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Influence of waste from ferroalloy production on the color and properties of clinker ceramics

Introduction

Various by-products are produced in the manufacture of ferroalloys. In plants producing ferroalloys, among others, ferromanganese and silicomanganese, due to the appropriate chemical composition of the product being modeled in the production process, significant amounts of waste dust with a high content of manganese are generated. Until now, the generated waste has not been used; it has only been transferred to a landfill. It is possible to use this waste for the production of Portland cement (Gomes-Pimentel et al. 2022; Larbi et al. 2024), autoclaved ceramic products (Zhou et al. 2014; Wang et al. 2019; Larbi et al. 2024),

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as well as for the production of building ceramics (Sikalidis and Zaspalis 2007; Stolboushkin et al. 2018; Pavlova et al. 2020; Zhang et al. 2023). Waste containing significant amounts of manganese can be used as pigments for coloring red ceramics, in particular clinker bricks (Sikalidis et al. 2007; Stolboushkin et al. 2018; Pavlova et al. 2020; Larbi et al. 2024). Manganese compounds, e.g., $(Al,Mn)_2O_3$, $(Ni,Mn)(Fe,Cr)_2O_4$ (Dziubak 2016), are used as pigments in the ceramic industry. Depending on the type and amount of admixture, as well as the chemical composition of the mass or enamel, it is possible to obtain yellow, purple, brown, purple, and black colors.

Particularly noteworthy is the waste dust generated during the production of silicomanganese, which can be used in its entirety as the basic raw material for the production of pigments. Such a solution allows for the management and disposal of waste stored so far in silos and promotes environmental protection.

The aim of the study was to analyze the possibility of color change by MnSi waste from the production of ferroalloys for coloring clinker masses. The scope of work included the characterization of waste (pigments) in terms of chemical composition, phase, and color, preparation of samples–bricks with different amounts of pigment addition, their firing and characterization in terms of the effect of the addition of pigments on the color of clinker bricks.

1. Materials and methods

Two wastes from the production of metal alloys differing in manganese and silicon content were used in the study. In the study, the fraction of waste powders (pigments) with a grain size of less than 0.12 mm was used. The chemical composition was determined using XRF X-ray fluorescence spectrometry methods. For this purpose, Thermo Fisher Scientific Inc., ARL Perform'x-9950730 type. Phase compositions of the samples were identified via X-ray diffraction analysis based on the ICDD databases. XRD analysis was performed using a Philips X'Pert Pro diffractometer (CuKa = 1.5406Å, $2\Theta = 20-90^{\circ}$). The number of phases was determined through the Rietveld quantitative phase analysis using High Score Plus software. Pigments (waste) in the amount of 1% wt. and 3% wt. were added to commercial Creaton and Röben clinker masses. The mass and waste of the appropriate amount were homogenized in the Controls mixer, 65-L0006/AM Automix type, and then brick-shaped samples were formed from the resulting mixtures. The next stage was the drying of prepared and seasoned samples in Binder chamber dryers at a temperature of up to 200°C. Dried samples were fired in a Czylok chamber furnace, type FCF-V40HC, at a temperature selected using a Misura high-temperature microscope, 3 HSM 1600 40 for each sample. The sintering temperature of mass C and mass C with the addition of 3% pigments 1 and 2 was 950°C. In contrast, the sintering temperature of mass C with the addition of 1% pigments 1 and 2 was 1,050°C.

In contrast, the sintering temperature of the R mass and the R mass with the addition of both pigments at 1 and 3% was 950°C. After firing, the samples, both without additives

and with the addition of pigments (MnSi waste), were subjected to quantitative color measurements. For color measurements, a Tri-Color spectrophotometer, SF80 type, was used. The color measurements were made in the spatial coordinate system CIEL*a*b* (where: L – brightness; a – measure of red and green; b – measure of yellow and blue). On the basis of the determined color parameters in the CIELab system, the color parameters in the spatial coordinate system CIEL*C*h° (where: L – brightness; C – saturation; h° – hue) were measured (Figure 2) (Konica Minolta 2007; Mokrzycki and Tatol 2011). The strength tests were carried out using a static testing press from Walter Bai AG, using the D-5000-S model. The measurement of the absorbability of the samples was carried out by hydrostatic weighing, determining the mass of the dry sample, its saturated mass in water, and the mass of the sample saturated with water in the air (PN-EN 771-1:2006; PN-EN 772-1:2002).

The following notations were used in the paper: MnSi waste no. 1 - pigment 1, MnSi waste no. 2 - pigment 2, Creaton clinker mass – C, Röben clinker mass – R.

2. Characterisation of raw materials

Table 1 presents the chemical composition of MnSi waste (pigments). The presented chemical composition shows that the waste dust used differ significantly in the content of manganese and silicon. Table 2 presents the phase composition of both wastes.

In both cases, there is a large number of compounds with a spinel structure that most likely contain manganese (Mn), aluminum (Al), magnesium (Mg), and iron (Fe) in their composition. Waste 2 is also characterized by a much higher content of hausmannite (Mn_3O_4) and birnessite ($MnO_2 \cdot H_2O$) compared to waste 1. The substitution of manganese for iron

Table 1. XRF chemical composition of manganese waste (pigments) MnSi used in the study (per oxides)

| Tabela 1. | Skład chemiczny | / XRF użytych w b | adaniach odpadów | MnSi (pigmentów) | w przeliczeniu na tle | enki |
|-----------|-----------------|-------------------|------------------|------------------|-----------------------|------|
|-----------|-----------------|-------------------|------------------|------------------|-----------------------|------|

| Chemical composition (% wt.) | Pigment 1 | Pigment 2 |
|--|-----------|-----------|
| Mn ₂ O ₃ | 32.30 | 55.70 |
| SiO ₂ | 33.50 | 17.60 |
| Al ₂ O ₃ | 4.54 | 5.07 |
| Fe ₂ O ₃ | 5.00 | 3.81 |
| CaO | 8.04 | 7.24 |
| MgO | 5.60 | 3.36 |
| K ₂ O | 4.39 | 3.51 |
| Na ₂ O | 3.53 | 2.19 |
| Other: ZrO ₂ , P ₂ O ₅ , Cr ₂ O ₃ | <1.00 | <1.00 |

| Phase composition (% wt.) | Pigment 1 | Pigment 2 |
|---|-----------|-----------|
| (Mg,Mn,Al,Fe) Spinels | 26.8 | 31.8 |
| Hausmannite (Fe)(Mn ₃ O ₄) | 14.1 | 32.1 |
| Birnessite (MnO ₂ ·H ₂ O) | 1.2 | 7.4 |
| Quartz (SiO ₂) | 0.7 | 0.9 |
| Sylvine KCl | 1.0 | _ |
| Arcanite (K ₂ SO ₄) | 9.2 | _ |
| Amorphous | 47.1 | 27.9 |

Table 2. Phase composition of manganese waste (pigments) MnSi used in the study

| Tabela 2. | Skład | fazowy | odpadów | MnSi | użytych | W | badaniach |
|-----------|-------|--------|---------|------|---------|---|-----------|
|-----------|-------|--------|---------|------|---------|---|-----------|

in hausmannite cannot be ruled out either. The low content of quartz (SiO₂) in both cases may suggest that most of the silicon present in the samples is in the amorphous phase. In addition, in the case of pigment 1, we observe the occurrence of sylvine (KCl) and arcanite (K₂SO₄), which are impurities resulting from the ferroalloy production process.

Figure 1 and Table 3 show the phase composition of the clinker masses used. In both cases, the following crystalline phases can be identified: quartz (SiO₂), kaolinite (Al₄[Si₄O₁₀] (OH)₈), illite ((K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂,(H₂O)]) and albite (NaAlSi₃O₈). In addition, the composition of the mass R includes augite ((Ca,Mg,Fe)₂Si₂O₆).



Fig. 1. X-ray diffraction pattern of the masses C (Creaton) and R (Röben)Rys. 1. Dyfraktogramy mas klinkierowych: C (Creaton) i R (Röben)

Table 3. Quantitative phase composition of masess used in the study

| | Tabela 3. Il | lościowy skłac | fazowy mas | klinkierowych | użytych w | badaniach |
|--|--------------|----------------|------------|---------------|-----------|-----------|
|--|--------------|----------------|------------|---------------|-----------|-----------|

| Phase composition (% wt.) | Mass C | Mass R |
|---|--------|--------|
| Quartz (SiO ₂) | 69.6 | 46.0 |
| Kaolinite (Al ₄ [Si ₄ O ₁₀](OH) ₈) | 14.8 | 14.8 |
| Illite ((K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ ,(H ₂ O)]) | 14.6 | 17.5 |
| Albite ((NaAlSi ₃ O ₈) | 0.9 | 6.5 |
| Augite ((Ca,Mg,Fe) $_2$ Si $_2$ O $_6$) | - | 15.3 |

3. Results and discussion

3.1. Phase composition of bricks without and with the addition of pigments after sintering

Figure 2 illustrates the phase composition of the fired R and C masses with the addition of pigments 1 and 2 in the amount of 3% wt. Table 4 presents the phase composition of clinker bricks made of Röben and Creaton masses without and with the addition of pigments 1 and 2 in the amount of 1% and 3% wt.

After sintering, crystallization of quartz, cristobalite, and haematite is observed for both C and R masses, regardless of the amount and composition of the pigment used (Table 4). However, no crystalline phase containing manganese has been identified. Most likely, manganese occurs in the amorphous phase, the share of which in all samples is over 50%. In the R mass samples, we observe unreacted augite and the crystallization of andesine, which forms crystals mixed with albite and anorthite; this may be due to the much higher albite content in the initial R mass (Table 3).

3.2. Color of bricks without and with the addition of pigments

On the basis of color measurements in the spatial systems CIEL*a*b* and CIEL*C*h°, it can be concluded that the addition of both pigments, i.e., pigment 1 with a lower Mn content and pigment 2 with a higher Mn content, the color of clinker bricks changes significantly. Regardless of the Röben or Creaton compound used, the color of the bricks without additives is yellow-orange-red. The color of the Röben mass contains a significant proportion of red +a (approx. 25 units) and yellow +b (approx. 40 units) (Figures 3 and 4). The saturation



Fig. 2. X-ray diffraction pattern of the masses C and R with the addition 3% wt. pigment 1 and pigment 2 Rys. 2. Dyfraktogramy mas C i R z dodatkiem 3% wag. pigmentów 1 i 2

is high, reaching 50 units. On the other hand, a color angle greater than 50° suggests that the color shade of the Röben bricks is orange (Figure 5). The color of bricks made of Creaton mass without additives can be characterized in a similar way (Figures 6 and 7). In the case of bricks made of Creaton mass, there is a significant proportion of red +a (over 30 units) and yellow +b (about 40 units) in the color. The color is saturated, as evidenced by the C parameter greater than 30. The saturation angle h^o equals approx. 45° , which suggests

| e 4. Quantitative phase composition of bricks made from masess C and R without and with the additions of both pigments after sintering process | sla 4. Ilościowy skład fazowy wypalonych cegieł wykonanych z mas C i R, bez i z dodatkiem obu pigmentów |
|--|---|
| Tabl | Tabe |

| | | | Mass C | | | | | Mass R | | |
|--|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Phase composition (% wt.) | * č | pigm | ent 1 | pigm | ent 2 | * C | pigm | ent 1 | pigm | ent 2 |
| | | 1% wt. | 3% wt. | 1% wt. | 3% wt. | K. | 1% wt. | 3% wt. | 1% wt. | 3% wt. |
| Quartz (SiO ₂) | 40.4 | 40.6 | 35.4 | 42.2 | 38.5 | 17.8 | 17.6 | 17.9 | 19.4 | 22.2 |
| Cristobalite – beta (SiO ₂) | 2.5 | 2.5 | 1.7 | 2.1 | 1.9 | I | I | I | - | I |
| Hematite (Fe ₂ O ₃) | 1.4 | 1.4 | 1.6 | 1.5 | 1.4 | 2.9 | 2.8 | 2.2 | 2.3 | 2.6 |
| Andesine ((NaAlSi ₃ O ₈) \cdot (CaAl ₂ Si ₂ O ₆)) | I | I | I | I | I | 18.1 | 19.4 | 14.4 | 18.3 | 13.7 |
| Augite ((Ca,Mg,Fe) ₂ Si ₂ O ₆) | I | I | I | I | I | 5.6 | 5.5 | 5.0 | 4.1 | 3.5 |
| Amorphous | 55.7 | 55.5 | 61.3 | 54.2 | 58.2 | 55.6 | 58.7 | 60.5 | 55.9 | 58.0 |

 C^* – mass without pigment, *R – mass without pigment.



Fig. 3. Color comparison of bricks without the addition of pigments and with the addition of pigment 1, made of Röben mass in the CIELab (a) and CIELCh (b) systems





Fig. 4. Color comparison of bricks without the addition of pigments and with the addition of pigment 2, made of Röben mass in the CIELab (a) and CIELCh (b) systems



that the color of Creaton brick is light orange (Figure 8). It should be added that the color of Creaton brick is lighter than that of a brick made of Röben mass. The L-brightness for Creaton brick is close to 60, and for Röben brick, it is close to 45.

The addition of MnSi pigments significantly changes the color of the bricks. With regard to the Röben mass, in the case of which the fired brick shows an intense orange color, it can be observed that the greater the addition of pigment 1 (with a lower Mn content), the lower the proportion of both components, i.e., red +a and yellow +b in color (Figure 3a).

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The color of the bricks becomes darker, as evidenced by the L parameter, the value of which decreases. The color angle h° for all samples without the addition and with the addition of pigment 1 oscillates around 50°, which suggests that the color is orange. On the other hand, the saturation of the brick color (parameter C) decreases after the addition of pigment 1 (Figure 3b) from 60 units to 20 units for a brick with a 3% addition of pigment 1, which indicates that the color of the bricks becomes grey. Similar color changes, but more intense, occur with the addition of pigment 2 (with a higher manganese content). In this case, the addition of pigment 2 causes a significant reduction in both parameters describing the color, i.e., +a and +b (Figure 4a), and above all, a significant reduction in color saturation, parameter C decreases from 45 to 15 after the addition of 1% of the pigment.

Figure 5 shows photos of brick fragments reflecting their actual color. In the lower right corner, the color generated in the graphics program on the basis of the measured parameters $L^*a^*b^*$ is presented. The images shown are consistent with the measured color parameters. The addition of both pigments noticeably changes the C saturation of the color, the color of bricks with a 3% addition of pigment 1 and a 3% addition of pigment 2 becomes grey (Figure 5).

The color of bricks made of Creaton mass is intense orange. Here, too, the color changes significantly after the addition of the pigments. Figure 6 illustrates the actual color of bricks made of Creaton mass. Bricks with the addition of both pigments, regardless of the amount added, change their color towards grey-brown (Figure 6). In the light of color measurements



Fig. 5. Photos of the color of bricks made of Röben mass



| n | nass Creaton |
|------------|-----------------------|
| L 62.02 | |
| a +33.92 | And the second second |
| b +45.87 | |
| pigment 1 | pigment 2 |
| 1% | 1% |
| ALL STREET | |
| 1 11 61 | 1 42.01 |
| | L 45.91 |
| a +17.05 | a +14.36 |
| D +18.05 | D+19.01 |
| 3% | 3% |
| | The second second |
| 1 10 11 | 1 44 70 |
| L 40.11 | L 41.78 |
| a +11.39 | a +9.41 |
| b +15.35 | b +16.09 |

Fig. 6. Photos of the color of bricks made of Creaton mass

Rys. 6. Zdjęcia koloru cegieł wykonanych z masy Creaton

in the spatial systems CIEL*a*b* and CIEL*C*h°, the addition of pigment 1 with a lower manganese content in the amount of 1% and 3% wt. causes a significant reduction, compared to the color of brick without additives, of the share of red +a from 30 units to 10–15 units and the share of yellow +b from over 45 units to about 20 units (Figure 7a). The color angle h° does not change significantly, it lies between 47 and 53°, which indicates the orange color. The C saturation of the color is significantly reduced from more than 50 units to 30 when the addition of pigment 1 is 1% wt. and when the addition of pigment 1 is 3% wt., the color saturation is only 20 units (Figure 7b). Therefore, the color is perceived by the human eye as grey-brown (Figure 6).



Fig. 7. Color comparison of bricks without the addition of pigments and with the addition of pigment 1, made of Creaton mass in the CIELab (a) and CIELCh (b) systems



Rys. 7. Porównanie barwy cegieł bez dodatku i z dodatkiem pigmentu 1 wykonanych z masy Creaton w układach CIELab (a) i CIELCh (b)

Fig. 8. Color composition of bricks without the addition of pigments and with the addition of pigment 2, made of Creaton mass in the CIELab (a) and CIELCh (b) systems

Rys. 8. Porównanie barwy cegieł bez dodatku i z dodatkiem pigmentu 2 wykonanych z masy Creaton w układach CIELab (a) i CIELCh (b) The addition of pigment with a higher manganese content changes the color of bricks made of Creaton mass, regardless of the amount of pigment added (Figure 8). The color of the bricks is darker, as evidenced by a lower value of the L parameter, less red +a and less yellow +b. The +a parameter, which is a measure of the red color, decreases from 30 units to 15 units when the addition of pigment 2 is 1% wt. and up to 10 units when the addition of pigment 2 is 3% wt. In contrast, the +b parameter decreases from 45 units to approximately 20 units for both addition quantities. The color angle h° increases from 54 to 60°, indicating a bright orange color. The bricks, as shown in Fig. 8, are not light orange due to the very low color saturation, which is about 20 units, so the actual color of the bricks is brown-grey (Figure 6).

Figure 9 illustrates the actual color of bricks without and with the addition of pigments. The graph is presented in a plane coordinate system +b = f(+a) and does not take into account the variable, which is the brightness L. In most cases, the brightness of bricks after the addition of pigments decreases compared to bricks without the addition of pigments (Figures 3–4 and 7–8). The L-brightness values of bricks with the addition of pigments are mainly from 38 to 45 units, except for bricks made of Röben mass with the addition of 3% of pigment 2 (L = 59). The graph shows one very important observation: the addition of pigments significantly reduces the C parameter, i.e., color saturation, which is manifested by the fact that the observer begins to perceive the color as grey or as a subdued color that is not very expressive. It can be light grey or dark grey, which depends on the L parameter, i.e. brightness.



Fig. 9. Graphic representation of the actual color of bricks made of Röben and Creaton masses without and with the addition of pigments

Rys. 9. Graficzne przedstawienie rzeczywistej barwy cegieł wykonanych z mas Röben i Creaton bez dodatku i z dodatkiem pigmentów

3.3. Functional properties of bricks with pigment additives

Figure 10 presents the results of measurements of the compressive strength of clinker bricks made of both tested masses without and with the addition of pigments. The results of the compressive strength measurements are compared with the water absorption measurements, which are also illustrated in Figure 10.

The presented results (Figure 10) show that both the composition of the pigment used and the amount of pigment have no influence on the values of the obtained compressive strengths. Regardless of the mass used (R and C) and the pigment used, all results are around 40 MPa Table 5.



Fig. 10. Results of measurements of compressive strength (a,c) and water absorption (b,d) of bricks made of Creaton and Röben masses, without and with the addition of pigments

Rys. 10. Wyniki pomiarów wytrzymałości na ściskanie (a,c) i nasiąkliwości (b,d) cegieł wykonanych z mas Röben i Creaton, bez i z dodatkiem pigmentów

| Mass | Compressive strength (MPa) | Mass | Compressive strength (MPa) |
|------------------------|-------------------------------|------------------------|-------------------------------|
| C – without pigments | 40.12±4.31 | R – without pigments | 37.62±2.94 |
| C – 1.0% wt. pigment 1 | 39.85±3.80 | R – 1.0% wt. pigment 1 | 39.47±2.89 |
| C – 3.0% wt. pigment 1 | 41.87±3.72 | R – 3.0% wt. pigment 1 | 37.92±3.44 |
| C – 1.0% wt. pigment 2 | 41.90±3.40 | R – 1.0% wt. pigment 2 | 41.91±4.51 |
| C – 3.0% wt. pigment 2 | 44.03±2.69 | R – 3.0% wt. pigment 2 | 40.47±3.30 |

Table 5.Normalised compressive strength of obtained materialsTabela 5.Znormalizowana wytrzymałość na ściskanie otrzymanych materiałów

 \pm confidence interval at 0.95 confidence level.

Shows normalized results of compressive strength (PN-EN 772-1:2002). The obtained results allow for the qualification of all obtained materials to the compressive strength class of 30 (PN-EN 771-1:2006). In the case of water absorption of samples fired from mass C, the amount of pigment added increases the absorbability. However, no differences were observed depending on the composition of the pigment used. In materials fired from R-mass, both the amount and composition of the pigment affect the absorbability. As in the case of materials obtained from the C mass, the absorbability increases with the amount of pigment added; in addition, a higher percentage of absorbability is observed for materials containing pigment with a higher silicon content and less manganese. The addition of pigments worsens the sinterability of the obtained materials. We observe an increase in water absorption to approximately 6–7%. From this point of view, it seems that the addition of waste (pigment) in the amount of 3% is the maximum value that can be introduced into the clinker mass.

Conclusions

The paper presents the results of research devoted to the utilization of industrial waste. One of the problematic wastes is waste from the production of ferroalloys containing significant amounts of manganese. In the literature, works can be found devoted to the utilization of this waste as additives–pigments in clinker ceramics and, more specifically, in ceramic masonry elements. MnSi pigments mainly contain manganese compounds in various oxidation states, which are responsible for the color. The study showed that the color of bricks with the addition of MnSi pigments changes. In the obtained materials containing the addition of pigment 1 and pigment 2, no crystalline phase containing manganese was observed. Most likely, manganese oxides occur in the amorphous phase, which affects the color of the bricks. The reduction in color saturation resulting from

the participation of hematite is most likely due to the addition of pigments (waste) to the clinker masses, which contain manganese compounds in lower oxidation states: $((Mg,Mn,Al,Fe) \text{ spinels} - \text{most often shades of gray, hausmannite (Fe)}(Mn_3O_4)) - \text{color from black to brown-red, birnessite }(MnO_2) - \text{black})$. The color of fired bricks made from R mass can be influenced by the augite present in the phase composition. Depending on the cations it contains, augite can be green, brown, or even black in color (https://www.mindat.org/min-419.html). The presented research shows that it is possible to change the color of clinker ceramics with the use of waste materials, which increases the available color palette of clinker ceramics.

It is important that these types of pigments do not significantly affect the phase composition of bricks and their functional properties, which does not limit their use in any way.

The results of the study encourage the use of MnSi waste in the production of building ceramics. Such utilization can contribute to reducing the environmental problem, e.g., deterioration of soil and water quality.

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The Authors have no conflict of interest to declare.

REFERENCES

- Dziubak, C. 2016. *Ceramic pigments: production and use (Pigmenty ceramiczne: wytwarzanie i stosowanie)*. Opole: Wydawnictwo Instytut Śląski (*in Polish*).
- Gomes-Pimentel et al. 2022 Gomes-Pimentel, M., Rubens Cardoso da Silva, M., de Cássia D., Viveiros, S. and Picanço, M.S. 2022. Manganese mining waste as a novel supplementary material in Portland cement. *Materials Letters* 309, DOI: 10.1016/j.matlet.2021.131459.
- Konica Minolta 2007. Color Measurement Fundamentals Color Control from Perception to Measurement (Podstawy pomiaru barwy kontrola barwy od postrzegania do pomiaru). [Online:] https://www.konicaminolta.pl/pl-pl/ urzadzenia-pomiarowe/centrum-wiedzy/pomiar-koloru/podstawy-pomiaru-barwy [Access: 2024-12-27] (in Polish).
- Larbi et al. 2024 Larbi, A., Chen, X., Khan, S.M. and Fangheng, T. 2024. Innovative Techniques for Electrolytic Manganese Residue Utilization: A Review. *Waste* 2(3), pp. 354–381, DOI: 10.3390/waste2030020.
- Mokrzycki, W. and Tatol, M. 2011. Color difference Delta E A survey. *Machine Graphics and Vision* 20(4), pp. 383–411.

[Online:] https://www.mindat.org/min-419.html [Access: 2024-12-27].

Pavlova et al. 2020 – Pavlova, I.A., Sapozhnikova, M., Farafontova, E.P. 2020. The Effect of Manganese-Containing Pigment on the Strength of Ceramic Bricks. *Materials Science Forum* 989, pp. 329–334, DOI: 10.4028/www. scientific.net/MSF.989.329.

- Polish Standard PN-EN 771-1:2006, Requirements for masonry units. Part 1: Ceramic masonry units (Polska Norma PN-EN 771-1:2006, Wymagania dotyczące elementów murowych. Część 1: ceramiczne elementy murowe) (in Polish).
- Polish Standard PN-EN 772-1:2002, Test methods for masonry units. Part 1: Determination of compressive strength (Polska Norma PN-EN 772-1:2002, Metody badań elementów murowych. Część 1: Określenie wytrzymałości na ściskanie) (in Polish).
- Sikalidis, C. and Zaspalis, V. 2007. Utilization of Mn–Fe solid wastes from electrolytic MnO₂ production in the manufacture of ceramic building products. *Construction and Building Materials* 21(5), pp. 1061–1068, DOI: 10.1016/j.conbuildmat.2006.02.009.
- Stolboushkin et al. 2018 Stolboushkin, A., Akst, D., Fomina, O. and Ivanov, A. 2018. Structure and properties of ceramic brick colored by manganese-containing wastes. *MATEC Web of Conference* 143, DOI: 10.1051/ matecconf/201814302009.
- Wang et al. 2019 Wang, Y., Gao, S., Liu, X., Tang, B., Mukiza, E. and Zhang, N. 2019. Preparation of non-sintered permeable bricks using electrolytic manganese residue: Environmental and NH3-N recovery benefits. *Journal* of Hazardous Materials 378, DOI: 10.1016/j.jhazmat.2019.120768.
- Zhang et al. 2023 Zhang, J., Li, R., Nie, D. and Zhang, Y. 2023. Preparation of building ceramic bricks using waste residue obtained by mutual treatment of electrolytic manganese residue and red mud. *Ceramics International* 49(13), pp. 22492–22505, DOI: 10.1016/j.ceramint.2023.04.083.
- Zhou et al. 2014 Zhou, C., Du, B., Wang, N. and Chen, Z. 2014. Preparation and strength property of autoclaved bricks from electrolytic manganese residue. *Journal of Cleaner Production* 84, pp. 707–714, DOI: 10.1016/j. jclepro.2014.01.052.

INFLUENCE OF WASTE FROM FERROALLOY PRODUCTION ON THE COLOR AND PROPERTIES OF CLINKER CERAMICS

Keywords

waste, ferroalloy, MnSi, color properties, CIEL*a*b* space system, CIEL*C*h° space system

Abstract

The paper presents research conducted as part of the project from priority axis 1 Knowledge economy of the Regional Operational Programme for the Małopolska Region for 2014–2020, entitled: "Małopolska Region for 2014–2020, entitled: "Development of a technology for the production of pigment for dyeing red ceramics with the use of MnSi waste generated in the production of ferroalloys with contract number RPMP.01.02.01-12-0497/17-00". On the basis of the studies of the phase composition of XRD, compressive strength, absorbability, and color measurements in the CIEL*a*b* and CIEL*C*h° color space, it has been shown that it is possible to use MnSi waste containing large amounts of manganese oxides, formed in the production of ferroalloys. The waste (pigments) used for the study differed significantly in the content of manganese and silicon. It was found that the addition of both pigments does not change the phase composition and does not have a significant effect on the functional properties of clinker bricks but changes their color. The color becomes less saturated.

WPŁYW ODPADÓW Z PRODUKCJI ŻELAZOSTOPÓW NA BARWĘ I WŁAŚCIWOŚCI CERAMIKI KLINKIEROWEJ

Słowa kluczowe

surowce odpadowe, MnSi, pomiary barwy, system przestrzenny CIEL*a*b*, system przestrzenny CIEL*C*h°

Streszczenie

W pracy przedstawiono badania zrealizowane w ramach projektu I osi priorytetowej gospodarki wiedzy regionalnego programu operacyjnego województwa małopolskiego na lata 2014-2020, pt.: "Opracowanie technologii produkcji pigmentu do barwienia ceramiki czerwonej z wykorzystaniem odpadu MnSi powstającego przy produkcji żelazostopów o numerze umowy RPMP.01.02.01-12-0497/17-00". Na podstawie badań składu fazowego metodą dyfrakcji promieniowania rentgenowskiego XRD, wytrzymałości na ściskanie, nasiakliwości wodnej i pomiarów barwy w przestrzeniach barw CIEL*a*b* i CIEL*C*h° wykazano, że istnieje możliwość wykorzystania odpadów MnSi zawierających duże ilości tlenków manganu, powstających w produkcji żelazostopów. Wykorzystane do badań odpady (pigmenty) w sposób istotny różniły się zawartością manganu i krzemu. Zastosowane dwie masy przemysłowe wykazywały natomiast różne zawartości SiO₂. Na podstawie przeprowadzonych badań stwierdzono, że dodatek obu pigmentów nie zmienia składu fazowego, nie ma istotnego wpływu na właściwości użytkowe cegieł klinkierowych takie jak wytrzymałość na ściskanie (ok. 40 MPa) i nasiąkliwość wodna (< 7%), ale zmienia ich barwę. Barwa staje się przede wszystkim mniej nasycona, co widoczne jest przez zmniejszanie się parametru C*. Cegły tracą barwę pomarańczowo-czerwoną, stają się szare. Należy jednak zaznaczyć, że postrzeganie barwy i odczucia z nią związane zależą od indywidualnego odbiorcy. Wyniki badań zachęcają do wykorzystania odpadów MnSi w produkcji ceramiki budowlanej.