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DETERMINING THE OPTIMAL COMPOSITION OF LOW-BASICITY SLAGS USING PEGMATITE FOR ELECTROMELTING PROCESSES

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This study focuses on the process of slag formation and its performance during steelmaking using carbon charge, when remelting alloyed scrap in electric steelmaking units, and in secondary metallurgy units. One of the relevant issues is the use of alternative materials, such as alkali aluminosilicates, capable of replacing conventional slag components without compromising the quality of the slag.

This study reports scientifically proven conditions for replacing fluorspar in the composition of slags used in remelting technologies and secondary metallurgy with domestic mineral raw materials – pegmatites, which contain up to 10–15% of the total alkali metal oxides Na_2O and K_2O.

The effect of Na_2O and K_2O on the rheological characteristics of the slag melt in the CaO-SiO_2+(Na_2O, K_2O) system has been confirmed. A series of experimental meltings was carried out to establish the slag-forming regime in a ladle-furnace when fluorspar in the solid slag-forming mixture is completely replaced with pegmatites.

A comparative analysis of the compositions of refining slags for the current industrial technology and the experimental technology has been performed. A significant increase in slag fluidity and a desulfurization level of the metal comparable to that of the current technology were established, despite a decrease in slag basicity to 1,8–2,0, which is consistent with the requirements of remelting technologies. Chemical analysis of the metal and slag compositions was conducted for the experimental meltings at the stages of semi-product melting and steel treatment in the ladle furnace. The metal from the experimental meltings fully met the requirements of the normative and technical documentation.

Thus, this work provides a theoretical justification for an innovative secondary-metallurgy technology using alkali aluminosilicate pegmatite as a part of slag forming mixtures. The metal quality indicators in terms of sulfur content confirm the effectiveness of the devised technology with partial or complete replacement of fluorspar with pegmatite during remelting or secondary steelmaking

Keywords: pegmatite, electric arc steel remelting, rheological properties of slag, refining of the melting

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1. Introduction

The current development of electric steelmaking is based on the concept of a technological scheme consisting of the following metallurgical stages:

1) smelting of semi-finished metal in an over-powerful electric furnace using alternative energy sources;

2) secondary steelmaking in a Ladle Furnace unit and a vacuum degasser;

3) casting of metal on continuous casting machines.

At all stages of metallurgical processes, an obligatory component of the technology is the use of slag systems that enable metal refining due to mass transfer reactions in the “metal-slag” system. An important physicochemical characteristic of slag systems is the viscosity of the slag. To obtain certain rheological parameters of the slag (melting point, fluidity) in the composition of the slag of remelting processes, up to 5% of fluorspar is present, in slags of out-of-furnace processing the content of fluorspar is 25...30%.

The technologies of secondary steelmaking operating at the enterprises determine the composition of solid slag-forming materials (SSM) for slag formation at the metal processing stage at LF. The technical regulations determine the standards for the consumption of a mixture of 10 kg/t of steel at a ratio of components of the lime/fluorspar mixture of 3/1.

The use of classical slag formation technology has significant disadvantages because fluorspar has a fairly high cost. Also, the use of fluorspar negatively affects the environment due to the instability of its compound with lime and the release of fluorine.

Therefore, studies on searching for new materials to be used in the composition of slags in remelting technologies and non-furnace processing are relevant and important for enabling sustainable development and competitiveness of metallurgy.

2. Literature review and problem statement

In [1], the possibilities of using refining slag with a low fluorine content were investigated. Oxides such as Al_2O_3, SiO_2, B_2O_3, and Li_2O were proposed as a replacement for fluorspar (CaF_2). The melting point of the slags and their desulfurization ability were determined. The authors of the study found that the melting point of the slag in the case of replacing the CaF_2 fraction with Al_2O_3 (CaF_2 < 4 wt. % and Al_2O_3 > 28 wt. %) is less than 1706 K. According to the authors, this slag is able to reduce the [S] content in steel to less than 0.0060 wt. %. When replacing CaF_2 with SiO_2, the melting point increases, and the desulfurization rate, on the contrary, decreases. It was found that the fluxing effect of B_2O_3 is stronger than that of CaF_2. At the same time, the melting point decreases to 1561 K, in the case of replacing CaF_2 with B_2O_3. It is shown that Li_2O can not only reduce the melting point of the slag but also improve the desulfurization rate. However, there are still unresolved issues related to the optimization of the slag composition in order to simultaneously ensure its key properties, namely: low melting point, high desulfurization capacity, stability of the slag as a multicomponent system. The objective reason is the complexity of the experimental assessment of the interaction of oxides under high-temperature conditions and the limited availability of low-fluoride compositions. One of the options for overcoming these difficulties may be the study of other oxides, for example, rare-earth or based on alkali aluminosilicates, capable of partially replacing CaF_2. That is why work [2] is relevant as it considers issues of using the rare-earth oxide La_2O_3 as a slag component.

The authors of [2] conducted a study on the evaporation and crystallization of fluoride in the slag CaF_2-CaO-Al_2O_3-(La_2O_3) for vacuum and electroslag remelting. They showed that the main volatile substances of the studied slag within 7.4 wt. % La_2O_3 content at 1723 K are CaF_2 and $AAlF_3$. It was found that the weight loss of the slag CaF_2-CaO-Al_2O_3-(La_2O_3) decreases with increasing La_2O_3 content both in the thermogravimetric experiment and under vacuum conditions. It was shown that the addition of La_2O_3 within 7.4 wt. % reduces the viscosity and melting point of the slag under study, and the change in viscosity is not the main reason for the inhibition of fluoride evaporation. Therefore, the following conclusions are drawn in the work: the vapor pressure of CaF_2 and AlF_3 at 1723 K decreases with increasing La_2O_3 content due to changes in the activity of the components and, thus, the evaporation of fluoride is weakened; the crystalline phases of the CaF_2-CaO-Al_2O_3 are $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$ and CaF_2, while the crystalline phases of the slag within the content of 7.4 wt. % La_2O_3 are $(CaLa)Al_3O_7$, $La(AlO_3)$ and CaF_2; the addition of La_2O_3 can reduce the crystallization temperature of CaF_2 and prevent the precipitation of $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$. However, similarly to work [1], there are unresolved issues regarding the simultaneous solution of complex issues related to ensuring a low melting point, fluidity of the slag and limiting the evaporation of fluorides in multicomponent systems. This is due to the difficulty of experimentally reproducing all thermodynamic and kinetic interactions of slag components and limited information on the interaction of rare earth oxides with other additives. A logical step to overcome these problems is to additionally study the influence of boron oxides, which are able to regulate slag crystallization and CaF_2 precipitation. This approach was used in [3].

In [3], it was demonstrated how B_2O_3 affects the kinetics of slag crystallization, morphology and phase composition of primary crystals in electroslag remelting of high-alloy alloys. It was found that the appropriate content of B_2O_3 added to the CaF_2-based slag should be about 1.0%, which makes it possible to limit the precipitation of CaF_2 crystals to achieve good ingot surface quality and stable operation of the plant. However, study [3] is limited only to the effect of B_2O_3 on crystallization and does not cover the issue of evaporation of fluorine compounds and the interaction of other slag components.

Thus, works [1–3] expand knowledge about slag systems based on CaF_2-CaO-Al_2O_3-(La_2O_3, La_2O_3, B_2O_3) and show the possibilities of limiting the CaF_2 content. But the authors of the above studies did not pay attention to the issues of using alkali metal oxides (Na_2O, K_2O) in the slag composition, which are widely available raw materials. This opens up prospects for further research to find alternative slag components capable of reducing the fluorine content without deteriorating its physicochemical properties.

In this sense, work [4] is interesting, which reports a study on the fluoride evaporation of slag CaF_2-CaO-Al_2O_3-MgO-TiO_2-(Na_2O-K_2O) with a low fluorine content for electroslag remelting. To elucidate the behavior of fluoride evaporation in the electroslag remelting process, the authors investigated the non-isothermal evaporation of low-fluoride slag based on CaF_2-CaO-Al_2O_3-MgO-TiO_2-(Na_2O-K_2O) using thermogravimetric analysis. Fourier transform infrared spectroscopy (FTIR) was applied to assess the change in the slag structure. It was found that the main substances that evaporate are CaF_2, KF and NaF, while the evaporation of MgF_2, AlF_3 and AlOF is less. KF evaporates at the early stage of the reaction, and CaF_2 evaporates in a significant proportion during the late reaction period. The results of Fourier transform IR spectroscopy showed that the addition of K_2O depolymerizes the network structure. At the same time, K_2O can depolymerize the network structure better than Na_2O. The limitation of the work is that the ratios of slag components that would ensure its rational rheological parameters are not determined. The influence of fluoride evaporation on the kinetics of desulfurization and the physicochemical properties of slag during industrial smelting is also not considered. The reasons for this may be the limitations of the experimental methodology and the complexity of complex modeling of multi-component systems at high temperatures.

One of the options for overcoming the above problems is the approach described in [5]. The work does not directly relate to steelmaking processes but rather to waste processing and fluoride extraction, but it provides information on the thermodynamic and chemical aspects of the behavior of CaF_2 in slags. The authors demonstrated the thermodynamic possibility of converting rare earth fluoride into their oxides by calcining CaO. The influence of calcining and leaching conditions on the leaching rate of rare earth elements was also investigated. The results of X-ray diffraction, scanning electron microscopy, and energy dispersive spectroscopy showed that during the calcination process, rare earth elements present in fluorite (CaF_2) in isomorphic form were converted into acid-soluble oxides. However, study [5] is limited to the thermodynamic and chemical aspects of the transformation of CaF_2 and rare earth metals during calcination. The questions of determining the melting temperature of slags, phase relations, oxide activity and sulfide capacity of slags remained open. These parameters are decisive for the controlled conduct of steel melting in metallurgical units. Thus, the results of [4, 5] indicate the need for further experimental and thermodynamic studies on slags with a low fluorine content and the addition of alkaline oxides to them to create optimal properties. Also very important for a deeper understanding of the mechanisms of behavior of multicomponent slag melts is the modeling of molecular dynamics of binary systems. Scientific research into this area is reported in [6].

In [6], molecular dynamics models of binary systems CaO-FeO, MgO-SiO_2, FeO-SiO_2, CaO-SiO_2 and ternary systems CaO-FeO-SiO_2 were built using pair potentials of Born-Mayer at a temperature of 1873 K. The potentials included effective dipole-dipole interactions for pairs Ca-Fe, Mg-Si, Fe-Si, and Ca-Si. The authors found the parameters of the dipole-dipole interaction by reducing the calculated Gibbs free energies of formation of binary systems CaO-FeO, FeO-SiO_2, MgO-SiO_2 and CaO-SiO_2 to experimental data. The thermodynamic properties of CaO-FeO-SiO_2 solutions were studied by converting several iron ions into calcium ions. This allowed them to calculate the increments of Gibbs free energy and the ratio of activity coefficients γCaO/γFeO in the ternary system. The disadvantage of [6] is that only a rather limited range of oxide systems is considered. Also, the interaction of Al_2O_3, CaF_2, alkali metal oxides Na_2O-K_2O in multicomponent slag systems based on CaO-Al_2O_3-SiO_2-CaF_2-Na_2O-K_2O is not taken into account. This limitation is associated with the complexity of parameterizing potentials for systems with a large number of components, as well as the complexity of their modeling. One of the ways to overcome these limitations is to step-by-step expand existing models of slag systems using empirical data obtained from the use of industrial slags. This direction of research is partially implemented in [7, 8].

Unlike previous studies, the quantitative composition of slag components was determined in [7, 8]. Thus, work [7] considers the quantitative substantiation of the composition of slag that does not contain fluorine for off-kiln processing in a ladle-furnace installation. For this purpose, the influence of the main components on the physical and metallurgical properties of slag was analyzed using theoretical analysis and laboratory tests. The following rational range of the composition of slag components was established: w(CaO) = 40–55 wt. %, w(SiO_2) = 2–6 wt. %, w(Al_2O_3) = 30–40 wt. %, w(MgO) = 6–8 wt. %, and w(CaO)/w(Al_2O_3) = 1.25–1.50. In [8], with our participation, it was proposed to use a slag of reduced basicity with the composition of 50%CaO-35%SiO_2-5%Al_2O_3-5%MgO-5%FeO for refining during the electrosmelting of steel. Changes in the content of alloying elements due to the remelting process were analyzed. It was confirmed that the loss of alloying elements depends, in addition to their chemical affinity for oxygen, also on the formation of compounds of the type CaO*MeO in the slag, where MeO oxide has an acidic nature of interaction. Thus, new knowledge was obtained regarding the physical properties and phase composition of the lime-iron slag of the CrO-FeO-SiO_2-(Me)O system, where Me is Mn, Cr, V, Mo. Thus, the advantage of studies [7, 8] is the confirmation of the possibility of carrying out refining processes under slags of reduced basicity without the use of fluorspar. At the same time, those studies did not consider the influence of pegmatite and alkali metal aluminosilicates, which are potentially capable of improving the rheological properties of slag and the stability of remelting processes. The reasons are the orientation of studies on classical oxide compositions without taking into account the available mineral raw materials – alkali aluminosilicates. One of the directions of expanding the results from [7, 8] is the introduction of predictive models of slag behavior, which makes it possible to take into account a larger number of components simultaneously.

Of significant scientific interest for modeling the chemical composition of slag during the remelting of high-alloy steel scrap is study [9], which predicts the chemical composition of refining slag using an artificial neural network. It is shown that the use of models of this class helps overcome the complexity of evaluating multicomponent slag systems and take into account the relationships between process parameters and slag composition. However, the model from [9] does not take into account the influence of alkali aluminosilicates, which limits its application for new types of slag. To improve the model in [9], it is necessary to additionally study the influence of alkali aluminosilicates on the properties of slag. This will make it possible to expand the range of its use and adapt it to the tasks of modern metallurgy.

Thus, our review of the literature [1–9] allows us to conclude that despite significant progress in studying the properties of metallurgical slags, there are a number of issues that require further research. The behavior of fluoride components under high-temperature conditions, the effect of their evaporation on refining processes and interaction with the lining have not been fully understood. Researchers have also overlooked the issue of using alternative materials, such as alkali aluminosilicates, which could replace conventional slag components without degrading its quality, enabling the use of Ukraine's raw material base.

3. The aim and objectives of the study

The purpose of our study is to determine the rational composition of slags of reduced basicity for electrosmelting processes using pegmatite as an alternative to fluorspar. This will make it possible to improve the efficiency of the course of physicochemical processes, increase the degree of assimilation of alloying elements, and reduce the negative impact on the environment.

To achieve the goal, the following tasks were set:

– to perform an analysis of the physicochemical properties of fluorspar (CaF_2) as a traditional flux of metallurgical slags, in order to determine its impact on the refining ability of the slag, which is necessary for comparison with alternative components;

– to scientifically substantiate the possibility of replacing fluorspar in the composition of slags of remelting technologies and off-furnace processing with mineral raw materials that are available in Ukraine – pegmatites, a rock-forming mineral, a product of crystallization of magmatic melts;

– to assess how Na_2O and K_2O in the composition of slags of the CaO-SiO_2 + (Na_2O, K_2O) system affect the rheological characteristics of the slag melt;

– to conduct a series of experimental melts using slag of the proposed composition and to perform comparative studies of experimental slags and slags of the current technology in order to draw conclusions about the effectiveness of the proposed slag composition.

4. Materials and methods

The object of our study is the process of formation and behavior of slag during steelmaking on a carbon charge, during the remelting of alloyed waste in electric steelmaking plants and in units for off-furnace steel processing. The possibility of replacing the conventional slag diluent CaF_2 with pegmatite is taken into account.

The main hypothesis of the study is that reducing the proportion of CaF_2 in the slag mixture or its complete replacement with natural alkaline aluminosilicates makes it possible to improve the properties of the slag (fluidity, melting point, refining ability).

The following assumptions were adopted when conducting the research. It was believed that the main properties of model slags can be described quite accurately by equilibrium thermodynamic dependences. Structural changes in slag systems CaO-Al_2O_3-SiO_2-MgO when CaF_2 and pegmatite are introduced into the composition are described quite correctly by calculation methods and laboratory models.

To simplify the analysis of model slag systems, the influence of components whose content does not exceed 1 wt % was considered absent. In this case, the process of slag formation was considered under quasi-stationary conditions, which are close to industrial conditions but do not reproduce them in full.

The study used generalized literature data on the physicochemical properties of CaF_2, thermodynamic behavior of oxide-fluoride systems, experimental results of determining the melting temperatures of pegmatite, CaO-pegmatite, CaO-CaF_2 mixtures. The methods included thermodynamic analysis of the CaO-CaF_2, CaO-Al_2O_3-SiO_2-CaF_2 and CaO-Na_2O-SiO_2, systems, as well as studies on the form and aggregate composition of slag mixtures using a high-temperature microscope MNO-2 Carl Zeiss. A TPP thermocouple (type S) was used to control the temperature in the sample heating zone. Based on the data obtained, the behavior of components in slag melts, their influence on viscosity, liquidus temperatures and desulfurization ability of slags during out-of-furnace steel processing were evaluated.

5. Results of investigating the rational composition of slags of reduced basicity

5. 1. Analysis of the physicochemical properties of fluorspar (CaF_2) as a conventional flux of metallurgical slags

The materials summarized by the authors of [10] indicate significant deposits of fluorspar in the eastern part of the Ukrainian Shield, on its southwestern and northern slopes. The authors of [10] note promising manifestations of fluorspar in the central part of the Ukrainian Shield, namely in the Kirovograd tectonic region.

According to [10], most deposits are not developed due to difficult hydrogeological and engineering-geological operating conditions. Several pressure aquifers, fault zones, and unstable carbonate rocks have been identified in the deposits. According to the authors, water breakthroughs into the mining works are possible when the zones are opened. Given the geological features of fluorite deposits and ore occurrences, strict requirements for the concentration of its enrichment from 10–12% to 80–90%, for the needs of the metallurgical industry, prerequisites are created for the import of this mineral raw material. Data on the physicochemical properties of calcium fluoride are summarized in Table 1.

The vapor pressure of CaF_2 at the solid-liquid phase transition (1418°C) is $1.6*10^{-6}$ atm. (0.16 Pa), and at the liquid-gas phase transition (2530°C) it reaches a value of 1 atm. (105 Pa). Obviously, in the combustion zone of electric arcs, prerequisites are created for intensive evaporation of CaF_2, which leads to significant changes in the composition of refining slags of secondary steelmaking. In the specified slags, the basic components of which are CaO and CaF_2, CaF_2 does not form compounds, which gives grounds to consider the structure of the slag as ionic-molecular. In work [11], a phase diagram of the CaO-CaF_2 system is given (Fig. 1).

Table 1

Physicochemical properties of calcium fluoride and its natural analog, the mineral fluorite CaF_2

Title	Units of measurement	Parameter value
Molecular weight	g	78.056
Chemical composition	wt %	51 Ca, 49 F
a-CaF_2, cubic lattice to 1151°C	nm	0.54626
Tetragonal syngony over 1151°C	–	Disorder modification
Density (mineral)	g/cm^3	3.1–3.2
Melting point	°C	1418
Boiling point	°C	2530
Entropy, S^0_{298}	J/(mol×K)	68.45
Heat capacity, C^0_p	J/(mol×K)	67.03
Enthalpy of melting, $\varDelta H^0_{melt}$	J/(mol×K)	30.0
Enthalpy of evaporation, $\varDelta H^0_{ev}$	J/(mol×K)	305 (2800 K)
Enthalpy of formation, $\varDelta H^0_{edu}$	J/(mol×K)	–1221.0
Gibbs energy change, $\varDelta G^0_{change}$	kJ/mol	–1168.0
Temperature of interaction with H_2O vapors	°C	>800
Maximum allowable concentration (toxic)	mg/m^3	2

Thermodynamic analysis of the CaO-CaF_2 system reveals a positive deviation of the CaF_2 activity values from Raoult's law $\alpha_i = f_i * N_i$ in the range of compositions enriched with CaF_2. The given thermodynamic characteristics confirm the phenomenon of stratification of CaO-CaF_2, SiO_2-CaF_2 melts into 2 liquids having the same CaF_2 activity values but differing in composition. The physical properties and thermodynamic characteristics of the behavior of CaF_2 in oxide melts determine the instability of the composition of refined slags during the out-of-furnace processing of steel both in the ladle-furnace unit and in the vacuum degasser VD.

Comparative analysis of slag compositions reveals that due to the interaction of slag with ladle lining refractories, partial oxidation of alloying and deoxidizers, the basic composition of the slag of the CaO-CaF_2 system is transformed into a multicomponent calcium oxide fluoride system CaO-MgO-Al_2O_3-SiO_2-CaF_2. The melting points (liquidus) of slags of this system can be estimated by analyzing the primary crystallization fields of the CaO-Al_2O_3-SiO_2-CaF_2 system (Fig. 2).

In studies [13], an ambiguous effect of CaF_2 additives on the compositions of the specified system was established. The presence of CaF_2 in an amount of up to 1.5% contributes to the mineral formation of primary slags. An excess of CaF_2 content of more than 5% not only leads to a decrease in the temperature of the nonvariant equilibrium points by 70–120°C but also shifts the fields of crystallization of helenite $2\,CaO \times Al_2O_3 \times SiO_2$ to the side of Al_2O_3-CaF_2. The fields of stability of calcium metasilicates $CaO \times SiO_2$, rankinite $3CaO \times 2SiO_2$ and anorthite $CaO \times Al_2O_3 \times 2SiO_2$ also decrease [12].

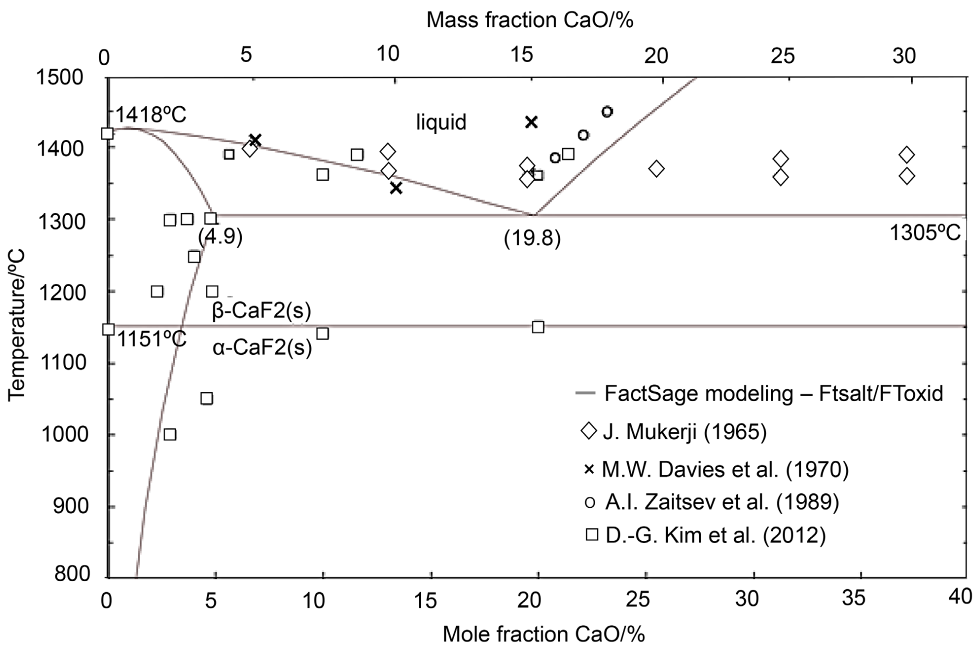


Fig. 1. CaO-CaF_2 system phase diagram [11]

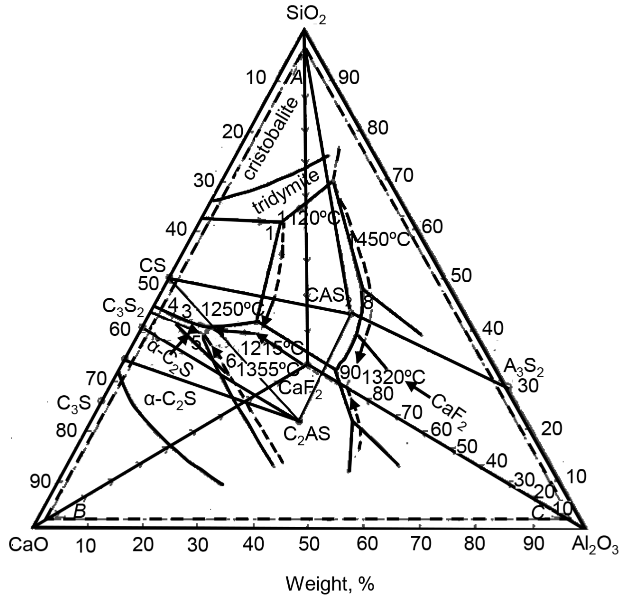


Fig. 2. Phase equilibria in the ternary system CaO-Al_2O_3-SiO_2 with 10% CaF_2 [12]

In the three-component system CaO-Al_2O_3-SiO_2 with 10% CaF_2, a significant increase in the concentration field of the existence of two miscible liquids is observed, limited by a curve with a beginning corresponding to 5% Al_2O_3 on the Al_2O_3-SiO_2 side and ending at the point of 27.6% CaO on the CaO-SiO_2 side (Fig. 2).

Chemical and mineralogical analysis of the composition of the phases formed as primary slags at the initial stages of melt crystallization reveals that CaF_2 does not participate in mineral formation reactions and exhibits (especially in a high-silica melt) the properties of a depolymerizer, breaking the chain structures Si:O:Si and increasing the content of oxygen anions in the melt according to the following scheme

$$(-\,Si - O - Si\,-) + 2F^- = 2(-\,Si - F) + O^{2-}. \qquad (1)$$

Obviously, the course of reaction (1) changes not only the physical properties of the melt, but also the oxidation potential of the slag system. The thermodynamic model of the behavior of CaF_2 in binary and more complex systems makes it possible to consider the properties of these systems on the basis of the theory of ionic solutions, assuming the activity of the element to be identical to its ionic particle.

By developing the theory of the structure of slags as associated solutions, we note the weak interparticle interaction of CaF_2 with the melt of the Al_2O_3-SiO_2 system. Thus, the participation of CaF_2 in the process of formation of primary slag melts is excluded, and the properties of liquid melts are approximated by the presence in their composition of complexes (associates) CaO×Al_2O_3, 2CaO×Al_2O_3 and SiO_2 networks.

Within the framework of this theory, the absence of such model structures as fluorine-containing molecules and complexes of the Me-F type (Ca-F, Si-F) is assumed. At the same time, spectroscopic studies of crystallized compositions of the C-A-S-F system have recorded the presence of $AF_x(AlF_6^{-3}$, AlF_4^-, $AlF_3^{2-})$ complexes, which indicates the participation of fluorine ions in the deformation of the crystallochemical structures of Al_2O_3. In the CaO-CaF_2 system, which exhibits positive deviations $\dot{a}_{CaF_2}$ in the region of increased CaF_2 contents, intermolecular interaction of components occurs, which makes it possible to estimate the value of the excess energy of mixing ΔG^E in terms of the theory of regular solutions (the heat of formation of the solution differs from zero ($H^E \neq 0$), the entropy of mixing is equal to the entropy of an ideal solution ($S^E = -RSx_i \ln x_i$)

$$\Delta G^E = L_1 \times x(CaO)[1 - x(CaO)] + \\ + L_2 \times [x(CaO)]^2 \times [1 - x(CaO)]^2, \qquad (2)$$

where x(CaO) is the molar share of CaO;

L_i – parameter ($L_1 = RT(3.84-0.00108T)$;

$L_2 = -RT(11.87-0.00472T)$ J.

Analysis of dependence (2) reveals that the influence of the temperature of the slag melt on the value of the mixing energy of the components ΔG^E is insignificant and the maximum value of ΔG^E is obtained for compositions with a high content of calcium fluoride. Thus, at the final stages of solidification of the mother liquor enriched with fluoride, as the most fusible component of the $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}CaF_2$ system, the formation of ordered phase structures occurs, containing the fluoride component $2CaO\times2SiO_2\times CaF_2$ (cuspidin), $12CaO\times7Al_2O_3\times CaF_2$.

In practice, metal refining with slags of the composition $CaO / CaF_2 = 3 / 1$ with a CaF_2 content within 20–10% by weight (the first value is the initial CaF_2 content, the second – during metal processing). Fluoride increases the content of oxygen anions in the melt due to the depolymerization reaction of structures $\left(SiO_4\right)_4^{4-}$ according to reaction (1), increases the basicity of the slag during reaction (3):

$$CaF_2 + 1/3Al_2O_3 = CaO + 2/3AlF_3, \qquad (3)$$

$$\lg Kp = -\frac{14677}{T} + 4.2296.$$

The specified physicochemical regularities of high-temperature interaction of components and phase components of the $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}CaF_2$ system determine the necessity of creating slag-forming compositions, which would be characterized by high desulfurizing ability, appropriate viscosity and provide conditions for refining steel.

One of the directions of scientific and technological searches for increasing the efficiency of steel production with processing in LF and VD with oxide-fluoride slags is to reduce the specific consumption of fluorspar, electric energy and refractories for lining the ladle furnace. When analyzing the influence of calcium fluoride contained in the slags of secondary steelmaking, its positive effect on reducing the melting point and, accordingly, the viscosity of ladle slags formed from solid slag-forming materials is noted. The disadvantages include the increased specific consumption of refractory materials, the high price of imported fluorspar, the negative impact of CaF_2 (MPC 2 mg/m^3) and fluoride volatile compounds (SiF_4, $t_{ign} = 95°C$; AlF_3, $t_{ign} = 1270°C$) on the environment.

The mentioned disadvantages of the use of fluorspar (reduced stability of ladle lining, formation of volatile fluorine-containing compounds) are a feature of out-of-furnace processing; therefore, research and development of technological solutions are being conducted to reduce their harmful effects. In study [3], attention was first focused on the impact of high concentrations of calcium fluoride in furnace slags, which is expressed in an increase in activity (a_{FeO}) and, therefore, the equilibrium content of dissolved oxygen in the metal.

It was noted above that calcium fluoride accelerates the dissolution of lime and increases the fluidity (viscosity decreases) of slags, as a result of which the rate of steel desulfurization increases, i.e., the influence of CaF_2 is manifested in the kinetics of the desulfurization process. In some retrospective studies it was noted that the presence of CaF_2 in basic slags can significantly increase its basicity and thus increase the degree of steel desulfurization. The authors of [13], probably for the first time in the literature of Ukraine, substantiated that the steel desulfurization coefficient S(CaO + MgO) by oxide-fluoride slags with increased CaF_2 does not increase, but decreases, which follows from the data given in Table 2.

Table 2

Value of the coefficient of steel desulfurization by slag

Content of CaF_2, %	The value of the coefficient of desulfurization of steel by slag in the ladle $\left(L_S = \frac{(\%S)}{[\%S]}\right)$	
	Σ(CaO + MgO) < 65%	Σ(CaO + MgO) > 65%
< 4.0	96 (17 melting sessions)	67 (19 melting sessions)
> 4.0	81 (6 melting sessions)	53.3 (8 melting sessions)

For the same slag, which is characterized by the sum of components S(CaO + MgO), an increase in the CaF_2 content in the slag > 4% reduces the sulfur distribution coefficient by 15%. Based on the data from experimental melts, the authors of [13] also came to the conclusion about "… lack of desulfurizing ability in calcium fluoride". In that work, the decrease in the desulfurizing ability of furnace oxide-fluoride slags was explained by an increase in the activity of ferric oxide, which follows from the expression

$$L_S = (S)/[S] = K_s a_{(CaO)} / a_{(FeO)}, \qquad (4)$$

where K_s is the equilibrium constant of the metal desulfurization reaction;

$a_{(CaO)}$ is the activity of the "free" concentration of calcium oxide, which is determined by the method from [13].

Thus, the oxygen and sulfur content in the metal, which are in equilibrium with oxide-fluoride slags, should be the lower, the less calcium fluoride in the slag.

The given physicochemical laws of high-temperature interaction of components and phase components of oxide-fluoride systems determine the need to create slag-forming compositions with a limited CaF_2 content.

One of the most important technological tasks implemented during secondary steelmaking at a ladle furnace unit (LF) is metal desulfurization by slag systems. In production practice, the efficiency of metal refining in most cases is determined by the indicators of slag basicity (B) and the final characteristic of the degree of desulfurization (η_S).

An integral assessment of the efficiency of the metal desulfurization reaction by slag systems is determined by achieving a balance between metal and slag, oxygen activity in the metal, and the composition of slag and metal, taking into account the relative weight of slag

$$\left[S\right]_{fin} = \frac{\alpha_{[O]}\left(\left(S\right)_{slag} + \frac{\left[S\right]_{in}}{m}\right)}{f_S * C_S + \frac{\alpha_{[O]}}{m}}, \qquad (5)$$

where S_{in}, S_{fin} – sulfur content in the metal before and at the end of desulfurization; $\alpha_{[O]}$ – oxygen activity in the metal; f_S – sulfur activity coefficient; C_S – sulfide capacity of slag; m – relative weight of slag (kg) per kg of steel.

Components of the PI, PI + LF technologies are the presence of refining slag with increased desulfurization capacity. Depending on the degree of oxidation, sulfur in slags can be in sulfide (1) or sulfate (2) forms [10]:

$$1/2S_{2_g} + O_s^{2-} = 1/2O_{2_g} + S_s^{2-}, \qquad (6)$$

$$K_{1,2} = \frac{\alpha_{S^{2-}} * p_{O_2}^{1/2}}{\alpha_{O^{2-}} * p_{S_2}^{1/2}},$$

$$1/2\mathrm{S}_{2_g} + 3/2\mathrm{O}_{2_g} + \mathrm{O}_s^{2-} = \mathrm{SO}_{4s}^{2-}\ , \tag{7}$$

$$\mathrm{K}_{1,3} = \frac{\alpha_{\mathrm{SO}_4^{2-}}}{\alpha_{\mathrm{O}^{2-}} * p_{\mathrm{S}_2}^{1/2} * p_{\mathrm{O}_2}^{3/2}}.$$

For the specified temperature and composition of the slag, the equilibrium concentration of sulfur is determined only by ratio $\left(p_{\mathrm{O}_2} / p_{\mathrm{S}_2}\right)^{1/2}$, but not by the absolute values, of the partial pressures of oxygen and sulfur.

At the same time, the partial pressure of oxygen determines the form of the presence of sulfur in the slag melt: at $p_{\mathrm{O}_2} \leq 10^{-5}$ atm. sulfur is in the slag in the form of sulfide ions (MeS); at $p_{\mathrm{O}_2} \leq 10^{-3}$atm. – in the form of sulfates ($\mathrm{MeSO_4}$).

The latter condition determines the mechanism of sulfur removal by means of its oxidation during electroslag remelting.

To assess the desulfurizing properties of slag systems, the parameter "sulfide capacity – C_S" is used [12]

$$K_1 * \frac{\alpha_\mathrm{O}}{\gamma_\mathrm{O}} = C_\mathrm{S} = (S) * \left(\frac{p_{\mathrm{O}_2}}{p_{\mathrm{S}_2}}\right)^{\frac{1}{2}}. \tag{8}$$

The characteristics of the sulfide capacity of slags of the ternary system $\mathrm{CaO\text{-}Al_2O_3\text{-}SiO_2}$ [12] indicate the maximum value of the $\mathrm{C_S}$ parameter in the range of the $\mathrm{CaO\text{-}Al_2O_3}$ composition, as the basis of slags for secondary steelmaking, used in foreign practice.

Calcium fluoride accelerates the dissolution of lime and increases the fluidity (viscosity decreases) of slags, as a result of which the rate of steel desulfurization increases, i.e., the influence of $\mathrm{CaF_2}$ is manifested in the kinetics of the desulfurization process.

Of some interest are the results of the experimental determination of the sulfur-absorbing capacity of slags of the $\mathrm{CaO\text{-}Al_2O_3\text{-}SiO\text{-}CaF_2}$ system [13].

According to the authors of [14], "at a $\mathrm{SiO_2}$ content of 10–15%, the replacement of part of $\mathrm{Al_2O_3}$ with $\mathrm{SiO_2}$ (C-A-S-F system) has a negligible effect on the sulfide capacity ...". In metallurgical practice, the state of the gas phases ($\mathrm{O_2}$, S) is very often replaced by a 1% solution of the components in the metal phase

$$C'_\mathrm{S} = (S) * \frac{a_\mathrm{O}}{a_\mathrm{S}}, \tag{9}$$

where α_0 and α_S are the activities of oxygen and sulfur in the metal, respectively. The relationship of C'_S and C_S can be converted through the relation

$$C'_\mathrm{S} = \left(-\frac{2{,}154}{T} + 3.166\right) * C_\mathrm{S}. \tag{10}$$

The sulfur partition coefficient between slag and metal (L_S) is determined from the following equation

$$L_\mathrm{S} = \frac{(S)}{[S]} = \frac{C'_\mathrm{S}}{f_\mathrm{S} * a_\mathrm{O}}. \tag{11}$$

Analyzing expressions (8) to (10), we can conclude that replacing $\mathrm{CaF_2}$ with an element with a high affinity for sulfur and reducing the viscosity of the slag melt should have a positive effect on the thermodynamic capabilities of desulfurization.

5. 2. Justifying the possibility of replacing fluorspar in the composition of slags of remelting technologies and non-furnace processing with pegmatite

Aluminosilicates are widely distributed in nature and occupy up to 50% of the volume of the upper part of the earth's crust. By composition, feldspars, the most common rock-forming minerals, are divided into two mineralogical series – plagioclase and alkali feldspars and include 23 minerals [15].

A certain practical interest in the use of alkali metal oxides ($\mathrm{Na_2O}$, $\mathrm{K_2O}$) in the composition of refining slags of non-furnace processing is the use of alkali aluminosilicates, especially pegmatite with a total content of $\mathrm{Na_2O}$ and $\mathrm{K_2O}$ of 10–15% by weight.

Pegmatites are natural mineral formations composed of feldspar, quartz, and muscovite $\mathrm{KAl_2(OH,\ F)_2AlSi_3O_{10}}$ (a group of micas with local accumulations of accessory, liquid-impregnated minerals).

The State Balance of Mineral Resources as of 01.01.2006, according to [10], approved 9 deposits, including pegmatite, one microgranodiorite, and one technogenic – Mazurovsk feldspar raw materials (Donetsk oblast). Pegmatite reserves in the subsoil, including developed deposits, are 8132.2 thousand tons, confirmed – 6567.2 thousand tons.

The phase components of the $\mathrm{Na_2O\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2}$ system, basic elements in the crystallochemical structure of pegmatite, are shown in Fig. 3.

Of the 18 tetrahedra of the specified system, which characterize the topology of the phases are in subsolidus equilibrium, 8 contain $\mathrm{Na_2O}$ oxide. The predominant interaction of $\mathrm{Na_2O}$ with $\mathrm{SiO_2}$ and $\mathrm{Al_2O_3}$ oxides present in the melt in the form of anions $[\mathrm{SiO_4}]^{4-}$, $[\mathrm{AlO_4}]^{4-}$ can be represented by the following reaction

$$n\ \mathrm{Na_2O} + m\ \mathrm{SiO_2} = \mathrm{Na}_{2n}\mathrm{Si}_m\mathrm{O}_{n+4}. \tag{12}$$

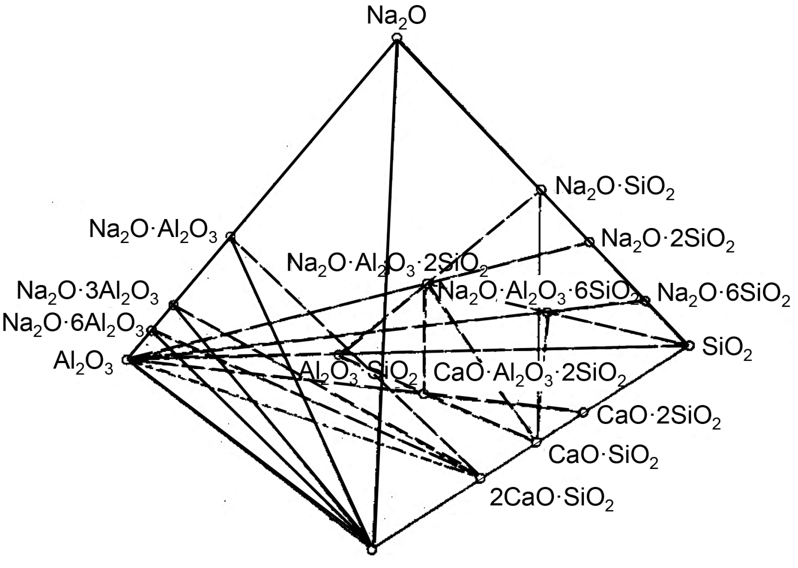


Fig. 3. Phase ratios in the subsolidus state of the $\mathrm{Na_2O\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2}$ system [15]

As a result of this reaction, n oxygen atoms belonging to Na_2O oxide are transferred to silicon. This results in the process of depolymerization of silica, which is represented by the scheme

$$Na_2O + \equiv Si-O-\left(Si\equiv\right) \rightarrow \left[\begin{matrix} Na-O- \\ Na-O- \end{matrix} Si=\right].$$

The destruction of structures with the main motif $[SiO_4]^{4-}$, $[AlO_4]^{4-}$ leads to a decrease in the viscosity of the melt and, as a consequence, to a decrease in the liquidus temperature of the melt.

The diagram of crystallization fields in the Na_2O-CaO-SiO_2 system shown in Fig. 4 confirms the presence of low-melting compounds at a content of 10–15 wt. % Na_2O.

Thus, a promising direction for improving the chemical composition of slag is the introduction of Na_2O-based components into the slag composition.

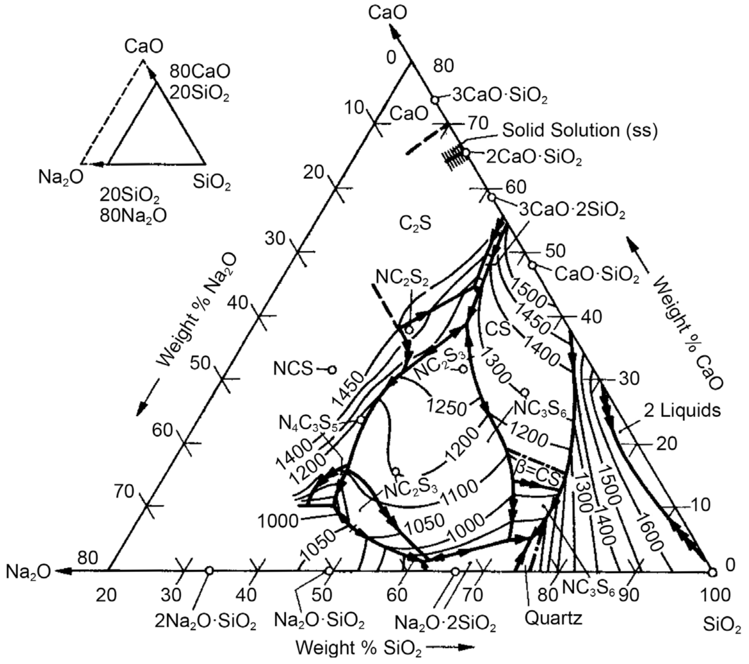


Fig. 4. Phase equilibrium in the system Na_2O-CaO-SiO_2 [12]

5. 3. Analyzing the influence of Na_2O and K_2O in the composition of slags of the CaO-SiO_2 + (Na_2O, K_2O) system on the rheological characteristics of the slag melt

To determine the rheological characteristics of slag melts, measurements of the melting temperatures of pegmatite, a mixture of lime and pegmatite (at a ratio of lime to pegmatites of 3:1), as well as a mixture of lime with fluorspar (at a ratio of lime to fluorspar of 3:1) were performed. Pegmatite supplied according to TU U 14.5-22141296-001-2002 has the following chemical composition, wt. % (): SiO_2 – 75.9; free quartz – 34.71; Al_2O_3 – 13.7; CaO – 0.73; MgO – 0.8; Fe_2O_3 – 0.7; K_2O – 3.5; Na_2O – 4.4; PPP – 0.34. Measurements were carried out on a high-temperature microscope MNO-2 Carl Zeiss. Temperature control in the heating zone of the sample was carried out according to the readings from the TPP thermocouple (type S). Before use, lime, pegmatite, and fluorspar were crushed to a fraction of 0.2–0.3 mm. Preparation of the studied mixtures was carried out by mixing the corresponding components for 30 min. Subsequently, the materials are compressed in the form of a cylinder with a diameter of 3 mm and a height of 4 mm.

Observations of changes in the shape and aggregate state of the studied samples are given in Table 3.

Based on the results of the experiment, the melting temperatures of the studied samples of oxide systems were determined. For pegmatite, the melting temperature corresponds to 1270°C, for a mixture of lime and pegmatite (at a ratio of 3:1) – 1342°C, and for a mixture of lime and fluorspar (at a ratio of 3:1) – 1363°C.

As follows from the results of the experimental determination of the melting onset temperatures of the components of the slag-forming mixture, pegmatite, as an independent component of the mixture, has a relatively low melting temperature (1270 °), which ensures earlier slag formation of SSM.

Thermochemical characteristics of pegmatite, taking into account its chemical composition (SiO_2 total – 75.9%, including free quartz 34.71%) indicate that the predominant amount of silica in pegmatite is associated with ultrabasic oxides in the form of MeO * SiO_2, MeO * $2SiO_2$ (Me = Na, K).

Table 3

Experimental determination of melting point for slag-forming mixtures

Material	Temperature, °C	Observation
Pegmatite	1158	The edges of the cylinder are rounded
	1190	Cylinder wall geometry changes (barrel)
	1220	Material has the appearance of a drop
	1240	Drop spreads over the substrate
	1270	Complete spreading over the substrate
Lime + Pegmatite (3:1)	1260	Material swelling is observed
	1310	Shrinkage and rounding of the cylinder edges
	1335	Changing the geometry of the cylinder walls (barrel)
	1341	The drop spreads over the substrate
	1342	Complete spreading over the substrate
Lime + fluorspar (3:1)	1110	Shrinkage of the cylinder
	1258	Changing the geometry of the cylinder walls (barrel)
	1343	The sample has the shape of a trapezoid
	1352	The drop spreads on the substrate
	1363	Complete spreading on the substrate

Below are thermodynamic data on the interaction of alkali metal oxides Na, K with silica:

$Na_2O * SiO_2$ sol. = $Na_2O * SiO_2$ liq.,

t_{melt}. = 1,089°C, (13)

$\Delta G_T = 51{,}748 - 38.0T$, J/mol,

$Na_2O * 2SiO_2$ sol. = $Na_2O*2SiO_2$ liq.,

t_{melt}. = 874°C, (14)

$\Delta G_T = 35{,}530 - 31.0T$, J/mol,

$K_2O * SiO_2$ sol. =
= $K_2O * SiO_2$ liq., t_{melt}. = 976°C, (15)

$\Delta G_T = 50{,}160 - 40.1T$, J/mol.

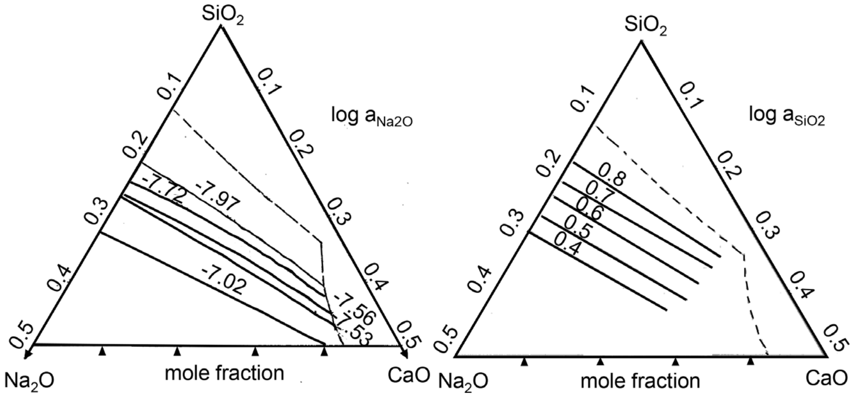
Table 4 gives values of the Gibbs energy for alkali metal silicates in the pegmatite structure at slag melt temperatures.

Table 4

Gibbs energy of alkali metal silicates in the temperature range of slag melt

Alkali metal silicate	Gibbs energy – ΔG_T, J/mol			
	1,500°C	1,550°C	1,600°C	1,650°C
$Na_2O * SiO_2$	15,626	17,526	19,426	21,326
$Na_2O * 2SiO_2$	19,433	20,983	22,533	24,083
$K_2O * SiO_2$	20,937	22,942	24,947	26,952

The calculated values of the Gibbs energy given above give grounds to assume the equally probable presence of silicates $Na_2O * SiO_2$, $Na_2O * 2SiO_2$, $K_2O * SiO_2$ in the pegmatite melt at temperatures of steelmaking processes. When slag is formed from components CaO and pegmatite, the basic composition of the initially formed slag is represented by phases of the CaO-SiO_2-Na_2O (K_2O) system, the activity of the components of which is shown in Fig. 5. As shown in the data of Fig. 5, the calculated values of the activities of Na_2O and SiO_2 do not depend on the phase components of the CaO-SiO_2-Na_2O system.



a *b*

Fig. 5. Logarithms of activity values in the CaO-Na_2O-SiO_2 system at 1400°C [12]: *a* — Na_2O; *b* — SiO_2

The sulfide capacity of melts of the CaO-SiO_2-Na_2O system is determined by both the absolute Na_2O content and the basicity CaO/SiO_2 of the slag (Fig. 6).

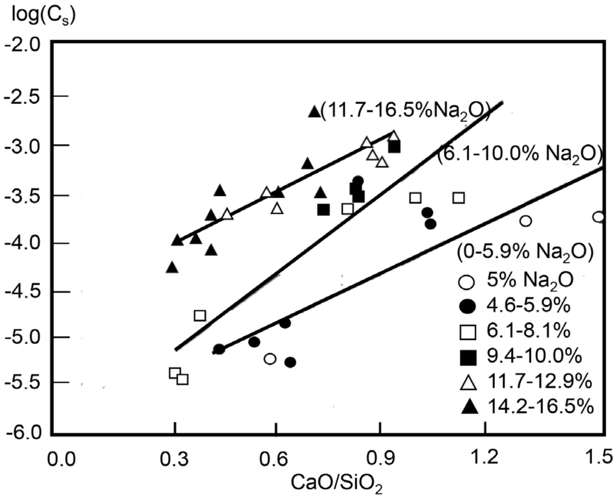


Fig. 6. Effect of Na_2O on sulfide capacity in the CaO-Na_2O-SiO_2 system at 1400°C [12]

The data in Fig. 6 indicate that to ensure the optimal composition of the refining slag in the ladle-furnace unit, it is necessary to limit the Na_2O content in the slag to £ 5% when using pegmatite since an increase in the pegmatite content clearly leads to a decrease in the basicity of the slag with a simultaneous decrease in the sulfide capacity.

5. 4. A series of experimental melts using slag of the proposed composition and analysis of the results

Under the conditions of an enterprise, the metal-semi-product was melted in EAF-190 and released through a bay window device, which excluded the ingress of furnace slag into the steel-pouring ladle with a capacity of 160 tons and made it possible to determine the effect of replacing fluorspar with pegmatite during out-of-furnace processing of steel using the following technology: pegmatite additive on the release of the metal-semi-product in a steel ladle with EAF-190 together with aluminum (AV91 DSTU 3753-98), carbon (LF VD), lime (TU 23.5-23365425-696: 2014), and ferroalloys.

Pegmatite from the Yeliseyevskoye deposit (Zaporizhzhya oblast) with a fraction of 20–90 mm was supplied according to the technological conditions of TU U 14.5-22141286-001-2002. The chemical composition of the pegmatite, determined in the samples submitted to the Center for Certification Testing of Non-Ferrous Metals, Standard Samples and Metrological Support for Analytical Control (certification certificate No. 3813-85 VL), is given in Table 5.

The chemical composition of the slag from the non-furnace treatment of steel is given in Table 6.

Data on the sulfur content in steel at the outlet from the EAF-190 furnace and at the end of the secondary steelmaking of the experimental melts are given in Table 7.

Table 5

Chemical composition of pegmatite supplied for experimental melting, protocol No. 455

Mass fraction of oxides, % by weight							
SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	K_2O	Na_2O	l.o.i.
75,2	13.2	1.21	1.1	0.6	2.1	6.1	0.34

Table 6

Chemical composition of slags with replacement of fluorspar by pegmatite

Mass fraction of oxides, % by weight							
SiO_2	Al_2O_3	CaO	MgO	MnO	S’	Na_2O	Slag basicity
19	20	57	8	0.5	1.9	6.1	1.7

Table 7

Initial $[S]_{in}$ and final $[S]_{fin}$ sulfur content and degree of steel desulfurization (η_s, %) during the out-of-furnace metal treatment of experimental melts

Application option	Number of melting sessions, pcs.	$[S]_{in}$, ppm	$[S]_{fin}$, ppm	η_s, %
Exploratory technology	242	(330…520) 430	(40…90) 60	86.0
Current technology	50	(370…540) 440	(20…70) 40	90.9

Note: in the columns $[S]_{in}$, $[S]_{fin}$, the minimum and maximum sulfur values are given in brackets, respectively, and the average values are given outside the brackets

The results of our analysis of the chemical composition of metal from the experimental melts, the results of studies on the metal macrostructure, as well as mechanical tests, indicate that the proposed technological solutions fully comply with the requirements from the regulatory and technical documentation.

6. Discussion of results based on investigating the rational composition of slags of reduced basicity

Our analysis of the physicochemical properties of fluorspar (CaF_2) as a conventional flux for metallurgical slags revealed the following:

– despite the fact that CaF_2 is an important component of slag, which is able to reduce the melting point and viscosity, there are several features of its application, which are associated with significant thermodynamic, technological, and environmental limitations;

– calculations of the thermodynamic activities of components in the CaO-CaF_2, CaO-Al_2O_3-SiO-CaF_2 systems using expressions (1) to (3) make it possible to draw conclusions about the instability of oxide-fluoride slags, their tendency to stratification, and an increase in FeO activity at a CaF_2 content of more than 4%. It should also be noted that the high partial pressure of CaF_2 vapors in the electric arc zone and the formation of volatile fluorine-containing compounds cause intensive evaporation and accelerated destruction of the lining;

– analysis of the structural parameters of slag melts (Fig. 2) confirms that CaF_2 does not participate in mineral formation, but performs the function of a depolymerizer, which, according to formula (4), is accompanied by an increase in the oxidation potential of the system;

– the established patterns (Table 2) show that with an increased CaF_2 content, the refining ability of slags decreases. This fact confirms the need to limit the proportion of CaF_2 in slag and search for alternative slag-forming components that make it possible to provide a stable structure, high desulfurization ability, and reduce the release of harmful elements.

Analyzing the above, it is necessary to note the qualitative difference of our results from previously published works [2, 4, 5]. The upper limit of the possible CaF_2 content in slag has been established, which does not lead to intensive evaporation of fluorine and deterioration of the refining properties of slag (up to 4%). Thus, it is shown that fluorspar cannot effectively provide the necessary physicochemical properties of the slag mixture.

Given the limitations of the use of CaF_2 in slags, it is proposed to use pegmatite as its replacement, which belongs to the class of alkali aluminosilicates and contains 10–15 wt. % Na_2O and K_2O, which provide its high refining properties. Unlike expensive components such as B_2O_3 and Li_2O, proposed for use in [1, 3], pegmatite, as a natural mineral formation consists of feldspar, quartz, and muscovite $KAl_2(OH, F)_2AlSi_3O_{10}$. A positive factor is its wide availability in Ukraine (according to the State Balance of Mineral Resources of Ukraine, its confirmed reserves are 6567.2 tons). The phase ratios of the main oxides included in the crystal chemical structure of pegmatite are shown in Fig. 3. Analysis of Fig. 3 allows us to conclude that out of 18 tetrahedral structures of this system Na_2O-CaO-Al_2O_3-SiO_2, 8 contain Na_2O oxide, which indicates its high chemical activity in melts. The predominant interaction of Na_2O with SiO_2 and Al_2O_3 oxides present in the melt in the form of anions $[SiO_4]^{4-}$, $[AlO_4]^{4-}$ is represented by reaction (11). The destruction of structures leads to a decrease in the viscosity of the melt and, as a consequence, to a decrease in the liquidus temperature of the melt. This fact is consistent with the phase diagram of the Na_2O-CaO-SiO_2 system (Fig. 4), where at a Na_2O content of 10–15 wt. %, low-melting compounds are formed. It is this property that determines the prospects for using pegmatite as a component of slag-forming systems. Therefore, according to the analysis of phase equilibria (Fig. 3, 4), thermochemical regularities (12) and structural transformations of aluminosilicate melts, the use of pegmatite as a replacement for fluorspar is scientifically justified and promising. This significantly and organically complements studies [7, 8], since the range of components capable of providing an effective level of refining capacity of slags is expanding.

According to the results of the experiment to determine the rheological characteristics, it was found that for pegmatite the melting point corresponds to 1270°C, for a mixture of lime and pegmatite (at a ratio of 3:1) – 1342°C, and for a mixture of lime with fluorspar (at a ratio of 3:1) – 1363°C. As shown in Table 3, pegmatite has the lowest melting point, which ensures earlier slag formation. The high content of bound silica in the form of Na and K silicates is confirmed by the thermodynamic characteristics of reactions (13) to (15), where the melting points and the ΔG_T dependence are given. Based on the data in Table 4, which shows the calculated values of Gibbs energy, we can conclude that the $Na_2O * SiO_2$, $Na_2O * 2SiO_2$, K_2O*SiO_2 phases can coexist in the pegmatite melt at temperatures of steelmaking processes. When CaO interacts with pegmatite, a slag system CaO-SiO_2-Na_2O (K_2O) is formed, the activity of the components of which is shown in Fig. 5. As can be seen from Fig. 5, *a*, *b*, the calculated values of the activities of Na_2O and SiO_2 do not depend on the phase components of the CaO-SiO_2-Na_2O system. The sulfide capacity of melts of the CaO-SiO_2-Na_2O system is determined by both the absolute Na_2O content and the basicity of the CaO/SiO_2 slag. It is shown (Fig. 6) that an increase in the Na_2O concentration above 5% leads to a decrease in the basicity of the slag with a simultaneous decrease in the sulfide capacity. Therefore, when using pegmatite, the Na_2O content in the refining slag should not exceed 5% to ensure optimal refining properties. The obtained data on the properties of slag systems CaO-SiO_2-Na_2O (K_2O) complement works [6, 9], which did not take into account the influence of Na_2O (K_2O) on the properties of the slag. Thus, the scientific basis of the properties of metallurgical slags is expanded. Taking into account our results in the developed artificial neural network [9] could make it possible to expand the possibilities of its use.

The results of industrial smelting confirmed the possibility of replacing pegmatite fluorspar with ensuring the required slag properties. The formation of slag with a basicity of 1.7 (Table 6) and an increased Na_2O content ensured stable reactivity. This fact is in good agreement with the calculated values of the Gibbs energy (Table 4), the values of the activities of Na_2O and SiO_2 (Fig. 5) and data on the effect of Na_2O on the sulfide capacity in the CaO-Na_2O-SiO_2 system (Fig. 6). It should be noted that the slag containing Na_2O showed reduced indicators of the degree of desulfurization (η_S – 86% versus 90.9) compared to the use of classical slag; however, the final sulfur content (60 ppm) fully complies with regulatory requirements (Table 7). A slight decrease in the degree of desulfurization due to the influence of Na_2O is compensated by earlier melting of pegmatite, which, in turn, contributes to the rapid formation of liquid slag and a stable process. Analysis of the macrostructures of the resulting steel and its mechanical properties confirmed the absence of negative effects when replacing CaF_2.

Thus, the devised technology for replacing fluorspar with pegmatites in the composition of slags of secondary steelmaking is not inferior to the indicators of the current technology in terms of technological characteristics. It meets the requirements of the import substitution concept, which is implemented at the enterprises of Ukraine. It should be noted that the use of our results is limited to arc steelmaking furnaces and secondary steelmaking units (ladle-furnace unit plant and vacuum degasser). The reason for this is that to ensure the refining properties of the proposed slag, high temperatures of 1600–1700°C are required, which provide the appropriate rheological characteristics. Units such as induction furnaces and oxygen converters, due to differences in temperature regimes and slag formation kinetics, do not allow for the proper formation of slag containing pegmatite.

The disadvantage of this study is that it does not sufficiently take into account the modes of electric arc heating. To ensure rational technical and economic indicators of metal smelting in arc steelmaking furnaces, it is important to link the obtained scientific results with the operating modes of the electric furnace transformer. Therefore, further development of research consists in improving the electrical modes in arc steelmaking furnaces and installing a "ladle-furnace" because slags of reduced basicity provide a reduction in the length of the electric arc. This makes it possible to supply more power to the furnace bath, thereby reducing the duration of melting.

7. Conclusions

1. Analysis of the physicochemical properties of fluorspar (CaF_2) as a conventional flux for metallurgical slags revealed the existence of significant disadvantages of its use. Calculations of the thermodynamic activities of components in the CaO-CaF_2, CaO-Al_2O_3-SiO-CaF_2 systems allowed us to draw conclusions about the instability of oxide-fluoride slags, their tendency to delamination and an increase in FeO activity at a CaF_2 content of more than 4%. It should be noted that the high partial pressure of CaF_2 vapors in the electric arc zone and the formation of volatile fluorine-containing compounds cause intensive evaporation and accelerated destruction of the lining. Analysis of the structural phases of the slag confirms that CaF_2 does not participate in mineral formation but performs the function of a depolymerizer, which is accompanied by an increase in the oxidation potential of the system. It was established that with an increased CaF_2 content, the refining ability of slags decreases. This fact confirms the need to limit the proportion of CaF_2 in the slag and to search for alternative slag-forming components that make it possible to ensure a stable slag composition, high desulfurization capacity, and reduction of the release of harmful elements.

2. Considering the limitations of the use of CaF_2 in slags, it is proposed to use pegmatite as its replacement, which belongs to the class of alkali aluminosilicates and contains 10–15 wt. % Na_2O and K_2O, which enable its high refining properties. A positive factor in the use of pegmatite is its wide availability in Ukraine. Analysis of the crystallochemical structure of pegmatite allows us to conclude that it has high chemical activity in melts. It is shown that the destruction of the $[SiO_4]^{4-}$, $[AlO_4]^{4-}$ structures leads to a decrease in the viscosity of the melt and, as a result, to a decrease in the liquidus temperature of the melt. It is this property that determines the prospects for the use of pegmatite as a component of slag-forming systems. Thus, the use of pegmatite as a replacement for fluorspar is scientifically sound and promising.

3. According to the results of the experiment to determine the rheological characteristics, it was found that for pegmatite the melting point corresponds to 1270°C, for a mixture of lime and pegmatite (at a ratio of 3:1) – 1342°C, and for a mixture of lime with fluorspar (at a ratio of 3:1) – 1363°C. Thus, the effect of the influence of Na_2O and K_2O in the composition of slags of the CaO-SiO_2 + (Na_2O, K_2O) system on the rheological characteristics of the slag melt (reduction in viscosity, reduction in the temperature of the onset of crystallization) was confirmed. In this case, unlike CaF_2, the evaporation of alkali metal oxides is reduced and the stability of the composition of the refining slag is ensured during metal processing in the ladle-furnace unit. At the same time, it is shown that an increase in the Na_2O concentration above 5% leads to a decrease in the basicity of the slag while simultaneously reducing the sulfide capacity. Therefore, when using pegmatite, the Na_2O content in the refining slag should not exceed 5% to ensure optimal refining properties.

4. A series of experimental melts was carried out, which regulates the slag formation mode at LF with complete replacement of fluorspar in the composition of SSM with pegmatites from the Yeliseyevskoye deposit (Zaporizhzhya oblast), supplied according to the technical conditions of TUU 14.5.-22141286-001-2002. A comparative analysis of the compositions of refining slags of the ladle-furnace unit of the current and experimental technologies was performed.

During the secondary steelmaking with slags using pegmatite, despite the reduction in the basicity of the slag to 1.8–2.0, a significant increase in the fluidity of the slag was recorded and the degree of metal desulfurization was achieved, commensurate with the indicators of the current technology. The chemical composition of the metal and slag of the experimental melts at the stage of smelting the semi-finished metal and processing the steel on the ladle-furnace unit was analyzed. It was established that the metal of the experimental melts fully met the requirements from the regulatory and technical documentation.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

Authors’ contributions

Yurii Proidak: Conceptualization, Investigation, Formal analysis, writing – original draft, Writing – review & editing; **Anton Gorobets**: Methodology investigation, Validation data curation, Writing – review & editing; **Oleksandr Zhadanos**: Conceptualization, Formal analysis, Methodology, Software; **Mariia Rybalchenko**: Validation, Investigation, Resources, Data curation

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