# THE DIAGRAM OF PHASE STRUCTURE OF THE OXIDE SYSTEM $MnO$-$MgO$-$CaO$-$SiO_2$-$Al_2O_3$

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## ABSTRACT

*A complete phase diagram of the system $MgO$-$MnO$-$CaO$-$Al_2O_3$-$SiO_2$ has been built and its mathematical model has been obtained. It is made up of 34 stable before melting elementary pentatopes of the coexisting phases.*

*The diagram of the phase structure of the system $MgO$-$MnO$-$CaO$-$Al_2O_3$-$SiO_2$ is determined to be cut into two main parts by the general plane of $MnO$-$MgO$-$2CaO{\cdot}SiO_2$-$Al_2O_3$, on both sides of which there are two pentatopes:*

*$CaO$-$MnO$-$MgO$-$2CaO{\cdot}SiO_2$-$Al_2O_3$ (high-basic, i.e. conventionally"calcic");*

*$SiO_2$-$MnO$-$MgO$-$2CaO{\cdot}SiO_2$-$Al_2O_3$ (low-basic, i.e. conditionally "silica").*

*The results obtained have been shown to allow to establish the phase proportions in the oxide melts of any composition as applied to the materials formed on the oxides of $MgO$-$MnO$-$CaO$-$Al_2O_3$-$SiO_2$ system and predict physical and chemical conditions in the processing technologies of the specified materials (including burden materials for the electric smelting of ferroalloys. The volume of required information for scientific analysis is reduced by several orders of magnitude.*

***KEY WORDS:*** *Diagram, pentatope, quasi-system, anorthite, slag, ferrosilicomanganese.*

The five-component system $MgO$-$MnO$-$CaO$-$Al_2O_3$-$SiO_2$ (where: M' is MnO, M is MgO, C is CaO, A is $Al_2O_3$, S is $SiO_2$) is composed from five quaternary oxide systems $MgO$-$MnO$-$Al_2O_3$-$SiO_2$, $MnO$-$CaO$-$Al_2O_3$-$SiO_2$, $MgO$-$MnO$-$CaO$-$Al_2O_3$, $MgO$-$MnO$-$CaO$-$SiO_2$, $MgO$-$CaO$-$Al_2O_3$-$SiO_2$. From them the phase diagrams were constructed for the system $MgO$-$MnO$-$Al_2O_3$-$SiO_2$, $MgO$-$MnO$-$CaO$-$Al_2O_3$, $MgO$-$MnO$-$CaO$-$SiO_2$, $MgO$-$CaO$-$Al_2O_3$-$SiO_2$ ( figures 1- 4) on the basis of thermodynamic data, topography peculiarities of the known state diagrams and other data on the equilibria as applied to the mentioned systems [1].

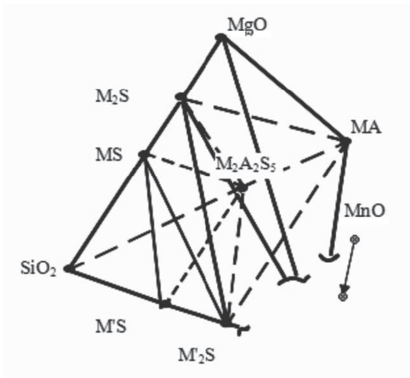
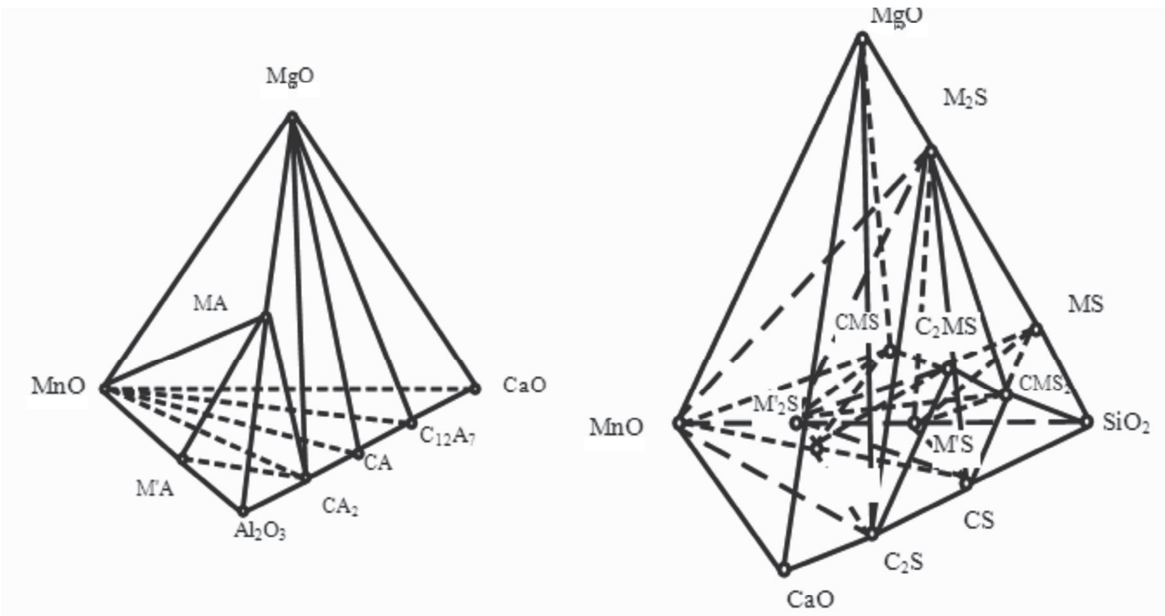



**Figure 1:** A scheme of a detail of the phase diagram of the system $MgO$-$MnO$-$Al_2O_3$-$SiO_2$

Based on the results of tetrahedration of the specified quaternary systems the easiest way to determine elementary polytopes of the general system $MgO$-$MnO$-$CaO$-$Al_2O_3$-$SiO_2$ is as follows:

congenial tetrahedra (distinguished only by one component) of the subsystems are written out and summed up to derive the resulting pentatope of the common system, as shown in table 1. Having searched through all the congenial tetrahedra of particular systems in terms of the data on the quasi-binarity of oxides one gets a constitutional diagram of the system MgO-MnO-CaO-$Al_2O_3$-$SiO_2$.




a) b)

**Figure 2:** Schemes of the phase diagrams of the systems (a) MgO-MnO-CaO-$Al_2O_3$ and (b) MgO-MnO-CaO-$SiO_2$

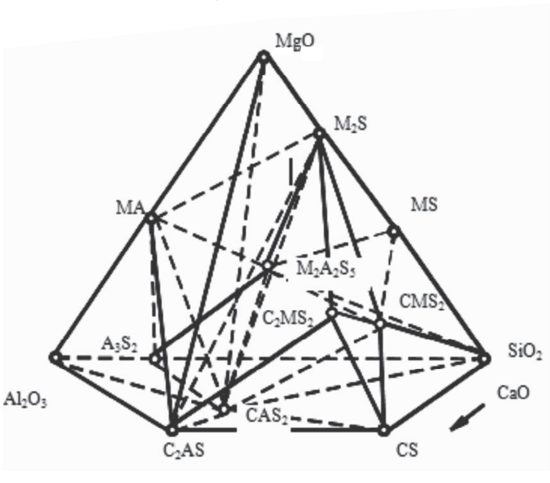



**Figure 3:** A scheme of a detail of the phase diagram of the system MgO-CaO-$Al_2O_3$ -$SiO_2$

The phase equilibria for manganese ferroalloy slag in the modal system M- M-M`-C-A-S have been determined. Eight of 34 quasi-systems stable at high temperatures disintegrate to 18 metastable derivatives to give 52 quasi-systems (stable and unstable in total). A breakdown of the common system is made in terms of all the components leading to particular boundary systems. The sum of the relative volumes of elementary pentatopes of the system MgO-MnO-CaO-$Al_2O_3$-$SiO_2$ is almost equal to the unit (0.99914), indicating the absence of "transitional" pentatopes at breakdown of the system (table 2).

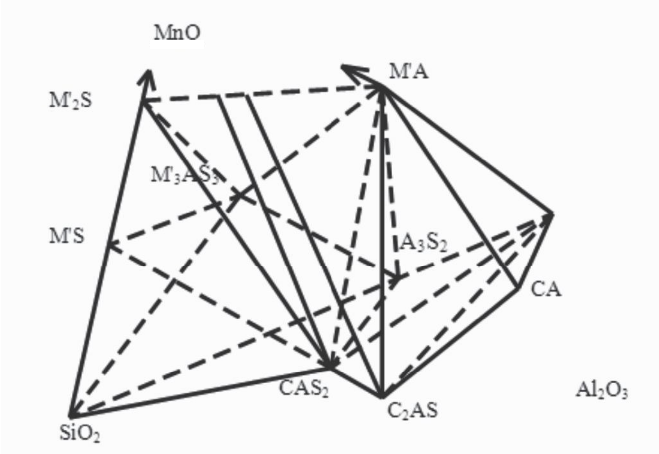



**Figure 4:** A detail of the phase diagram of the system MgO-CaO-$Al_2O_3$-$SiO_2$

**Table 1:** Determination of the resulting pentatopes of M-M`-C-A-S system based on the data of tetrahedration of its particular systems

| **Particular systems** | **Initial tetrahedra** | | |
|---|---|---|---|
| M-C-A-S | S-MA-$A_3S_2$-$CAS_2$ | A-MA-$CA_2$-$C_2AS$ | - |
| M`-C-A-S | S-$A_3S_2$-$CAS_2$-M`$_3AS_3$ | A-$CA_2$-M`A-$C_2AS$ | $C_2S$-M`$_2$S-$C_2AS$-M` |
| M-M`-C-A | - | A-$CA_2$-M`A-MA | - |
| M-M`-C-S | - | - | $C_2S$-M`$_2$S-$C_2MS_2$-M` |
| M-M`-A-S | S-MA-$A_3S_2$-M`$_3AS_3$ | - | - |
| Common system | Resulting pentatopes | | |
| M-M`-C-A-S | S-MA-$A_3S_2$-$CAS_2$-M`$_3AS_3$ | A-$CA_2$-MA-M`A-$C_2AS$ | M`-$C_2S$-M`$_2$S-$C_2MS_2$-$C_2AS$ |

For all the obtained secondary polytopes of the system MgO-MnO-CaO-$Al_2O_3$-$SiO_2$ including those with incongruent oxides (in total 52 quasi-systems) we have obtained mathematical models, so-called equations of transformation. These mathematical models allow to calculate the amounts of secondary oxides in melts of the system MgO-MnO-CaO-$Al_2O_3$-$SiO_2$ based on the content of primary oxides determined by means of the chemical analysis. These calculations are given in Table 3 [2].

The obtained diagram of the phase structure of the system MnO-MgO-CaO-$Al_2O_3$-$SiO_2$ is a complete one and it covers almost all compositions of slag melts of the processes of the ferroalloy and steel productions [3].

The presence of the general cross-section in the form of MnO-MgO-2CaO·$SiO_2$-$Al_2O_3$ being the basis for two pentatopes: CaO-MnO-MgO-2CaO.$SiO_2$-$Al_2O_3$ (high-basic - "calcic" one) and $SiO_2$-MnO-MgO-2CaO·$SiO_2$-$Al_2O_3$ (low-basic - "silica" one) has been revealed.

However, the second, main, pentatope is of interest for the ferroalloy and steel making processes whereas the first one is of interest for the flux, cement and refractory industries. The whole diagram of phase structure of the initial system actually consists of these two very complex in their structure pentatopes inside which all the others quinary quasi-systems are located (figure 5).

The results obtained allow to establish a list of pentatopes inside which all the possible slag compositions of the ferrosilicomanganese melting process are located. Under these conditions it is possible to choose among them those slag compositions that provide a high recovery of manganese and silicon into the metal.

**Table 2:** Pentatopes of the system $MgO-MnO-CaO-Al_2O_3-SiO_2$

| № | Pentatopes | Elementary volumes |
|---|---|---|
| 1 | $S-MA-A_3S_2-CAS_2-M`_3AS_3$ | 0,01765 |
| | including: | |
| | a) $S-A_3S_2-(M_2A_2S_5)-CAS_2-M`_3AS_3$ | (0,008605) |
| | b) $MA-A_3S_2-(M_2A_2S_5)-CAS_2-M`_3AS_3$ | (0,009060) |
| 2 | $S-MA-M_2S-CAS_2-M`_3AS_3$ | 0,01737 |
| | including: | |
| | a) $S-(MS)-M_2A_2S_5-CAS_2-M`_3AS_3$ | (0,01216) |
| | b) $(MS)-M_2S-(M_2A_2S_5)-CAS_2-M`_3AS_3$ | (0,00521) |
| 3 | $S-M`_2S-M_2S-CMS_2-CAS_2$ | 0,03818 |
| | including: | |
| | a) $S-(M`S)-(MS)-CMS_2-CAS_2$ | (0,02056) |
| | b) $(M`S)-(MS)-M`_2S-CMS_2-CAS_2$ | (0,00616) |
| | c) $(MS)-M_2S-M`_2S-CMS_2-CAS_2$ | (0,01146) |
| 4… | $S-M`_2S-M_2S-M`_3AS_3-CAS_2$ | 0,01676 |
| | including: | |
| | a) $S-(M`S)-(MS)-M`_3AS_3-CAS_2$ | (0,00909) |
| | b) $(M`S)-(MS)-M_2S-M`_3AS_3-CAS_2$ | (0,00387) |
| | c) $(MS)-M_2S-M`_2S-M`_3AS_3-CAS_2$ | (0,00503) |
| …7 | $A-CA_2-MA-M`A-C_2AS$ | 0,00549 |
| 8 | $A-MA-M`A-CAS_2-C_2AS$ | 0,01537 |
| 9… | $M`-CA_2-MA-M`A-C_2AS$ | 0,007898 |
| …20 | $CS-CAS_2-CMS_2-C_2AS-M`_2S$ | 0,01012 |
| 21 | $CS-C_2MS_2-CMS_2-C_2AS-M`_2S$ | 0,005153 |
| 22 | $M`-C_2MS_2-CMS_2-C_2AS-M_2S$ | 0,03033 |
| 23 | $M`_2S-CMS_2-CAS_2-C_2AS-M_2S$ | 0,02091 |
| 24 | $M`_2S-M-CAS_2-C_2AS-MA$ | 0,06676 |
| 25 | $M`_2S-M`-C_2MS_2-C_2AS-C_2S$ | 0,01064 |
| | including: | |
| | a) $C_2S-M`-C_2MS_2-C_2AS-(CM`S)$ | (0,005741) |
| | b) $M`_2S-M`-C_2MS_2-C_2AS-(CM`S)$ | (0,004905) |
| 26 | $MA-M`A-A_3S_2-M`_3AS_3-CAS_2$ | 0,008855 |
| 27 | $MA-M`A-M`-M`_2S-CAS_2$ | 0,01002 |
| 28 | $MA-M`A-M`_2S-M`_3AS_3-CAS_2$ | 0,005758 |
| 29 | $CMS_2-M`-M`_2S-M_2S-C_2AS$ | 0,01940 |
| 30 | $CAS_2-M`-M`_2S-M_2S-C_2AS$ | 0,01270 |
| 31 | $CAS_2-M`A-M`-MA-C_2AS$ | 0,02212 |
| 32 | $CMS_2-M`-M`_2S-C_2MS_2-C_2AS$ | 0,004211 |
| 33 | $M_2S-M`_2S-M`_3AS_3-MA-CAS_2$ | 0,01417 |
| 34 | $M-M_2S-M`_2S-CAS_2-C_2AS$ | 0,02238 |
| | | 0,99914 |

The quasi-system $SiO_2-CaO{\cdot}SiO_2-CaO{\cdot}Al_2O_3{\cdot}2SiO_2-2MnO{\cdot}SiO_2-CaO{\cdot}MgO{\cdot}2SiO_2$ is the most significant of the total list of 34 pentatopes of the system $MgO-MnO-CaO-Al_2O_3-SiO_2$. In this system in the area of primary crystallization of anorthite ($CaO/SiO_2$ = 0,2-0,4; more than 20% of $Al_2O_3$ and about 4-8% of MgO) a high temperature in the reaction zone of the furnace can be provided that will result in reducing loss of manganese with slag and increasing the degree of recovery of manganese and silicon into the metal, and, consequently, to reducing the electric power consumption.

**Table 3:** Mathematical models for calculating the equilibrium contents of secondary components (minerals in the oxide melts or phases in the oxide materials in the subsolidus state) in quasi-systems of the system $MgO$-$MnO$-$CaO$-$Al_2O_3$-$SiO_2$

| № | Quasi-systems and their mathematical models |
|---|---|
| 1 | $S$-$MA$-$A_3S_2$-$CAS_2$-$M_3'AS_3$: |
| | $S = +1S_o-0{,}392A_o-1{,}426C_o+0{,}995M_o-0{,}658M_o'$; $MA = +3{,}533M_o$; $A_3S_2 = +1{,}392A_o-2{,}523C_o-3{,}528M_o-0{,}667M_o'$; $CAS_2 = +4{,}95C_o$; $M_3'AS_3 = +2{,}325M_o'$. |
| 2 | $S$-$MA$-$M_2S$-$M_3'AS_3$-$CAS_2$: |
| | $S = +1S_o+0{,}294A_o-2{,}671C_o-0{,}745M_o-0{,}987M_o'$; $MA = +1{,}394A_o-2{,}527C_o-0{,}668M_o'$; $M_2S = -0{,}688A_o+1{,}248C_o+1{,}745M_o+0{,}329M_o'$; $M_3'AS_3 = +2{,}325M_o'$; $CAS_2 = +4{,}95C_o$. |
| 3 | $S$-$M_2'S$-$M_2S$-$CMS_2$-$CAS_2$: |
| | $S = +1S_o-0{,}293A_o-1{,}607C_o-0{,}745M_o-0{,}422M_o'$; $M_2'S = +1{,}422M_o'$; $M_2S = 0{,}691A_o-1{,}253C_o+1{,}745M_o'$; $CMS_2 = -2{,}130A_o+3{,}861C_o$; $CAS_2 = +2{,}732A_o$. |
| 4 | $S$-$M_2'S$-$M_2S$-$M_3'AS_3$-$CAS_2$: |
| | $S = +1S_o-0{,}885A_o-0{,}534C_o-0{,}745M_o-0{,}422M_o'$; $M_2'S = -2{,}969A_o+5{,}379C_o+1{,}422M_o'$; $M_2S = +1{,}745M_o$; $M_3'AS_3 = +4{,}854A_o-8{,}795C_o$; $CAS_2 = +4{,}95C_o$. |
| 5. | $S$-$CS$-$M_2'S$-$CMS_2$-$CAS_2$: |
| | $S = +1S_o-0{,}589A_o-1{,}07C_o-1{,}493M_o-0{,}423M_o'$; $CS = -1{,}143A_o+2{,}07C_o-2{,}882M_o$; $M_2'S = +1{,}422M_o'$; $CMS_2 = +5{,}376M$; $CAS_2 = +2{,}732A_o$. |
| 6… | $A$-$MA$-$M'A$-$A_3S_2$-$CAS_2$: |
| | $A = -2{,}546S+1A_o+3{,}633C_o-2{,}533M_o-1{,}439M_o'$; $MA = +3{,}533M_o$; $M'A = +2{,}439M_o'$; $A_3S_2 = +3{,}546S_o-7{,}583C_o$; $CAS_2 = +4{,}95C_o$. |
| …31 | $M$\`-$M$\`$A$-$MA$-$CAS_2$-$C_2AS$: |
| | $M' = +0{,}391S_o-0{,}694A_o+0{,}422C_o+1{,}76M_o+1M_o'$; $M'A = -0{,}953S_o+1{,}694A_o-1{,}030C_o-4{,}294M_o$; $MA = +3{,}533M_o$; $CAS_2 = +3{,}087S_o-1{,}653C_o$; $C_2AS = -1{,}525S_o+3{,}261C_o$. |
| 32 | $M$\`-$M_2$\`$S$-$C_2MS_2$-$CMS_2$-$C_2AS$: |
| | $M' = -2{,}367S_o+1{,}401A_o-0{,}007C_o+7{,}072M_o+1M_o'$; $M_2S = +3{,}367S_o-1{,}993A_o+0{,}010C_o-10{,}06M_o$; $C_2MS_2 = -5{,}365A_o+4{,}88C_o-6{,}795M_o$; $CMS_2 = +4{,}269A_o-3{,}883C_o+10{,}78M_o$; $C_2AS = +2{,}688A_o$. |
| 33 | $M_2S$-$M_2$\`$S$-$M_3$\`$AS_3$-$MA$-$CAS_2$: |
| | $M_2S = +0{,}584S_o-0{,}517A_o-0{,}312C_o+1{,}309M_o-0{,}246M_o'$; $M_2'S = -2{,}517S_o-0{,}740A_o+6{,}726C_o+1{,}876M_o+2{,}486M_o'$; $M_3'AS_3 = +4{,}116S_o+1{,}210A_o-10{,}99C_o-3{,}067M_o-1{,}739M_o'$; $MA = -1{,}182S_o+1{,}046A_o+0{,}632C_o+0{,}881M_o+0{,}499M_o'$; $CAS_2 = +4{,}95C_o$. |
| 34 | $M$-$M_2S$-$M_2$\`$S$-$CAS_2$-$C_2AS$: |
| | $M = -1{,}341S_o+2{,}384A_o-1{,}449C_o+1M_o+0{,}566M_o$\`; $M_2S = +2{,}341S_o-4{,}16A_o+2{,}53C_o-0{,}989M_o$; $M_2'S = +1{,}422M_o'$; $CAS_2 = +5{,}486A_o-4{,}989C_o$; $C_2AS = -2{,}709A_o+4{,}909C_o$. |

The production of manganese alloys is known to have started in Kazakhstan only since 1993.

The first attempts to produce them were made in the JSC "Khimprom" (at the present time it is Taraz Metallurgical Plant) in the phosphoric furnaces having the transformer capacity of 48 MVA. Later the production of ferrosilicomanganese was organized.

A larger-scale production was introduced at Aksu ferroalloy plant. Its ferrosilicium furnaces having the transformer capacity of 33 MVA began to produce ferrosilicomanganese.

For the first time we started to produce carbon ferromanganese in 2000-2001 in Temirtau Electrometallurgical plant in the carbide furnaces having the transformer capacity of 60 MVA. Further we transferred those furnaces to the smelting of ferrosilicomanganese.

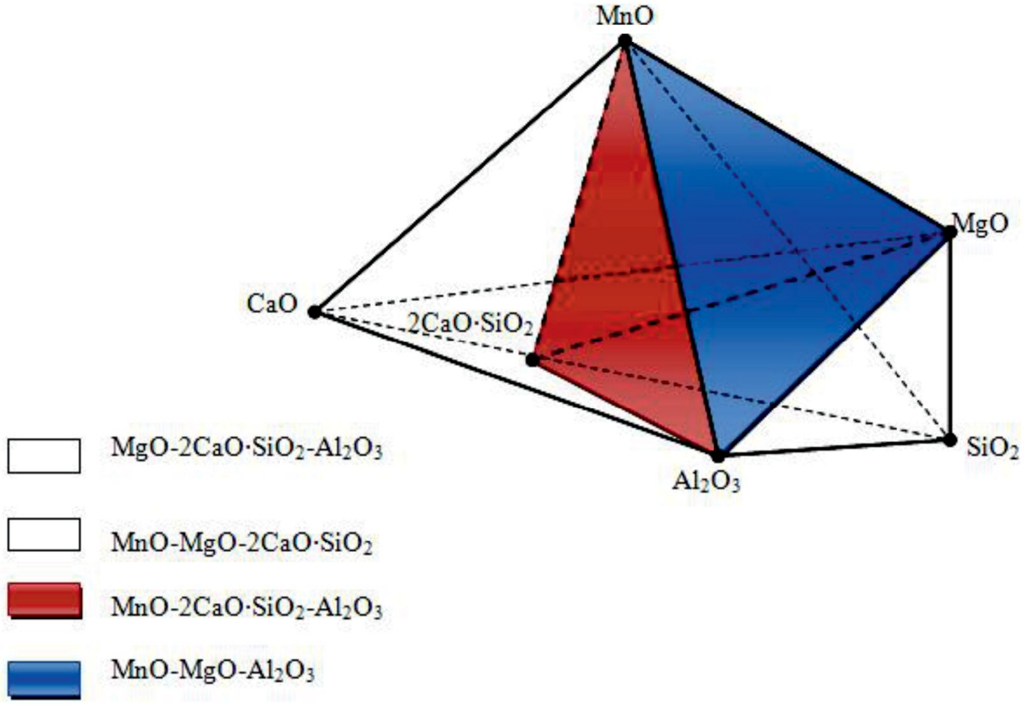



**Figure 5:** The common concentration space of the system $MgO$-$MnO$-$Al_2O_3$-$SiO_2$-$CaO$

## CONCLUSION

The compositions of such slag due to their low electroconductivity provide the formation of high-temperature slag in the furnace that contributes to the effective work of the former ferrosilicon furnaces when smelting of manganese alloys in shop-floor number № 1 of Aksu Ferroalloy Plant (JSC "TNK" Kazchrome").

## REFERENCES

[1] Gabdullin T.G., Taknov T.D., Baisanov S.O., Buketov E.A. Physicochemical properties of manganese slag / Alma-Ata: Nauka, 1984.- 232 p.
[2] Akberdin A. A. The balance method of calculation of equilibrium phase composition of multi-component systems//KIMS: Almaty.- 1995, № 3. – P. 92-93.
[3] Tolymbekov M. Zh. Dynamics of phase equilibria in melted slag obtained by the method of direct doping of steel with oxide materials / Melts: Ekaterinburg. – 2003, № 2. – P. 68-74.