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Polymorphic transformations of dicalcium silicates in steel slags used in the production of road aggregates

Introduction

Steel slags belong to a group of metallurgical waste that is being recycled and used on a large scale. The favorable results of physical and mechanical parameters have an impact upon the possibilities of their use, mainly in road construction, e.g. as an additive in the production of cement binders (Hager 2013), as a substitute for rock aggregates in unbound layers of road substructures (Sherwood 1995), and in the production of asphalt and mineral mixtures (Shi 2004; Reddy et al. 2006; Alanyali et al. 2009; Fidancevska et al. 2009; Sofilić et al. 2010). The wide possibilities for using steel slags, while limiting the use of natural resources and enabling the recycling of waste, make this material increasingly considered as a future-proof solution, especially for the production of road aggregates. As already mentioned, steel slags, due to their properties, can compete with natural aggregates (Collins and Sherwood 1995; Dunster 2002; Rai et al. 2002; Iacobescu et al. 2011; Sorlini et al. 2012; Wawrzeńczyk et al. 2016). Xu and Li (Xu and Li 2009) even commented on steel slags in the

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context of future-oriented and ecological materials used in construction, while Shen et al. (Shen et al. 2004) also proposed the consideration of the possibilities of recovering metals from slags where mainly iron may be present in the form of small, spherical precipitates which are not separated from the slag during the smelting process (Wieczorek and Jonczy 2019).

However, before using steel slags as a road construction material, it is necessary to conduct additional tests of their chemical composition, which usually includes elements from the group of heavy metals: Cr, Zn, and Pb. Particular attention to the chemical composition of slag samples is also linked to the determination of their alkalinity, which is affected by the content of calcium oxide. The increased content of CaO in the chemical composition of slags significantly reduces the possibility of them releasing heavy metals.

When analyzing the possibilities of the economic use of slags, as well as when assessing whether it is a material that is safe for the environment, attention should also be paid to the phase composition of slags (Jonczy and Stanek 2013). In various expert opinions, this aspect is either ignored or treated as a secondary issue. Meanwhile, there may occur transformations of phase components, and consequently, changes in their volume, which is a particularly undesirable phenomenon in the context of the use of slags as construction materials, especially in their use in road construction. In this context, special attention should be paid to dicalcium silicates, which are usually one of the basic phase components of steel slags (Groves 1983; Shi 2004). The presence of some of their polymorphs may cause the deterioration of the slags' physical as well as mechanical properties and thus constitute an obstacle to their secondary use (Kim and Hong 2004). This paper describes dicalcium silicates occurring in open-hearth slags from which aggregate is produced, and includes, as a comparison, an analysis of the occurrence of dicalcium silicate polymorphs in slags constituting a by-product of steel production in EAF and LF furnaces.

The aim of the work was to characterize steel slags with regard to the selection of the research method for the detection of dicalcium silicates in slags. During the research, particular attention was paid to the effectiveness of the technique of dicalcium silicate detection.

1. Characteristics of dicalcium silicates

In the conditions of a metallurgical furnace, calcium silicates crystallize when the content of calcium oxide in the alloy increases. The presence of CaO is related to the flux added to the sinter mixture, which is most often limestone or dolomite. The type and amounts of calcium silicates formed depend on the alkalinity of the environment.

Dicalcium silicates form four basic polymorphs:

- α-$Ca_2[SiO_4]$,
- α'-$Ca_2[SiO_4]$,
- β-$Ca_2[SiO_4]$,
- γ-$Ca_2[SiO_4]$.

The polymorph α-$Ca_2[SiO_4]$ represents high-temperature dicalcium silicates; it is stable within the temperature range of 1425°C to 2130°C and it does not occur in slags, because the highest sinter temperature of self-melting mixtures does not exceed 1350°C. The remaining polymorphs of dicalcium silicates are a frequent component of steel slags, but the possibility of their crystallization largely depends on the temperature and cooling rate of the slag alloy. The pattern of the formation of polymorphs of dicalcium silicates was presented by Henning and Knöfel (Henning and Knöfel 1982). They found that at the temperature of 440–510°C calcium orthosilicate is formed, probably γ-$Ca_2[SiO_4]$, which then turns into α'-$Ca_2[SiO_4]$ at 820–850°C, appearing in slags most often in the glaze mass in an elongated cigar-shaped form. What is characteristic for this polymorph is the presence of polysynthetic twinning and cleavage perpendicular to the elongation of the crystals.

During slow cooling of the alloy, at a temperature of about 670°C, the polymorph α'-$Ca_2[SiO_4]$ transforms into β-$Ca_2[SiO_4]$. This is an undesirable component as it is not stable and transforms into γ-$Ca_2[SiO_4]$ during the cooling of the sinter. Such a transformation is usually accompanied by an increase in the phase volume by 11–12%, which causes internal stresses and the possibility of the formation of additional cracks, and ultimately causes the disintegration of the sinter – thus reducing its strength (Alanyali et al. 2009; Setién et al. 2009). Silicate γ-$Ca_2[SiO_4]$ is stable below 850°C, while up to the temperature of 675ºC it retains the structure of olivine. The transition from β-$Ca_2[SiO_4]$ into γ-$Ca_2[SiO_4]$ has been reported by scientists numerous times (Juckers 2002), but the temperature at which this transformation occurs is disputed; it is reported to be at around 400°C or in a range slightly higher than 550–560°C (Smith et al. 1965; Rajczyk 1990; Chan et al. 1992). Additionally, the β-$Ca_2[SiO_4]$ polymorph is a dangerous component as it shows high hydration susceptibility, even greater than γ-$Ca_2[SiO_4]$.

As already mentioned, the formation of individual polymorphs of dicalcium silicates largely depends on the cooling rate of the alloy. It must be noted that the period when the crystallization may occur is very short. During the cooling of the slag alloy, e.g. in slag pits, it takes about 1 minute to lower the temperature from 1400°C to 800°C. It is slower afterwards. From the beginning of the cooling process, vitrification, i.e. the formation of glaze, takes place in the alloy. The slower the cooling, the greater the possibility of the formation of crystalline phases, which usually occur as fine crystallites embedded in the glaze (Ghose et al. 1983; Green et al. 2018).

The α'-$Ca_2[SiO_4]$ polymorph, which crystallizes as one of the first phases, behaves in different ways depending on the course of the cooling process:

- It can be stabilized and remain in the slag phase composition; its transition to a low temperature variant is difficult due to the presence of Fe^{2+} ions in its structure, which constitute a kind of stabilizer.
- It can transform into β-$Ca_2[SiO_4]$, which remains as one of the phase components.
- It transforms into γ-$Ca_2[SiO_4]$.
- It transforms into β-$Ca_2[SiO_4]$, and then γ-$Ca_2[SiO_4]$ along with an increase in volume by about 11–12% (Gutt 1963).

Based on research using high-temperature X-ray analysis, Smith et al. (Smith et al. 1965) distinguished two phases (α'_L-$Ca_2[SiO_4]$ and β_L-$Ca_2[SiO_4]$) and found that under certain conditions, β_L-$Ca_2[SiO_4]$ is not transformed into γ-$Ca_2[SiO_4]$ and thus does not cause sinter crushing.

Dicalcium silicates may be accompanied by a tricalcium silicate: alite Ca_3SiO_5. Its presence in slags indicates that the alloy was cooled quite quickly as it is then preserved in sinters in a metastable form. During the cooling of the alloy, alite is stable in the temperature range of 1200–1900°C; below 1200°C, it decomposes into $2CaO \cdot SiO_2$ and CaO.

Dicalcium silicates and free CaO present in steel slags are the components responsible for possible volumetric instability (Gutt 1965; Gutt and Russell 1977; Taylor 1990; Cioroi et al. 2010), which must be excluded according to the methods provided for in the standard PN-EN 1744-1+A1:2013-05 when using slag in construction, especially for the production of aggregates.

2. Research material

The tests were performed on five samples of aggregate based on steel slag constituting waste from steel production in the open-hearth process. For several decades, the slags were stored in a dump, but now they are used for the production of road aggregate by one of the largest companies in Upper Silesia, focusing on the disposal of steel slags and producing aggregates based on them (Figure 1). Aggregate samples were taken directly from the production line.

The tested aggregate is gray, fine-grained, and has a porous texture (Figure 2).

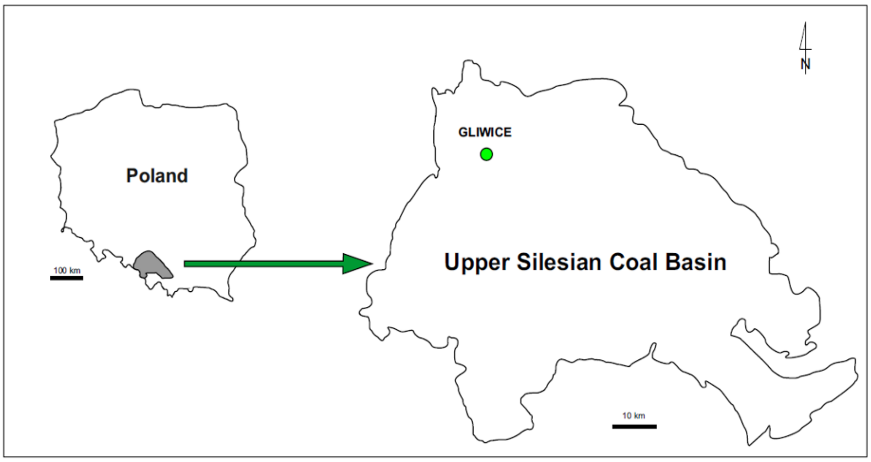


Fig. 1. Location of the research area

Rys. 1. Lokalizacja obszaru badań

Fig. 2. Aggregate based on open-hearth slag

Rys. 2. Kruszywo na bazie żużla martenowskiego

For comparison, tests were also performed on two samples of slags from the current production of active steelworks, where the metallurgical process is based on the use of steel scrap subject to metallurgical treatment in EAF (electric arc furnaces). One waste sample was collected from an EAF, and the other from a LF (ladle furnace), where steel-refining processes are performed, consisting in its refining and the final regulation of chemical composition and temperature (Figure 3).

Fig. 3. Steel slag from an EAF (electric arc furnace) on the left, from a LF (ladle furnace) on the right

Rys. 3. Żużel stalowniczy, z pieca EAF (po lewej), z pieca LF (po prawej)

3. Research methods

The research included:
- Total Digestion ICP and ICP/MS,
- X-ray diffraction method (XRD),

- scanning electron microscopy,
- determination of the decomposition of dicalcium silicate according to PN-EN 1744-1+A1:2013-05 standard (Taylor 1990).

Chemical composition tests were carried out at Activation Laboratories Ltd. – ACTLABS in Canada using spectrometric methods – total digestion ICP and ICP/MS. In the ICP method, a sample weighing 0.25 g was digested first in hydrofluoric acid and then in a mixture of nitric acid and perchloric acid. The samples were brought into solution with aqua regia. The samples were analyzed using an Agilent 735 ICP spectrometer. In the ICP/MS method, the etched samples were diluted and analyzed using a Perkin Elmer Sciex ELAN 6000, 6100 or 9000 ICP/MS spectrometer.

The SiO_2 content in slags was determined by melting with an alkaline flux such as Na_2CO_3. The obtained results were converted into the share of Si.

Using X-ray diffraction (XRD), the phase composition of slag samples was characterized. The following equipment was used during the measurements: a PANalytical XPERT PRO MPD powder diffractometer with an X-ray tube and a Cu anode, a X'Celerator counter, a graphite monochromator, and also a spinner. For the range of angles of 5–80° 2Θ at lamp parameters of 30 mA and 40 kV, X-ray diffractograms were made. To characterize the individual phases, the HighScore software from PANanalytical and the ICDD PDF-4+ database, were used. The quantitative analysis of the phase composition was performed using the standard Rietveld method and the SIROQUANT program. Corrections were applied in the analyses for the anomalous scattering of X-rays and for the effect of microabsorption. The unit cell parameters were determined by the Rietveld method only for those phase components for which the diffraction spectrum was well developed. The results of unit cell parameter determinations were compared with catalog data from the ICCD PDF 4+2012 database to identify solid solutions.

During the scanning electron microscopy tests, a HITACHI S-4700 field-emission scanning electron microscope with a NORAN Vantage EDS analysis system was used. Secondary electron SEM images were taken for bulk preparations while YAG BSE backscattered electron images were taken for thin samples. The research was conducted using an accelerating voltage of 20 kV and the counting time of each analysis – 100 s.

The determination of the decomposition of dicalcium silicate according to the method presented in the PN-EN 1744-1+A1:2013-05 standard is aimed at revealing the inversion of an unstable b form of dicalcium silicate into a g form in air-cooled blast furnace slags. According to the procedure, the effects of such transformations manifest themselves as yellow, brown, or cinnamon discolorations visible in UV light on the surface of fresh fractures of the slag pieces. Therefore, the estimation has a qualitative dimension and the test result is largely the result of a subjective judgement of the observer. Slag with discoloration visible in UV light against a violet background is considered prone to disintegration, and its use in construction is in most cases excluded. It is not clear whether the degradability is proven by the fluorescence of the dicalcium silicate γ-$Ca_2[SiO_4]$ only.

4. Research results

The chemical composition of tested slags is presented in Table 1.

Table 1. Chemical composition of aggregate based on open-hearth slags and slags from EAF and LF

Tabela 1. Skład chemiczny kruszywa na bazie żużli martenowskich oraz żużli z pieca EAF i LF

Element	Quantitative share (% wt)		
	aggregate based on open-hearth slag*	slag from EAF**	slag from LF**
Li ppm	14.04	11.5	11.23
Na %	0.22	0.06	0.05
K %	0.26	0.01	0.01
Mg %	3.58	2.20	3.13
Ca %	12.06	15.67	35.23
Ba ppm	607.40	1266.67	375.33
Al %	2.84	2.15	4.90
Si %	11.68	5.26	10.40
Pb ppm	789.74	24.23	35.53
P %	0.151	0.173	0.005
S %	0.14	0.09	0.71
Fe %	10.62	32.13	0.42
Ni ppm	89.94	28.33	16.33
Cu ppm	389.06	252.67	44.00
Zn ppm	2512.42	327,00	31.93
Cd ppm	14.48	0.13	1.13
Ti %	0.22	0.20	0.16
V ppm	261.40	624.67	115.33
Cr ppm	3169.60	>5000.00	86.20
Mo ppm	16.36	45.63	2.23
W ppm	79.60	157.00	0.80
Mn ppm	7013.20	>10000.00	7106.67

* Average value from five analyses.
** Average value from three analyses.

The aggregate based on open-hearth slags is generally dominated by three elements: Ca, Si and Fe, which occur in comparable amounts. The following heavy metals are also present: Pb, Cu, Zn, Cr and Mn.

Fe (32.13%) is present in the highest amounts in EAF slag, while the average content of Ca and Si in this slag is, respectively 15.67%, and 5.26%. Moreover, significant amounts of Cr and Mn were found – their content exceeds the limit of quantification.

Table 2. Results of qualitative and quantitative analysis of the phase composition of aggregate based on open-hearth slags (XRD)

Tabela 2. Wyniki jakościowej i ilościowej analizy składu fazowego kruszywa na bazie żużli martenowskich (XRD

Component	Quantitative share (%)				
	sample 1	sample 2	sample 3	sample 4	sample 5
Amorphous phase	51.2	30.0	44.9	41.8	32.4
Dicalcium Silicate α'-$Ca_2[SiO_4]$ with Mg^{2+} substitutions	–	3.2	–	–	–
Dicalcium Silicate ß-Ca_2SiO_4	–	–	2.5	16.2	8.4
Wustite FeO	–	2.5	2.4	13.6	4.8
Magnetite Fe_3O_4	–	6.8	3.0	1.9	3.5
Hematite Fe_2O_3	6.9	2.0	0.6	–	–
Spinel $MgAl_2O_4$	3.6	5.0	2.2	–	–
Brownmillerite-Srebrodolskite $Ca_2(Fe,Al)_2O_5$	–	–	1.2	4.5	1.4
Mayenite $Ca_{12}Al_{14}O_{33}$	–	–	–	–	1.3 ± 0.2
Quartz ß-SiO_2	7.9	30.2	22.9	4.0	8.9
Cristobalite SiO_2	–	0.8	0.5	8.7	0.1
Tridymite SiO_2	–	–	1.7	–	–
Anorthite $CaAl_2Si_2O_8$	10.5	–	–	–	–
Augite $(Mg,Fe,Ti,Al)(Ca,Na,Mg)(Si,Al)_2O_6$	5.8	–	–	–	–
Gehlenite-Åkermanite $(Ca,Mg)_2AlSi_2O_7$	–	4.6	–	–	–
Kirschsteinite-Monticellite $CaFeSiO_4$-$CaMgSiO_4$	–	3.8	–	–	3.8
Mullite $Al_6Si_2O_{13}$	13.2	–	–	–	–
Microcline $KAlSi_3O_8$	–	2.3	2.7	–	1.8
Calcite $CaCO_3$	0.9	7.6	14.1	9.2	21.1
Aragonite $Ca(CO)_3$	–	–	–	–	2.8
Brucite $Mg(OH)_2$	–	–	–	–	5.6
Portlandite $Ca(OH)_2$	–	–	–	–	0.8
Hydrocalumite $Ca_4Al_2O_6Cl_210H_2O$	–	–	0.6	–	3.2

In the slag from the LF, Ca is the dominant element, its amount exceeds 35%. The amount of Si is 10.40% and Fe is only 0.42%. Among the heavy metals, the presence of Mn is also noticeable.

The main component of the slags is an amorphous phase, which should be equated with a glassy phase. Crystalline phases occur in smaller amounts in the form of fine crystallites. Based on the results of the X-ray diffraction method, the presence of dicalcium silicates in the studied aggregate based on open-hearth slags was noted. Although their presence was not observed in all samples (Table 2).

The α'-$Ca_2[SiO_4]$ polymorph at an amount of over 3% was found in only 1 sample, while β-$Ca_2[SiO_4]$ was found in three out of five analyzed samples. The content of β-$Ca_2[SiO_4]$ is quite diversified and ranges from 2.5 to 16.2%. γ-$Ca_2[SiO_4]$ was not found in the open-hearth slags.

For comparison, an analysis of two samples of slags other than open-hearth from the steel production process was performed. The first sample was waste from the production of the EAF and the second from the production of the LF. The results of the X-ray analysis for these samples are presented in Table 3.

Table 3. Results of the qualitative and quantitative analysis of the phase composition of slags from the EAF and LF furnace

Tabela 3. Wyniki jakościowej i ilościowej analizy składu fazowego żużli z pieca EAF i LF (XRD)

Component	Quantitative share (%)	
	EAF furnace slag	LF furnace slag
Amorphous phase	54.5	13.6
Dicalcium silicate α'-$Ca_2[SiO_4]$ with Mg^{2+} substitutions	2.1	57.0
Dicalcium silicate β-Ca_2SiO_4	17.7	1.0
Dicalcium silicate γ-Ca_2SiO_4	–	15.4
Alite Ca_3SiO_5	–	1.5
Wustite FeO	19.8	–
Magnetite Fe_3O_4	3.7	–
Mayenite $Ca_{12}Al_{14}O_{33}$	–	2.1
Quartz β-SiO_2	–	0.2
$Ca_2Al_2SiO_7$ Gehlenite	–	1.6
Gehlenite-Åkermanite $(Ca,Mg)_2AlSi_2O_7$	2.2	–
Clinoenstatite $MgSiO_3$	–	6.7
Yeelimite $Ca_4Al_6(SO)_4O_{12}$	–	0.8

In the EAF furnace slag, the content of dicalcium silicates is similar to the slag analyses from the open-hearth process, on the basis of which the tested aggregate was produced. The α'-$Ca_2[SiO_4]$ polymorph is present in small amounts (about 2%). The dominant silicate phase is β-$Ca_2[SiO_4]$ (over 17%).

In the slag from the LF furnace, a significant content of α'-$Ca_2[SiO_4]$ with substitutions of Mg^{2+} ions was found, its content reaching 57%, making it the dominant slag-building phase. In addition to α'-$Ca_2[SiO_4]$, β-$Ca_2[SiO_4]$ appears at an amount of 1%, as well as γ-Ca_2SiO_4, the content of which exceeds 15%.

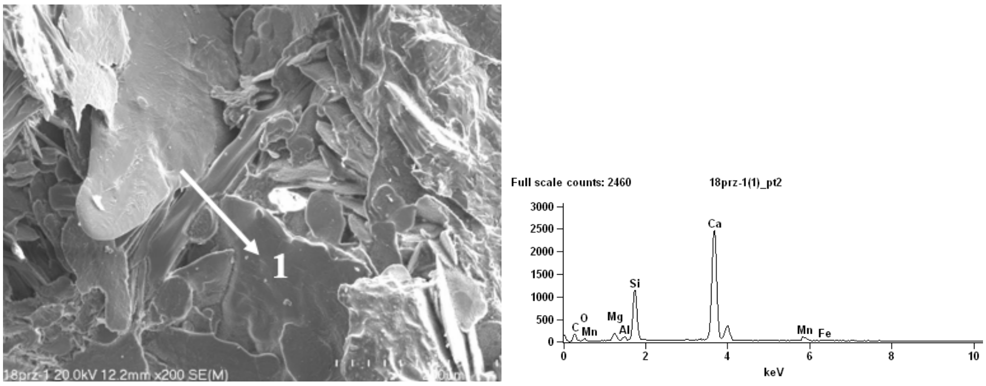
The detectability and thus the possibility of determining the individual polymorphs of dicalcium silicates during the X-ray structure analysis largely depends on the degree of crystallinity of the phase components (Jonczy 2016). Dicalcium silicates in slags generally occur as fine crystallites surrounded by glaze, which often makes it difficult to determine the lattice parameters of basic cells for their particular polymorphs. In the case of the tested slags, several analyses were possible (Table 4).

Observations using scanning electron microscopy enabled determination of the morphology of the dicalcium silicates (Figures 4 and 5).

Table 4. Lattice parameters of the basic cell of individual polymorphs of dicalcium silicates

Tabela 4. Parametry sieciowe komórek elementarnych poszczególnych odmian polimorficznych krzemianów dwuwapniowych

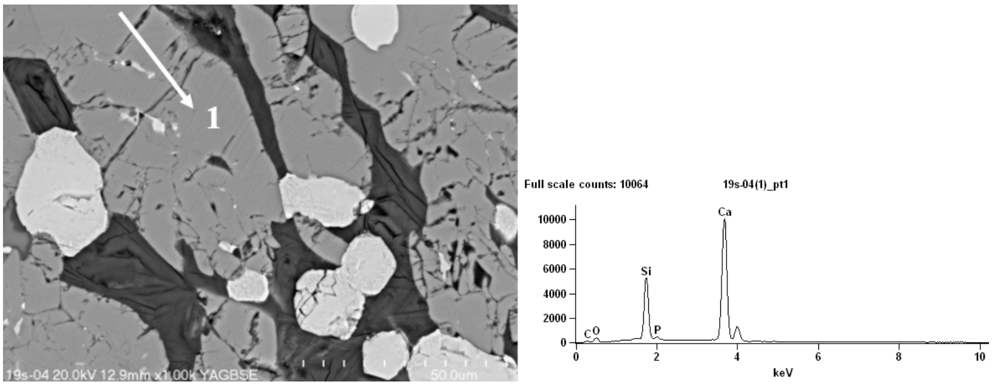
Slag type	Phase	Basic cell lattice parameters		
		a	b	c
Open-hearth slag	β-$Ca_2[SiO_4]$	5.518	6.764	9.329
LF furnace	β-$Ca_2[SiO_4]$	5.523	6.756	9.317
	γ-$Ca_2[SiO_4]$	5.084	11.214	6.757
EAF furnace	α'-$Ca_2[SiO_4]$	10.959	18.402	6.767
		10.984	18.488	6.759
		10.917	18.421	6.776
		10.907	18.432	6.782
	β-$Ca_2[SiO_4]$	5.509	6.760	9.315
		5.509	6.760	9.318
		5.509	6.760	9.315
		5.508	6.761	9.312
Literature data: Mindat.org: https://www.mindat.org/min-9574.html	α'-$Ca_2[SiO_4]$	10.9	18.34	6.73
	β-$Ca_2[SiO_4]$	5.50	6.74	9.29
	γ-$Ca_2[SiO_4]$	5.074	11.211	6.753



Point 1 according to Figure 4	Oxide content (wt. %)						Σ
	SiO_2	Al_2O_3	FeO	MnO	MgO	CaO	
	27.84	1.39	1.44	4.15	4.85	60.34	100.00

Fig. 4. Dicalcium silicates in aggregate based on open-hearth slag, SEM

Rys. 4. Krzemiany dwuwapniowe w kruszywie na bazie żużli martenowskich, SEM



Point 1 according to Figure 5	Oxide content (wt. %)			Σ
	SiO_2	P_2O_5	CaO	
	32.14	2.40	65.45	100.00

Fig. 5. Dicalcium silicates in aggregate based on open-hearth slag, BSE

Rys. 5. Krzemiany dwuwapniowe w kruszywie na bazie żużli martenowskich, BSE

However, it should be noted that out of 100 analyzed micro areas, only a few had well-formed plates of dicalcium silicates. In most cases, as already mentioned, these silicates occur in the form of fine crystallites embedded in the glaze.

A total of 50 LF slag samples were subjected to UV light observations, as only in this type of slag, based on XRD analysis, was the presence of γ-$Ca_2[SiO_4]$ found. The tests were carried out on fresh fractures of slag pieces. The observed surfaces ranged from a few to several dozen cm^2. According to the assumptions of the PN-EN 1744-1+A1:2013-05 standard, the presence of γ-Ca_2SiO_4 dicalcium silicate is indicated by yellow, brown, or cinnamon stains visible against a violet background. Due to the fact that the presence of γ-$Ca_2[SiO_4]$ was confirmed in the phase composition tests in the slag from the LF furnace (15% content), a positive test result was to be expected in at least one series of samples. Selected test results are shown in Figures 6–9. None of the tested slag samples presented discoloration under UV light at both 366 nm and 395 nm wavelengths.

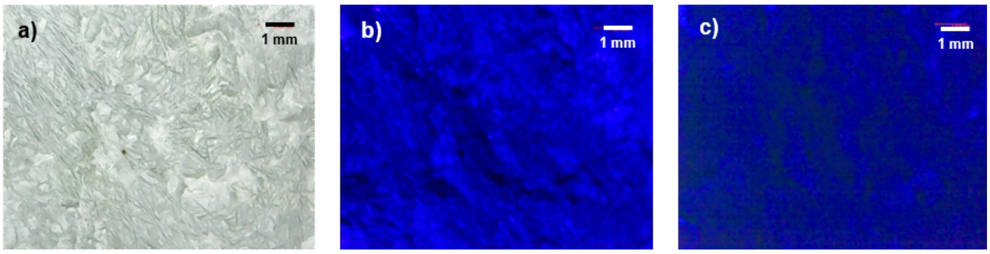


Fig. 6. Surface of the piece of slag from the LF furnace (sample 1) observed
a) in visible light; b) under UV light with a wavelength of 395 nm;
c) under UV light with a wavelength of 366 nm; 50× magnification

Rys. 6. Powierzchnia fragmentu żużla z pieca LF (próbka 1) obserwowana
a) w świetle widzialnym; b) w świetle UV o długości fali 395 nm;
c) w świetle UV o długości fali 366 nm; powiększenie 50×

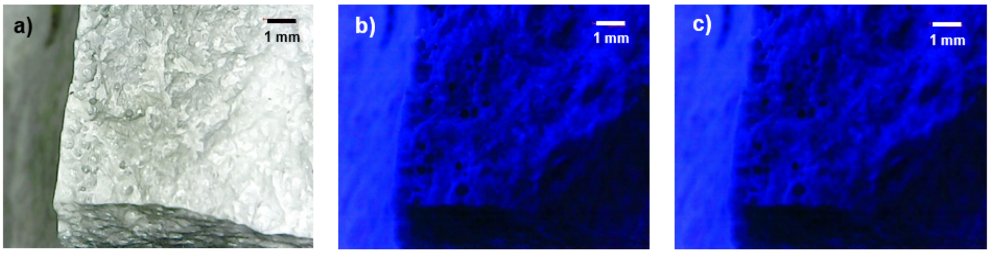


Fig. 7. Surface of the piece of slag from the LF furnace (sample 2) observed
a) in visible light; b) under UV light with a wavelength of 395 nm;
c) under UV light with a wavelength of 366 nm; 50× magnification

Rys. 7. Powierzchnia fragmentu żużla z pieca LF (próbka 2) obserwowana
a) w świetle widzialnym; b) w świetle UV o długości fali 395 nm;
c) w świetle UV o długości fali 366 nm; powiększenie 50×

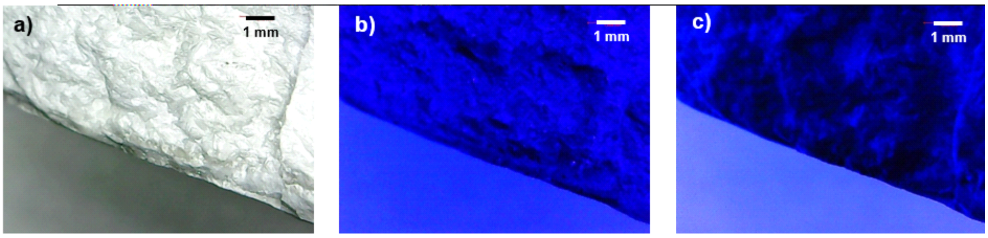


Fig. 8. Surface of the piece of slag from the LF furnace (sample 3) observed
a) in visible light; b) under UV light with a wavelength of 395 nm;
c) under UV light with a wavelength of 366 nm; 50× magnification

Rys. 8. Powierzchnia fragmentu żużla z pieca LF (próbka 3) obserwowana
a) w świetle widzialnym; b) w świetle UV o długości fali 395 nm;
c) w świetle UV o długości fali 366 nm; powiększenie 50×

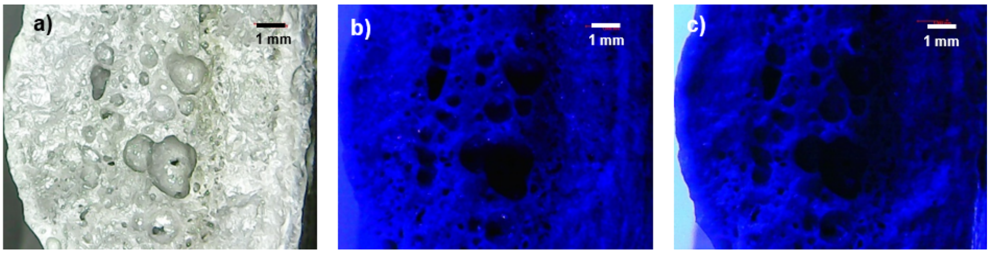


Fig. 9. Surface of the piece of slag from the LF furnace (sample 4) observed
a) in visible light; b) under UV light with a wavelength of 395 nm;
c) under UV light with a wavelength of 366 nm; 50× magnification

Rys. 9. Powierzchnia fragmentu żużla z pieca LF (próbka 4) obserwowana
a) w świetle widzialnym; b) w świetle UV o długości fali 395 nm;
c) w świetle UV o długości fali 366 nm; powiększenie 50×

5. Discussion

Dicalcium silicates present in the tested aggregate based on open-hearth slags were found in four out of five tested samples. These are represented by two polymorphs: α'-$Ca_2[SiO_4]$ and β-$Ca_2[SiO_4]$. The content of α'-$Ca_2[SiO_4]$ is relatively low – its presence was found only in one sample (about 3%). It should be noted that in this sample, β-$Ca_2[SiO_4]$ was not determined, but the α'-$Ca_2[SiO_4]$ variant was accompanied by tricalcium silicate Ca_3SiO_5. In three subsequent samples α'-$Ca_2[SiO_4]$ was absent, but β-$Ca_2[SiO_4]$ appeared in varying amounts (from 2.5 to 16.2%). In the first case, where α'-$Ca_2[SiO_4]$ was preserved in the aggregate phase composition, this may indicate its stabilization and, at the same time, the fairly rapid cooling of the slag alloy, which is also indicated by the presence of tricalcium silicate. In the second group of samples, α’-$Ca_2[SiO_4]$ transformed into β-$Ca_2[SiO_4]$, which also remained one of the components of the analyzed aggregate.

For comparison, the content of dicalcium silicates was determined in two types of slags constituting waste from steel production based on melting in EAF and LF. The proportion of dicalcium silicates in the EAF slag was similar to their proportion in the slag from the open-hearth process. By contrast, the slag from the LF was characterized by a completely different phase composition with a strong prevalence of β-$Ca_2[SiO_4]$ (57%) accompanied by γ-$Ca_2[SiO_4]$ (15%).

Based on the analysis of the basic cell lattice parameters of individual polymorphs of dicalcium silicates, it was established that the basic cell lattice parameters differed slightly from the literature data. In the case of α’-$Ca_2[SiO_4]$, it may be related to substitutions in the structure of Mg^{2+} ions (Tables 2 and 3). In some cases, P_2O_5 substitutions were found in the internal structure of dicalcium silicates (Figure 5), which is a quite common phenomenon because the dicalcium silicate polymorph β-$Ca_2[SiO_4]$ can form a solid solution with $3CaO{\cdot}P_2O_5$, while the content of P_2O_5 itself can reach 10%. Mixing with other elements of dicalcium silicates is quite common, for example Kriskova et al. (Kriskova et al. 2014) found admixtures of chromium ions in dicalcium silicates crystallizing in EAF furnace slags.

The conducted mineralogical and chemical studies show that the transformation of β-$Ca_2[SiO_4]$ into γ-$Ca_2[SiO_4]$ takes place only in the conditions of the metallurgical furnace and during the cooling of the slag alloy. In the tested open-hearth slags, γ-$Ca_2[SiO_4]$ was not found in their phase composition, while the β and α polymorphs were preserved. It should be noted that during the over 100-year period of storage of the slags in the dump, under hypergenic conditions, no further transformations of silicates took place and γ-$Ca_2[SiO_4]$ was not formed. Contrary to open-hearth slags, γ-$Ca_2[SiO_4]$ was found in the slags formed as a by-product in the LF furnace. This phase had to form under the conditions of the metallurgical process as the samples of these slags were taken from the current production of the metallurgical furnace and they were not stored.

During slow cooling of the alloy at a temperature of around 670°C, α’-$Ca_2[SiO_4]$ transforms into β-$Ca_2[SiO_4]$, which is not stabilized and turns into γ-$Ca_2[SiO_4]$during the cooling of the sinter. Such a transformation is connected with an increase in the phase volume by 11–12%, which is a reason for internal stresses and the possibility of the formation of additional fractures and ultimately results in the disintegration of the sinter, thus reducing its strength.

During the research, attention was paid to the validity of the research techniques used. Doubts were raised concerning the effectiveness of the method of confirming the susceptibility of slag to decay as a result of the inversion of the unstable form of β-$Ca_2[SiO_4]$ into γ-$Ca_2[SiO_4]$ described in the PN-EN 1744-1+A1:2013-05 standard.

Doubts seem justified here, especially given that, contrary to the assumptions of the method, the form β-$Ca_2[SiO_4]$ which is commonly present in slags and does not disintegrate, also showed a color different from purple (orange) under UV light (Adegoloye et al. 2013, 2016). As part of the research, observations were performed on freshly fractured pieces of steel slag in UV light with a wavelength of 395 nm and a recommended length of 366 nm (20 W fluorescent lamps). Both wavelengths fall within the range of 300 to 400 nm as specified by the standard, which is important in further considerations, as cases of observations under UV light with a wavelength of 254 nm have been documented, which did not enable observations of fluorescence and gave false test results (Nikolaides 2014).

This method has proven to be unreliable while maintaining all standards and using the correct tools. It seems that in the situation of using LF furnace slag as an artificial aggregate, especially on a large scale, e.g. in communication construction, taking the test results according to the method described in the PN-EN 1744-1+A1:2013-05 standard as decisive is very risky. Absolute certainty of the presence of γ-$Ca_2[SiO_4]$ in the slag, indicating its decay, is provided by chemical and phase composition (XRD) tests at the very least, possibly supplemented by observations and measurements using scanning electron microscopy.

Conclusions

Based on the conducted analyses, the following conclusions were drawn:

- Dicalcium silicates constitute one of the basic components of steel slags. Two polymorphs were found in open-hearth slags and slags from EAF production: α'-$Ca_2[SiO_4]$ and β-$Ca_2[SiO_4]$. β-$Ca_2[SiO_4]$ was also found in the slags from the LF, as was γ-$Ca_2[SiO_4]$.
- It was confirmed that the transformation of β-$Ca_2[SiO_4]$ into γ-$Ca_2[SiO_4]$ takes place only during the metallurgical process, as evident by the fact that after an over 100-year storage period for the open-hearth slag containing β-$Ca_2[SiO_4]$, no γ-$Ca_2[SiO_4]$ was found. This polymorph did not form in conditions of the metallurgical furnace, nor did it occur as a result of the transformation of β-$Ca_2[SiO_4]$ under hypergenic conditions.
- Comprehensive determination of the phase composition of slags, with the use of appropriately selected research methodology, especially in terms of the presence of the γ-$Ca_2[SiO_4]$ polymorph, is of key importance prior to the secondary use of this material. It has been determined that the most accurate test results are obtained using the XRD technique. The method of determining the decomposition of dicalcium silicate in accordance with the PN-EN 1744-1+A1:2013-05 standard proved to be unreliable.

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REFERENCES

Adegoloye et al. 2013 – Adegoloye, G., Beaucour, A.L., Ortola, S. and Noumowe, A. 2013. Mineralogical characterisation of EAF and AOD slags using ultraviolet fluorescence. *Proceedings of the Third International Slag Valorisation Symposium, The Transition to Sustainable Materials Management*. Leuven, Belgium, 19–20 March 2013, pp. 347–350.

Adegoloye et al. 2016 – Adegoloye, G., Beaucour, A. L., Ortola, S. and Noumowe, A. 2016. Mineralogical composition of EAF slag and stabilised AOD slag aggregates and dimensional stability of slag aggregate concretes. *Construction and Building Materials* 115, pp. 171–178.

Alanyali et al. 2009 – Alanyali, H., Çöl, M., Yilmaz, M. and Karagöz, Ş. 2009. Concrete Produced by Steel-Making Slag (Basic Oxygen Furnace) Addition in Portland Cement. *International Journal of Applied Ceramic Technology* 6, pp. 736–748.

Chan et al. 1992 – Chan, C.J., Kriven, W.M. and Young, J.F. 1992. Physical stabilization of the β → γ transformation in dicalcium silicate. *Journal of the American Ceramic Society* 75, pp. 1621–1627.

Cioroi et al. 2010 – Cioroi, A.M., Nistor Cristea, L. and Cretescu, I. 2010. The treatment and minimization of metallurgical slag as waste. *Environmental Engineering and Management Journal* 1, pp. 101–106.

Collins, R.J. and Sherwood, P.T. 1995. *Use of waste and recycled materials as aggregates: standards and specifications, report prepared by the Building Research Establishment (BRE) for the Department of the Environment*. London: HMSO.

Dunster, A.M. 2002. Blast furnace slag and steel slag as aggregates: a review of their uses and applications in UK construction. *Third European Slag Conference, Proceedings Manufacturing and Processing of Iron and Steel Slags*, UK, pp. 21–29.

European Standard EN 1744-1+A1:2013-05, Tests for chemical properties of aggregates, Part 1, Chemical analysis.

Fidancevska et al. 2009 – Fidancevska, E., Vassilev, V., Hristova-Vasileva, T. and Milosevski, M. 2009. On a possibility for application of industrial wastes of metallurgical slag and tv-glass. *Journal of the University of Chemical Technology and Metallurgy* 44(2), pp. 189–196.

Ghose et al. 1983 – Ghose, A., Chopra, S. and Young, J.F. 1983. Microstructural characterization of doped dicalcium silicate polymorphs. *Journal of Materials Science* 18(10), pp. 2905–2914.

Green et al. 2018 – Green, D.J., Hannink, R.H.J. and Swain, M.V. 2018. *Transformation toughening of ceramics*. Boca Raton: CRC Press.

Groves, G.W. 1983. Phase transformations in dicalcium silicate. *Journal of Materials Science* 18, pp. 1615–1624.

Gutt, W. 1963. High-temperature phase equilibria in the partial sys-tem 2CaO · SiO_2-2MgO · SiO_2-$A1_2O_3$ in the quaternary system CaO-SiO_2-$A1_2O_3$-MgO. *Journal of the Iron and Steel Institute* 201, pp. 532–536.

Gutt, W. and Russell, A.D. 1977. Studies of the system CaO-SiO_2-$A1_2O_3$-MgO in relation to the stability of blast furnace slag. *Journal of Materials Science* 12, pp. 1869–1878.

Hager, I. 2013. Behaviour of cement concrete at high temperature. *Bulletin of the Polish Academy of Sciences: Technical Sciences* 61, pp. 3–10.

Henning, O. and Knöfel, D. 1982. *Baustoffchemie*. Wiesbaden: Bauverlag.

Iacobescu et al. 2011 – Iacobescu, R.I., Koumpouri, D., Pontikes, Y., Şaban, R. and Angelopoulos, G. 2011. Utilization of EAF metallurgical slag in “GREEN” belite cement. *UPB Scientific Bulletin, Series B* 73(1), pp. 1454–2331.

Jonczy, I. 2016. Microstructures of metallurgical slags. *Archives of Metallurgy and Materials* 61(1), pp. 61–66.

Jonczy, I. and Stanek, J. 2013. Phase composition of metallurgical slag studied by Mössbauer spectroscopy. *Nukleonika International Journal of Nuclear Research* 58(1), pp. 127–131.

Juckers, L.M. 2002. Dicalcium silicate in blast-furnace slag: a critical review of the implications for aggregate stability. *Mineral Processing and Extractive Metallurgy* 111, pp. 120–128.

Kim, Y.-M. and Hong, S.-H. 2004. Influence of minor ions on the stability and hydration rates of β-dicalcium silicate. *The Journal of the American Ceramic Society* 87, pp. 900–905.

Kriskova et al. 2014 – Kriskova, L., Pontikes, Y., Zhang, F., Cizer, Ö., Jones, P.T., Van Balen, K. and Blanpain, B. 2014. Influence of mechanical and chemical activation on the hydraulic properties of gamma dicalcium silicate. *Cement and Concrete Research* 55, pp. 59–68.

Mindat.org [Online:] https://www.mindat.org/min-9574.html [Accessed: 2021-02-27].

Nikolaides, A. 2014. *Highway engineering. Pavements, Materials and Control of Quality*. Boca Raton: CRC Press.

Rai et al. 2002 – Rai, A., Prabakar, J., Raju, C.B. and Morchalle, R.K. 2002. Metallurgical slag as a component in blended cement. *Construction and Building Materials* 16(8), pp. 489–494.

Rajczyk, K. 1990. Effect of a reducing atmosphere on the properties of dicalcium silicate. *Cement and Concrete Research* 20, pp. 36–44.

Reddy et al. 2006 – Reddy, A.S., Pradhan, R.K. and Chandra, S. 2006. Utilization of basic oxygen furnace (BOF) slag in the production of a hydraulic cement binder. *International Journal of Mineral Processing* 79(2), pp. 98–105.

Setién et al. 2009 – Setién, J., Hernández, D. and González, J. J. 2009. Characterization of ladle furnace basic slag for use as a construction material. *Construction and Building Materials* 23, pp. 1788–1794.

Shen et al. 2004 – Shen, H., Forssberg, E. and Nordström, U. 2004. Physicochemical and mineralogical properties of stainless steel slags oriented to metal recovery. *Resources, Conservation & Recycling* 40, pp. 245–271.

Sherwood, P.T. 1995. Alternative materials in road construction, London: Thomas Telford.

Shi, C. 2004. Steel slag – its production, processing, characteristics, and cementitious properties. *Journal of Materials in Civil Engineering* 16(3), pp. 230–236.

Shi, C. and Hu, S. 2003. Cementitious properties of ladle slag fines under autoclave curing conditions. *Cement and Concrete Research* 33, pp. 1851–1856.

Smith et al. 1965 – Smith, D.K., Majudor, A. and Ordway, F. 1965. The crystal structure of γ-dicalcium silicate. *Acta Crystallographica* 18, pp. 787–795.

Sofilić et al. 2010 – Sofilić, T., Merle, V., Rastovčan-Mioč, A., Ćosić, M. and Sofilić, U. 2010. Steel slag instead natural aggregate in asphalt mixture. *Archives of Metallurgy and Materials* 55(3), pp. 657–668.

Sorlini et al. 2012 – Sorlini, S., Sanzeni, A. and Rondi, L. 2012. Reuse of steel slag in bituminous paving mixtures. *Journal of Hazardous Materials* 209–210, pp. 84–91.

Taylor, H.F.W. 1990. Cement Chemistry, London: Academic press.

Wawrzeńczyk et al. 2016 – Wawrzeńczyk, J., Juszczak, T. and Molendowska, A. 2016. „Determining equivalent performance for frost durability of concrete containing different amounts of ground granulated blast furnace slag. *Bulletin of the Polish Academy of Sciences: Technical Science*s 64, pp. 731–737.

Wieczorek, A.N. and Jonczy, I. 2019. Mineralogical and chemical characteristics of metallic precipitations in selected types of steelmaking slags and in blast furnace slags. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 35(4), pp. 69–84.

Wyderko-Delekta M. and Bolewski A. 1995. *Mineralogy of sinters and ores* (*Mineralogia spieków i grudek rudnych*). Kraków: AGH Publishing House (*in Polish*).

Xu, D. and Li, H. 2009. Future resources for eco-building materials: I. Metallurgical slag. *Journal of Wuhan University of Technology, Materials Science Ed*ition 24(3), pp. 451–456.

POLYMORPHIC TRANSFORMATIONS OF DICALCIUM SILICATES IN STEEL SLAGS USED IN THE PRODUCTION OF ROAD AGGREGATES

Keywords

steel slag, dicalcium silicate, artificial aggregate

Abstract

This paper presents results of mineralogical and chemical research connected with the polymorphic transformations of dicalcium silicates in aggregate based on open-hearth slag and also slags from the current production of EAF (electric arc furnaces), and LF (ladle furnaces). Particular attention

was paid to the transformation of the polymorph β-$Ca_2[SiO_4]$ into the variant γ-$Ca_2[SiO_4]$, which is undesirable from the perspective of using steel slags in road construction. A full mineralogical characterization of the tested metallurgical slags enabled the verification of the effectiveness of detecting the decomposition of dicalcium silicate in observations in UV light in line with the PN-EN 1744-1+A1:2013-05 standard. On the basis of the conducted research, it was found that in the aggregate based on open-hearth slags and in the EAF furnace slag, dicalcium silicates are mainly represented by the β-$Ca_2[SiO_4]$ polymorph, accompanied by α'-$Ca_2[SiO_4]$. The slag from the LF furnace was characterized by a different composition, with a strong advantage (57%) of the α'-$Ca_2[SiO_4]$ variety, with a 1% share of the β-$Ca_2[SiO_4]$ and 15% of the γ-$Ca_2[SiO_4]$.

It was found that the transformation of β-$Ca_2[SiO_4]$ into γ-$Ca_2[SiO_4]$ can take place only under certain conditions in the metallurgical process, but the process is not influenced by hyperergenic factors, as evidenced by the fact that after more than 100 years of storage of open-hearth slag, on the basis of which the aggregate was produced, it was primarily marked with all the variants of β-$Ca_2[SiO_4]$, without the polymorph γ-$Ca_2[SiO_4]$.

The comprehensive characterization of the slag phase composition requires use of an appropriately selected research methodology; this is of key importance prior to the secondary use of this material, especially in the presence of the γ-$Ca_2[SiO_4]$ polymorph. It has been determined that the most accurate test results are obtained using the XRD technique. The method of determining the decomposition of dicalcium silicate according to the PN-EN 1744-1+A1:2013-05 standard proved to be unreliable. It seems that in the situation of using LF slag as an artificial aggregate, taking the test results according to the method described in the PN-EN 1744-1+A1:2013-05 standard as being decisive is very risky, especially on a large scale (e.g. in communication construction).

PRZEMIANY POLIMORFICZNE KRZEMIANÓW DWUWAPNIOWYCH W ŻUŻLACH STALOWNICZYCH STOSOWANYCH DO PRODUKCJI KRUSZYWA DROGOWEGO

Słowa kluczowe

żużel stalowniczy, krzemiany dwuwapniowe, kruszywa sztuczne

Streszczenie

W artykule przedstawiono wyniki badań mineralogiczno-chemicznych dotyczące przemian polimorficznych krzemianów dwuwapniowych w kruszywie na bazie żużli martenowskich, a także w żużlach z bieżącej produkcji pieca elektrycznego EAF (*Electric Arc Furnace*) oraz pieca kadziowego LF (*Ladle Furnace*). Szczególną uwagę zwrócono na przeobrażenia polimorfu β-$Ca_2[SiO_4]$ w odmianę γ-$Ca_2[SiO_4]$, co jest niepożądanym zjawiskiem z punktu widzenia wykorzystania żużli stalowniczych w budownictwie drogowym. Pełna charakterystyka mineralogiczna badanych żużli posłużyła do weryfikacji skuteczności wykrywania rozkładu krzemianu dwuwapniowego w obserwacjach w świetle UV zgodnie z normą PN-EN 1744-1+A1:2013-05. Na podstawie przeprowadzonych badań stwierdzono, że w kruszywie na bazie żużli martenowskich oraz w żużlu z pieca EAF krzemiany dwuwapniowe są reprezentowane przede wszystkim przez odmianę β-$Ca_2[SiO_4]$, której towarzyszy α'-$Ca_2[SiO_4]$. Żużel z pieca LF charakteryzował się natomiast odmiennym składem, z sil-

ną przewagą (57%) odmiany α'-$Ca_2[SiO_4]$, przy 1% udziale odmiany β-$Ca_2[SiO_4]$ oraz przy 15% zawartości odmiany γ-$Ca_2[SiO_4]$.

Stwierdzono, że przemiana β-$Ca_2[SiO_4]$ w γ-$Ca_2[SiO_4]$ może zachodzić tylko w określonych warunkach w procesie metalurgicznym, na proces ten nie mają natomiast wpływu czynniki hipergeniczne, o czym może świadczyć fakt, że po około 100-letnim okresie składowania żużla martenowskiego, na bazie którego wyprodukowano kruszywo, oznaczono w nim przede wszystkim odmianę β-$Ca_2[SiO_4]$, nie stwierdzając polimorfu γ-$Ca_2[SiO_4]$.

Kompleksowa charakterystyka składu fazowego żużla wymaga zastosowania odpowiednio dobranej metodyki badawczej, zwłaszcza pod kątem obecności polimorfu γ-$Ca_2[SiO_4]$, co ma kluczowe znaczenie przed wtórnym wykorzystaniem tego materiału. Stwierdzono, że najdokładniejsze wyniki badań uzyskuje się przy użyciu techniki XRD. Metoda oznaczania rozkładu krzemianu dwuwapniowego wg normy PN-EN 1744-1+A1:2013-05 okazała się zawodna. Wydaje się, że w sytuacji wykorzystania żużla po produkcji pieca LF jako kruszywa sztucznego, zwłaszcza na dużą skalę, np. w budownictwie komunikacyjnym, przyjęcie wyników badań zgodnie z metodą opisaną w normie PN-EN 1744-1+A1:2013-05 jako decydujące jest bardzo ryzykowne.