Assessment of preliminary suitability of Fe- and Cr-rich waste material for the production of building ceramics

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Abstract. This paper presents laboratory research on assessment of preliminary suitability of stainless steel waste material in building ceramics production. Application of the waste material in building ceramics production is innovative and might be environmentally friendly way to utilize it and to improve/modify the properties of the ceramic products. The waste was used as an additive to kaolinite-illite and montmorillonite-illite clay type. Selected properties of ceramics materials such as water adsorption, firing shrinkage, open porosity, apparent density, frost resistance, compressive strength and leaching of chromium and iron were determined. Improvement of the mechanical properties of the fired material and its colour intensification were observed. The studies confirmed the possibility of the utilization of this kind of waste material in production of building ceramics.

1 Introduction

Stainless steel is an iron-chromium alloy with minimum chromium amount of 11 %, which is their key alloying element. The addition of chromium above 11% creates a durable protective layer on the steel surface - a passive layer that provides anti-corrosive protection to the surface. To effectively prevent corrosion, the chromium contained in the steel must be fully dissolved in the solid solution and must not be in the form of chromium carbides [1].

Stainless steel mechanical processing is the final stage of the manufacturing process of many steel objects. It generates Fe- and Cr-rich wastes difficult to recycle. Use of the waste material in building ceramics production might be environmentally friendly way to utilize it and to improve the properties of the ceramic products. This topic has not been directly discussed in scientific literature yet, but it seems to have a great application potential. This paper presents laboratory research on assessment of preliminary suitability of stainless steel waste material in building ceramics production.

Until now attempts have been made to solidificate stainless steelmaking dust with clay in 1:1 ratio [2]. It was found that gained product can be used for the production of bricks or disposal and landfill. Research on use of stainless steel waste as pigment for ceramics was conducted [3-4]. Articles [5-6] presents the results of research on the use of this type

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of pigment in the production of black ceramic tiles. Discussed work concerns the use of waste in the form of dust. Waste used in this work has a stainless steel fiber-like form mixed with fine grained mineral matter.

2 Materials and methods

2.1 Materials

Ceramic masses for building ceramics were prepared from two type of clay sediments popular in Poland: Triassic sediment signed as “P” and Miocene sea-sediment signed as “Z”. As an additive Fe- and Cr-rich stainless steel waste was used.

Clays used in the research was milled to granulation below 2 mm. Fe- and Cr-rich steel waste was used without preparation. It was added to clay in an amount 30% by weight (Table 1).

Table 1. Dry mixes composition

Mass symbol	The content of raw clay [% mas.]	The content of waste [% mas.]
P	100 clay P	-
P30	70 clay P	30
Z	100 clay Z	-
Z30	70 clay Z	30

Water was added to the dry mixes until plastic consistency of masses was reached. The samples were hand-moulded. After drying, they were fired with the rate of temperature increase 100°C/h to 950°C with one hour temperature curing in 600°C and maximum temperature.

2.2 Methods

Chemical analysis of clay sediments and steel waste were performed using WDXRF method (WDXRF Axios maX PANalytical, with 4 kW Rh lamp). Mineral composition of clays was carried out by XRD method (Seifert-FPM XRD7 analyser). According to the method described in [7] untreated, burnt in 560°C and treated by ethylene glycol clays were examined (2 θ measuring range was 4-30°). Thermal characteristics of ceramic masses components were characterized by simultaneous thermal analysis using NETZSCH STA 449 F3 Jupiter® and by evolved gases analysis using mass spectrometer QMS 403 Aëolos (heating rate 10°C/min, atmosphere: synthetic air, dynamic flow 40 ml/min). For complete characterization of steel waste its microstructure was observed using a scanning electron microscope FEI Nova 200 Nanos with EDS attachment.

Masses were characterised by mixing water content, drying shrinkage and volume density of dried samples.

Final materials were examined by their color, firing shrinkage, loss of weight upon firing, water adsorption, open porosity, apparent density, frost resistance, compressive strength according to method described in [7-9]. Leachability of chromium and iron were examined according to the standard PN-EN 12457-2 [10] and determined by inductively coupled plasma mass spectrometry ICP-MS method. The leachates with 1:10 dilution were analysed

using a Perkin Elmer ELAN 6100 spectrometer. Analysis of the phase composition of final materials was carried out by XRD method (Phillips PW-1040 analyser, in the 2θ measuring range $5-60^\circ$).

3 Results and discussion

3.1 Characteristic of raw materials

Chemical compositions of the mass components are presented in Table 1. Clay P is red Triassic sediment from the deposit in Silesia (Poland). Its colour is from high hematite content which is reflected in high Fe_2O_3 content (Table 2). It can be use in clinker and porous ceramics (bricks, hollow bricks) production [7].

Clay Z is Miocene sea-sediment from the deposit from southern Poland. High content of CaO is a confirmation of calcareous characteristic of clay raw material. The chemical composition is closely related to the mineralogical composition, which is accurately described in the further part of the work.

Table 2. Chemical compositions of the mass components.

Oxide	Content [% mas.]											
	Clay P			Clay Z			Waste					
SiO ₂	58.14			52.1			1.65					
Al ₂ O ₃	17.99			16.4			7.48					
Fe ₂ O ₃	9.81			4.5			55.20					
TiO ₂	1.07			0.61			0.01					
CaO	0.43	1.51	1.82	9.15	11.35	15.32	0.28	16.35	16.54			
MgO	1.08			2.20			16.07					
K ₂ O	0.20	0.31		3.50	3.97		0.02	0.19				
Na ₂ O	0.11			0.47			0.17					
SO ₃	0.07			0.42			0.07					
Cr ₂ O ₃	-			-			11.39					
Cl ⁻	-			-			1.92					
MoO ₃	-			-			0.14					
MnO	-			-			0.21					
L.O.I. (in 1000°C)	8.50			10.18			5.17 (in 465 °C)					
total	97.39			99.53			99.78					

The main chemical components of the waste are: Fe_2O_3 and Cr_2O_3 from stainless parts. Alkaline oxides, Al_2O_3 , SiO_2 and Cl originate from abrasive parts, such as corundum and mechanical processing fleece with talc [11-12]. Loss on ignition is given before Fe oxidation.

XRD analysis of clay sediments are given in Fig. 1-2. They show that the P-clay is a raw material of a kaolinite-illite character. It also contains small amounts of chlorite and β -quartz. The remaining minerals in the sample were identified by simultaneous thermal analysis.

Fig. 1. P-clay XRD (N – untreated, P – burnt in 560°C for 2 hours, G – treated by ethylene glycol, *cts – Counts Per Step; Ch – chlorite; I – illite; K – kaolinite; Q – quartz)

Fig. 2. Z-clay XRD analysis (N – untreated, P – burnt in 560°C for 2 hours, G – treated by ethylene glycol, *cts – Counts Per Step; M – montmorillonite; Ch – chlorite; I – illite; K – kaolinite; Q – quartz, C - calcite)

Fig. 3. DTA/EGA analysis of waste

Clay-Z is a montmorillonite-illite-kaolinite sediment. It contains also chlorite and calcite minerals. Calcite is characteristic component of calcareous clay raw materials. It consists of smaller amount of β -quartz than P-clay.

Fig. 3 presents simultaneous thermal analysis with separated evolved gases analysis of steel waste. Small double peak in ion current for $m/z = 18$ is present up to 275°C. It is due to water release from the material. In the range of 275 to 465°C simultaneously increase in water and carbon dioxide ion current combined with a weight loss is observed. This is probably related to the combustion of organic matter. Increase in carbon dioxide ion current is observed also at around 700°C. It may be caused by decomposition of carbonates. The most important thermal effect on the DTA curve is observed from around 600 to 800°C. It is exothermal oxidation of Fe from steel. It is associated with about 27% mass increase on TG curve and decrease in ion current on m/z -32 EGA curve which is due the decrease of oxygen concentration in the atmosphere near of the sample. During oxidation of Fe, also volume of the oxidized material increases.

Fig. 4. SEM micrograph of waste W.

Fig. 4 presents SEM micrograph of Fe- and Cr-rich waste. It has the form of steel fibres with remains of abrasive and polishing materials. Fibres have different length and width and they are intertwined with each other.

3.2 Properties of masses

Table 3 presents properties of the masses after drying. Water absorption of both masses after the waste addition slightly increased (respectively by about 5% for P-clay and 12% for clay-Z). Despite this, drying shrinkage of P-clay with waste addition is smaller than P-clay without addition. It is due to fibrous form of the waste. Bulk density of masses based on P-clay with the waste addition is higher than bulk density of P-clay without its content. Drying shrinkage and bulk density after drying of masses based on Z-clay are slightly different.

Table 3. The properties of the masses after drying

Mass symbol	W [% mas.]	W SD [% mas.]	Ss [%]	Ss SD [%]	qs [g/cm ³]	qs SD [g/cm ³]
P	20.22	0.05	8.65	0.21	1.97	0.02
P30	21.14	0.25	7.65	0.20	2.09	0.02
Z	24.60	0.05	10.18	0.17	1.87	0.01
Z30	27.48	0.10	10.36	0.26	1.89	0.01

W - mixing water content, Ss – drying shrinkage, qs – bulk density after drying,

3.3 Properties of materials after firing

Fig. 5 presents colours of samples after firing. In both cases addition of the waste intensifies colour of clay matrix. According to [13] colour change is occurring as result of the valence variation of Fe, new phases and the outward diffusion of Fe. From red in case P-clay sample colour changes to brown in case of masses with waste. From light orange in case Z-clay sample colour changes to gray-brown in case of masses with waste. According to XRD results (Fig. 6) it is due to higher hematite and magnetite content in samples with the waste. Reddish colour of P-samples is probably triggered by the higher amount of Fe_2O_3 in P-clay (Table 2) and hematite amount in P-material.

Firing temperature	P	P30	Z	Z30
950°C

Fig. 5. Colours of samples after firing.

Table 4 presents properties of the materials after firing. In both cases high temperature expansion was observed for masses with the waste addition. It is probably due to iron oxidation during firing (Fig. 3). By the same phenomenon, masses of samples increase causing a decrease in firing weight loss. Water absorption and open porosity increases by the waste addition, but increase is higher for material made of Z-clay.

Fig. 6. XRD results of samples after firing (Q – quartz, Cr – crystobalite, H – hematite, M – magnetite, Hd – hedenbergite, A – anhydrite, C – corundum).

Despite the increase in porosity the apparent density increases with the waste addition. It is due to its higher real density than densities of clays. Fe- and Cr-rich waste stainless steel waste addition causes increase in compressive strength (by 11% and 31% respectively for P- and Z-material).

Each material is fully frost resistant according to methods shown in PN-B-12012:2007 [9] standard intended for unprotected type clay masonry units. According the standard PN-EN 771-1:2011+A1:2015 [8], this means that they can be used for masonry materials unprotected against external factors. The factor limiting this use is the

high water absorption values (>6%). Therefore, they should be considered as suitable for use as materials for masonry protected against external factors.

Table 4. The properties of the materials after firing

Mass	Sf [%]	SD Sf	Fwl [%]	SD Fwl [%]	Aw [%]	SD Aw [%]	Po [%]	SD Po [%]	qp [g/cm ³]	SD qp [g/cm ³]	FR	Rsc [MPa]	SD Rsc [MPa]
P	1.11	0.08	6.99	0.00	13.27	0.07	27.22	0.09	1.97	0.01	Y	49.95	0.97
P30	-0.01	0.10	-2.35	0.03	13.84	0.24	29.21	0.18	2.20	0.01	Y	55.31	0.90
Z	2.07	0.11	12.12	0.02	14.11	0.09	25.53	0.12	1.81	0.01	Y	51.04	0.83
Z30	-0.28	0.19	1.64	0.08	20.08	0.07	37.72	0.09	1.90	0.01	Y	66.93	0.30

Sf – firing shrinkage, Fwl – firing waste loss, Aw – water absorption, Po – open porosity, qp – apparent density, FR – frost resistance, Y – full frost resistance, Rsc – compressive strength, SD – standard deviation

Table 5. Leaching tests results

Element\symbol	P0	P3	Z0	Z3
Cr	0.0004	0.0008	0.0009	0.0044
Fe	0.008	0.048	0.003	0.003

Table 5 presents leaching tests results. According to [14] acceptable value of total chromium leachability is 70 mg/l. There are no requirements for iron leaching. Higher chromium leachability was observed for material from Z-clay with stainless steel addition. Higher iron leachability was observed for material from P-clay with stainless steel addition. This issue requires a more detailed analysis.

4 Conclusions

In this paper the possibility use of Fe- and Cr-rich waste material from stainless steel elements mechanical processing in the production of building ceramics was analysed. As the basic constituent two types of clays was used: Triassic sediment signed as “P” and Miocene sea-sediment signed as “Z”. The waste was added to clay in an amount of 30% by mass. Firing process temperature was 950°C.

Research of final ceramic materials confirmed suitability of use of the waste in the production of dark-coloured building ceramic products, especially as materials for masonry protected against external atmospheric factors.

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