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Crystalline Phases in the Waste Foundry Sands Based on Quartz Sand Matrix

Fazy krystaliczne w zużytych masach formierskich na osnowie piasku kwarcowego

This paper characterizes the crystalline phases present in waste foundry sands prepared based on a quartz sand matrix. The main component of the examined waste is quartz, which is accompanied by its polymorphic forms: tridymite and cristobalite. In addition to quartz, iron oxides such as magnetite, hematite and occasionally wüstite, and grains represented by metallic iron precipitation and Cu-Zn-Pb polymetallic aggregates were found. A particular emphasis was placed on the magnetite present in relatively high amounts, characterized by variable chemical composition, associated with the presence of numerous admixtures of chromium and titanium, which may suggest presence of chromite and titanomagnetite.

Keywords: foundry sand, quartz sand, phase composition

Introduction

Waste foundry sands represent one of by-products in the foundry industry. It is estimated that ca. 550,000 tonnes of waste molding and core sands are produced every year in Poland; the dominant percentage of them is compounds with bentonite, whereas smaller percentage is observed for those with inorganic and organic binders [1].

In the foundry industry, liquid metal for castings is commonly poured into sand molds. Foundry sands represent a mixture to which, in addition to quartz sand, other components such as water, bentonite, coal dust (so-called green sand) or inorganic or organic binders are added. Waste foundry sands, with sand percentage reaching essentially more than 90%, can be regenerated in the foundry. The regeneration

process consists in the treatment of spent foundry sands, leading to the recovery of at least one of the components. The regenerate obtained has properties similar to fresh sand, which makes it possible to be re-used for production of foundry sand. In practice, all types of waste foundry sand, both with organic and inorganic binders, are subjected to mechanical or thermal regeneration [2-5]. Since the 1950s, Foundry Research Institute in Kraków, Poland, has been conducting research and development works in the field of quartz sand regeneration, using e.g. dry mechanical, pneumatic and thermal methods [1].

The problems of regeneration of the sand matrix of the waste foundry sand is related to green logistics, which includes activities leading to the re-use of the basic component i.e. sand matrix (mainly quartz). The used sand that is not regenerated represents a waste or a by-product of foundry processes. In sands with bentonite, the regeneration processes mainly focus on sand recovery and rarely on recovery of bentonite and coal dust [4, 5].

Analysis of data from various countries indicate that production of 1 Mg of castings made of iron alloys consumes from 1.6 to 1.2 Mg of fresh sand, with this value in Poland being 1.0 Mg of sand. The results obtained from the 20 largest Polish foundries showed that about 50% of foundry waste is re-used, while the remaining part is discharged to dumping sites. It is estimated that about 250,000÷3,500,000 Mg of foundry sand is transported to dumping sites every year [6].

Waste foundry sands, with their main component being quartz sand, often contain minerals representing oxides of various metals. Furthermore, they may also contain fine metallic inclusions. Due to their presence, this material can be regarded as a secondary source of their recovery. All such initiatives, aimed at secondary waste management require detailed research, including mineralogical analyses, which provide essential information on the phase composition of the waste [7-9].

The aim of this paper was to present a qualitative characterization of the phase composition of waste foundry sand produced based on the quartz sand matrix.

1. Foundry sands: a literature review

Sands represent a group of loose clastic rocks with a grain size of 0.1 to 2.0 mm; their mineral composition includes minerals resistant to weathering, with quartz being the dominant component.

Sands are classified based on various characteristics:
– mineral composition: quartz, arkose, and greywacke sands,
– structure: coarse, medium, and fine-grained sands,
– sedimentation environment: dune, river, beach, and glacial sands [10].

Kozłowski [11] classified sands according to their application: for production of glass, molding, filling, construction and production of silicate products. Sands are characterized by high sintering temperature and are the basic raw material for preparation of foundry and core sands used to manufacture steel castings, iron castings and non-ferrous metal castings. There are two main types of foundry sands:

quartz sands and clayey sands (called natural). Furthermore Kozłowski [11] also enumerates: glauconite sands, quartz dusts and loam.

Foundry sands are composed first and foremost of grains of the sandy fraction with size from 0.02 to 3.3 mm, and a binder containing grains smaller than 0.02 mm. In pure quartz sands, the content of binder does not exceed 2% and the mineral composition is similar to glass sands with a quartz concentration of up to 98%. In the clayey (natural) sands, the percentage of clay minerals increases to 35%. Binder may contain minerals from the kaolinite group, colloidal silica and dusts consisting primarily of fragmented quartz. The undesirable components in foundry sands include sodium, potassium, calcium, magnesium and iron. The content of iron compounds which cause burns and penetrations on the castings cannot exceed 0.5%, while the amount of carbonates can not be greater than 0.3%, because their presence leads to creation of gas bubbles in the casting [11-13].

Molding compounds are prepared from foundry sands and specific additives. Molding materials are generally divided into two groups: main materials and auxiliary molding materials, i.e. additives to foundry sands. The main materials include: quartz sands with a quartz content of not less than 98.50%, foundry sands with clay content reaching 50% (mild foundry sands - clay content up to 8%, medium-strong foundry sands - clay content 8÷15%, strong foundry sands - clay content 15÷50%) and clays in which the clay content exceeds 50%. Auxiliary materials include: varnish, oil, cement, rosin, dextrin, sulphite lye and coal dust.

If properly selected, both in qualitative and quantitative terms, molding materials form molding compound after mixing. Their characteristics include plasticity, binding quality that ensures shock resistance and metallostatic pressure of the metal, resistance to high temperature of the molten metal, adequate gas and vapour permeability during casting and metal cooling processes, the ability to maintain reusability in the form of admixtures for new compounds, easiness of detaching from the walls of the finished casting, adequate strength, and uniform density in the entire mold [14-16].

The foundry sands and, consequently, molding materials can be re-used after obtaining castings; Joseph et al. [17] emphasized the necessity and opportunities for reuse and recycling of used molding materials. Foundry sand can consist of freshly mixed molding materials, but also materials previously used for molding, with their percentage constituting of up to 70% of the total molding compound. The waste materials are sifted through sieves that ensure separation of impurities and too large sand grains and then returned to the foundry plant material circulation [18].

2. The scope of the research and methodology

The scope of the research included waste foundry sand stored with other types of waste on one of the old dumping sites in the Upper Silesia region of Poland. Three samples of waste with mass of about 2 kg each, with different macroscopic characteristics, were designated for testing.

In order to present the mineralogical characterization of waste and to identify chemical composition of the phases that form the waste, the following tests were performed: phase identification using X-ray diffraction, X-ray spectral analysis in micro-areas and spectrometric examinations to determine the content of selected metals.

Identification of phases by X-ray diffraction was performed at the Institute of Non-Ferrous Metals in the Department of Powder and Composite Materials in Gliwice using the XRD 7 X-ray diffractometer (Seifert-FPM). Co Kα characteristic radiation and Fe filter were used. The analysis was performed for 2θ angles ranging from 10° to 100°, which corresponds to the range of interplanar distances d_{hkl} from 1.027 to 0.1168 nm. Identification of the crystal phases present in the samples was made based on the Seifert software and PDF-2 catalogue data from 2007 by ICDD. The test powder material was placed in an aluminium cuvette, with the X-ray area of approximately 0.5 cm^2. The tested samples responded to the effect of the magnet field to various degree. For this reason, phase composition analyses of the part enriched with the magnetic fraction were additionally performed for each sample. The sample was prepared by obtaining a small amount of powder with a strong permanent magnet and then applying it to the substrate covered with a binder.

X-ray spectral analysis in micro-areas was performed at the Institute of Non-Ferrous Metals (Department of Materials Engineering and Powder Metallurgy) in Gliwice, using the JEA 8230 X-ray microanalyzer (JEOL). The analyses were performed for metallographic sections that were sputtered with gold to discharge the electric charge: the unspecified maximum in X-ray spectra for the energy of 2.13 keV represents the gold Mα line. Surface X-ray distributions of elements were prepared using the energy-dispersion method (EDS). Point quantitative analyses of selected grains were performed by means of a wavelength-dispersive model (WDS), at voltage of 15 kV and beam current of 30 nA.

Spectrometric examinations aimed to analyse the content of selected metals in the sands studied were conducted at the Institute of Ceramics and Building Materials, Department of Refractory Materials in Gliwice. 0.5 g of the sample was weighed into a platinum dish and calcined at 700°C for 1 h to remove free carbon. After cooling, the sample was moistened with several drops of water and 1 cm^3 of 20% (v/v) sulphuric acid solution and 10 cm^3 of 40% hydrofluoric acid solution (m/m) were added. Then, the acids were evaporated to remove SiO_2 from the sample. The evaporation of the acids was performed in triplicate. The dry residue after removal of SiO_2 was dissolved in 30 ml of a 12% (v/v) hydrochloric acid solution. The solution was filtered into a 250 ml flask. After washing with hot water, the drain with the residue was incinerated and the residue was melted with 1 g of a mixture of anhydrous sodium carbonate and sodium tetraborate (1:1) at 1100°C for 10 minutes. The alloy was dissolved in 20 ml of a 12% hydrochloric acid solution (v/v) and mixed with the filtrate in a 250 ml flask. The obtained solution was filled to the line and analysed. Concentrations of Cr, Cu, Fe, Mn, Pb, Ti, V, Zn were determined by means of inductively coupled plasma - optical emission spectroscopy (ICP-OES), using a Shimadzu ICPE 9800 atomic emission spectrometer with inductively-coupled

plasma with a Teflon sample insertion system allowing for working with hydro-fluoric acid.

3. Results

In macroscopic terms, the examined waste differed in their colour: sample 1 was grey, sample 2 was brown-red (showing the presence of oxidized iron compounds, most probably hematite), sample 3 - black (associated with the addition of coal dust). The structure of all samples was psammite, from fine- to medium-grained, the grains of the crumb material showed a good degree of coating and a high degree of sorting. The waste texture was loose.

Phase identification by X-ray diffraction (Figs. 1-3) revealed that SiO_2 quartz is the main phase in all samples, which is due to the fact that the dominant component of the waste is quartz sand. In samples 1 and 3, diffraction lines of low intensity were also determined, corresponding to other polymorphic forms of quartz (probably tridymite or cristobalite), but their distinction was difficult due to the insignificant intensity of the line.

In addition to quartz, lines coming from Fe_3O_4 magnetite or α-Fe iron were observed for each sample on general diffractograms. In sample 1, reflexes from the recrystallizing $CaCO_3$ calcite were also recorded.

Analysis of the magnetic fraction of each sample yielded additional information. In sample 1 enriched with the magnetic fraction, in addition to quartz and calcite, phases with magnetite Fe_3O_4, hematite Fe_2O_3 and α-Fe structures were identified. In this group, magnetite was found in the largest amounts. In sample 2 enriched in the magnetic fraction, in addition to quartz, α-iron and oxides with the magnetite and hematite structures, and probably wüstite FeO, were found. It was difficult to distinguish the dominant phase in this sample. In a part of sample 3 enriched with the magnetic fraction, in addition to quartz, reflections coming from the compounds with the magnetite structure and α-Fe were observed.
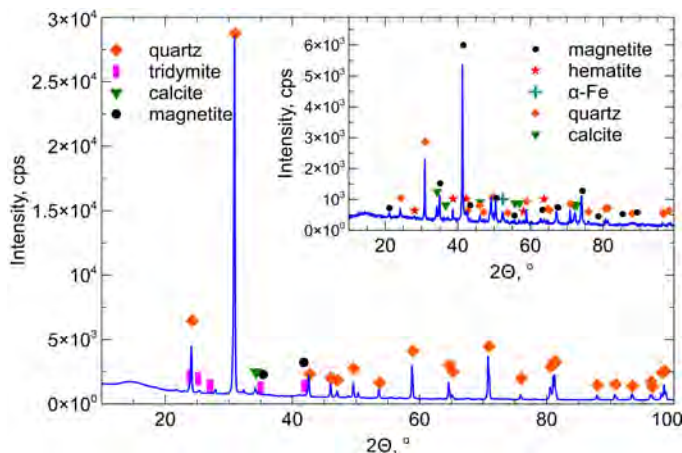

Fig. 1. X-ray diffraction pattern of sample 1 with the identification of crystalline phases; the inset shows diffraction pattern of the sample 1 enriched with a magnetic fraction
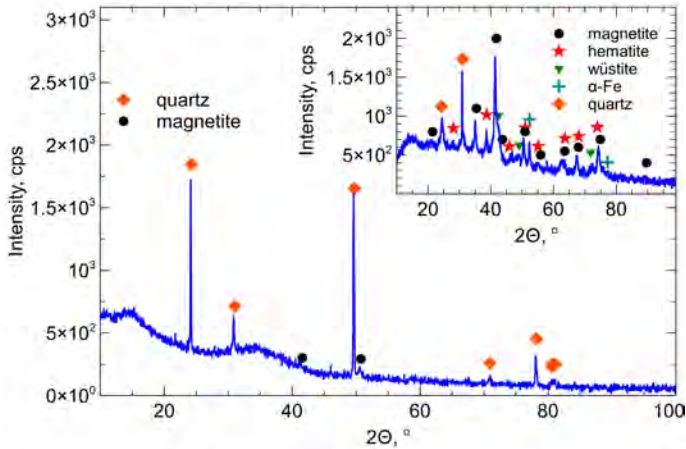
Fig. 2. X-ray diffraction pattern of sample 2 with the identification of crystalline phases; the inset shows diffraction pattern of the sample 2 enriched with a magnetic fraction
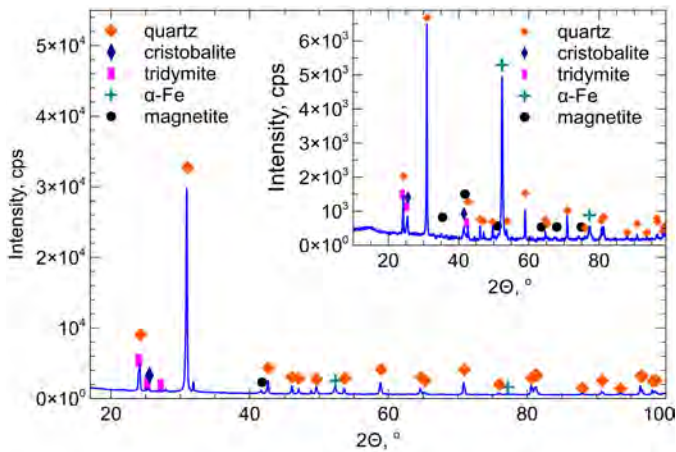

Fig. 3. X-ray diffraction pattern of sample 3 with the identification of crystalline phases; the inset shows diffraction pattern of the sample 3 enriched with a magnetic fraction

The examinations by means of X-ray spectral analysis in micro-areas demonstrated that in addition to the dominant quartz and, consequently, SiO_2 silica present in the waste, metal oxides, especially iron oxide, were also accumulated. This compound is often accompanied by admixtures of other metals, including titanium and chromium. Substitutions of these elements are characteristic of magnetite, whose presence in all samples was found based on phase identification by X-ray diffraction.

Metallic precipitations are present in the waste, mainly iron, accompanied by Cu-Zn-Pb aggregates.

Example analyses to identify the presence of components that accompany quartz dominant in the wastes are shown in Figures 4-6 and in Tables 1-3.
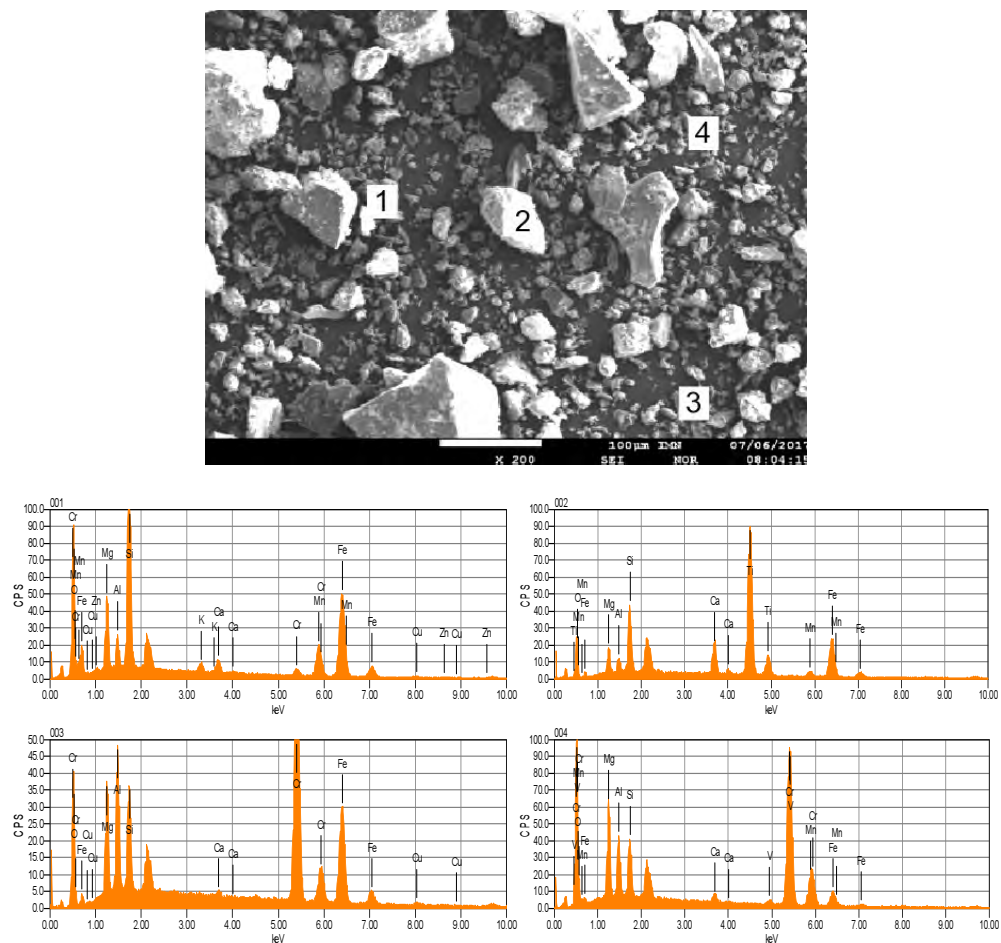
Fig. 4. Microphotography of sample 1 with EDS spectra

Table 1. **Elemental phase composition in sample 1; points of analysis according to Figure 4**

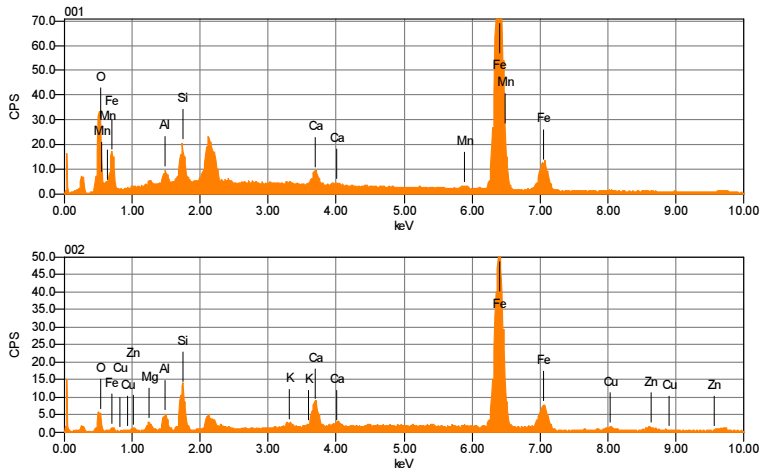| Analysis no.	Element, wt.%												
	O	Si	Al	Ca	K	Mg	Fe	Mn	Ti	V	Cr	Cu	Zn
1	33.0	11.1	1.8	1.3	0.8	4.6	29.2	14.6	–	–	2.3	0.8	0.7
2	31.5	4.5	1.0	4.4	–	2.1	19.6	3.6	33.2	–	–	–	–
3	13.9	3.2	4.3	0.3	–	4.1	19.8	–	–	–	53.3	1.1	–
4	26.1	2.6	2.7	0.7	–	5.1	4.2	8.4	–	0.7	49.5	–	–

Fig. 5. Microphotography of sample 2 with EDS spectra

Table 2. **Elemental phase composition in sample 2; points of analysis according to Figure 5**

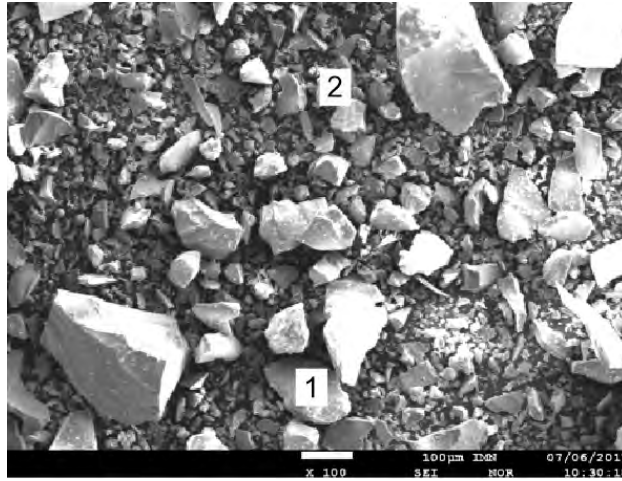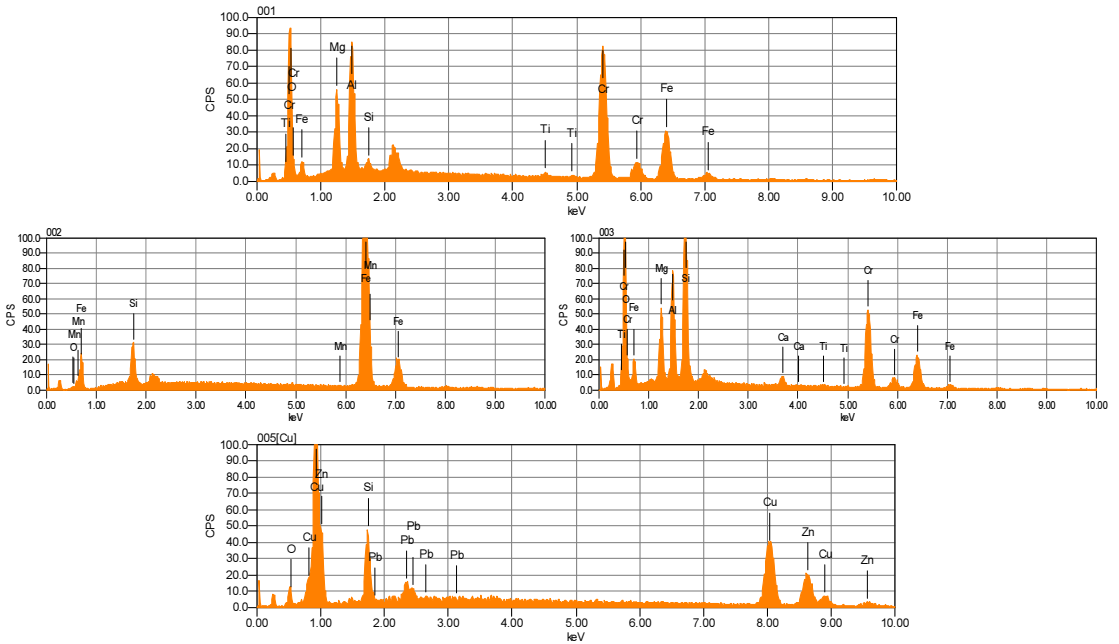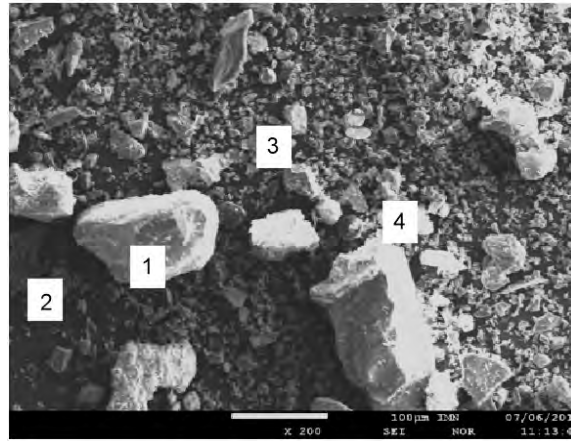| Analysis no.	Element, wt.%									
	O	Si	Al	Ca	K	Mg	Fe	Mn	Cu	Zn
1	16.8	1.9	0.7	1.3	–	–	78.00	1.3	–	–
2	6.1	3.1	1.3	3.1	0.4	0.8	77.8	–	3.3	4.3

Fig. 6. Microphotography of sample 3 with EDS spectra

Table 3. **Elemental phase composition in sample 3; points of analysis according to Figure 6**

Analysis no.	Element, wt.%											
	O	Si	Al	Ca	Mg	Fe	Mn	Ti	Cr	Cu	Pb	Zn
1	25.7	0.6	6.8	–	4.8	17.0	–	0.4	44.8	–	–	–
2	0.7	2.6	–	–	–	96.5	0.3	–	–	–	–	–
3	37.0	9.8	5.7	1.0	4.1	12.3	–	0.3	29.8	–	–	–
4	4.5	4.5	–	–	–	–	–	–	–	52.1	4.5	34.4

In sample 1, presence of metal oxide phases was mainly found. Each phase was characterized, to various extent, by the presence of iron (4.2÷29.2 wt.%), followed by manganese (3.6÷16.6 wt.%) and chromium (2.3÷53.3 wt.%); in one analysis, titanium was determined at 33.2 wt.%. Based on the percentage of individual elements in subsequent points of the analysis and their combination with the examinations using phase identification by means of X-ray diffraction, the presence of a solid solution of FeO-MnO-MgO (Table 1, analysis 1), magnetite containing a significant admixture of titanium can be identified, commonly termed titanomagnetite (Table 1, analysis 2), and $FeCr_2O_4$ chromite (Table 1, analysis 3 and 4) was found.

In sample 2, the tests revealed a significant percentage of iron-rich metallic precipitates and admixtures of other metals. Their presence in the waste could be observed already during macroscopic observations as black particles with a characteristic metallic gloss.

Sample 3 contained mainly metallic iron precipitations with an admixture of Mn (Table 3, analysis 2). The presence of Cu-Zn metallic aggregates with Pb admixture was occasionally recorded (Table 3, analysis 4). Among the oxide phases, the presence of chromite was noticeable (Table 3, analysis 1 and 3).

Due to the significant percentages of the phases rich in metals, additional spectrometric examinations were performed to determine the concentrations of selected metals in individual samples. The results are shown in Table 4.

Table 4. **Concentrations of individual metals in waste samples tested in the study**

Element	Sample No./Content, wt.%		
	1	2	3
Cr	0.19 ±0.03	0.05 ±0.01	0.15 ±0.03
Cu	0.02 ±0.01	0.81 ±0.09	0.05 ±0.01
Fe	3.08 ±0.24	13.45 ±2.01	14.58 ±2.08
Mn	0.15 ±0.03	0.21 ±0.03	0.58 ±0.04
Pb	0.01 ±0.01	0.94 ±0.06	< 0.01
Ti	0.07 ±0.01	0.39 ±0.04	0.07 ±0.01
V	0.01 ±0.01	0.11 ±0.03	0.01 ±0.01
Zn	0.02 ±0.01	0.75 ±0.05	0.03 ±0.01

The tests revealed that the dominant metal in all samples was iron, with its lowest concentration found in sample 1 (3.08%). In samples 2 and 3, the iron concentration was 13.45 and 14.58%, respectively.

In addition to iron in sample 1, the presence of Cr (0.19%) and Mn (0.15%) was noticeable, while in sample 2, higher concentrations were observed for Pb (0.94%), Cu (0.81%), Zn (0.75%), titanium (0.39%), Mn (0.21%), and V (0.11%). Compared to samples 1 and 3, sample 2 was characterized by the lowest concentration of Cr (0.05%). In addition to iron, sample 3 also contained substantial amounts of Mn (0.58%) and Cr (0.15%).

4. Discussion

The phase composition determined in the tested samples of waste foundry sands unequivocally indicated that the main component was quartz sand. In addition to quartz, phase composition was also characterized by two polymorphic modifications: tridymite and cristobalite, with their presence resulting from allotropic transformations that occurred during production of castings using molds made of quartz sand. During cooling at 1713°C, α-crystallite is released, and next, at 1470°C, its transition is observed, with remodelling into α-tridymite. At 870°C, transition is also observed, with remodelling into α-quartz. At 572°C, α-quartz turns into β-quartz [2, 14].

Among the remaining components, the presence of iron oxide is noticeable. It can be presumed that it is mainly associated with magnetite, which, during phase identification by X-ray diffraction, was determined for each sample in quite substantial amounts. Furthermore, X-ray spectral analysis demonstrated that iron oxide is doped with other elements, i.e. titanium and chromium. These metals, in addition to magnesium, manganese and vanadium, represent admixtures characteristic of magnetite. They are also found in magnetite that forms accumulations among natural sandy sediments, e.g. in Baltic sands [19].

In addition to the oxide phases, metallic precipitation occurs quite frequently in the tested wastes; they are mainly associated with the presence of small metallic iron precipitations, whereas polymetallic aggregates rich in copper and zinc with an admixture of lead were found in sample 3.

A similar phase composition in waste foundry sands was documented by Neymbwe et al. [20], who, in addition to quartz, found the presence of tridymite and cristobalite. These researchers also demonstrated the presence of wüstite. In the waste foundry sands tested in the present study, wüstite was also observed in sample 2. This phase rarely occurs in nature, but it is a frequent component of alloys, including heat-resistant steel, where during its smelting at a temperature of about 560°C, iron oxidation is relatively slow and magnetite is formed. Above this temperature, the scale is mainly formed by FeO - wüstite, crystallizing with an excess of oxygen atoms.

Spectrometric studies, similar to phase analyses, showed that the dominant metal in the waste studied is iron. As could be expected already from macroscopic observations, the smallest amount of this element was found in sample 1, characterized by a grey colour, whereas in samples 2 and 3, with brown-red and black colours, respectively, iron concentrations ranged from 13.45 to 14.58%.

In sample 1, in addition to iron, Cr and Mn are present in larger amounts, and, in individual analyses, titanium is also observed. These elements were also dominant in the chemical composition of oxide phases determined during X-ray spectral analysis in micro-areas. Based on the examination in micro-areas and using phase identification by means of X-ray diffraction, solid solution of FeO-MnO-MgO, magnetite, titanomagnetite, chromite, hematite, and α-iron were found.

In sample 2, in addition to the considerable amount of iron, the presence of Cu, Mn, Pb, Ti, V, Zn was also observed. Only the Cr concentration was lower compared to the respective values in samples 1 and 3. These elements are primarily associated with metallic inclusions, which, as mentioned above, represent, in addition to the quartz and iron oxide phases (magnetite, hematite and occasionally present wüstite), one of the main components of sample 2. The presence of these phases was also recorded in X-ray diffraction patterns.

Sample 3 was characterized by the highest concentration of Fe (14.58%), accompanied by Mn and Cr. X-ray spectral analysis in micro-areas demonstrated that chromium forms its own phase (chromite), while manganese is part of metallic iron inclusions. Both manganese and chromium are elements characterized by geochemical relationship with iron and, due to similar values of ionic radii, they can replace each other. The presence of α-iron and a substantial concentration of magnetite were found during phase identification by means of X-ray diffraction.

The accumulation of magnetite and metallic precipitations in the sands studied is likely to suggest the opportunities for their recovery. Such examinations, aimed to separate heavy minerals from sands, were performed by e.g. Łuszczkiewicz and Kaczmarek [21] for glass sands from Tomaszowskie Kopalnie Surowców Mineralnych "Biała Góra". In the case of the waste examined in the present study, it can be initially claimed that this material could offer a secondary source of obtaining heavy minerals and metals. The research is of preliminary character, and, in the case of making decisions regarding the reuse of waste, qualitative analyses should also be performed.

Conclusions

The findings of the present study lead to the following conclusions:
- The phase composition of the waste foundry sand based on the quartz sand matrix is dominated by quartz, accompanied by its polymorphic forms of tridymite and cristobalite.
- In addition to quartz, iron oxides were also found in the waste, such as magnetite, hematite, and occasionally wüstite, and grains represented by the precipitations of metallic iron and Cu-Zn-Pb polymetallic aggregates.
- Magnetite is characterized by variable chemical composition depending on the presence of various admixtures of chromium and titanium. In some analyses, the concentrations of Cr and Ti were quite substantial, suggesting the presence of oxide minerals (chromite and titanomagnetite, respectively).
- The presence of magnetite admixtures and metallic precipitates in the waste could indicate a potential secondary source of their recovery. However, in such cases, qualitative examinations should be supplemented with analyses aimed to estimate concentrations of individual components in the waste and the amount of stored waste.

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Streszczenie

    W odlewnictwie powszechnie odlewy wykonywane są w formach piaskowych. Sporządzone na bazie piasku masy formierskie stanowią mieszaninę, do której oprócz piasku kwarcowego dodawane są: woda, bentonit, pył węglowy oraz spoiwa nieorganiczne lub organiczne. Zużyte masy formierskie, w których udział piasku dochodzi do około 90%, są na ogół poddawane w odlewni wewnętrznemu odzyskowi (czyli regeneracji), ale część z nich trafia na składowiska. Odpady mas formierskich, których głównym składnikiem jest piasek kwarcowy, w swoim składzie często zawierają minerały reprezentujące tlenki różnych metali, ponadto mogą być w nich obecne drobne wytrącenia metaliczne. Z uwagi na ich obecność materiał ten może stać się wtórnym źródłem ich odzysku. W artykule scharakteryzowano, pod względem jakościowym, skład fazowy zużytych mas formierskich sporządzonych na osnowie piasku kwarcowego. Do badań ze zwałowiska pobrano 3 próbki materiału odpadowego charakteryzujące się odmienną barwą: szarą, brązowo-czerwoną i czarną, które poddano identyfikacji faz metodą dyfrakcji rentgenowskiej oraz rentgenowskiej analizie spektralnej w mikroobszarach; ponadto przy użyciu metod spektrometrycznych oznaczono zawartość wybranych metali występujących w odpadach. Na podstawie przeprowadzonych badań stwierdzono, że w składzie fazowym wszystkich analizowanych odpadów dominujący udział ma kwarc, obok którego oznaczono jego dwie polimorficzne odmiany: trydymit i krystobalit - ich obecność jest wynikiem przemian alotropowych dokonujących się w trakcie wykonywania odlewów w formach z mas kwarcowych. Oprócz kwarcu w odpadach występują dość znaczne ilości tlenków metali oraz wytrąceń metalicznych, co znalazło swoje odzwierciedlenie w udziale poszczególnych metali w składzie chemicznym odpadów. W próbce 1 obok dominującego żelaza w większych ilościach występują Cr i Mn, ponadto w pojedynczych analizach zaznacza się udział Ti. Pierwiastki te były również wskazane jako główne w składzie chemicznym faz tlenkowych oznaczonych podczas rentgenowskiej analizy spektralnej w mikroobszarach. Na podstawie tych badań oraz przy wykorzystaniu identyfikacji faz metodą dyfrakcji rentgenowskiej wśród faz tlenkowych wyróżniono: roztwór stały FeO-MnO-MgO, magnetyt, tytanomagnetyt, chromit, a także hematyt. Obok nich stwierdzono występowanie α-żelaza. W próbce 2 obok dość znacznej ilości żelaza zaznacza się obecność: Cu, Mn, Pb, Ti, V, Zn. Pierwiastki te są przede wszystkim związane z wtrąceniami metalicznymi, które obok kwarcu i faz tlenkowych żelaza (magnetytu, hematytu i sporadycznie występującego wüstytu) stanowią jeden z głównych składników próbki 2. Próbka 3 charakteryzuje się najwyższym, wśród badanych odpadów, udziałem Fe, któremu towarzyszą Mn i Cr. Rentgenowska analiza spektralna w mikroobszarach wykazała, że chrom tworzy własną fazę - chromit, natomiast mangan wchodzi w skład wytrąceń metalicznych żelaza. Podczas identyfikacji faz metodą dyfrakcji rentgenowskiej potwierdzono obecność α-żelaza, wykazano również dość znaczący udział magnetytu. Obecność w badanych odpadach domieszek magnetytu oraz wytrąceń metalicznych mogłyby wskazywać na potencjalne źródło ich pozyskiwania.

Słowa kluczowe: formy piaskowe, piasek kwarcowy, skład fazowy