound by a natural binder – an egg yolk emulsion. Place on the panel from which the sample was taken – 2. The ob-

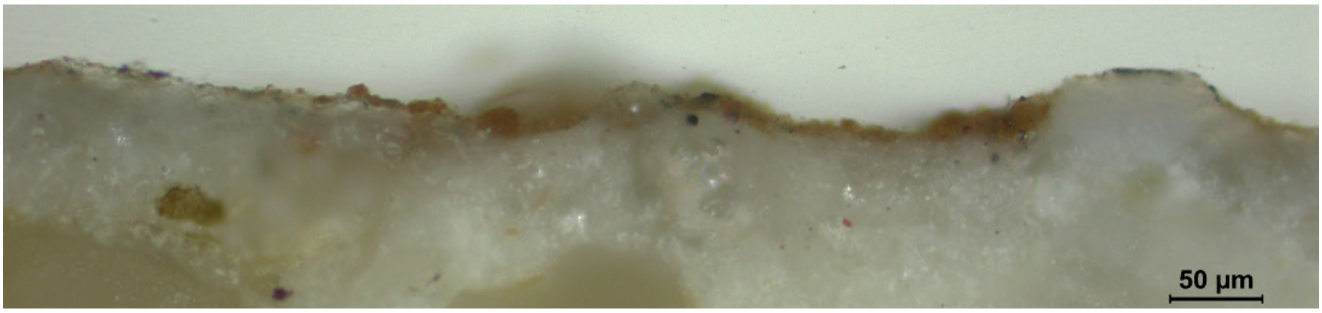


Fig. 5 The industrial pigment S079 Keim, bound by a natural binder, observation in VIS

Rys. 5 Pigment przemysłowy S079 Keim, związany naturalnym spoiwem, obserwcja w VIS

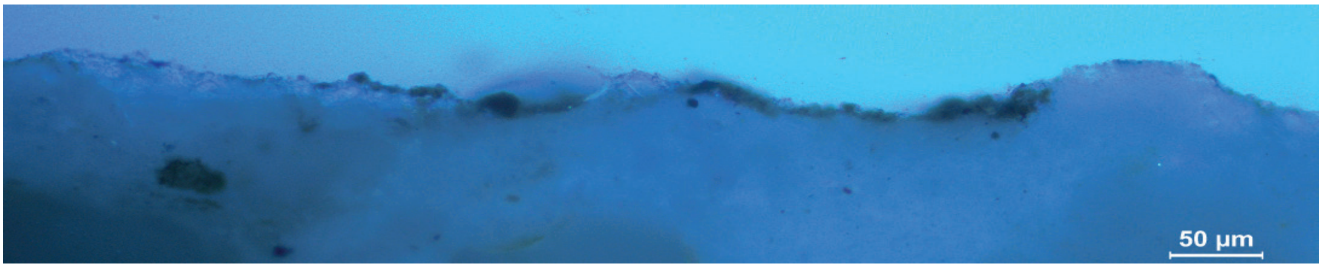


Fig. 6 The industrial pigment S079 Keim, bound by a natural binder, observation in UV

Rys. 5. Krzywe płynięcia wg modelu Binghama, zawiesin sporządzonych z popiołu K-1 bez dodatku cementu

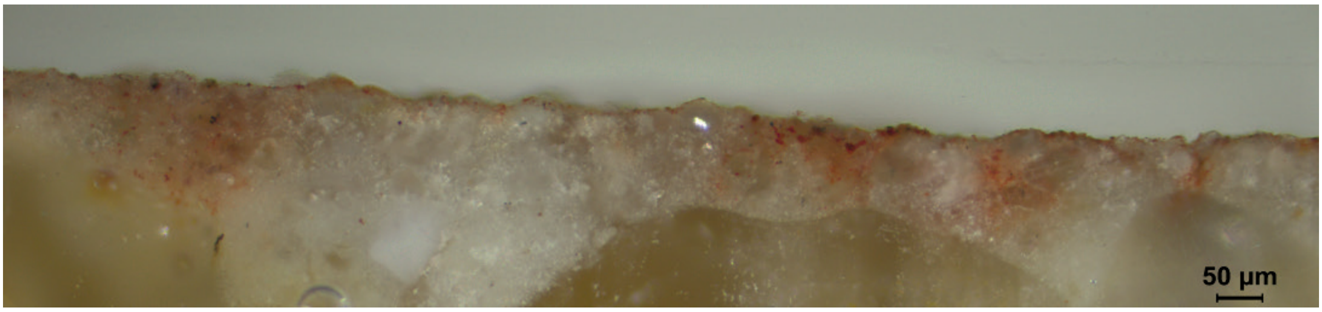


Fig. 7 The examined pigment K.O.Krakow, bound by a natural binder, observation in VIS

Rys. 7 Badany pigment K.O.Krakow, związany naturalnym spoiwem, obserwacja w VIS

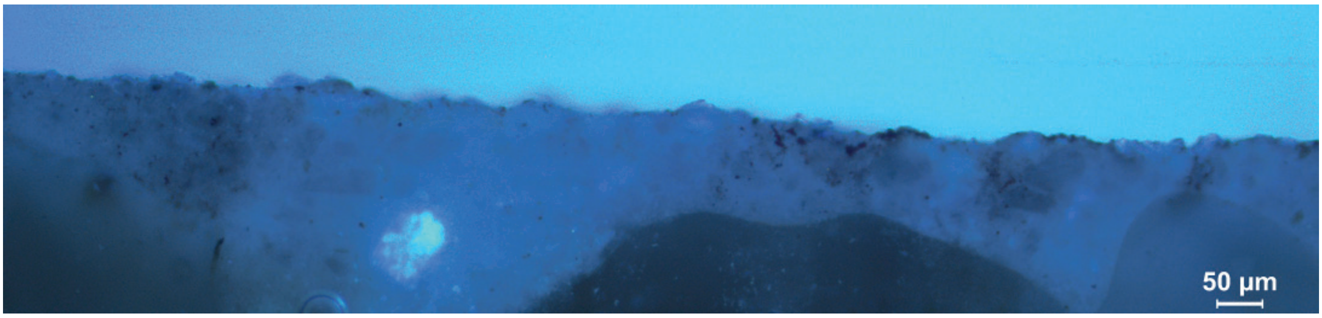


Fig. 8 The examined pigment K.O.Krakow, bound by a natural binder, observation in UV

Rys. 8 Badany pigment K.O.Krakow, związany naturalnym spoiwem, obserwacja w UV servation took place in VIS and in UV light (see Figures 7, 8).

The sample from polished section 3 contained the S079 Keim industrial pigment, bound by a synthetic binder – Primal SF 016. Place on the panel from which the sample was taken – 3. The observation took place in VIS and in UV light (see Figures 9, 10).

The sample from polished section 4 contained the pigment under examination, K.O.Krakow, bound by a synthetic binder – Primal SF 016. Place on the panel from which the sample was taken – 1. The observation took place in VIS and in UV light (see Figures 11, 12).

The ability of adhesion of the K.O.Krakow pigment and the S079 Keim industrial pigment to the ground layer (a lime plaster) was confirmed. In images taken in visible light, the filler (POLYLITE 32032) can be recognized in the top part; under this substance, it is possible to recognize the colour layer composed of a pigment mixed with the binder and the plaster substance can be recognized in the bottom part – see the scheme in Figure 4. The pigment under examination and the comparative industrial pigment were used in the colour surface layer. They were mixed with two binder types – a natural (egg yolk emulsion) and a synthetic binder (Primal SF 016).

Through observation in visible light, similarities in distribution, shape and adhesion of both the grains of the pigment under examination and the grains of the industrial segment were observed in all samples (see Figures 5, 7, 9 and 11). The types of the binder used cannot be identified through examination in visible light. UV light is used for these purposes. The synthetic binder fluoresces and shows as bright shining dots in the surface layer; a natural binder does not fluoresce. The pigment grains stay on the surface of the binder.

Observation in UV light confirmed the presence of a synthetic binder in the sample from polished section 3 of the S079 Keim industrial pigment (see Figure 10) and in the sample from polished section 4 of the K.O.Krakow pigment under examination (see Figure 12). The remaining samples did not fluoresce in UV light, which confirmed the presence of a natural binder.

Infrared and Raman spectroscopy

The analyses were conducted at the molecular spectrometry laboratories of the Prague Institute of Chemical Technology (VŠCHT). Red iron-based inorganic pigments were analysed. As regards the samples of pure pigments, the spectrums were measured using infrared spectroscopy and Raman spectroscopy. As regards the samples of the pigments used in the paint, the analysis focused on the stability of the pigment grains using Raman spectroscopy.

Infrared spectroscopy was performed using the Nicolet 6700 FTIR spectrometer (Thermo-Nicolet, USA) in connection with the GladiATR single-reflection diamond ATR accessory, reflectance measurement, DTGS detector, measurement parameters: spectrum range: 4000-400 cm^{-1}, resolution: 4 cm^{-1}, number of spectrum accumulations: 64, Happ-Genzel apodization.

Raman microspectroscopy was performed using the Nicolet DXR dispersion Raman microscope (Thermo Scientific, USA), equipped with the Olympus confocal microscope. A laser with a wavelength of 532 nm and an input power of 10 mW was used as the excitation source. The samples were measured at a 100% capacity of the laser, the duration of a pulse was 5 seconds and there was 1 spectrum accumulation. These parameters prevent the sample from suffering thermic damage. A dispersion grating with 900 grooves/mm and a 50µm pinhole was used. A multichannel air-cooled CCD camera served as the detector. A microscope objective with 50x magnification and a long working distance was used for the measurement.

The spectrums were computer processed using Omnic 8.0 (Nicolet Instruments Co., USA) and identified using the spectrum library of VŠCHT Prague.

Analyses of powder preparations of the pure pigments

Samples of pure powder preparations of the pigments were analysed before their application in the paint on the lime ground.

Sample 051112/1 Keim Farben S079 (S079 Keim) – this was a powder industrial pigment (S079 Keim) that was used for a comparison with the pigment under examination designated as K.O.Krakow (fly ash generated by the incineration of sewage sludge from a wastewater treatment plant in Krakow) before its application in in the paint on the lime ground.

Sample 051112/4 K.O.Krakow P1-1 (K.O.Krakow) – this was a powder preparation of the pigment under examination (K.O.Krakow – fly ash generated by the incineration of sewage sludge from a wastewater treatment plant in Krakow) that was used for a comparison with the S079 Keim industrial pigment before its application in the paint on the lime ground.

The results of analyses for the individual samples of the pure powder pigments before their application in the paint on the test panel with a lime plaster are

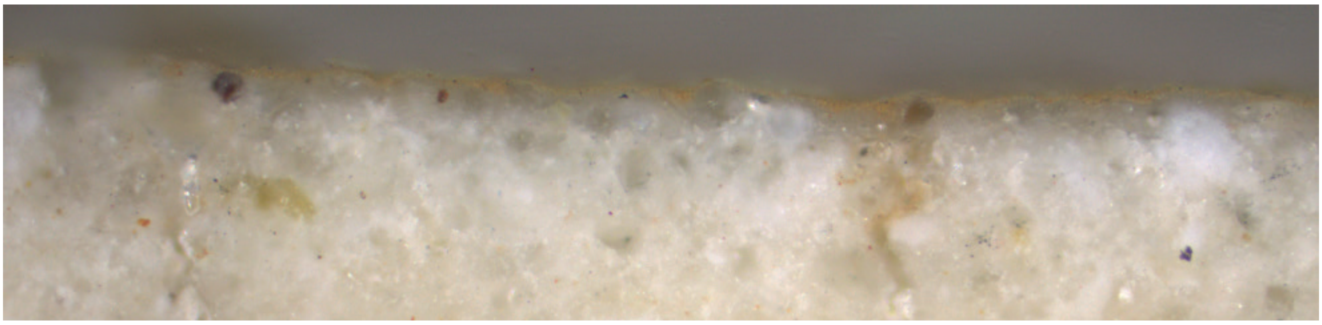


Fig. 9 The industrial pigment S079 Keim, bound by a synthetic binder, observation in VIS

Rys. 9 Pigment przemysłowy S079 Keim, związany spoiwem syntetycznym, obserwcja w VIS

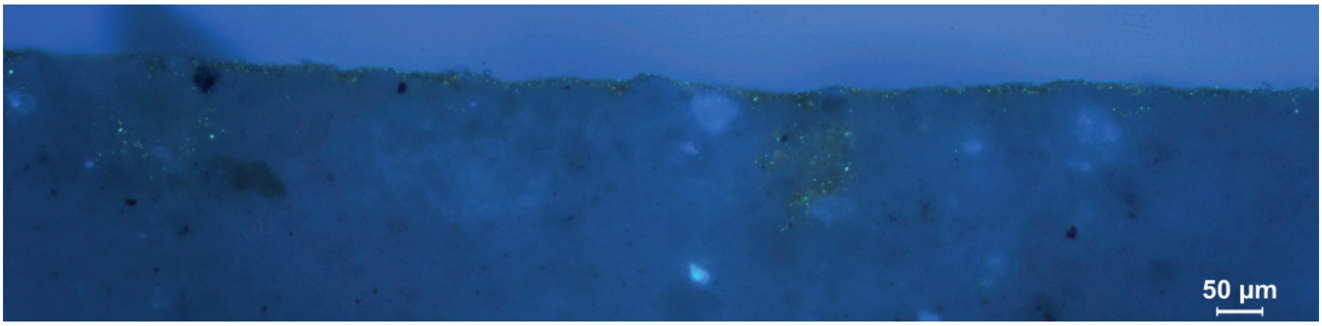


Fig. 10 The industrial pigment S079 Keim, bound by a synthetic binder, observation in UV

Rys. 10 Pigment przemysłowy S079 Keim, związany spoiwem syntetycznym, obserwcja w UV

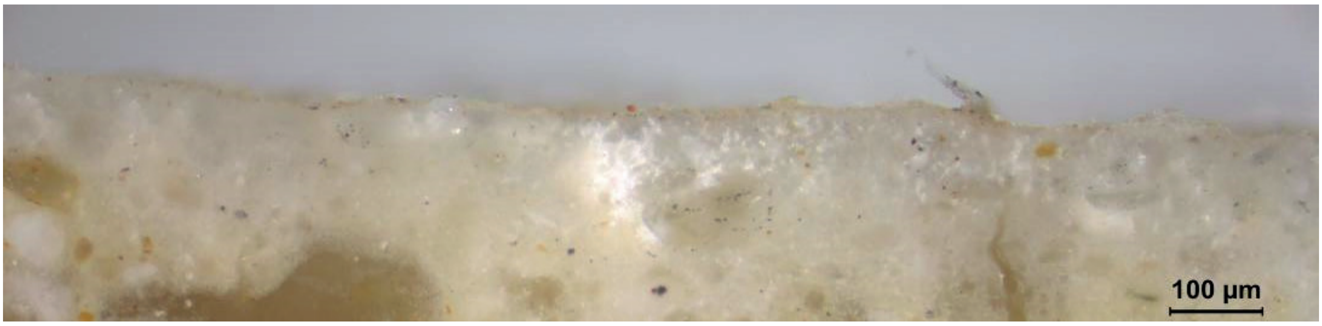
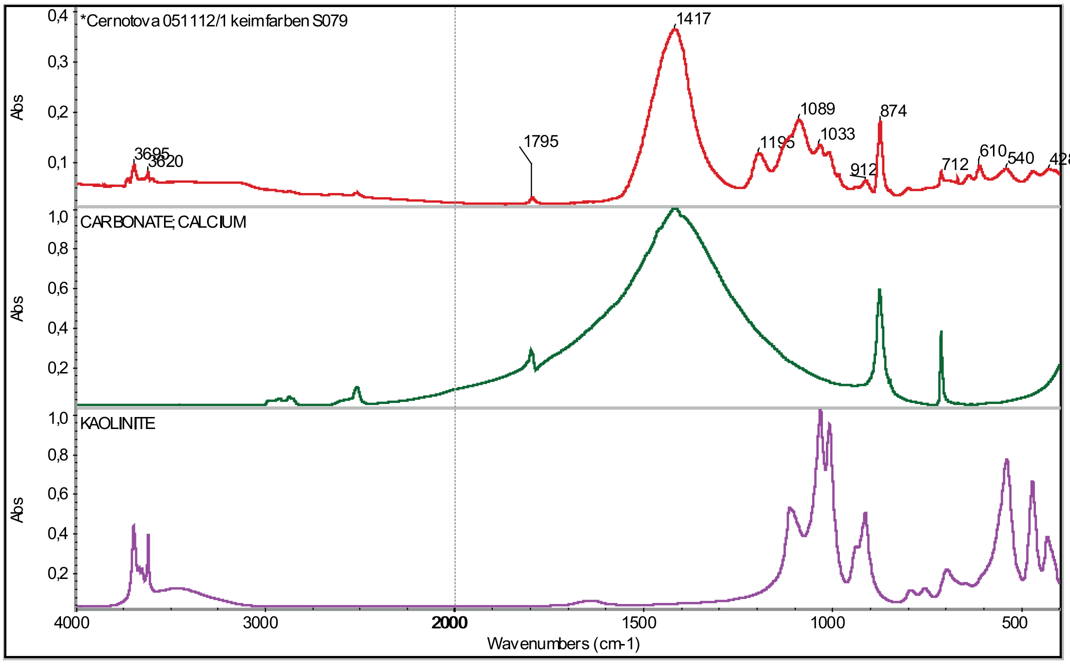


Fig. 11 The examined pigment K.O.Krakow, bound by a synthetic binder, observation in VIS

Rys. 11 Badany pigment K.O.Krakow, związany spoiwem syntetycznym, obserwacja w VIS

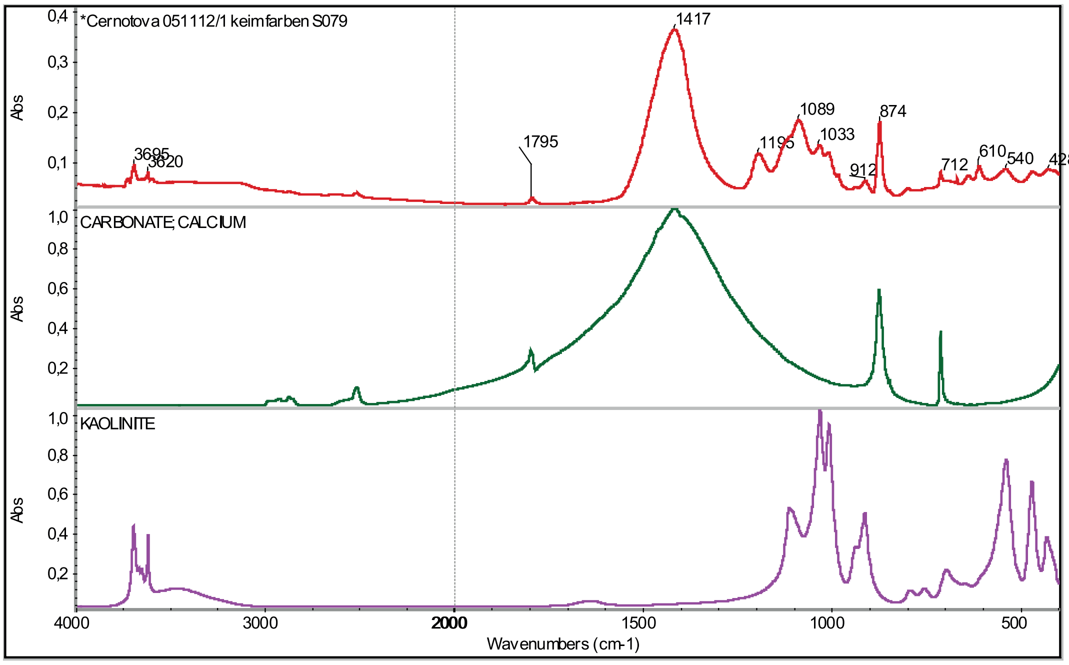
Fig. 12 The examined pigment K.O.Krakow, bound by a synthetic binder, observation in UV

Rys. 12 Badany pigment K.O.Krakow, związany spoiwem syntetycznym, obserwacja w UV



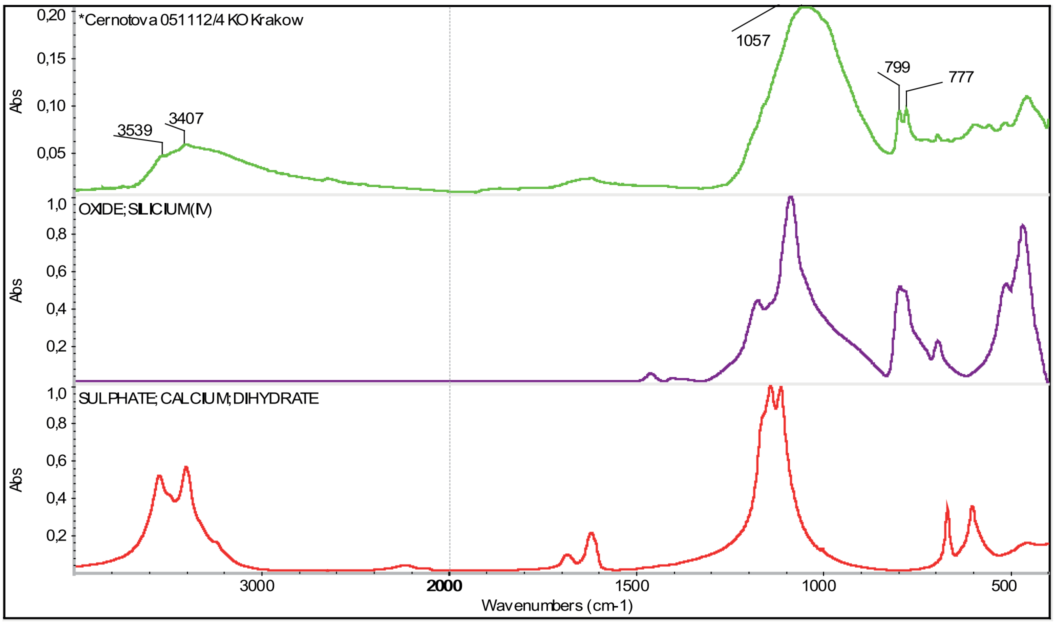
Graph 1 IR spectrums of the sample 051112/1 Keim farben S079

Graf. 1 Widmo IR próbki 051112/1 Keim farben S079



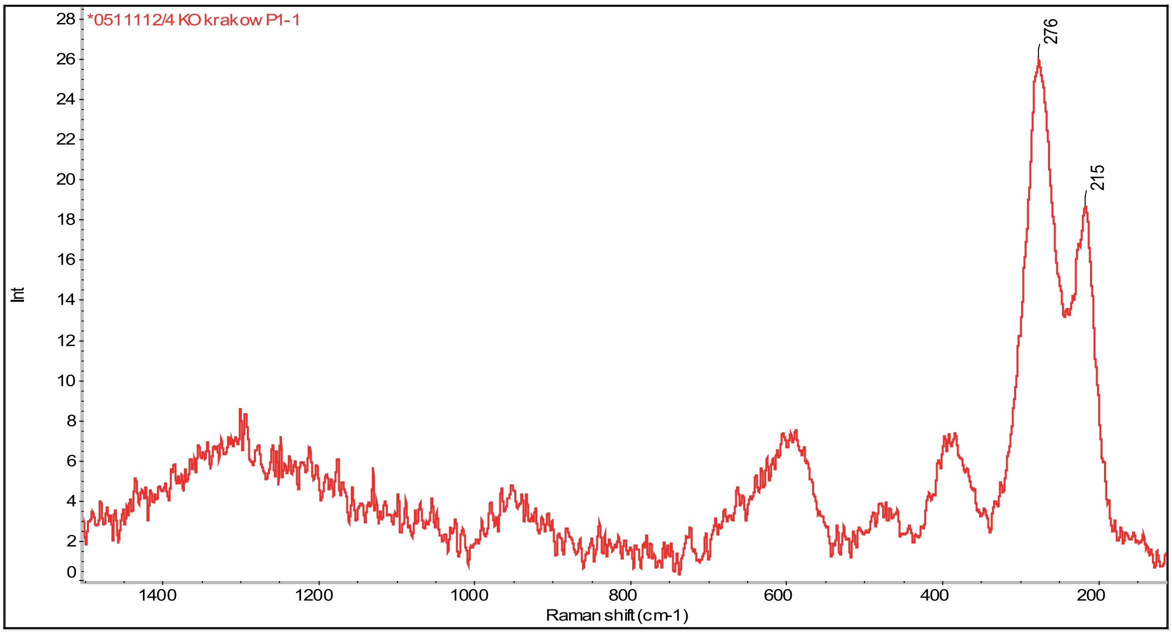
Graph 2 The Raman spectrum of the sample 051112/1 Keim farben S079

Graf. 2 Widmo ramanowskie próbki 051112/1 Keim farben S079



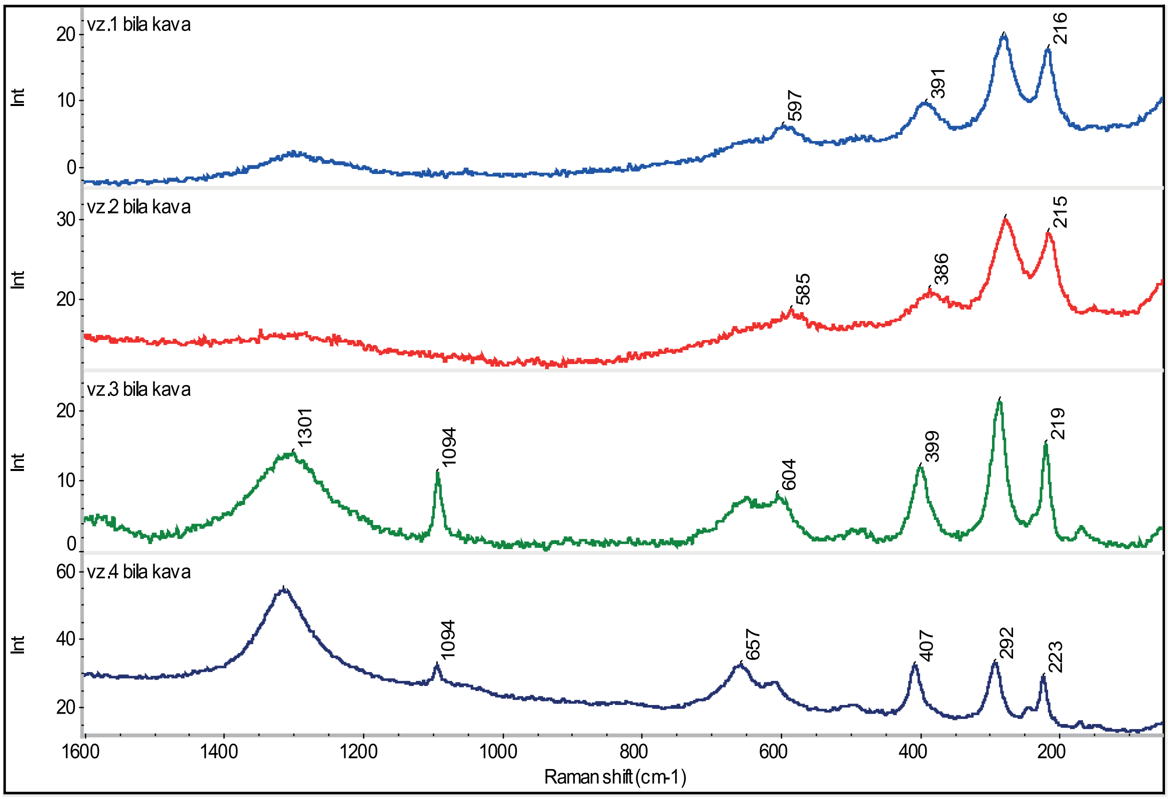
Graph 3 IR spectrums of the sample 051112/4 K.O.Krakow P1-1

Graf. 3 Widmo IR próbki 051112/4 K.O.Krakow P1-1



Graph 4 The Raman spectrum of the sample 051112/4 K.O.Krakow P1-1

Graf. 4 Widmo ramanowskie próbki 051112/4 K.O.Krakow P1-1



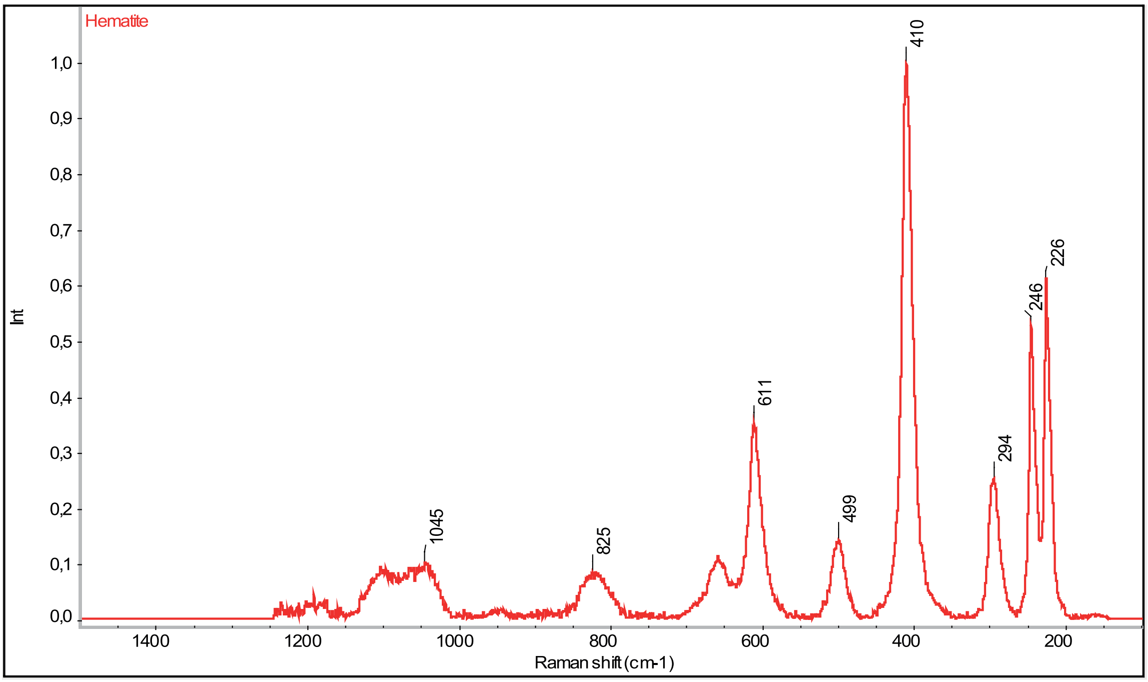
Graph 5 The Raman spectrums of the shade of the samples – white coffee

Graf. 5 Wido ramanowskie szlifu próbki – biała kawa

Tab. 1 Legend for Graph 5 of the Raman spectrums of the shade of the samples – white coffee.

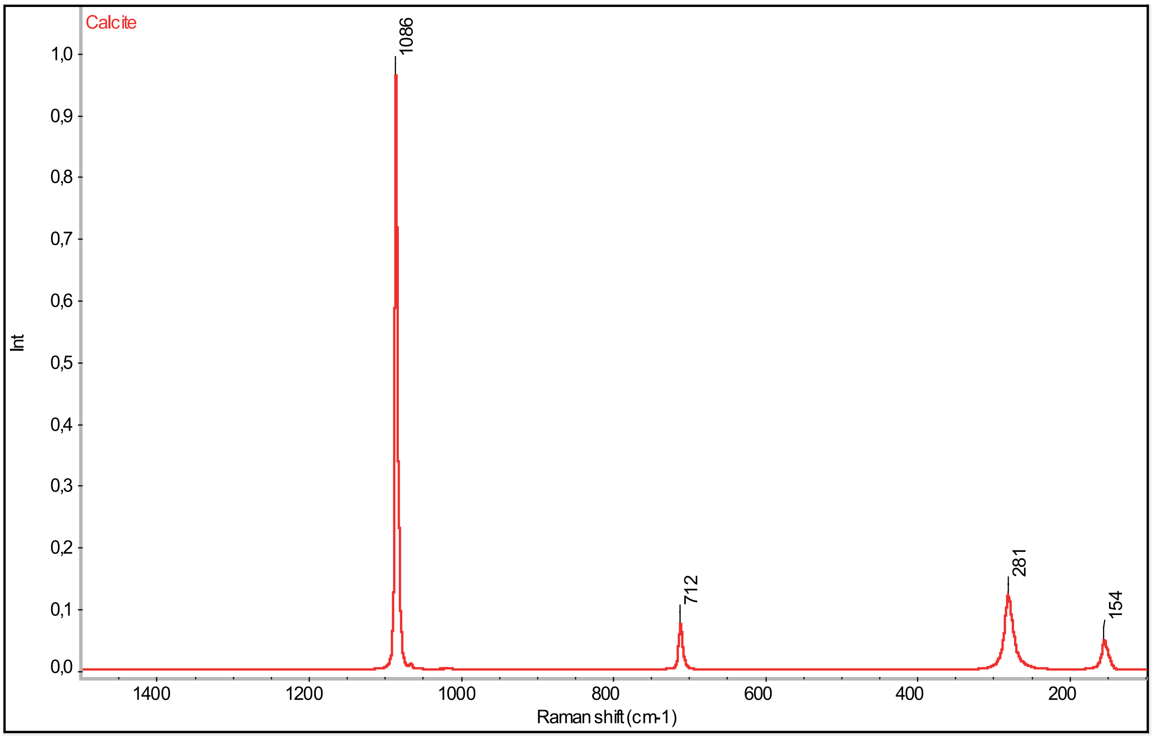
Tab. 1 Legenda do Rys. 5. Widmo ramanowskie szlifu próbki – biała kawa

Designation of the sample	Industrial pigment	Examined pigment	Synthetic binder	Natural binder
s. 1 white coffee		051112/4 K.O.Krakow P1-1	✓	
s. 2 white coffee		051112/4 K.O.Krakow P1-1		✓
s. 3 white coffee	051112/1 Keim farben S079		✓	
s. 4 white coffee	051112/1 Keim farben S079			✓



Graph 6 The standard Raman spectrum of hematite

Graf. 6 Standardowe widmo ramanowskie



Graph 7 The standard Raman spectrum of calcite

Graf. 7 Standardowe widmo ramanowskie kalcytu shown in the following Graphs 1 – 4.

- 051112/1 Keim farben S079 – the following pigment composition was identified in the sample using infrared spectroscopy. The pigment is composed predominantly of calcium carbonate and aluminosilicate based on kaolinite. The sample spectrum resulting from the measurement is shown in Graph 1, including the spectrums of the selected standards from the spectrum library. The characteristic Raman spectrum of the sample is shown in Graph 2. In the sample, it is possible to identify Fe_2O_3 in the form of hematite (226, 294, 410, 499, 611 cm-1 bands) and $CaCO_3$ in the form of calcite (154, 281, 712, 1086 cm^{-1} bands).

- 051112/4 K.O.Krakow P1-1 – the following substances were identified in the sample: calcium sulfate dihydrate, silicon dioxide and hematite. The spectrums resulting from the measurement are shown in Graphs 3 and 4.

The industrial pigment designated as S079 Keim is composed predominantly of calcium carbonate and aluminosilicate based on kaolinite. It also contains Fe_2O_3 in the form of hematite and $CaCO_3$ in the form of calcite. Based on an analysis of red iron-based inorganic pigments, the presence of hematite was identified in the pigment under examination before its use in the paint. The pigment under examination designated as K.O.Krakow (fly ash generated by the incineration of sewage sludge from a wastewater treatment plant in Krakow) contains calcium sulfate dihydrate, silicon dioxide and hematite.

Analyses of samples of the pigments used in the paint

Samples of the pigments used in the secco paint were analysed; they contained a colour layer and a ground layer. Sample 1 contained the examined pigment bound with a synthetic binder from the test panel (place from which the sample was taken: 1). Sample 2 contained the examined pigment bound with a natural binder from the test panel (place from which the sample was taken: 2). Sample 3 contained the industrial pigment bound with a synthetic binder from the test panel (place from which the sample was taken: 3). Sample 4 contained the industrial pigment bound with a natural binder from the test panel (place from which the sample was taken: 4).

The pigment samples used in the paint were measured using Raman spectroscopy. The Raman spectrum of the shade trivially designated as white coffee for the samples of light colour pigments 051112/1 Keim Farben S079 and 051112/4 K.O. Krakow P1-1, bound with a synthetic or natural binder and used in the paint on a lime ground, is shown in Graph 5. The legend for Graph 5 is contained in the following Table 1.

The standard Raman spectrum of hematite is shown in Graph 6 and the standard Raman spectrum of calcite is shown in Graph 7. The samples might have contained further components whose concentration was below the detection threshold of the selected method or whose absorption bands are situated beyond the selected spectrum range of the analysis (e.g., oxides, sulphides, halides, etc.)

The analysis of the pigments used in the paint focused on particles corresponding to the red pigments used in the colour shade that was designated as white coffee in the general trivial designation of the shade spectrum of the samples of pure pigments. The pigment under examination contained Fe_2O_3 in the form of hematite. A comparison of the shade in terms of pigment aging or the binder used showed that there had not been any significant spectrum changes of the pigments following their use in the paint. It can be inferred from the spectrums resulting from the measurements that neither a different environment nor aging has any influence on the pigment particles.

The above analyses of changes in the physical and chemical properties of the pigment under examination, namely fly ash generated by the incineration of sewage sludge from a wastewater treatment plant in Krakow (K.O.Krakow), following its application on a test panel, have confirmed that this pigment can be used for artistic purposes. It has been confirmed that this pigment is able to compete with industrial pigments and also that these secondary raw materials can be utilized and recycled.

Literatura - References

1. *Černotová, L.; Tora, B.; Čablík, V.; Čablíková, L.: A Comparison of Pigments and Waste Industrial Pigments. Inżynieria Mineralna, 2012, vol. 30, No. 2, s. 65–72. ISSN 1640-4920 Dostupné z: <http://www.potopk.republika.pl/archiwum.html>*
2. *Kępys, E.; Pomykała, R.; Pietrzyk, J.: Właściwości popiołów lotnych z termicznego przekształcania komunalnych osadów ściekowych. Inżynieria Mineralna - Journal of the Polish Mineral Engineering Society, 2013. s.11-18, č.1 (31)2013 PL ISSN 1640-4920*

Streszczenie

Celem badan było przeprowadzenie weryfikacji mozliwości wykorzytsnia popiołów lotnych ze spalania komunalnych osadów ściekowych jako pigmentu do malarstwa ściennego.
Badania próbek obejmowało rozdrabnianie pigmentu oraz jego wykorzytsanie w malarstwie ściennym na panelu testowym, starzenie próbek w komorze starzenia oraz porównanie z pigmentem handlowym z wykorzystnaiem mikroskopii, spektrometrii w podczerwienie oraz ramanowskiej.

Słowa kluczowe: utylizacja odpadów, malarstwo ścienne, pigmenty, spalanie komunalnych osadow ściekowych, panel testowy,