The investigation of phosphorus chemical bond in the manganese-ore materials

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ABSTRACT

The order of phosphorus chemical bond in the monomineral differences, oxide and carbonate concentrates of manganese ores has been investigated using X-ray photoelectron spectroscopy and by means of theoretical analysis based on the quantum chemistry. The phosphorus is in four energy states expressed by bond energy: 132.4; 133.3; 134.5 and 135.8 eV. The chemical shift of P2*p*-levels is driven by phosphorus chemical bond with cations being present in manganese ores and being in different valence state; formation of island, ring and chain orthophosphates and di-orthophosphates; transfer of electron density from the phosphorus atom to the central modifying cations. Thus, the presence of direct chemical bond of phosphorus and manganese in the manganese-ore minerals has been clearly established.

1. INTRODUCTION

The order of phosphorus chemical bond in the oxide and carbonate manganese ores determines foremost the choice of technology for beneficiation and production of low-phosphorus manganese raw materials using mechanical, chemical, hydro- and electrometallurgical methods, as well as the efficiency of their implementation in the production.

The dephosphorization degree of max 30% is mainly achieved due to the impossibility of complete separation of manganese and phosphorus using the existing methods of manganese ore beneficiation (washing, gravity jigging, magnetic separation, flotation). However, there is no unambiguous scientific explanation of this fact in literature and further thorough examination of fine structure of manganese ore mineral constituents and disclosure of order of phosphorus chemical bond in the manganese-ore minerals are of great importance.

The member of the Academy of Sciences A.G. Betekhtin [1], in his earlier papers, gave suggestions that the major part of phosphorus in the manganese ores is bonded with manganese and this bond is distinguished by absorption nature.

The investigations [2-4] established the connection between manganese and phosphorous content in the products at all beneficiation stages. The IR spectrometry demonstrated that phosphorus is mainly represented by orthophosphate group $[PO_4]^{3-}$ with predominant bond with manganese. The inclusions with P, Ca, Fe complex has been revealed in the mineral composition differences of psilomelane ($MnO{\cdot}MnO_2{\cdot}nH_2O$) and pyrolusite ($MnO_2$). The pyrolusite ore component includes manganapatite containing (in %) 6.0 P_2O_5; 3.90 MnO; 61.01 MnO_2; 3.23 CaO; 0.87 MgO; 4.33 SiO_2; 1.87 Al_2O_3; 1.98 (Na_2O + K_2O); 1.91 CO_2; 0.64 F; 3.12 H_2O, in which the isovalent substitution of Ca^{2+} by cation Mn^{2+} may occur. Mn-containing phosphates are represented by mangan-fluorapatite (Ca_{5-x}, Mn_x) $(PO_4)_3F$ and silica-fluorapatite $(Ca_{10-x}, Mn_x)(PO_4)_2$ $(Si_4)_3F_2$. In the gangue, phosphorus appears as francolite $Ca_5\,(PO_4CO_2)_3F$, fluorapatite $Ca_{10}\,(PO_4)_6F_2$ and hydrohylapatite $Ca_5(PO_4)_3OH$. The carbonate apatite is the main P-containing mineral in the gangue almost in all carbonate manganese ores and bonded with manganocalcite and calcium rhodochrosite [5].

However, there is a standpoint [6] that the main part of phosphorus is in close association with non-metallic minerals, which are located between the crystalline individuals of oxide manganese minerals.

The analysis of manganese ore beneficiation does not support this argument [6], since the dephosphorization degree does not exceed 30% irrespective of the ore-grain release degree at various beneficiation stages.

When washing the base ores, phosphorus being under transformation into sludge is represented by calcium phosphates, however, over 85% of phosphorus remains in the washed ore, which evidences its close bond with ore component.

During gravity preparation with increase in the density of fractions from 2.4 to 3.2 g/cm^3, and, consequently, with Mn content growth, the phosphorus redistribution is attributed to the ore oxidation degree and the ratio of $\frac{\%P}{\%Mn}$ in the final product grows, when manganite ($MnO{\cdot}OH$) compound increases in the ores.

The investigations of magnetic separation products show that considerable part of phosphorus in them is represented by Mn-containing minerals and its absolute content increases directly proportional to the manganese increase in the concentrate. Only up to 15% of phosphorous is removed in tailings.

The study of possibility to beneficiate mineral differences of manganese ores: carbonate apatite, manganite, pyrolusite, psilomelane (Ca, Mn) CO_3 and calcium rhodochrosite (Mn, Ca) CO3 using flotation methods demonstrated that pyrolusite, manganocalcite and psilomelane are harder to be beneficiated. Thus, the direct relationship between the manganese and phosphorous recovery into marketable products has been evidenced.

In the paper [6], the correlation relationship between the manganese and phosphorus content in the beneficiated and non-beneficiated ore fractions is explained by the mechanical redistribution of phosphate components, mainly related to non-metallic grains of the gangue that, in our opinion, is debatable.

2 EXPERIMENT

The presence of fine-grained phosphorous in the ores (2-4 μm) imposes restrictions on possibilities of the conventional investigation methods. In the present paper, the order of phosphorus chemical bond has been investigated based on the analysis of bond energies of external electron levels of phosphorus atom in different manganese-ore materials. The samples of the main mineral differences of oxide ores from Nikopol deposits – pyrolusite (β-MnO_2), manganite ($MnO_2 \cdot Mn(OH)_2$), psilomelane ($MnO \cdot MnO_2 \cdot nH_2O$), as well as oxide and carbonate concentrates, the chemical composition of which is presented in Table 2.1, were used as the investigation objects.

Table 2.1: Chemical composition of manganese minerals and concentrates, % wt

Material	MnO	MnO_2	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	LOI
Natural materials:											
pyrolusite manganite	**4.6**	**79.80**	**0.9**	**4.6**	**0.12**	**2.12**	**0.90**	**0.46**	**0.33**	**0.595**	**9.06**
psilomelane	**31.3**	**49.20**	**1.1**	**3.4**	**0.17**	**13.40**	**0.20**	**0.56**	**0.24**	**0.612**	**5.32**
Concentrates:	**4.3**	**62.30**	**2.3**	**9.2**	**1.15**	**1.30**	**1.44**	**1.04**	**0.76**	**0.573**	**7.36**
oxide											
carbonate	**8.1**	**57.15**	**6.05**	**16.1**	**2.94**	**2.71**	**1.05**	**1.46**	**0.62**	**0.530**	**10.2**
	37.3	**-**	**3.85**	**11.9**	**2.00**	**12.10**	**2.22**	**0.31**	**0.22**	**0.480**	**29.6**

The investigations were carried out with electron spectrometer ES-2402, which makes it possible to evaluate the electronic structure of solids by energy distribution of electrons emitted under X-ray exposure. The X-ray tube with magnesium anode and maximum permitted capacity of 300 W (anode current is 30 mA, anode voltage is 10 kV) was used as X-ray source. The vacuum in the analytical chamber of the spectrometer was $1 \cdot 10^{-7}$ Pa.

The absolute spectrometer resolution measured by $4f_{7/2}$-golden peak was 1.2 eV, when the analyzer transmission energy *Ean* is 50 eV and intensity is $5 \cdot 10^{-4}$ imp/s. The spectrometer was calibrated by Fermi edge in nickel using magnesium radiation. The bond energies at the extreme points of energy range were E_{bond} (Au$4f_{7/2}$) = 84.0 and E_{bond} (Cu$2p$) = 932.6 eV. The scanning voltage assigned by the program was set within 0.09 eV at U_{scan} = 1000 V, which was controlled by digital voltmeter. The reproducibility of Au$4f_{7/2}$ line maximum position was ± 0.025 eV. The closed circuit with anode cooling by distilled water was used to reduce the leak current of X-ray tube anode.

The aluminum shields with inlet and outlet openings for X-ray photon beam and photoelectron flux respectively were used to eliminate the inequality of the surface charging of the non-conductive specimens in question. *C*1*s*-line was used as calibration spectrum for recording the surface charging magnitude. The magnitude of maximum bond energy of 285.0 eV was set for the above mentioned line. The time for one spectrum accumulation was 10-50 minutes. The selected scanning pitch was 0.025 eV.

The material powders prepared by abrasion of coarse-grained samples in air (in the agate mortar) were employed as investigation objects.

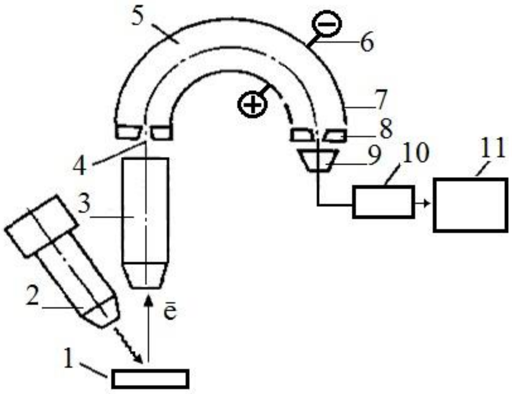

Figure 2.1: Schematic diagram of X-ray photoelectron spectrometer ES-2402

The schematic diagram of the above described spectrometer is presented in Fig. 2.1. The ionizing radiation flux from X-ray tube *2* is directed to the specimen *1* with the area of 1 cm^2, fixed on the manipulator in the analytical chamber. The electrons emitted by the specimen enter the electron-optical lens *3*, which focuses them onto the entrance slit *4* and restrains to the transmission energy of electric analyzer *5* equipped with spherical capacitor *6*. Using the adjusting electrode *7*, the electron flow through the exit slit *8* is directed to the detector *9*, which is represented by channel electron multiplier that enables immediate recording of the spectrum and its transmittance to the counter *10*, compatible with ECM *11*, which makes discrete recordings of spectra of emitted electrons.

The electrons emitted by the sample, entering the hemispherical analyzer, are subjected to the spatial separation induced by the electrostatic field, depending on their kinetic energy, and enter the channel electron multiplier (with the relevant energy), which is represented by the device with continuous diode surface. The signal is extracted in the single-electron pulse counting mode. The pulses, from output of the electron multiplier, successfully enter the pulse counter through the matching unit, where they are amplified, discredited by amplitude and transmitted to the ECM data entry for collection and processing.

3. RESULTS

The experimental data obtained during the investigations are presented as spectrograms, which coordinate the intensity I, imp/s at the given point and the bond energy E_{bond}, eV (Fig. 3.1).

The X-ray photoelectron spectra of the main levels of phosphorus - P2*p*, manganese - Mn2*p*, calcium - Ca2*p*, silicon - Si2*p*, potassium - K2*p*, oxygen - O1*s* were taken, interpreted and analyzed. The spectrum of the main phosphorus level with maximum of E_{bond} = 285.0 eV used for further adjustments of other spectra in case of deviations of spectrum E_{bond} from the tabulated value, as provided by standard procedure [7, 8] was taken as reference.

Table 3.1 shows the experimental values of bond energies (E_{bond}) of electronic 2p-levels of phosphorus for the materials in question.

Table 3.1: Bond energies of internal electron 2p-level of phosphorus of monomineral fractions and concentrates of manganese ores

Material	Ebond, *EV*, corresponding to the peaks			
	1	2	3	4
Natural materials:				
pyrolusite	132.4	133.3	134.4	135.8
manganite	132.4	133.3	134.4	135.8
psilomelane	132.5	133.3	134.4	135.8
Concentrates:				
oxide	132.4	133.3	134.5	135.8
carbonate	132.5	133.5	134.4	135.8

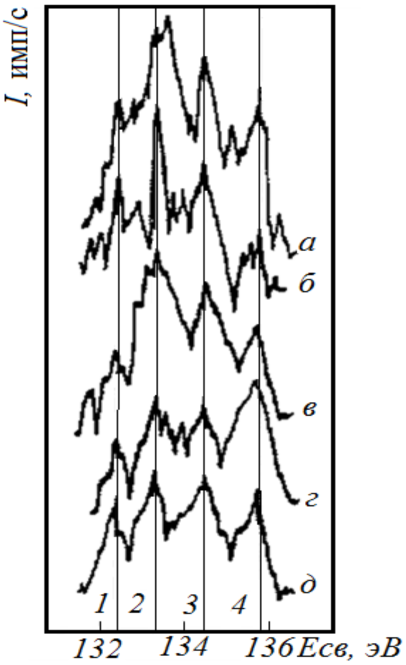

Figure 3.1: X-ray photoelectron spectra of electron 2*p*-levels of phosphorus in the manganese-ore materials: *a* — pyrolusite; *b* — manganite; *c* — psilomelane; *d* — oxide concentrates; *e* — carbonate concentrate.

The sequential comparison of spectra for mineral differences and concentrates demonstrated that phosphorus appears in the main four peaks (*1-4),* corresponding to E_{bond} = 132.4; 133.3; 134.5 and 135.8 eV (Fig. 3.1). All four types of peaks are most clearly expressed for oxide manganese concentrate (Fig. 3.1 *d*).

X-ray photoelectron spectroscopy based on the photo-effect phenomena using monochromatic X-ray makes it possible to determine the energy of electron levels of phosphorus atom in question on the basis of the measured kinetic energy of photoelectrons.

The fundamental equation used to describe the photoelectron process is Einstein's equation:

$$h\nu = E_{kin}^{'} + E_{K}^{'f} - E^{i} , \qquad (3.1)$$

where, $h\nu$ is photon energy; E^{i} is total initial atom energy; $E_{kin}^{'}$ is kinetic energy of knock-on electron; $E_{K}^{'f}$ is total atom energy in the final state after electron departure from state with quantum number K:

$$E_{K}^{'f} = E_{K}^{f} - E^{r} , \qquad (3.2)$$

where, E^{r} is recoil energy (Er = 0.1 eV for valence lithium electrons and 0.04 eV for sodium at excitation energy of $h\nu$ = 1500 eV) and it can be ignored. Subsequently, the expression (2.1) simplifies to:

$$h\nu = E_{kin}^{'} + E_{K}^{f} - E^{i} , \qquad (3.3)$$

where, $E_{K}^{f} - E^{i}$ is energy required for removal of electron at infinity with zero kinetic energy that characterizes the bond energy level:

$$E_{bond(K)} = E_{K}^{f} - E^{i} , \qquad (3.4)$$

subsequently:

$$E_{bond} = h\nu - E_{kin}^{'} . \qquad (3.5)$$

If we know hv and E'_{kin} of knock-on electrodes, we can estimate the bond energy of external electron levels of phosphorus atom. As part of the electrostatic model of chemical shift:

$$E_{bond} = Kq + E_{Mad} - E_{rel} , \qquad (3.6)$$

where, q is effective atom charge in the compound; E_{Mad} is Madelung potential describing the interaction of electrons of atom in question with nuclei and electrons of the entire molecule; E_{rel} is relaxation energy describing the impact of changes in the atom wave functions after photoelectron removal, as well as redistribution of electron density between the atoms in the molecule.

4. DISCUSSIONS

Each chemical element has its own specific number of values for E_{bond} for inner electrons. The changes in the charge configuration in the valence shell of element atom attributed to the change in degree of its oxidation, coordination and bond character result in variations of E_{bond} of core levels (chemical shift), which is the main source of information about chemical bond character.

As it is known from quantum chemistry [9], the valence serves as a quantitative measure of atom capability to form the chemical bonds. However, well-defined bond corresponds to each integral-valued valence state in the molecule. These bonds differ in energy, length, polarity and orientation in space (σ -, π -bonds). We can evaluate the character of chemical bond accompanied by the recombination of valence electronic atom shell and electron collectivization based on the bond energy of internal electron levels of phosphorus as the main characteristic of valence state of phosphorus atom in combination. The character of chemical bond is described by chemical structure of molecules (topology), spatial structure (nuclei location and motion in space) and electronic structure (orientation and location of electron density).

The chemical shift (ΔE_{bond}) of internal electron levels serves as a characteristic of atom state change during its transmission from element into compound (molecule). The bond energy of inner electron in the free atom is composed of interaction energy between the electron and atomic nucleus, kinetic energy, энергии interaction energy with other electrons and valence electrons.

In conjunction with electron bond energy in the atom, the bond energy of the mentioned electron with other electrons and nuclei will be added. Since the wave function of inner electron is different from zero in the immediate vicinity of its nucleus and overlapping of wave functions of electrons of other atoms is extremely small, the wave function of inner atom electron slightly changes during transformation from the atom to the compound. As a consequence, the change in bond energy during transformation from the free atom to the compound will be mainly caused by the changes in the interaction energy of inner electron with valence electrons [8]. Thus, the value of chemical shift is determined by difference of bond energies in the compound and in the atom:

$$\Delta E_{bond} = E_{bond\,(M)} - E_{bond\,(A)} \qquad (4.1)$$

The bond energy of internal electron 2*p*-levels of phosphorus equal to 130.1 eV [8] was taken as reference one.

The changes in the bond energy or chemical shift ΔE_{bond}, as the analysis shows, is primarily attributed to the variation of the valence state of the atom itself and the valence state of atoms of the nearest neighbors, spatial (nuclear) and electronic structure of the compound and motives included in it.

It has been established that chemical shift of inner electrons in the compound depends linearly on the total number of valence electrons n and formal oxidation level N:

$$\Delta E_{bond} = CnN, \qquad (4.2)$$

where, C is a constant. The positive chemical shift of X-ray electron line of the element in the compound has the upward trend, when the formal positive oxidation degree increases. However, the ranges of bond energy values for different oxidation degrees may be overlapped. The shift of X-ray electron line depends on the formal oxidation degree of the element and the negative charge of the complexes. When the positive oxidation degree increases, the electron density on the element decreases and the general upward trend of bond energy with oxidation degree level is observed.

To determine the oxidation degree of the element by chemical shift of X-ray electron line, it is necessary to take into account the immediate environment character of the element in question. When the oxidation increases by one unit, the line shift increases by about 1 eV, if the anionic complexes remain unchanged [8].

Let us analyze the changes in the bond energy (E_{bond}) and chemical shift (ΔE_{bond}) of internal electron 2p-levels of phosphorous in the isoelectronic compounds of type $Me_n[P_xO_y]^{z-}$ in terms of the impact of change in the valence condition of the nearest neighboring cation *Me* and in the charge of phosphorus-oxide complex $[P_xO_y]^{z-}$. Keeping in mind the principles [8] established for oxides [8], it is conceivable that for the phosphate compounds $Me_n[PO_4]^{3-}$ (*Me* is modifying cation; P is phosphorus-element-structure-forming agent), the shift ΔE_{bond} of electron 2p-levels of phosphorus shall increase along with the increase of valence state of modifying cation. With due regard for the complex chemical composition of pyrolusite, manganite, psilomelane, oxide and carbonate manganese concentrates in question (Table 2.1), it is reasonable to expect that bond energy of internal electron 2p-levels of phosphorus shall vary due to the different valence state of neighboring modifying cations (К^{+}, Na^{+}, Ca^{2+}, Мп^{2+}, Мп^{3+}, Мп^{4+}, Fe^{3+}).

It is usual that phosphorus as element-structure-forming agent forms the orthophosphate motive $[PO_4]^{3-}$ with all the modifying cations. The linear dependence ΔE_{bond}-nN (Fig. 4.1) meets the regular changes ΔE_{bond} of electron 2p-level of phosphorus in the compounds with various modifying cations of II period. In such a case, the following compounds $K_3^{+}[PO_4]^{3-}$, $Ca_3^{2+}[PO_4]_2^{3-}$, $Fe^{3+}[PO_4]^{3-}$, $Mn_3^{2+}[PO_4]_2^{3-}$, $Mn^{3+}[PO_4]^{3-}$, $Mn_3^{4+}[PO_4]_4^{3-}$ are formed. It is evidence that there is a direct bond of phosphorus with manganese in the valence state Mn^{2+}, Mn^{3+}, Mn^{4+}, the presence of which has been established upon the obtained results of spectra of electron 2p-levels of manganese.

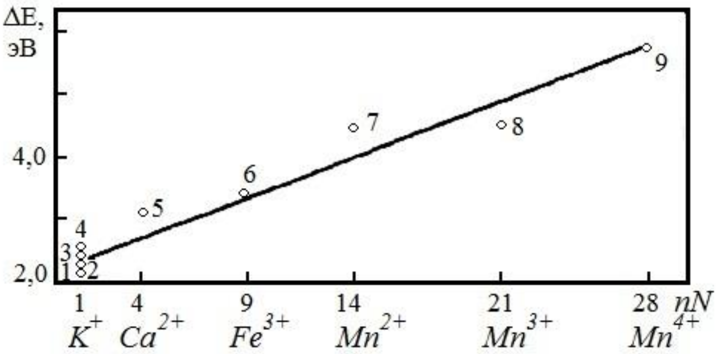

Figure 4.1: The relationship between the chemical shift of P2p-levels and formal oxidation level of modifier in the compounds: *1* — Ag_3PO_4; *2, 3* — К_3PO_4; *4* — Na_3PO_4; *5* — $Ca_3(PO_4)_2$; *6* — $FePO_4$; 7 — $Mn_3(PO_4)_2$; *8* — $MnPO_4$; *9* — $Mn_3(PO_4)_4$. *1, 2, 4, 6* — the present papers [8]; *3, 5,* 7-9 — the results of the present paper.

The peaks of bond energies of core electron levels of phosphorus of high intensity for mineral differences of pyrolusite, manganite, and psilomelane identify the presence of its crystal-chemical bond with 3d-transition metals Mn^{2+}, Mn^{3+}, Mn^{4+}, Fe^{3+} and cannot be explained only be gangue presence, as evidenced in the paper [6].

As noted previously, the chemical shift of the internal electron levels of element-structure-forming agent of phosphorus in combination with the same modifying elements is also determined by the negative charge (z) value of complex anion $[P_xO_y]^{z-}$.

The basis of spatial coordination of dimeric phosphorous oxide P_4O_{10} is represented by molecule-cell with tetrahedral packing of four oxygen atoms around one phosphorous atom at six bridging oxygen atoms O^M, bonding the phosphorous atoms and four unbound oxygen atoms O^O. If the phosphorus oxide dimer is polymerized by modifying cations Mn^{2+}, Mn^{3+} и Mn^{4+} the phosphorous-oxide motives of island $[PO_4]^{3-}$, ring $[P_3O_9]^{3-}$ and chain $[P_3O_{10}]^{5-}$ types and diorthophosphate $[P_2O_7]^{4-}$ (Fig. 4.2) may be released.

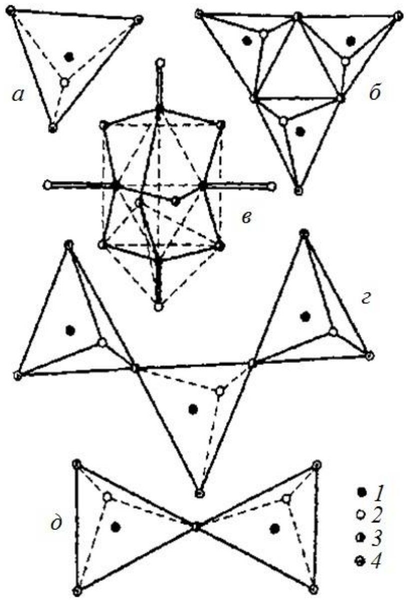

Figure 4.2: Topology (structure formula) of dimeric phosphorous oxide molecule and spatial structure of phosphorus-oxide motives of tetrahedral coordination: *a* — island orthophosphate motive $[PO_4]^{3-}$; *b* — ring motive $[P_3O_9]^{3-}$; *c* — dimer P_4O_{10}; *d* — chain motive $[P_3O_{10}]^{5-}$; *e* — diorthophosphate motive $[P_2O_7]^{4-}$; *1* — phosphorus atom; *2* — unbound oxygen (O^O); *3* — bridge oxygen (O^M); *4* — end oxygen (O^K).

Table 4.1: Chemical shift of 2p-levels of phosphorus for various phosphorus-oxide motives in the compounds with Na [8] and Mn (data indicated in the present paper)

Metal	**ΔE_{bond}, eV for motive**			
	$[PO_4]^{3-}$	**$[P_3O_9]^{3-}$**	**$[P_2O_7]^{4-}$**	**$[P_3O_{10}]^{5-}$**
Na	**2.2**	**2.3**	**3.0**	**4.0**
Mn	**3.1**	**3.1**	**4.4**	**5.7**

The comparison of calculated values ΔE_{bond}, phosphorus of 2p-levels (Table 4.1) for manganese phosphate with literature data for analogous sodium phosphates shows that regular increase of shift ΔE_{bond} is observed with increase in the negative charge (Z) of anion $[P_xO_y]^{z-}$ with change in the valence state of neighboring modifying cation from Na^+ to Mn^{4+}. In such a case, the more the cation valence is, the greater the value of ΔE_{bond}, phosphorus of 2p-levels is. The reason for change in the bond energy of each atom in the compound is a redistribution of electron density between the modifier atoms and the structure-forming agent atoms in the complex anionic motives. In these conditions, when the chemical shift of internal electron levels of atom in the compound increases, the electron density for the atom is reduced.

Thus, the increase in the bond energy of 2p-levels of phosphorus, which is observed after coordination of phosphorus-oxide motive by transition metal (Mn) shows the transfer of density from the phosphorus atom to the central atom. When the negative charge (*z*) anion $[P_xO_y]^{z-}$ in the row $[PO_4]^{3-} \rightarrow [P_2O_7]^{4-} \rightarrow [P_3O_{10}]^{5-}$ changes, the number of oxygen atoms is decreased by 1 phosphorus, from 4 to 3.5 and 3.3 respectively and the number of bridging oxygen atoms increases from 0 to 1 and 2.

The bridging oxygen atoms (O^M) in the anionic motives are more stably bonded than the end ones (O^K) and the bond energy O^M in the complexes is greater than bond energy O^K.

Relying on theoretical analysis of experimental and literature data and considering the complex chemical composition of natural manganese minerals, oxide and carbonate concentrates, it is possible to state that four energy states of internal electron 2p-levels of phosphorus are attributed to the difference of valence conditions of the nearest neighboring modifying cations K^+, Na^+, Ca^{2+}, Fe^{3+}; manganese presence in three valence states (Mn^{2+}, Mn^{3+}, Mn^{4+}); change of structural motive $[PO_4]^{3-}$ within one coordination group in the form of ring $[P_3O_9]^{3-}$ and chain $[P_3O_{10}]^{5-}$ ortho- and diorthogroups $[P_2O_7]^{4-}$ with increase in the bridging oxygen portion; transfer of electron density from the phosphorus atom as a structure-forming agent to the central modifying atom - manganese.

In X-ray photoelectron spectrograms, the peaks *1* and 2 (Fig. 3.1) complies with orthophosphates K_3PO_4, $(KNa)_3PO_4$ with E_{bond} = 132.4 and $Ca_3(PO_4)_2$ with E_{bond} =133.3 eV, in which the island tetrahedrons $[PO_4]^{3-}$ have no common bond; the bridging oxygen O^M is not available at three end oxygen atoms O^K (Fig. 4.2). This energy state of internal electron 2p-levels of phosphorus in the specimen in question is attributable to the phosphorus inclusion in the mineral composition of apatite, hydrohylapatite, fluorapatite, carbonate apatite and manganapatite. In the apatite structure, the calcium and oxygen (fluorine) atoms are combined into rhombohedral prism of two types, which are bonded with PO_4-tetrahedrons. The last one can be interchanged in the carbonate apatite: $[PO_4]^{3-} \leftrightarrow [CO_3OH\ ]^{3-}$.

The peaks *3* and *4* (Fig. 3.1) are attributable to the formation of diorthophosphates (E_{bond} = 134.5 eV) on the basis of phosphorus-oxide motives $[P_2O_7]^{4-}$ with one bridging oxygen atom O^M and four end oxygen ions O^K, transferring the electron density from the phosphorus atom to the central atom on the basis of 3*d*-transition metals Mn^{2+}, Fe^{3+}, which form the complexes of type $[Mn_2P_2O_7]$, $[(Mn,Fe)_2P_2O_7]$, $[Fe_4(P_2O_7)_3]$. The peak *4* (E_{bond} = 135.8 eV) distinguishes the formation of diorthophosphate $[P_2O_7]^{4-}$ and chain fluorophosphates motives $[P_3O_{10}]^{5-}$ on the basis of Mn^{2+}, Mn^{3+}, Mn^{4+}. The high bond energy of the third and fourth energy states of internal electron 2p-levels of phosphorus complies with formation of phosphate complexes on the basis of manganite $MnO_2\cdot Mn(OH)_2$ and psilomelane $MnO\cdot\ MnO_2\cdot H_20$, in which the absorbed phosphorus can replace the hydroxyl groups OH.

The investigations dedicated to the order of phosphorus chemical bond in the manganese concentrates and monomineral differences of manganese ores made it possible to line out the route of transformation $P_4O_{10}\rightarrow[PO_4]^{3-}$ [10-11], which, with due regard to the carbon reduction processes, can be represented by the sequential row $Mn[P_3O_9]_2\rightarrow Mn_5[P_3O_{10}]_2\rightarrow Mn_2[P_2O_7]\rightarrow Mn_3[PO_4]_2$ according to the equations:

$$1{,}5P_4O_{10} + 3MnO = Mn_3[P_3O_9]_2 \quad (4.3)$$

$$Mn_3[P_3O_9]_2 + 18C = 3MnP_2 + 18CO \quad (4.4)$$

$$1{,}5P_4O_{10} + 5MnO = Mn_5[P_3O_{10}]_2 \quad (4.5)$$

$$Mn_5[P_3O_{10}]_2 + 20C = Mn_5P_6 + 20CO \quad (4.6)$$

$$1{,}5P_4O_{10} + 6MnO = 3Mn_2[P_2O_7] \quad (4.7)$$

$$Mn_2[P_2O_7] + 7C = 2MnP + 7CO \quad (4.8)$$

$$1{,}5P_4O_{10} + 9MnO = 3Mn_3[PO_4]_2 \quad (4.9)$$

$$Mn_3[PO_4]_2 + 8C = Mn_3P_2 + 8CO \quad (4.10)$$

The changes in the manganese-phosphorus ratio in the course of sequential polymerization $P_4O_{10}\rightarrow[PO_4]^{3-}$, as well as carbon quantity per phosphorus unit, required for neutralization of excess charge, are presented in Table 4.2.

Table 4.2: The changes in the ratios of $\frac{Mn}{P}$ and $\frac{C}{P}$ for reactions (3.3-3.10)

Parameter	Polymerization and reduction reactions			
	(3.3-3.4)	(3.5-3.6)	(3.7-3.8)	(3.9-3.10)
$\frac{Mn}{P}$	0.5	0.833	1.0	1.5
$\frac{C}{P}$	3.0	3.33	3.5	4.0

5. SUMMARY

As can be seen from the above, the experimental investigations of bond energy of internal electron 2p-levels of phosphorus in the pyrolusite, manganite, psilomelane, oxide and carbonate concentrates and theoretical analysis of the obtained results made it possible to establish that phosphorus is in four strongly pronounced energy states. This is attributable to the following factors: presence of chemical bond between phosphorus-oxide motives $[PO_4]^{3-}$ and modifying cations – the main components of manganese ores in various valence state: K^+, Na^+, Ca^{2+}, Mn^{2+}, Fe^{3+}, Mn^{3+}, Mn^{4+}; formation of more complex ortho- and diorthophosphate motives $[P_3O_9]^{3-}$, $[P_2O_7]^{4-}$ и $[P_3O_{10}]^{5-}$, directly connected with modifying cations Mn^{2+}, Mn^{3+}, Mn^{4+}; transfer of electron density from the phosphorus atom – structure-forming agent to the central atom of transition metal (Fe, Mn) – modifying element.

The analysis of the identified model of manganese and phosphorus co-reduction during carbon reduction melting of ferromanganese using flux-free method with simultaneous production of marketable alloy and charge manganese slag demonstrates that for each phosphorus unit for its removal from anionic skeleton of enhanced negativity it is required to increase the input of acceptor atoms of carbon reduction, the quantity of which per unit of phosphorus increases from 3 to 4. The priority accompanying condition is a mandatory manganese reduction, which increase as long as the phosphorus concentration in the slag decreases.

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