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**IDENTIFICATION OF THE Si-F BONDS AND PHASE COMPOSITION
OF SELECTED SLAGS FROM THE CaO-SiO₂-CaF₂ SYSTEM USING
INFRARED SPECTROSCOPY**

**IDENTYFIKACJA WIĄZAŃ Si-F ORAZ SKŁADU FAZOWEGO
WYBRANYCH ŻUŻLI Z UKŁADU CaO-SiO₂-CaF₂
ZA POMOCĄ SPEKTROSKOPII W PODCZERWIENI**

The CaO-SiO₂-CaF₂ phase system was investigated for selected slags using infrared spectroscopy. Si-O, Si-O(Si) and Si-F bonds were found in the slags and the type of occurring phases and chemical compounds was determined. The Si-F type bonds occurred only a larger content of CaF₂. Using the examination results, the stages of the reaction of formation of the SiF₄ gaseous phase were proposed. An important role has been found to be played by Si-F bonds that initiate two stages of the reaction of formation of the SiF₄ gaseous phase. In the slags containing 4.02% and 9.88% of CaF₂, no Si-F bonds were identified.

Badano układ fazowy CaO-SiO₂-CaF₂ dla wybranych żużli przy użyciu spektroskopii w podczerwieni. Opisano układ żużlowy CaO-SiO₂-CaF₂ oraz metodykę badawczą. Stwierdzono wiązania Si-O, Si-O(Si) i Si-F w badanych żużlach oraz określono rodzaj występujących faz i związków chemicznych. Wiązania typu Si-F występowały tylko przy większej zawartości CaF₂. Wykorzystując wyniki badań zaproponowano etapy zachodzącej reakcji tworzenia się fazy gazowej SiF₄. Stwierdzono istotną rolę wiązań Si-F, które inicjują dwa etapy reakcji tworzenia gazowej fazy SiF₄. W żużlach zawierających 4,02% i 9,88% CaF₂ nie stwierdzono wiązań Si-F.

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1. Introduction

The CaO-SiO₂ slag system shows very close similarity to the CaO-SiO₂-CaF₂ system. This similarity is associated the existence of very similar types of slag occurring in the both systems. Because of a little research exploration of the CaO-SiO₂-CaF₂, this analysis was based on the CaO-SiO₂ system. Studies performed by numerous authors, e.g. [1], [2], indicate that Si-O silicon and oxygen bond has a typical ionic-covalent nature. It involves π electrons, therefore this type of bond in the structure of silicates has a bond order greater than one. The order of the silicon-oxygen bond in the isolated SiO₄ anion is equal to 1.29 and is consistent with the bond order calculated by quantum mechanics methods [3], [4]. The magnitude of bond order is a value that characterizes covalent bond. For ionic bond, the main characterizing feature are the charges of atoms forming the bond. Thus, the both concepts are used for describing the Si-O silicon and oxygen bond with ionic-covalent bonding. Charges on atoms forming a covalent-ionic bond are defined by various authors as follows, e.g.: effective charge, residual charge, net charge, bond charge, etc. The concept of effective charge was defined by Görlich [1] as the charge of an additional atomic core without covalent atoms. The following two conclusions result from numerous scientific studies concerning the character of Si-O bonds in silicates [2, 5, 6]:

- the Si-O bond is a bond being equally ionic and covalent, and
- this bond involves the π bonding orbital formed from non-bonding p electrons of oxygen and the non-populated d orbital of silicon.

The frequency of occurrence of the Si-O(Si) bridge bond in calcium silicates increases proportionally to the degree of polycondensation of the silicates. To compare the two types of bond in the anionic structure it should be stated in some simplification that the percentage of covalent bond will be greater with the participation of the Si-O bond and smaller in an anion in which Si-O(Si) bonds occur.

In the structure of calcium orthosilicates the β -Ca₂SiO₄ form has a bonding order equal to 1.31, whereas the bonding order of the γ -Ca₂SiO₄ form is 1.28, which can be explained by the considerable shortening of the Si-O bond length in the β -Ca₂SiO₄ form in relation to β -Ca₂SiO₄ form. Using Ohwady's model [7], Handke calculated the charge of silicon and oxygen, the total charge of the anion SiO₄⁻⁴ and the charge of the calcium cation. Based on these data, Handke determined the fraction of ionic bond in the Si-O according to the following relationship:

$$\%I_{\text{Si-O}} = \frac{q_{\text{Si}}}{4n} \cdot 100 \quad (1)$$

where: n — bonding order, $+q_{\text{Si}}$ — charge of the Si atom in the SiO₄⁴⁻ ion
Calculation data are shown in Table 1 below.

It can be seen from the above Table that the percentage share of ionic bond in particular combinations is dependent on the spatial structure. In the calcium silicates of the CaO-SiO₂-CaF₂ system, being basic in character, an excess of the CaO component occurs, which results in free oxygen ions, O²⁻F¹⁻, coexisting in the liquid phase. Free

TABLE I

Results of the calculation of Si-O bonds according to [6]

Charge parameter	SiO ₄ ⁴⁻	γ in orthosilicate	β Ca in orthosilicate
+q _{Si}	2.25	2.62	2.77
-q _O	1.56	1.63	1.55
-q(SiO ₄ ⁴⁻)	4.00	3.90	3.43
+qCa ²⁺	-	1.95	1.72
%I _{Si-O}	44	51	53

tetrahedrons and calcium cations also appear. For the larger concentration of SiO₂ in calcium silicate and the atom ratio Si/O = 1/3, O²⁻ oxygen ions do not exist in the liquid slag phase. Then, the ionic structure is based on Si-O bonds and Si-O(Si) bridge bonds that are capable of forming chain- or ring-type structures.

The character of structures forming in liquid slags with a higher degree of polycondensation (SiO₂ concentration) is complicated by additional Si-F bonds formed by fluorine ions. The character of bonding in the Si-O(Si) bridge, because of the complexity of its chemical composition of spatial structure, is difficult for direct investigation. Therefore, infrared spectroscopy examination methods, as well as Raman spectroscopy are applied. The infrared spectroscopy is useful because of the properties of the calcium cation sublattice, whose frequencies of vibrations are much lower than those inside the silicate-oxygen and silicate-fluorine-oxygen anions. This makes possible good separation of these vibrations in the spectra of calcium silicates, which facilitates the identification of particular spectra of compounds and phase structures. The band ranges in the part of spectra within the 400–1800 cm⁻¹ infrared range in the adsorption spectra of calcium silicates, are of interest. Introducing calcium fluoride, CaF₂, into the CaO-SiO₂ system causes the coexistence of two forms of free F⁻ ions related to calcium cations or Si-F bonds to coexist. According to Baak [8], also CaF⁺ forms may exist, which, however, has not been confirmed by experiments and is not accepted by many authors [9, 10].

The aim of the present investigations was an attempt to explain the mechanism of formation of Si-F combinations in CaO-SiO₂-CaF₂ slags within a specific concentration range. The use of the infrared spectroscopy should enable the identification of the phase composition of these slags.

2. Experimental

Two series of samples were made from CaO-SiO₂-CaF₂ system to undergo the tests slags. Their chemical composition is shown in Table 1 and in the ternary diagram (Fig. 1) with appropriate slag tests indicated.

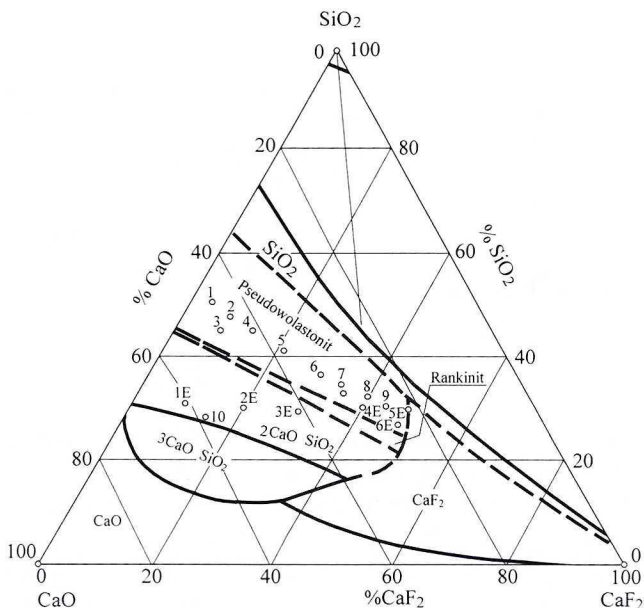


Fig. 1. The CaO-SiO₂-CaF₂ phase system of slags [17]

The first test series is characterized by a nearly constant SiO₂ concentration, being approximately 30 wt. %, and variable CaO and CaF₂ concentrations within the range 10–60 wt. %. The second test series features a constant basicity index, %CaO/%SiO₂ = 1, and variable CaF₂ concentrations within the range 4–50 wt. %. The latter test series was prepared so that the composition of slags examined belonged to the field of pseudo-wollastonite. Moreover, several additional tests were forseen, in order to confirm the assumption saying that the calcium orthosilicate phase prevents the formation of Si-F combinations in the slag.

Slags for tests were prepared by remelting of the initial components, i.e. CaO, and CaF₂, in a Tamman furnace in tungsten or molybdenum crucibles. The remelting of slags was done at temperature 50 K above the liquidus for about 1 hour, and then the slags were intensively cooled with compressed argon. The purpose of intensive cooling was to retain the phase and ionic slag structure existing in the liquid state. The next operation was grinding to a grain size below 200 μm, and preparation of samples with standard concentration (i.e. 1.6 mg of slag and 600 mg KBr). Such samples were investigated using a Fourier infrared spectrometer, type FTS-14 V DIGILAB. This spectrometer possesses an internal wavelength standard (laser He-Ne), which assures a high accuracy of determining the location of absorption bands. The Fourier spectrometer features a high resolution. Advantages provided by this apparatus when measuring the spectra of solids are reported by Handke [6, 11]. The spectra in the medium infrared range 400–1800 cm⁻¹, presented in this study, were measured at the constant values of the basic parameters and calculations of the interferogram, that is resolution and the sampling density 1 cm⁻¹.

3. Discussion of results

Figure 2 and 3 present interferograms of the absorption spectrum in the medium infrared range obtained for the $\text{CaO-SiO}_2\text{-CaF}_2$ slags using the Fourier spectrometer. Taking into consideration studies by H a n d k e [6], K u m a r and W a r d [12, 13], the phase fields of particular slags were identified, and qualitative evaluation was made by the relative comparison of the number of Si-F type bonds which were determined at the infrared

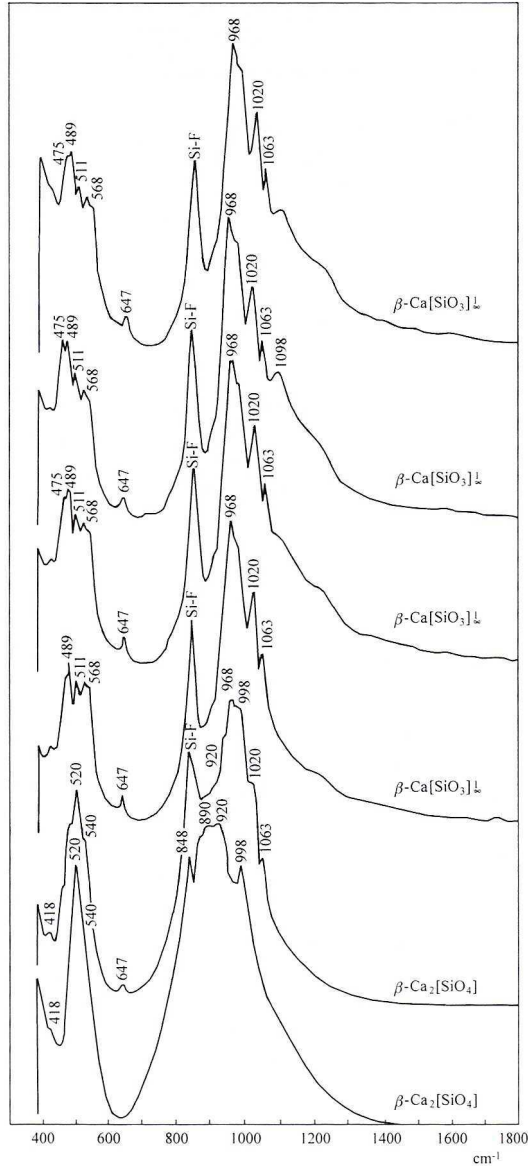


Fig. 2. Medium infrared-range absorption spectra for the calcium silicates of the $\text{CaO-SiO}_2\text{-CaF}_2$ slag system, Series I

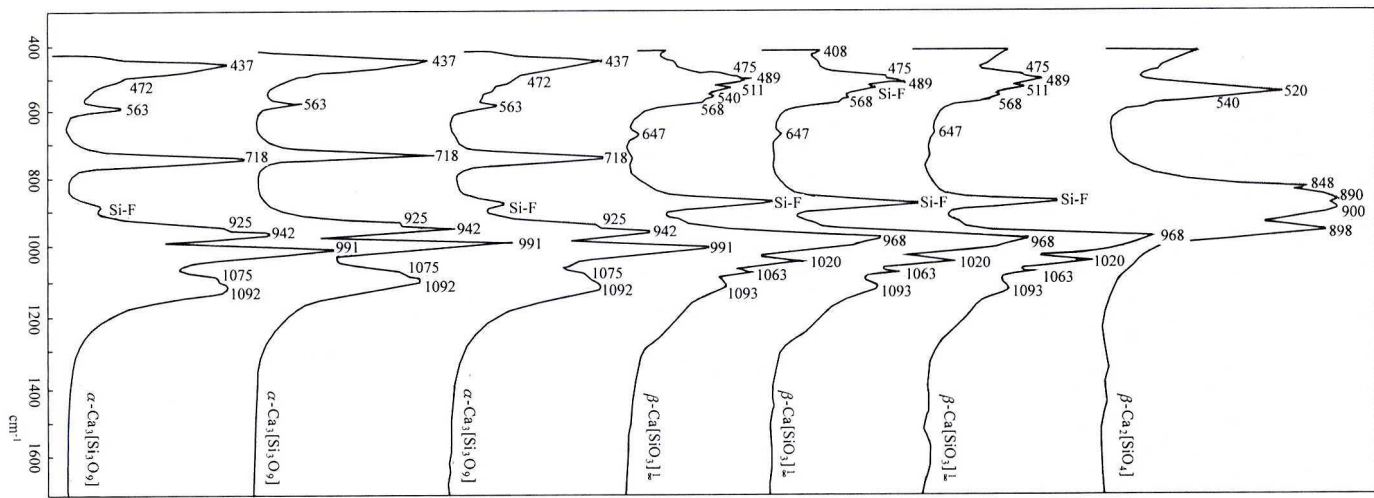


Fig. 3. Medium infrared-range absorption spectra for the calcium silicates of the $\text{CaO-SiO}_2\text{-CaF}_2$ slag system, Series II

spectrum equal to $\nu = 852 \text{ cm}^{-1}$. Table 1 shows the results of this identification, i.e. the height of the peak and its surface area in mm^2 . The selection of the chemical composition of slag samples in Series I was done in such a manner so to avoid the phase field of rankinite, Ca_3SiO_7 , whose one characteristic peak of the infrared spectrum length $\nu = 847 \text{ cm}^{-1}$ is situated close to spectrum of the Si-F bonding, which could cause difficulties in identifying the separation of the two infrared spectral bands.

To make a relative comparison of the number of Si-F bonds in the slags of Series I (slags 1E to 6E) and II (slag tests 1 to 10), two diagrams of the relationship of the height and surface area of the Si-F bonding peak versus CaF_2 slag concentration were plotted for each series. The peak area was calculated using various methods including planimeter, the Lorentz function, and the Gaussian function with background correction procedure. The minimum deviation of the peak area from the average value was obtained using the Gaussian function. The composition of the samples for the II Series was from the field of wollastonite. The data concerning types of phases found for both series of slag samples are shown in Table I

It can be stated based on the test results shown in Figs. 2 and 3 and in Table 1 that slags Nos. 1E and 2E have the structure of calcium orthosilicate, $\beta\text{-Ca}_2[\text{SiO}_4]$, for which the predominant form of combinations is the SiO bonding. For the $\beta\text{-Ca}_2[\text{SiO}_4]$ structure, characteristic infrared absorption spectra occur with the following peak bands: 520 cm^{-1} , 848 cm^{-1} , 920 cm^{-1} , and 998 cm^{-1} . Calcium orthosilicate appears in five crystalline forms. The low-temperature form $\gamma\text{-Ca}_2[\text{SiO}_2]$ is stable and is characterized by an olivine-type structure. The other forms, i.e. β , α_1 , α_{II} and α have similar topological structures. Calcium cations in these structures, as well as the mentioned above phase β , have the coordination

TABLE 2

Chemical composition of slag samples subjected to examination using an infrared spectrometer

No.	%CaO	%SiO ₂	%CaF ₂	%CaO/%SiO ₂	Si-F Bonds Average Peak Height, mm	Si-F Bonds Average Peak Surface Area, mm ²
1E	59.88	29.93	9.86	2.0	—	—
2E	49.81	29.87	20.10	1.6	29.5	126.0
3E	39.90	30.02	29.80	1.3	51.0	220.0
4E	29.889	29.95	39.84	1.0	54.5	228.0
5E	19.92	29.91	49.95	0.66	55.0	246.0
6E	16.95	25.43	57.81	0.67	54.5	246.0
1	47.90	47.84	4.02	1	—	—
2	45.86	45.92	7.95	1	6.0	14.5
3	48.98	43.01	7.98	1.15	—	—
4	42.36	42.24	15.04	1	14.5	42.5
5	39.01	38.82	21.87	1	54.0	198.0
6	34.90	34.78	30.05	1	58.0	205.0
7	32.49	32.40	34.94	1	55.0	199.0
8	29.35	29.18	40.16	1	52.5	195.0
9	24.91	24.91	49.87	1	51.0	175.0
10	62.86	21.90	15.02	2.8	—	—

TABLE 3

Results of the identification of phases occurring in slag samples using absorption spectra in the medium infrared range.

Note: The CaF_2 phase was examined by an X-ray method.

Sample No.	Type of Main Phase	Bonding Type	Type of Supplementing Phase
Series I			
1E	Calcium orthosilicate $\beta\text{-Ca}_2[\text{SiO}_4]$	Si-O	CaF_2
2E	Calcium orthosilicate $\beta\text{-Ca}_2[\text{SiO}_4]$	Si-O Si-F and SiO(Si)	$\text{CaF}_2 + \beta\text{-CaSiO}_3$ 1
3E	Wollastonite $\beta\text{-Ca}[\text{SiO}_3]$ 1	Si-O Si-O(Si) Si-F	CaF
4E-5E	Wollastonite $\beta\text{-Ca}[\text{SiO}_3]$ 1	Si-O Si-O(Si) Si-F	CaF
6E	Wollastonite $\beta\text{-Ca}[\text{SiO}_3]$ 1	Si-O Si-O(Si) Si-F	CaF
Series II			
1	Cyclowollastonite $\alpha\text{-Ca}_3[\text{Si}_3\text{O}_9]$	Si-O Si-O(Si) Si-O	CaF_2
2	Cyclowollastonite $\alpha\text{-Ca}_3[\text{Si}_3\text{O}_9]$	Si-F Si-O (Si)	CaF_2
3	Cyclowollastonite $\alpha\text{-Ca}_3[\text{Si}_3\text{O}_9]$	Si-O Si-O (Si)	CaF_2
4	Cyclowollastonite $\alpha\text{-Ca}_3[\text{Si}_3\text{O}_9]$	Si-O Si-F Si-O (Si)	CaF_2
5-9	Wollastonite $\beta\text{-Ca}[\text{SiO}_3]$ 1	Si-F Si-O (Si) Si-O	CaF_2
10	Calcium orthosilicate $\beta\text{-Ca}_2[\text{SiO}_4]$		CaF_2 Ca_2SiO_4 CaO calcium oxy-orthosilicate

number in the middle of 6, while in the second part of 8. Calcium silicates in this group of orthosilicates are characterized by rich and diverse polymorphism and a diversified degree of polycondensation of SiO_4^{4-} tetrahedrons. The $\beta\text{-Ca}_2[\text{SiO}_4]$ contains single tetrahedrons in its structure. Slag 1E was found not to contain Si-F combinations, which would suggest that it had a large contribution of single tetrahedrons and free oxygen ions and the sublattice of the calcium cations Ca-F and Ca-O. In the Ca-O combination, the bonding distances for the coordinating numbers are 247 pm and 250 pm, respectively [14]. The bonding distances for Si-O in these structures are 163 on the average, and they

are smaller than those in the γ - Ca_2SiO_2 form. In slag 2E, a gradual transformation of the β - $\text{Ca}_2[\text{SiO}_2]$ form towards the wollastonite form is visible. The share of β - $\text{Ca}_2[\text{SiO}_2]$ phase can be estimated at approximately 80%, but the structure of tetrahedrons is more complicated. Therefore, the appearance of Si-F combinations of an infrared spectrum band length of 852 cm^{-1} is possible in this structure.

In slag 3E the β - $[\text{SiO}_3] 1_\infty$ structure, or that of chain wollastonite, appears, where tetrahedrons are joined by the corners. The occurrence of the β - $[\text{SiO}_3] 1_\infty$ that is para-wollastonite, is also possible. In this type chain polyanions appear in a tri-alternating manner. Para-wollastonite possesses the monoclinic symmetry $P_{21}/a/C_{2n}^3$, while wollastonite has triclinic symmetry P_1/C_1 . The wollastonite structure β - $[\text{SiO}_3] 1_\infty$ was identified based on the following characteristic infrared band peaks: 489 cm^{-1} , 511 cm^{-1} , 568 cm^{-1} , 647 cm^{-1} , 968 cm^{-1} , 1020 cm^{-1} , and 1063 cm^{-1} . The average distance of the non-bridge bonding Si-O is 167.4 pm and is larger than the distance for silicon and oxygen in the bridge bonding, which is 160.3 pm [15]. In contrast to slag 2E, the structure in slag 3E is much better for the formation of Si-F type bonds.

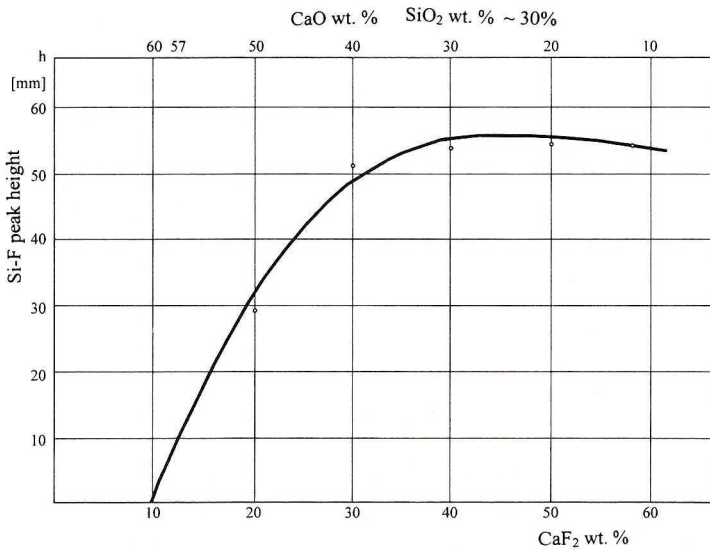


Fig. 4. Dependence of peaks heights for Si-F type bonds in the $\text{CaO-SiO}_2\text{-CaF}_2$ slag on the percentage concentration of CaF_2 for Series I of slag tests, function $-h = -49.978 + 6.0501 (\% \text{CaF}_2) - 0.1122 (\% \text{CaF}_2)^2 + 0.0006701 (\% \text{CaF}_2)^3$

In the slag 4-6E with a typical wollastonite structure, there is a tendency to the saturation of anion lattice with fluorine due to the limited slag concentration up to 30% SiO_2 . Therefore, the number of Si-F in these slags stabilizes, which can be observed from the dependence of peak surface area (or peak height) versus CaF_2 concentration (Figs. 4 and 5). Moreover, in slags 5E and 6E, a small amount of a vitreous phase can be seen, which is rich in silica.

Summarizing the above results, one can conclude that at a specific concentration of SiO_2 in slag of the $\beta\text{-Ca}[\text{SiO}_3]$ 1_∞ structure and at CaF_2 concentration of 0.24–0.50 mole fraction, the maximum number of Si-F type bonds occur. Moreover, the presence of the CaF_2 phase in the samples 1E-6E indicates that two types of bonding of fluorine combined with calcium and silicon form in the slag, which was also confirmed by the examination of slags carried out by the DSH X-ray method.

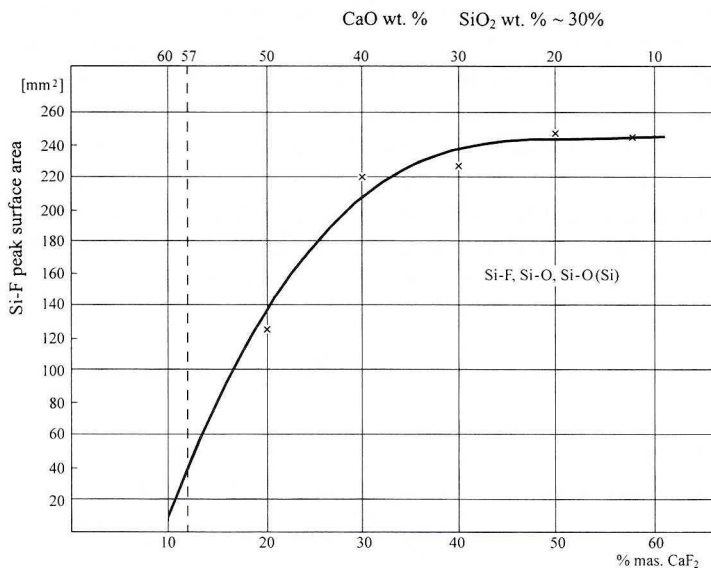


Fig. 5. Dependence of peak surface area for Si-F type bonds in the $\text{CaO-SiO}_2\text{-CaF}_2$ slag on the percentage concentration of CaF_2 for Series I of slag tests (E);

$$\text{function } s = -215.312 + 26.245 (\% \text{CaF}_2) - 0.5022 (\% \text{CaF}_2)^2 + 0.00322 (\% \text{CaF}_2)^3$$

Series II (slag tests 1-10) belonged to the phase field of wollastonite (except for slag No. 10). Slags 1-3 have the structure of pseudo-wollastonite, so-called cyclowollastonite $\alpha\text{-Ca}_3[\text{Si}_3\text{O}_9]$. This is a high-temperature phase which transforms into the $\beta\text{-Ca}[\text{SiO}_3]$ 1_∞ wollastonite at 1378 K. The cyclowollastonite structure is characterized by the following infrared spectra with the maximum peaks at: 718 cm^{-1} , 925 cm^{-1} , 942 cm^{-1} , 991 cm^{-1} , 1075 cm^{-1} and 1092 cm^{-1} . The existence of this structure confirms the effectiveness of fast cooling which enabled retaining the original structure of the liquid state of slag. The conservation of structure of the anionic lattice may indicate that fluorine ions in liquid slag can stabilize this type of structure. The cyclowollastonite possesses a sublattice of Ca^{2+} cations forming octahedral layers with the interconnecting rings formed from the connections of three octahedrons. Calcium cations, Ca^{2+} , take on the coordination number 8 in this structure.

In addition to the Si-O bonding, there are also Si-O(Si) bridge bonds. The distance of calcium cations from the oxygen in the bridge structure is 254 pm, being longer than that in the similar structure of β -wollastonite (238.5 pm). The calcium-oxygen octahedral layers connecting the Si_3O_9 rings are arranged in such a manner that non-bridge oxygen

ions laying in planes perpendicular to the ring plane join the top and the bottom of the octahedral layers [17]. The ability of the cyclowollastonite structure to add fluorine is reduced. This can be observed on the example of slags Nos. 2 and 3. The both slag samples have identical CaF_2 concentrations being approximately 8%, but they differ in the values of basicity index, which is 1 for slag 2 and 1.15 for slag 3.

In the slag No. 2, small amount of Si-F bonds are observed, whereas no such bonds were found in the slag No. 3, in spite of the fact that a similar phase composition remained in both slag samples. An increase of the slag concentration of CaO resulted in the formation of the cyclowollastonite structure that prevented fluorine from adding to the anionic lattice. The increase of the CaF_2 concentration up to 15% in slag No. 4 with basicity index equal to 1 caused an increase in the number of Si-F bonds in the cyclowollastonite structure in comparison with sample No. 2. The decreasing SiO_2 concentration and increasing CaF_2 concentration in slags Nos. 5 and 6 resulted in a further increase in the number of Si-F bonds in the β -wollastonite structure up to the maximum level. In the last Nos. 7-9, belonging to the phase β of wollastonite, a reduction of the fluorine amount in the anionic structure was observed, probably because of the decrease of SiO_2 concentration in those slags. This indicates (Figs. 6 and 7) close relationships between the number of Si-F bonds in the structure β of wollastonite and the SiO_2 to CaF_2 ratio in liquid slag.

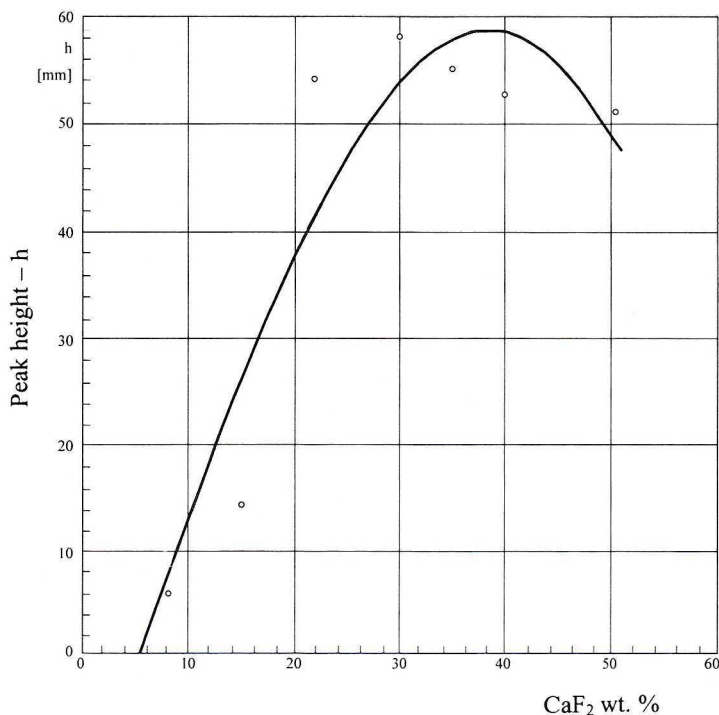


Fig. 6. Dependence of peak height for Si-F bonds in the CaO-SiO₂-CaF₂ slag (wollastonite field) on the percentage concentration of CaF₂ for the tests of Series II; function $h = -0.00049 (\% \text{CaF}_2) - 0.01228 (\% \text{CaF}_2)^2 + 3.15303 (\% \text{CaF}_2) - 16.2117$

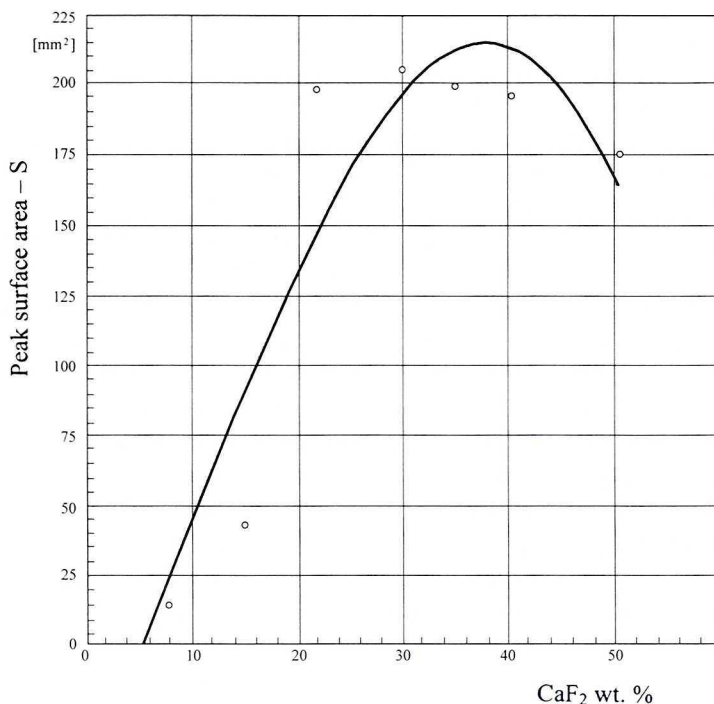
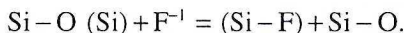


Fig. 7. Dependence of peak surface area for SiF bonds in the CaO-SiO₂-CaF₂ (the wollastonite field) on CaF₂ concentration for the tests of Series II; function $S = -0.00325 (\%CaF_2)^3 + 0.06610 (\%CaF_2)^2 + 9.20645 (\%CaF_2) - 52.8393$

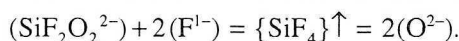
The slag No. 10 contained enhanced CaO content and had a different chemical composition. Therefore, the structure found in slag No. 10 was that of calcium orthosilicate, β -Ca₂SiO₄ with infrared spectra showing the characteristic peaks 520, 540, 848, 900, 920 and 998 cm⁻¹. This slag is similar to slag 1E, but differed slightly in the chemical composition and phase structure manifested by clearer contours of the 522 cm⁻¹ and 452 cm⁻¹ peaks, which is the reason for the fragments of the Ca₂SiO₄ CaO structure to appear. This is a polytypicality of calcium oxy-orthosilicate that can be written as Ca₂SiO₄·CaO. or Ca₃SiO₅ [16]. In the oxy-orthosilicate structure, various high-temperature forms exist, which differ in the arrangement of free tetrahedrons. In these conditions, combinations of fluorine with silicone are unlikely to happen. Therefore, no Si-F combinations were found in the structure of calcium orthosilicate and oxy-orthosilicate in slag No. 10.

In the CaO-SiO₂-CaF₂ slag system examined, the change of Si-to-O atomic ratio in the silicate structure to 1:3 causes a change in the geometrical structure of tetrahedrons from para-wollastonite to the wollastonite structure, in which combinations of tetrahedrons into a ring or chain structure form. In these structures Si-O and Si-O (Si) bridge bonds occur, therefore this will be a ionic-covalent bonding with prevalent ionic

bonding. The Si-F combinations were also found. They change the parameters of the silicate-oxygen crystalline lattice and in a consequence they cause the reaction of formation of the SiF_4 compound. Si-F bonds forming in the liquid state can, in dependance on SiO_2 concentration, either fix the existing geometrical structure of the lattice or disturb (for higher SiO_2 content) the geometric equilibrium of the lattice. This leads to lattice rebuilding with simultaneous occurrence of the following reaction:



SiFO_3^{3-} will follows in the tetrahedron.



The release of the gaseous SiF_4 and the oxygen ions O^{2-} leads to the geometrical rebuilt of the anionic silicate lattice and cationic calcium sub-lattice. This causes a shift in the silicon-to-oxygen ratio towards 1:4.

4. Conclusions

From the investigations carried out using infrared spectroscopy, the following conclusions can be drawn:

1. In $\text{CaO-SiO}_2\text{-CaF}_2$ type slags with the structure of calcium orthosilicates and oxy-orthosilicates no S-F bonds have been identified in the silicate-oxygen structure and no reaction of formation of the SiF_4 compound has been found to proceed.
2. In $\text{CaO-SiO}_2\text{-CaF}_2$ type slags with para-wollastonite and wollastonite structures, the Si-F bonding has been identified in the silicate structure and the reaction of formation of the SiF_4 compound has been found to proceed.
3. In $\text{CaO-SiO}_2\text{-CaF}_2$ type slags with para-wollastonite and wollastonite structures the number of Si-F bonds in the silicate structure increases with increasing SiO_2 and CaF_2 concentrations and the occurrence of the reaction of SiF_4 formation is related to the number of Si-F bonds in the slag.

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