

# THE STUDY OF SILICON CHEMICAL BOND IN MODELED SILICATE SYSTEMS AND MANGANESE ORES USING X-RAY PHOTOELECTRON SPECTROSCOPY

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## ABSTRACT

The nature of silicon chemical bonds in modeled samples of such systems as MnO-SiO<sub>2</sub>, MnO-CaO-SiO<sub>2</sub>, in oxide and carbonate manganese concentrates, manganese charge slags, metallic manganese melting and ferrosilicon-manganese slags was studied by means of X-ray photoelectron spectroscopy. It was found out that SiO<sub>2</sub> → [Si<sub>x</sub>O<sub>y</sub>]<sup>z-</sup> transformation with various silicon-oxygen motives formation in a range of SiO<sub>2</sub> → [Si<sub>4</sub>O<sub>10</sub>]<sup>4-</sup> → [Si<sub>4</sub>O<sub>11</sub>]<sup>6-</sup> → [Si<sub>2</sub>O<sub>6</sub>]<sup>4-</sup> → [Si<sub>3</sub>O<sub>15</sub>]<sup>10-</sup> → [Si<sub>2</sub>O<sub>7</sub>]<sup>6-</sup> → [SiO<sub>4</sub>]<sup>4-</sup>; decrease in the number of cross-linking bonds; increase in effective and formal charges of simple tetrahedron; increase in the number of external cation-modifiers Mn, Ca, Mg, Fe that are able to form channels for excess electron charge release affect the binding energy and the chemical change of the frame electron 2p-levels of silicon.

## 1. INTRODUCTION

Manganese ores and concentrates, charge slags and slag-heaps of metallic manganese, ferromanganese and ferrosilicon-manganese meltings represent multicomponent oxide systems SiO<sub>2</sub>-CaO-MnO-MgO-Al<sub>2</sub>O<sub>3</sub> which contain from 20% to 50% of SiO<sub>2</sub>. Functional properties of such materials have been analyzed in numerous theoretical and empirical studies. However, silicon chemical bonds (oxyanions in particular) which influence more effective extraction of manganese and silicon into alloys are still being discussed.

In manganese ores and quartzite silica occurs not only as a free mineral (α-quartz), but also as a part of various complex silicates. In high-manganese charge slag and slag-heaps received from manganese ferroalloy meltings silicon atoms that are coordinated by oxygen anions are considered to be structural units of various silicates with different arrangement of oxyanion motives [1-3].

The structure of SiO<sub>2</sub> elementary unit of silicate-ion [SiO<sub>4</sub>]<sup>4-</sup> has been fundamentally studied by the scientists [4-6]. It has been found that the length of Si-O bond (0.161 nm) remains the same during the silica transformation from a solid state to a liquid one. Direct empirical study of simple tetrahedron SiO<sub>4</sub> with various arrangements is complicated, that is why the researches [7-10] are focused on the development and improvement of computational methods and data analyses in terms of electron composition.

Si-O chemical bond in simple tetrahedron SiO<sub>4</sub> is formed due to hybrid sp<sup>3-</sup> orbitals of silicon atom and hybrid orbitals of oxygen atom which are intermediate between sp<sup>-</sup> and sp<sup>2-</sup> orbitals. The interaction energy of valence electrons of silicon and oxygen atoms in silicate-ion [SiO<sub>4</sub>]<sup>4-</sup> which has been calculated with 'magic' Mulliken formula [10] is

mainly defined by the given effective silicon charges  $\mu_{Si^{4+}}$  and  $\mu_{O^{2-}}$  that equal 3.283 and 1.925, respectively. The calculated atomization energy  $E_{am} = 1805,14$  and average binding energy  $E_{Si-O}^{cp} = 451$  kJ/Mol correspond with the data provided by researchers [11].

It has been determined [12] that the full effective negative charge changes from 4 down to 0.856 in the process of condensation [SiO<sub>4</sub>]<sup>4-</sup> → SiO<sub>2</sub>. Silicon positive effective charge has been determined to change from 0.803 up to 1.348. With the help of mathematical methods by outlining clusters which contain ion [SiO<sub>4</sub>]<sup>4-</sup> surrounded by a number of cations and which imitate fragments of silicate crystal lattices, the influence of closest monocations on fundamental properties of silicon-oxygen tetrahedrons has been defined. Such clusters as 4q<sup>+</sup>[SiO<sub>4</sub>]<sup>4-</sup>; 6q<sup>+</sup>[SiO<sub>4</sub>]<sup>4-</sup>; and 12q<sup>+</sup>[SiO<sub>4</sub>]<sup>4-</sup> have been analyzed. Comparison of properties in silicon-oxygen tetrahedrons in clusters as fragments of a silicate crystal lattice and in hydroxyl groups from Si(OH)<sub>4</sub> to [SiO<sub>4</sub>]<sup>4-</sup> has shown that in the condensed systems the influence of closest tetrahedron environment – i.e. outer-sphere ligands in oxygen atoms – is, first of all, defined with the ability of the latter to create effective channels for extra electron charge escape. Well-known principles of crystal chemistry of silicates introduced by Pauling C. Linus [5] and developed by Belov V. Nikolay [13] were supplemented by Lasarev N. Adrian et al. [12] with one more statement: the average length of Si-O bond in tetrahedron is determined by its full charge and the configuration of the closest environment. Certain analogy concerning the effect of protonation on the ion [SiO<sub>4</sub>]<sup>4-</sup> in Si(OH)<sub>4</sub> molecule and its condensation has been drawn. There are similarities in the ways of modifications of silicon-oxygen tetrahedron electron composition while changing from [SiO<sub>4</sub>]<sup>4-</sup> ion to Si(OH)<sub>4</sub> molecule during the transfor-

mation towards silicon dioxide group, i.e. the increase in the degree of system condensation and the changes in Si:O proportion range from 1:4 to 1:2.

This research has become up-to-date due to the lack of study of the nature of silicon chemical bond in manganese silicate systems [14, 15] alongside with multicomponent structure of both manganese mineral raw materials and slags.

## 2. EXPERIMENTAL

The nature of silicon chemical bond in manganese silicates has been studied in terms of defining binding energy of silicon frame electron levels  $E_{ce}(Si\ 2p)$  and chemical changes  $\Delta E_{ce}(Si\ 2p)$ . Using binding energy ( $E_{ce}$ ) and chemical changes ( $\Delta E_{ce}$ ) of internal electron levels as a main characteristic of silicon atom valence state in a bond, the nature of chemical bond accompanied by changes of atom valence shells and electron collectivization can be determined.

The idea of using X-ray photoelectron spectroscopy technique (XPS) for analyzing the nature of silicon chemical bond in manganese silicates has been accepted as a result of conducted research of phosphorus chemical bond in manganese ore minerals and concentrates [16].

Electron spectrometer ЭС-2402 has been used for analysis according to the described technique [16]. The chemicals used in the present study are given in Table 2.1. They include: the modeled samples of MnO-SiO<sub>2</sub> and MnO-CaO-SiO<sub>2</sub> systems, prepared by alloying “pure for analysis” oxides in argon atmosphere; the representative samples of oxide and carbonate manganese concentrate from Nikopol deposit; samples of industrial finishing slags received from metallic manganese and ferrosilicon-manganese melting; charge manganese slag.

**Table 2.1:** Chemical composition of the analyzed samples containing manganese

Samples	Component content, Mass %										
	MnO	MnO <sub>2</sub>	F <sub>2</sub> O <sub>3</sub> / FeO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	LOI
Modeled:											
MnO-SiO <sub>2</sub>	54.2	–	–	45,8	–	–	–	–	–	–	–
MnO-SiO <sub>2</sub> -CaO	38.0	–	–	47,5	–	14,5	–	–	–	–	–
Slags:											
charge											
metallic manganese	53.66	–	–/0,3	28,6	5,4	7,6	2,8	0,8	0,2	0,012	–
ferrosilicon-manganese	19.16	–	–/0,2	25,2	3,8	45,7	4,3	0,74	0,12	0,018	–
Concentrate:											
Oxide	21,16	–	–/0,2	49,8	9,7	12,9	4,9	0,52	0,16	0,011	–
Carbonate	8,10	57,15	6,05/–	16,10	2,94	2,71	1,05	1,46	0,62	0,53	10,2
	37,30	–	3,85/–	11,90	2,00	12,10	2,22	0,31	0,22	0,48	29,6

## 3. RESULTS

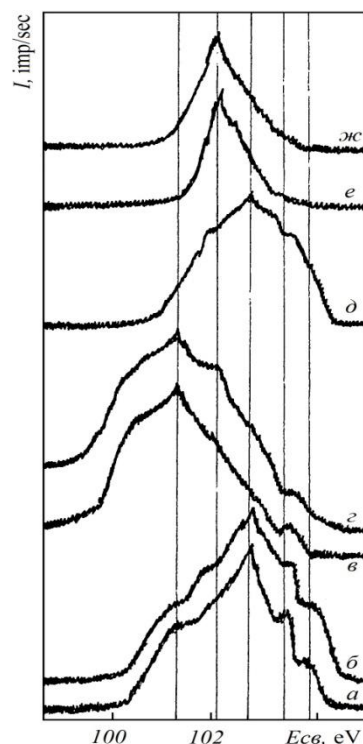
The results are presented in Figure 3.1 and Table 3.1.

As a result of comparison of the value of binding energy of Si2p-level and the analysis of changes in concentrates, charge and finishing slags, as well as modeled synthesized samples, clearly distinguished peaks  $E_{ce}(Si\ 2p)$  for the modeled samples and unclear nature of their maximum level for slags have been observed. It can be possibly explained by the presence of continuous range of transformations from SiO<sub>2</sub> to [Si<sub>x</sub>O<sub>y</sub>]<sup>z</sup> in the slag structure.

The change of electron composition of silicon atom in terms of chemical bond formation or transformation affected by external modifiers (Mn, Ca, Mg) as well as identification of the type of the bond based on well-known analogues is estimated by the chemical changes ( $\Delta E_{ce}$ ) of silicon frame electron levels which is defined as a difference of  $E_{ce}$  silicon internal frame electron levels in a molecule and atom:

$$\Delta E_{ce}(Si\ 2p) = E_{ce}^M(Si\ 2p) - E_{ce}^A(Si\ 2p). \tag{1}$$

The binding energy of silicon internal electron 2p-levels  $E_{ce}^A(Si\ 2p)=99,5\text{ eV}$  [17] is considered to be initial.



**Figure 3.1:** XPS spectra of silicon electron 2p-levels in modeled synthesized samples with silicon content, in manganese concentrates and industrial manganese slags: *a* – oxide concentrates; *b* – carbonate concentrates; *c* – charge slag; *d* –metallic manganese slag; *e* – ferrosilicon-manganese slag; *e* - MnO-SiO<sub>2</sub>; *f* -MnO-CaO-SiO<sub>2</sub>.

Chemical change of frame electron levels of  $\Delta E_{cb}$  element is directly proportional to the number of valence electrons (*n*) and nominal degree of oxidation (*N*):

$$E_{cb} = cnN \tag{2}$$

It also correlates with the effective charge of atom in a molecule:

$$\Delta E_{cb} = Kq_A + \sum (x)q_x / r_{Ax}, \tag{3}$$

where  $q_A$  and  $q_x$  are effective charges of *A* and *x*, respectively;  $r_{Ax}$  is a distance from electron to the analyzed atom.

**Table 2.1:** The binding energy of silicon internal electrons of 2p-level in analyzed samples

Samples	Peak indices of $E_{cb}$ , eV					O/Si
	max	1-st	2-d	3-d	4-th	
Modeled:						
MnO-SiO <sub>2</sub>	102,6	–	–	–	–	3,0
MnO-SiO <sub>2</sub> -CaO	102,4	–	–	–	–	3,0
Concentrate:						
oxide	103,0	101,6	102,4	103,4	103,7	–
carbonate	103,2	101,7	102,5	103,5	103,8	–
Slags:						
charge	101,6	–	–	103,8	–	4,0
ferrosilicon- manganese	102,9	–	102,3	103,7	–	2,7
metallic manganese	101,6	102,0	–	103,6	–	4,8

Proportional dependence can be seen between formal charge and both silicon and silicon-anion [SiO<sub>4</sub>]<sup>4-</sup> effective charges.

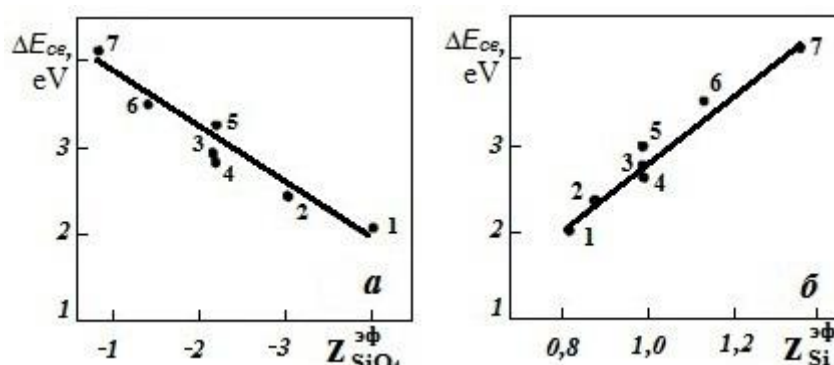
Thus, the authors have calculated the formal charges for some silicate-anion motives which represent the group of single and double chain inosilicates, ring and sheet silicates that have the defined value of  $E_{ce}(Si\ 2p)$ . The value of the formal charge of a single simple tetrahedron ( $z^{\phi}$ ) in  $[Si_xO_y]^{z-}$  motive has been defined as  $z/x$  relation:  $z^{\phi} = z/x$ .

#### 4. DISCUSSION

The calculation of the value of the effective charges for existing silicate motives and systems is quite complex due to a range of assumptions that include, first of all, the determination of limits of electron density distribution. For the following analysis the similar systems with silicon-oxygen motives have been chosen. They have similar formal charge of a simple single tetrahedron where binding energy values  $E_{ce}(Si\ 2p)$  are defined in reference literature. It is assumed that calculated parameters correspond to the accepted similar motives as it is indicated in Table 4.1. Figure 4.1

shows the dependence of  $\Delta E_{ce}(Si\ 2p)$  on the effective charge of  $[SiO_4]^{4-}$  silicate-ion ( $z_{SiO_4}^{\phi}$ ) and included in it silicon atom ( $z_{Si}^{\phi}$ ) for systems with different silicon-oxygen motives. The dependence proves that the criteria used in this article are reasonable as linear type of dependence retains. However, for existing multicomponent silicate systems (manganese concentrates, slags) the effective charges can be hardly defined. That is why the value of the formal charge ( $z^{\phi}$ ) of a simple tetrahedron in silicon-oxygen motives has been used for analysis.

Linear dependence of  $\Delta E_{ce}(Si\ 2p)$  and  $z^{\phi}$  (Fig. 4.2) for the bonds and test samples corresponds well with fundamentals of quantum chemistry of molecular systems and explains the type of  $\Delta E_{ce}(Si\ 2p)$  changes for all test samples.



**Figure 4.1:** The dependence of chemical changes ( $\Delta E_{ce}$ ) of  $Si\ 2p$  –levels on the silicate-ion effective charge of  $[SiO_4]^{4-}$  (a) and included in it silicon atom (b) for such compounds as: 1 -  $CaMg[SiO_4]$ ; 2 -  $Ca_2Mg[Si_2O_7]$ ; 3 -  $Ca_3[Si_3O_9]$ ; 4 -  $CaMn_4[Si_5O_{15}]$ ; 5 -  $CaMg[Si_2O_6]$ ; 6 -  $Al_4[Si_4O_{10}] \cdot (OH)_8 \cdot nH_2O$ ; 7 -  $\alpha$ - quartz.

**Table 4.1:** Changes in formal and effective charges during the process of polymerization of protonated silicon oxyanions and similar silicate-ions.

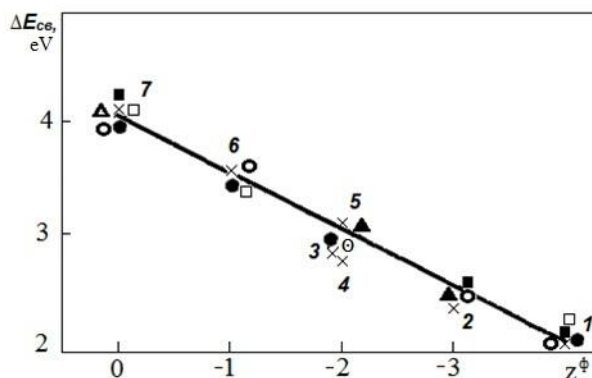
Parameter	System				
	$Si(OH)_4$	$Si(OH)_3O^-$	$Si(OH)_2O^{2-}$	$Si(OH)O^{3-}$	$[SiO_4]^{4-}$
Formal charge ( $z^{\phi}$ )	0	-1	-2	-3	-4
Effective charge ( $z^{\phi}$ ):					
$SiO_4$	-0,856	-1,472	-2,201	-3,053	-4,000
Si	+1,348	+1,128	+0,980	+0,877	+0,803
$O^M$	-0,551	-0,595	-0,637	-0,674	-
$O^K$	-	-0,813	-0,953	-1,084	-1,201
$O^K/Si$ Ratio	0	1	2	3	4
Similar motive or system	Silica $SiO_2$	Sheet sili- cates $[Si_2O_5]^{2-}$ $[Si_4O_{10}]^{4-}$	Chain inosilicates $[Si_2O_6]^{4-}$ $[Si_4O_{11}]^{6-}$ Ring silicates $[Si_3O_9]^{6-}$ $[Si_5O_{15}]^{10-}$	Diorthosilicates $[Si_2O_7]^{6-}$	Orthosilicates $[SiO_4]^{4-}$

The chemical changes of inner electron levels of the element, i.e. structure-forming element of silicon within the complex silicon compounds, are determined by the value of the negative formal charge  $z^\phi$  together with the other factors. Polymerization of silicon dioxide  $\text{SiO}_2 \rightarrow [\text{Si}_x\text{O}_y]^{z^-}$  is accompanied with the charge accumulation within the elementary silicate-ion, the increase of  $z^\phi$  from 0 till -4, and substitution of cross-linking bonds into finishing ones that leads to the changes of the binding energy. The defined interrelation of effective charges  $z^{\text{eff}}$  and  $z^\phi$  brings to the following conclusion: the changes in the number of external modifiers of Mn, Ca, Mg redistribute the binding electron density and pose the atom of oxygen closer to the modifier.

The changes in the binding energy  $E_{ce}$  (Si 2p) of the test samples correlate with the changes of the structural motive in the process of  $\text{SiO}_2$  polymerization with silicate formation that include two-layer stack of kaolinite group  $[\text{Si}_4\text{O}_{10}]^{4-}$ ; double anion chains  $[\text{Si}_4\text{O}_{11}]^{6-}$  (double chain metasilicates); single anion chains  $[\text{Si}_2\text{O}_6]^{4-}$ , both ring silicates  $[\text{Si}_3\text{O}_9]^{6-}$  and  $[\text{Si}_5\text{O}_{15}]^{10-}$ , and the groups of silicates with isolated tetrahedrons: ortho- and diorthosilicates –  $[\text{SiO}]^+$  and  $[\text{Si}_2\text{O}_7]^{6-}$ .

It increases the number of oxygen atoms by 1 silicon atom relatively in a row  $2 \rightarrow 2,5 \rightarrow 2,75 \rightarrow 3 \rightarrow 3,5 \rightarrow 4$  and decreases the number of cross-linking oxygen atoms ( $\text{O}^M$ ):  $2 \rightarrow 1,5 \rightarrow 1,25 \rightarrow 1 \rightarrow 0,5 \rightarrow 0$ .

XPS spectra of modeled samples of MnO-SiO<sub>2</sub> and MnO-CaO-SiO<sub>2</sub> systems are presented by the peaks where  $E_{ce} = 102,6$  and  $102,4$  eV relatively (see Figure 3.1) that corresponds to rhodonite and bustamite minerals. Rhodonite comprises coordinate group  $[\text{Si}_5\text{O}_{15}]^{10-}$  and is reflected in the structural formula  $\text{Mn}_5[\text{Si}_5\text{O}_{15}]$ . MnO-CaO-SiO<sub>2</sub> system sample can correspond to bustamite which is rhodonite-wollastonite group. Bustamite is rhodonite that contains calcium. It is a mineral that changes from rhodonite to wollastonite. The difference in  $E_{ce}$  (Si 2p) is, first of all, explained by the unequal length of the motive that is formed around the modifier. Wollastonite (wollastonite chain) corresponds to the triple tetrahedron orientation which means that every third tetrahedron has the equal position according to the axis of symmetry, whereas in rhodonite it corresponds to every fifth tetrahedron.



**Figure 4.2:** The dependence of chemical changes ( $\Delta E_{ce}$ ) Si 2p-levels on the formal charge ( $z^\phi$ ) of a simple tetrahedron for the test samples and some compounds: ×(1-7) - data [17]; 1-CaMg[SiO<sub>4</sub>]; 2-Ca<sub>2</sub>Mg[Si<sub>2</sub>O<sub>7</sub>]; 3-Ca<sub>3</sub>[Si<sub>3</sub>O<sub>9</sub>]; 4-CaMn<sub>4</sub>[Si<sub>5</sub>O<sub>15</sub>]; 5-CaMg[Si<sub>2</sub>O<sub>6</sub>]; 6-Al<sub>4</sub>[Si<sub>4</sub>O<sub>10</sub>]·(OH)<sub>8</sub>·n H<sub>2</sub>O; 7- $\alpha$ -cristobalite; received results in the present study: ▲ -MnO-SiO<sub>2</sub>; ⊙ — MnO-CaO-SiO<sub>2</sub>; ▲ -charge manganese slag; ■ - metallic manganese slag; □ - ferrosilicon-manganese slag; ● -oxide concentrate; ⊙ - carbonate concentrate.

XPS spectra of oxide and carbonate concentrates represent a complex pattern, as it is seen in Figure 3.1 a, b. The results reported in Table 3.1 show that both to the left and to the right of the maximum peak where  $E_{ce}=103,0$  and  $103,2$  eV for oxide and carbonate concentrates there are peaks that correspond to the definite energy state of the silicon inner electron level. It shows that the character of changes in XPS spectra for both concentrates is almost identical. The shift of carbonate concentrate peaks towards higher values is explained by the influence of carbonate groups  $[\text{CO}_3]^{2-}$  that cause the increase of  $E_{ce}$ . The first peak where  $E_{ce} = 101,6 - 101,7$  eV corresponds to the silicates of olivine group with ortho- and diortho-silicate-ions  $[\text{SiO}_4]^{4-}$  and  $[\text{Si}_2\text{O}_7]^{6-}$  which are reflected in a general formula  $\text{R}_2[\text{SiO}_4]$ , where R —  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ . The first three cations form individual silicates (tephroite —  $\text{Mn}_2[\text{SiO}_4]$ ) and isomorphous compounds (knebelite —  $(\text{Mn,Fe})_2[\text{SiO}_4]$ ), calcium forms double salt (monticellite —  $\text{Ca, Mg}[\text{SiO}_4]$ ).

It is shown in the research [15] that in minerals and slags of  $\text{Me}_2\text{SiO}_4$  (Me — Be, Mg, Ca, Mn, Fe, Ni, Zn) type  $\text{Be}^{2+}$  coordination is quaternary;  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$  is hexad;  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$  is hexad and above. It is noted that  $\text{Be}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$  cannot be isomorphically substituted with other cations.

Manganese hexad coordination in silicates matches the chosen mathematical model of the cluster that is used by the authors for the theoretical analysis as well as the data [18] taken from the theory of chemical elements structure and compounds based on statistic model of atom electron composition in the framework of the Periodic system. The peaks where  $E_{ce} = 102,0 - 102,1$  eV demonstrate that silicon appears in silicate anions with single chains of pyroxene

$[\text{Si}_2\text{O}_6]^{6-}$ , wollastonite  $[\text{Si}_3\text{O}_9]^{3-}$ , rhodonite  $[\text{Si}_5\text{O}_{15}]^{10-}$  groups where bustamite is likely to be the leading complex which matches modeled samples most of all.

The maximum peak where  $E_{ce} = 103,0 - 103,2$  eV corresponds with continuous tetrahedron sheets (double chain metasilicates) with the anion  $[\text{Si}_4\text{O}_{11}]^{6-}$  or dimetasilicates  $[\text{Si}_8\text{O}_{22}]^{12-}$  of the amphibole group as well as with the silicates of kaolinite group with two-layer stacks with anions  $[\text{Si}_4\text{O}_{10}]^{4-}$  that is typical for clay gang of manganese ores.

Anion part of dimetasilicates  $[\text{Si}_2\text{O}_5] \cdot (\text{OH})$  forms hexa-rings where silicon can be substituted with aluminium that forms aluminosilicate ion  $[(\text{SiAl})_4\text{O}_{10}]$ . To the right of the maximum peak there are two other peaks where  $E_{ce} = 103,4 - 103,5$  and  $103,7 - 103,8$  eV for oxide and carbonate concentrates, respectively. The first peak reflects the chemical changes of silica which is presented by silicon hydroxyls. The second corresponds to quartz, lechatelierite and  $\alpha$ -cristobalite whose existence is proved in the research [19]. Silicon hydroxyl groups can react with manganese hydroxyls through adsorption or  $\text{OH}^-$ ,  $\text{Cl}$ ,  $\text{F}$ ,  $[\text{PO}_4]^{3-}$ ,  $[\text{CO}_3]^{2-}$  anion exchanges.

Unclear nature of maximum level for industrial manganese slags shown in figure 3.1 *c-e* are first of all explained by their multicomponent structure as well as forming a range of silicate-ion groups on the basis of two silicon oxyanions:  $[\text{SiO}_4]^{4-}$  and  $[\text{Si}_2\text{O}_7]^{6-}$  for metallic manganese and charge slags and  $[\text{Si}_3\text{O}_9]^{6-}$  and  $[\text{Si}_2\text{O}_6]^{4-}$  for ferrosilicon-manganese slags.

Metallic manganese slags are mainly presented (in decreasing order) by the following components that comprise silicon: glaucophroite  $\text{CaMn}[\text{SiO}_4]$ , tephroite  $\text{Mn}_2[\text{SiO}_4]$ , calcium orthosilicate  $\text{Ca}_2[\text{SiO}_4]$ , rankinite  $\text{Ca}_3[\text{Si}_2\text{O}_7]$ , and stishovite. The basis of charge slag comprises tephroite  $\text{Mn}_2[\text{SiO}_4]$ , monticellite –  $\text{Ca,Mg}[\text{SiO}_4]$ , picrotephroite  $(\text{Mn,Mg})_2[\text{SiO}_4]$ , spessartite  $\text{Mn}_3\text{Al}_2[\text{SiO}_4]_3$ , and  $\alpha$ -quartz.

X-ray structural, IR spectroscopic, micro X-ray spectral and differential thermal analyses have proved that in slowly cooled industrial slags of ferrosilicon-manganese there appear silicon comprising phases: bustamite  $\text{Mn}_4\text{Ca}[\text{Si}_5\text{O}_{15}]$ , rhodonite  $\text{Mn}_5[\text{Si}_5\text{O}_{15}]$ , enstatite  $\text{Mg}_2[\text{Si}_2\text{O}_6]$ , aluminosilicate  $\text{Ca}_{1,82}\text{Al}_{3,64}\text{Si}_{10,36}\text{O}_8$ , and  $\alpha$ -quartz. The existence of free  $\text{SiO}_2$  in metallic manganese slags can be explained by additional decomposition of  $\text{Ca}_2[\text{SiO}_4]$  into molecular  $\text{CaO}$  and stishovite (artificial silica) under extremely high pressure created in a closed vessel, that is caused by the transformation of  $\beta$ - $\text{Ca}_2[\text{SiO}_4]$  into  $\gamma$ - $\text{Ca}_2[\text{SiO}_4]$  accompanied by the increase in the volume by 12,3%.

As it has been shown [20], the existence of  $\alpha$ -quartz and ferrosilicon-manganese slags is explained by the liberation of cristobalite in the process of crystallization. The existence of the peaks at XPS spectra for metallic manganese slags where  $E_{ce} = 103,69$  eV and ferrosilicon-manganese slags where  $E_{ce} = 103,8$  eV correspondingly is explained by the existence of the silica phase.

## 5. CONCLUSIONS

The results of studying binding energy of the silicon frame electron levels in modeled samples of  $\text{MnO-SiO}_2$ ,  $\text{MnO-CaO-SiO}_2$  systems, both manganese oxide and carbonate concentrates, manganese slags alongside with theoretical analysis of silicate-ion  $[\text{SiO}_4]^{4-}$  structure and properties in terms of their electron composition proves that the chemical changes of silicon internal electron levels are affected by transformation of  $\text{Si-O-Si} \rightarrow \text{Si-O-Si-O-M}$  bonds, i.e.  $\text{SiO}_2 \rightarrow [\text{Si}_x\text{O}_y]^z$ ; crystal chemical structure changes in a range of  $\text{SiO}_2 \rightarrow [\text{Si}_4\text{O}_{10}]^{4-} \rightarrow [\text{Si}_2\text{O}_6]^{6-} \rightarrow [\text{Si}_5\text{O}_{15}]^{10-} \rightarrow [\text{Si}_2\text{O}_7]^{6-} \rightarrow [\text{SiO}_4]^{4-}$  and electron composition of silicon-oxygen tetrahedron.

The substitution of cross-linking bonds into finishing ones leads to the accumulation of the negative charge on an elementary silicate-ion  $[\text{Si}_x\text{O}_y]^z$ . It also leads to the increase of its effective and formal charge as well as decrease of effective charge on silicon atom.

The rise in number of external modifiers (Mn, Ca, Fe, Mg) decreases the binding energy of silicon frame electron levels  $E_{ce}$  (*Si 2p*) resulted from conventional average radius  $\bar{r}$  Si-O changes. Alongside with the increase in the formal charge of a simple tetrahedron during  $\text{SiO}_2 \rightarrow [\text{SiO}_4]^{4-}$  transformation the binding electron density redistributes closer to the oxygen atom which is oriented towards modifier.

Electron density redistribution towards silicon atom and the decrease in balance distance ( $\text{Si-O}^K$ ) in silicate manganese meltngs causes extra thermodynamic difficulties in breakages of Si-O-Mn bonds while reducing the cation of manganese modifier. It also determines the inevitability of both manganese and silicon reduction as a result of the relation of final oxygen with the structure-forming element and modifier. The formation of longer manganese-based silicate chains compared to magnesium- and calcium-based ones can indicate their immediate disordering affected by various factors (like heating, the presence of reductants).

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