

# THE INFLUENCE OF OXISULFIDES ON LOSSES OF NICKEL AND COBALT IN SLAGS

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## ABSTRACT

Laboratory investigations made it possible to define more accurately the composition of oxisulfide as a FeO-FeS solution into which nickel, cobalt, and copper can transfer. At certain mole ratios of FeO and FeS homogeneous melt can be produced and separation into two or three layers is possible.

During oxidation of nickel matte containing less than 40% Ni, oxisulfide is formed in the absence of SiO<sub>2</sub> or if slag is formed with a basicity of over 0.8.

The presence of oxisulfide increases the nickel and cobalt losses in slags and results in an increase of the conventional equilibrium constant along with a lower nickel content and higher iron content in the matte.

Practical recommendations have been worked out as to how to use the possibility of oxisulfides formation or how to prevent their formation.

## INTRODUCTION

Based on the technical nature of losses of nickel, some authors [1,2] have recommended (in order to minimize losses) to overheat slag to reduce its viscosity, select a slag composition with a maximum interfacial tension, create appropriate conditions for coagulation of fine sulfide particles and their settling.

The authors of [3,4] have different viewpoint with respect to the mechanism of losses and assume that the distribution of nickel and cobalt between the smelting products is subject to the law of mass action (LMA) and may be described by the equilibrium constant:

$$K = \frac{(Me) [Fe]}{[Me] (Fe)} \quad (1)$$

Where *Me* is Ni and Co; in parentheses the *Me* content in slag and in square brackets in alloy. By developing these ideas, I.D. Reznik [5-8] studied in detail the mechanism of the equilibrium distribution of nickel and cobalt between the phases and found that in commercial smelting and converting processes the near to equilibrium distribution was reached.

From these results it was concluded that the transfer of nickel and cobalt to slag is interrelated with the iron distribution. The minimum losses are attained with incomplete transfer of iron to the slag when its part remains in the metallic alloy or in the matte, i.e., when smelting to produce low-grade alloy or matte. Overheating of slag has adverse effects and its temperature should slightly exceed the fluidity temperature; the phase separation proceeds quickly eliminating the necessity of an additional settler.

## DISTRIBUTION OF NICKEL AND COBALT BETWEEN SMELTING PRODUCTS

The equilibrium constants of the reactions schematically described by Equations (2) to (5) have been studied:



When calculating the constants, the total content of nickel and cobalt in the smelting products was taking into account without considering the activities, assuming that the relation of nickel and iron activities in the matte and the nickel and iron activities in the slag are close to unity. As a result of such calculation a value was obtained which is called “conventional equilibrium constant”.

As can be seen from Figures 1 and 2, in the system of metal alloy/slag, the value of the conventional equilibrium constant  $K_{\text{Ni/Fe}}$  at a temperature of 1300°C is equal to 0.005 and does not depend on the nickel content of the alloy; the value of  $K_{\text{Co/Fe}}$  is 0.03.

The fields of the values of the equilibrium constants calculated by the analysis of the smelting products from commercial processes are plotted over the curves of Figures 1 and 2, which confirms their similarity to the equilibrium distribution in industrial processes.

To modify Equation (1) by moving the metal content of slag to the right-hand side of the equation we obtain:

$$(Me) = K \frac{[Me] (\text{Fe})}{[\text{Fe}]} \quad (6)$$

and it follows, that the metal content of slag is directly proportional to the metal content of the alloy and iron content of slag.

The comparatively high value of  $K_{\text{Co/Fe}}$  in relation to  $K_{\text{Ni/Fe}}$  explains the cause of the higher losses of cobalt in slags.

A different picture has been obtained when smelting to produce sulfide alloy using Reactions (4) and (5). For high grade mattes, the value of  $K_{\text{Ni/Fe}}$  was 0.005, similar to the system with the metallic alloy. But as the nickel content of the matte decreased and the iron content rose, the value of the conventional equilibrium constant increased to as high as 0.050 in low grade mattes as shown in Figure 1. A similar increase in the “cobalt” constant is shown in Figure 2.

## CHARACTER OF NICKEL LOSSES IN SLAGS

We believe that equilibrium criteria have decisive significance in the process of formation of losses of nickel and cobalt.

Since under commercial conditions the nickel and cobalt distribution between matte and slag, characterized by a conventional equilibrium constant, taking into account the total nickel content of slag, fits well into the curves obtained in laboratory experiments and is continuously reproduced in industrial practice, as well as statistically confirmed relation between the nickel content of slag, nickel content of matte and iron content of slag, we have made a conclusion that the law of mass action is substantiated under the conditions of industrial processes.

Another proof of the insignificant role of mechanical losses of nickel in slag is that although both nickel and cobalt are simultaneously present in the melt each metal reports to slag with its own constant and the Ni:Co ratios in matte and slag are different, whereas “entangling” of

matte particles in slag would result in an equal ratio. The necessity of taking into account the total amount of nickel in slag, confirmed by the mentioned conclusions, substantiates the presence of nickel and cobalt in slag in the ion form.

The equilibrium constants increase with slag cleaning, since various amounts of oxisulfides are present in sulfide solutions. Of course, in the past we also paid attention to an increase in oxygen content of low-grade mattes, which was determined as the balance  $\Delta = 100 - (\text{Ni} + \text{Fe} + \text{S})$  and amounted to 10% or more, but we could not attribute the increase in losses to this fact at that time.

## **STUDIES OF THE EFFECT OF OXISULFIDES ON NICKEL AND COBALT LOSSES IN SILICATES SLAGS**

As a result of studies carried out in the Gintsvetmet Institute carried out in cooperation with the Urals Division of the Russian Academy of Sciences, it was found that in the system nickel matte/slag there was present oxisulfide dissolved or in the form of separate phase consisting mainly of the FeO-FeS alloy [9-11].

The laboratory tests of silicate iron-calcium slag cleaning using low-grade metallized matte resulted in production of matte with 8.8% Ni and slag with 0.17% Ni (Table 1). The basicity of slag  $B = \text{CaO}:\text{SiO}_2 = 0.57$  is only slightly different from that of the feed slag. The sulfur loss by the balance was 11%, which confirms a low degree of desulfurization. The equilibrium constant fits well within the curve in Figure 1.

In smelting with slag with elevated CaO content (Table 1) and with the same matte, three layers were separates, i.e., matte, slag and oxisulfide in-between. Matte was significantly enriched and metallized: it contained 23.2% Ni and only 9.3% S. The slag had a basicity of  $B=1.03$  and low nickel content (0.09%); the equilibrium constant was 0.007.

The oxisulfide yield was 35% of the feed slag weight; it contained 1.8% Ni, 13.4% S. About 26.7% Ni, 41.9% Fe and 65.7% S reported to the oxisulfide. The conventional equilibrium constant between matte and oxisulfide was 0.070, characterizing transfer of a large amount of nickel into oxisulfide. No desulfurization was observed.

A comparison of two smelting runs indicated that an increase in the CaO content of feed slag resulted in formation of oxisulfide, but the calcium oxide added to slag intentionally remained in the slag and did not report to oxisulfide.

In some smelting runs we investigated the behavior of cobalt. For example, in one run when smelting to produce slag with  $B = 1.04$ , we obtained matte with 29.0% Ni and 2.6% Co; oxisulfide with 3.2% Ni and 0.65% Co; and slag with 0.17% Ni and 0.26% Co. The equilibrium constants of matte/slag were:  $K_{\text{Ni/Fe}} = 0.007$ ;  $K_{\text{Co/Fe}} = 0.13$ ; and constants between matte and oxisulfide  $K_{\text{Ni/Fe}} = 0.079$  and  $K_{\text{Co/Fe}} = 0.16$ . The following amounts transferred to individual products: 67% Ni, 35% Co and 7% Fe to matte; 29% Ni, 35% Co, 44% Fe to oxisulfide; and 3.4% Ni, 30% Co, and 49% Fe to slag.

According to the nuclear gamma-resonance spectroscopy, the oxisulfide produced contained 17.6% FeS, 68.8% FeO and Fe<sub>3</sub>O<sub>4</sub>, including 13.4% S and 17.6% O<sub>2</sub>. A polished section of oxisulfide examined on a Kamebax microscope indicated the presence of 4 phases as shown in Table 2.

Investigation of the oxisulfide composition has confirmed that it is based on a FeS-FeO solution with ferronickel dissolved in it. Much nickel and cobalt reports to this solution; a certain amount of nickel and cobalt is dissolved in troilite; wustite and silicate do not virtually contain any amounts of these metals.

To study the role of calcium oxide in the amount of oxisulfide produced, a series of smelting runs were performed to model a process of sulfides oxidation in the presence of slag by adding different amounts of Fe<sub>2</sub>O<sub>3</sub>. It is seen from Figure 3 that the maximum yield of oxisulfide took place in the case of low-grade feed mattes and slag basicity  $B = 0.8-1.0$ . With

an increase in the nickel content of feed matte, the yield of oxisulfide decreased; with 40% Ni in matte no oxisulfide in the form of a separate phase was formed. An increase in the  $\text{SiO}_2$  content and a decrease in the slag basicity also resulted in lower oxisulfide yields; at  $B < 0.3$  no oxide was formed. Figure 4 shows transfer of nickel, cobalt and iron into all three phases in the case of different mattes and at a basicity = 0.9.

## **STUDY OF CONDITIONS FOR OXISULFIDE FORMATION IN THE PROCESS OF Ni MATTE OXIDATION IN THE ABSENCE OF FLUXES**

The conditions for oxisulfide formation were studied under laboratory conditions [4, 10, 11]. The experimental procedure consisted of smelting commercial mattes with additions of wustite to model the process of matte oxidation in the absence of fluxes in an argon stream at  $1250^\circ\text{C}$ . The feed mattes contained 12 and 27% Ni and were highly metallized.

The oxidation process can be graphically represented on a triple phase diagram combining the feed matte composition with the triangle apex FeO:A-B-FeO (Figure 5).

As long as “oxidation” proceeds the melt composition changes from point A toward FeO and when a certain mole ratio of FeO in the feed to remaining FeS is reached, the melt separates into two phases. As can be seen from Figure 5, the border of the separation field has a shape of an arc in which the end points correspond to 25% FeO, 63% ( $\text{Ni}_3\text{S}_2 + \text{Ni}$ ) and 70% FeO, 2% ( $\text{Ni}_3\text{S}_2 + \text{Ni}$ ), while the composition of the melt at the arc dome is 9-15% FeO, 27-33% ( $\text{Ni}_3\text{S}_2 + \text{Ni}$ ) and 58% (FeS + Fe). The dotted line shows the transition zone.

Saturation of the melt with oxygen up to point B occurs under conditions of homogeneity; oxisulfide is formed. With a further increase in the FeO content, separation of oxisulfide into two layers begins; the composition of each layer or phase is determined by canodes, two of which C-D and M-N are shown in Figure 5.

In the transition zone (at point B), where the smelting products separation is unstable, the nickel content of both phases is almost similar.

The lower layer at point C contains 50% ( $\text{Ni}_3\text{S}_2 + \text{Ni}$ ) and 10% FeO; the upper equilibrium layer (point D) contains 4.8% ( $\text{Ni}_3\text{S}_2 + \text{Ni}$ ) and 55% FeO; at point M (with more addition of FeO to the melt) it contains up to 58% ( $\text{Ni}_3\text{S}_2 + \text{Ni}$ ) and this phase with respect to the Ni:S ratio approaches the high-grade nickel matte; the corresponding upper layer (point N) is low in nickel: only 1.5%  $\text{Ni}_3\text{S}_2$ , being similar with respect to Ni content to converter slag, but it is oxisulfide.

Thus, it has been demonstrated that the higher nickel content of the sulfide phase, the lower nickel content of the equilibrium oxisulfide phase. The identified relationship contradicts to the general rule mentioned above: “the richer the matte, the richer the slag”. However, we consider distribution of nickel (and cobalt) in different systems: in case of regular matte and silicate slag, the separation of products of the exchange reaction  $\text{NiO} + \text{FeS}$  or  $\text{NiO} + \text{Fe}$  is rather efficient according to its equilibrium constant and the Ni content of slag actually increases with higher grade of matte; in an oxisulfide system the phase separation is incomplete due to elevated mutual solubility and the oxisulfide layer is always richer than the silicate slag layer.

Some smelting runs were also performed with copper-nickel matte produced by electrothermal smelting. In this case either homogenous melt or two layers were produced, but no rich sulfide prills. We assume that this is attributed to the low degree of metallization of initial matte. This problem requires additional investigation.

The studies conducted suggest the following mechanism of oxisulfide formation. As a result of iron oxide replacement in slag with a stronger base, i.e., calcium oxide, the activity of FeO in slag increases. The “liberated” FeO is dissolved in low-grade matte up to the saturation level, depending on the FeS concentration in matte, which results in separation of matte into

oxisulfide containing of FeO and FeS and matte enriched in nickel. Addition of SiO<sub>2</sub> binds FeO, prevents formation of oxisulfide and dissociates the latter. Along with matte enrichment in nickel, its FeS content decreases and the oxisulfide yield becomes lower.

Low-grade nickel mattes with up to 10% Ni contain 4-13% oxygen in the form of dissolved FeO and such mattes are in essence oxisulfides in which no separation has occurred due to the fact that they did not reach the solubility limit.

The investigations conducted have revealed the character of nickel matte converting under commercial conditions at initial stages of blowing prior to addition of quartz flux: this process proceeds without evolution of SO<sub>2</sub>, the melt remains homogeneous; when a second layer is formed, its tapping is accompanied by transfer of a large amount of “matte” into ladles, because it is not slag tapped but oxisulfide with elevated contents of nickel, copper and cobalt.

## DISCUSSION OF RESULTS

Figure 6 shows a comparison of the effect of nickel content in matte on the oxisulfide yield according to Figure 3 and on the value of conventional equilibrium constant according to Figure 1, where results of melting runs with slag basicity of 0.4-0.5 are presented.

The symbatic character of the both relationships confirms the direct connection between nickel loss and the presence of oxisulfide: the lower nickel content and higher iron content of the matte, the more oxisulfides are dissolved and the higher is the value of the conventional equilibrium constant, which characterizes an increase in the nickel content of slag.

Investigation of the role of oxisulfide has reputed the objections of the proponents of the theory of mechanical losses of nickel in slag and confirms the validity of the law of mass actions as a main regulator of nickel and cobalt distribution between the smelting products in commercial smelting processes.

The identified relation of oxisulfides with nickel loss in slag suggests some recommendations for commercial implementation:

- when converting nickel and copper-nickel mattes it is necessary to add quartz and produce acidic slags; if there are some delays with quartz addition, slag should be tapped only after the nickel content (or nickel + copper) in the converter mass reaches at least 40%;
- the converting process can be accelerated at initial stages by blowing matte without quartz and tapping oxisulfide melt; this would speed up the process, because sulfur is removed not only by oxidation by oxygen blowing, but also as a result of FeS dissolution in oxisulfide. If the tapped melt is fed to a slag-cleaning furnace and quartz is added, oxisulfide dissociates into sulfidizer, FeS, and fayalite slag, which ensures nickel and cobalt recovery into matte. The authors have patented this process with some specific features;
- in the case of converter slag cleaning, formation of oxisulfide should be prevented by addition of silica and metallization of matte;
- provide sulfidizing agent for smelting of oxide products to produce matte on the basis of oxisulfide with low disulfurization in the process of its preparation and use, which has been also patented by the authors.

## CONCLUSIONS

As a result of laboratory studies conducted, the composition of oxisulfide was determined more accurately as a FeO-FeS solution into which nickel, cobalt and copper can report. At certain mole ratios of FeO to FeS, homogeneous melt may be formed with possible separation into two layers (matte and oxisulfide) or in the presence of slag-forming constituents into three layers (matte, oxisulfide, slag).

Conditions required for oxisulfide formation were determined in the process of nickel matte oxidation: absence of silica or presence of silicate-calcium slags with elevated basicity in the order of  $\text{CaO}:\text{SiO}_2 = 0.8-1.0$ ; the nickel content of matte does not exceed 40%.

The presence of dissolved oxisulfide in low-grade nickel matte or separation of oxisulfide into a separate “slag” layer results in an increase in nickel loss in slag, and as a consequence, in higher conventional equilibrium constants as compared with constants for high-grade mattes free of oxisulfide.

Taking into account the presence of oxisulfide it has been confirmed that commercial smelting and converting processes are close to an equilibrium of exchange reactions between oxides and sulfides of nickel and iron, which permits prediction and control of transition of nickel into slags.

The investigated relationships in the nickel behavior is also valid to the full extent for cobalt. Practical recommendations have been offered as to how avoid formation of oxisulfides in certain cases, and how to use them in other cases.

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Table 1

## Results of cleaning of slags with different basicity using low-grade metallized nickel matte

Feed materials and smelting products	Weight, g	Content, %							Distribution, %				Conve ntional equilibrium constant, matte/slag  K <sub>Ni/Fe</sub>
		Ni	Fe	S	SiO <sub>2</sub>	CaO	Σ	O <sub>2</sub> **	Ni	Fe	S	CaO	
Feed slag, B = 0.52													
Input													
Matte	6.0	4.9	70.8	18.8	-	-	94.5	5.5	-	-	-	-	-
Slag	30.0	1.0	40.7	1.4	26.5	13.8	95.0*	-	-	-	-	-	-
Output													
Matte	6.2	8.8	61.7	17.3	-	0.9	88.7	11.3	91.4	25.3	61.6	1.4	0.032
Slag	29.8	0.17	37.6	2.2	24.4	14.0	89.0*	-	8.6	74.7	38.4	98.6	-
Feed slag, B = 1.04													
Input													
Matte	6.0	4.9	70.8	18.8	-	-	94.5	5.5	-	-	-	-	-
Slag	30.0	1.1	38.6	1.8	19.9	20.7	93.1*	-	-	-	-	-	-
Output													
Matte	2.2	23.2	58.1	9.3	-	0.3	90.9	9.1	70.4	7.6	9.4	0.1	0.007
Oxisulfide	10.5	1.8	65.8	13.4	1.9	3.3	86.2*	13.8	26.7	41.9	65.7	5.7	0.070***
Slag	25.3	0.09	32.8	2.1	22.1	22.5	89.2*	-	2.9	50.5	24.9	94.2	-

\* Fe calculated on the basis of FeO;

\*\* O<sub>2</sub> by balance

\*\*\* Between matte and oxisulfide

Table 2

**Oxisulfide phase composition**

Phases	Content, %							Identified minerals
	Fe	S	O	Ni	Co	Ca	Si	
Light-pink	44.8	46.8	5.5	1.7	0.8	0.04	0	FeS (troilite)
Dark	42,2	0.05	56.6	0.05	0.07	0.7	0.02	FeO (wustite)
Black	5.0	0.5	57.4	0.02	0.01	16.8	10.3	CaFe, SiO <sub>4</sub> (hedenbergite)
Light-color	43.6	0.1	0	48.4	6.7	0	0	Ferronickel



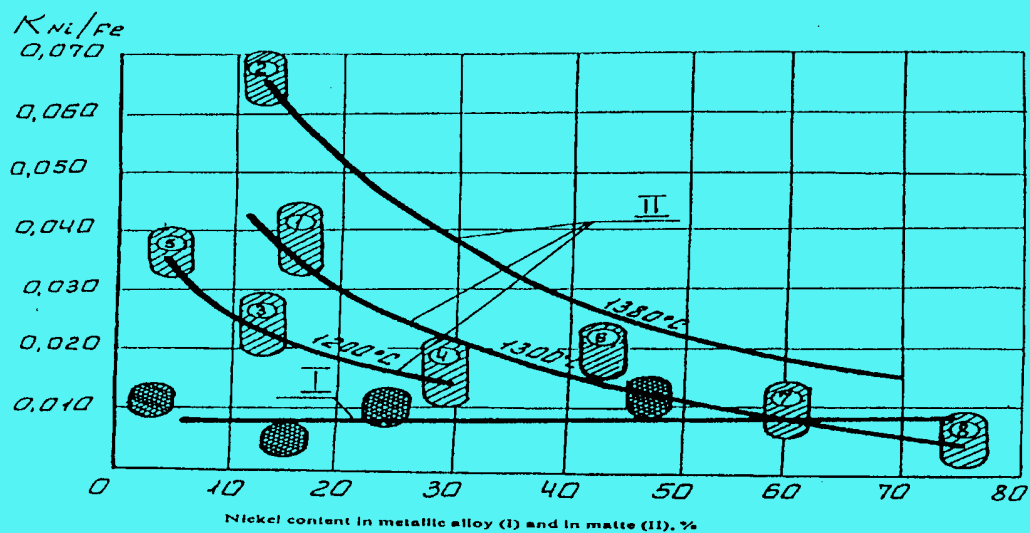


Figure 1 - The dependence of the conventional equilibrium constant  $K_{Ni/Fe}$  on nickel content in the metallic alloy (I) in the matte (II) in laboratory smelting tests at different temperatures  
 ● - metallic alloy smelting at the smelter  
 ⊗ - matte smelting at the smelter (the slag basicity  $B=0,4$ ):  
 1,2 - blast smelting of nickel agglomerate; 3,4,5 - blast smelting of the converter slags; 6,7,8 - matte converting

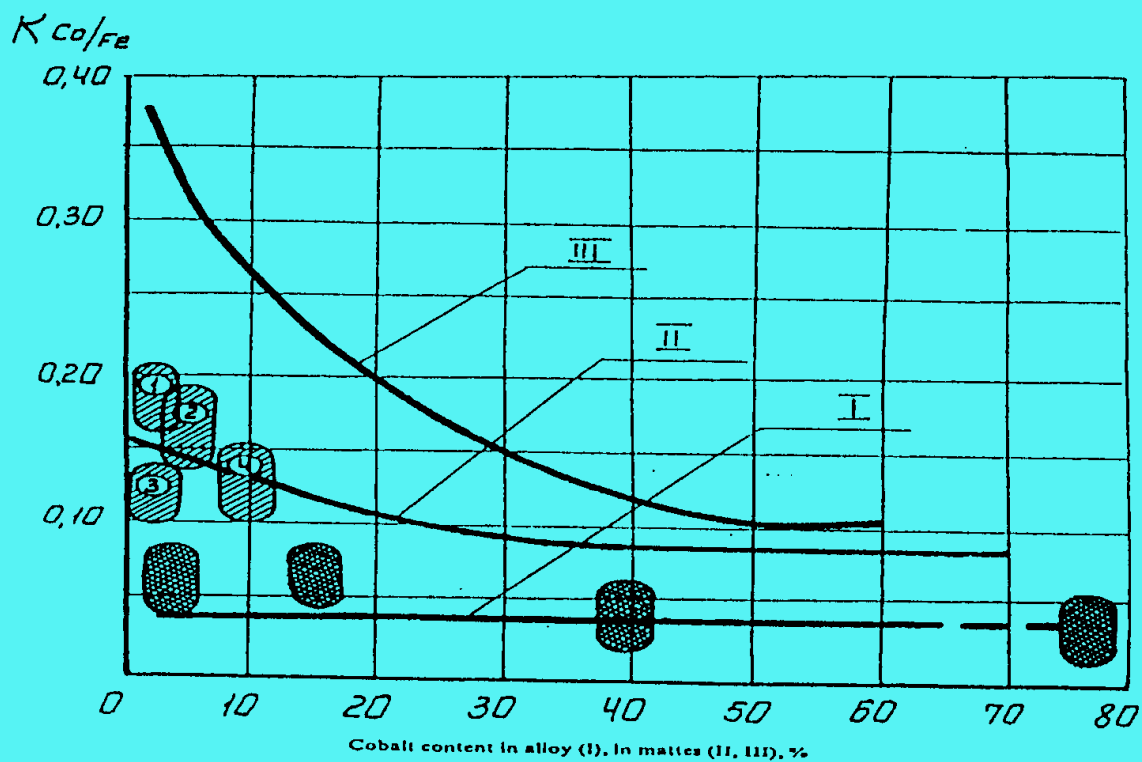


Figure 2 - The dependence of the conventional equilibrium constant  $K_{Co/Fe}$  on the cobalt content in the metallic alloy (I), metallized matte (II), matte (III) in laboratory smelting tests

- - alloy smelting at the smelter
- ▨ - matte smelting at the smelter:  
1,2,3 - blast smelting of the converter slags; 4 - blast smelting of the nickel agglomerate (see Fig. 1)

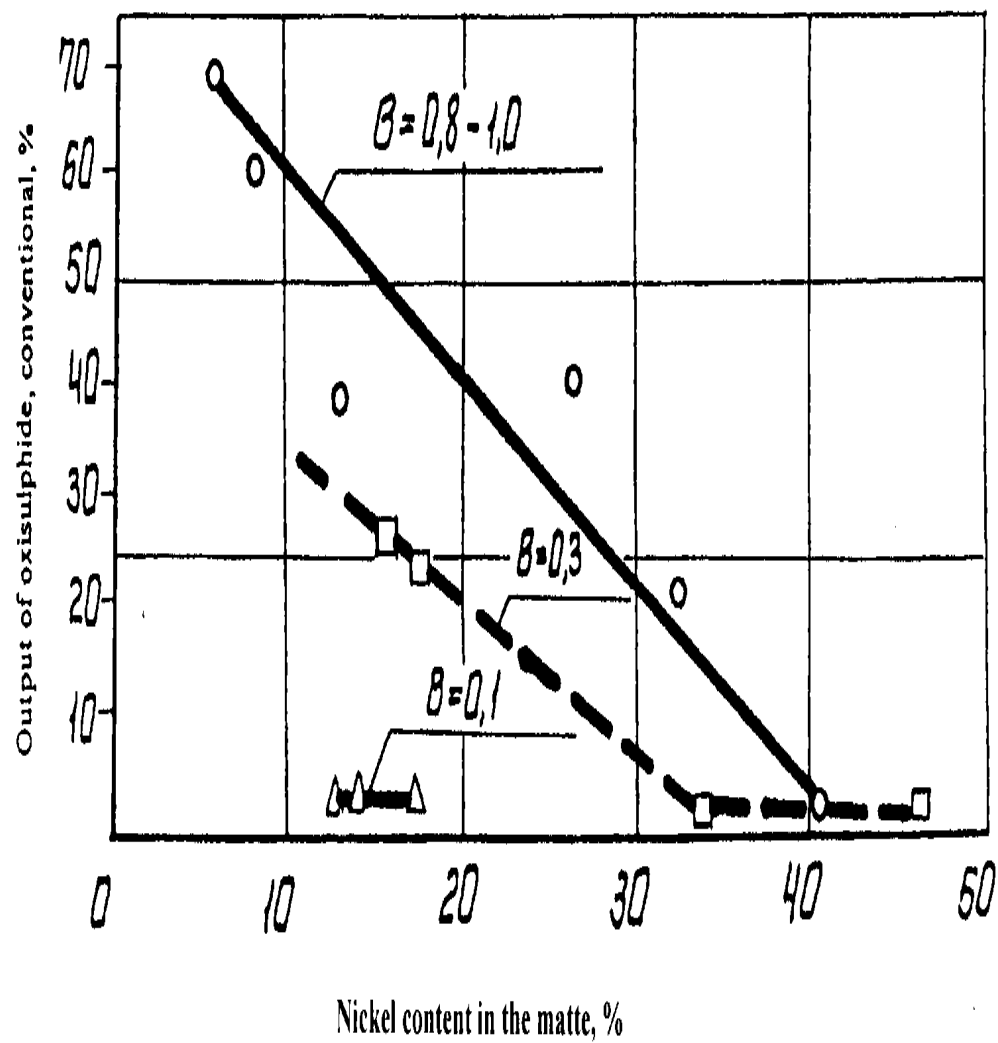


Figure 3 - The influence of the slag basicity (B) and nickel content in the matte on the output of oxisulphide phase at matte oxidation at 1300°C

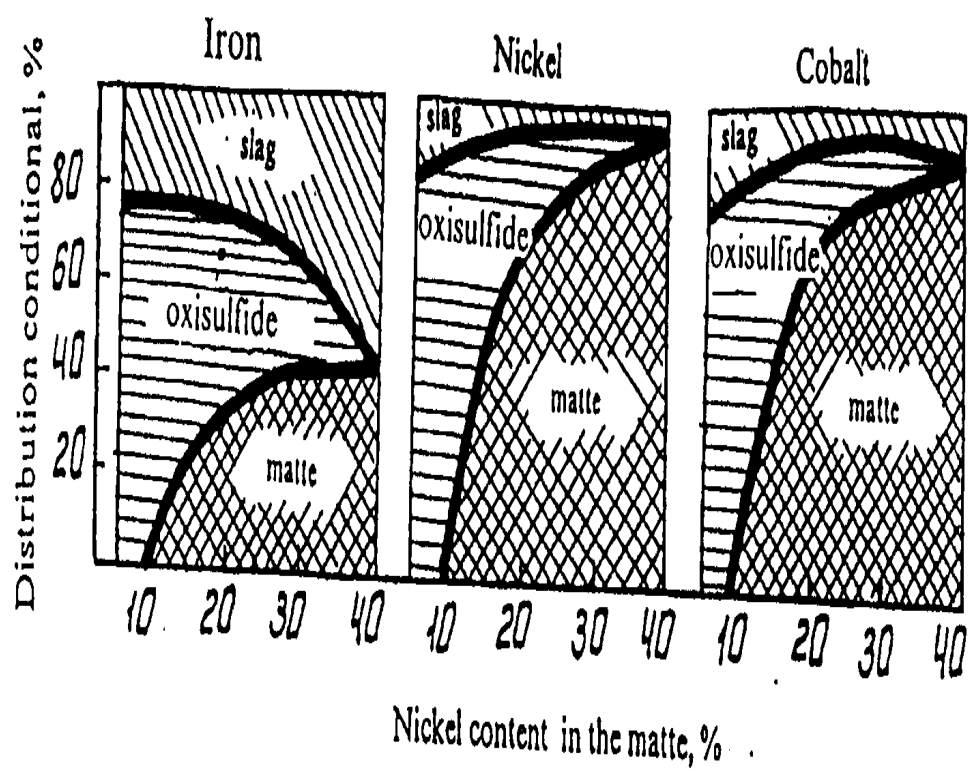


Figure 4 - The influence of the nickel content of the matte on the distribution of metals in the products of smelting at the slag basicity 0,9

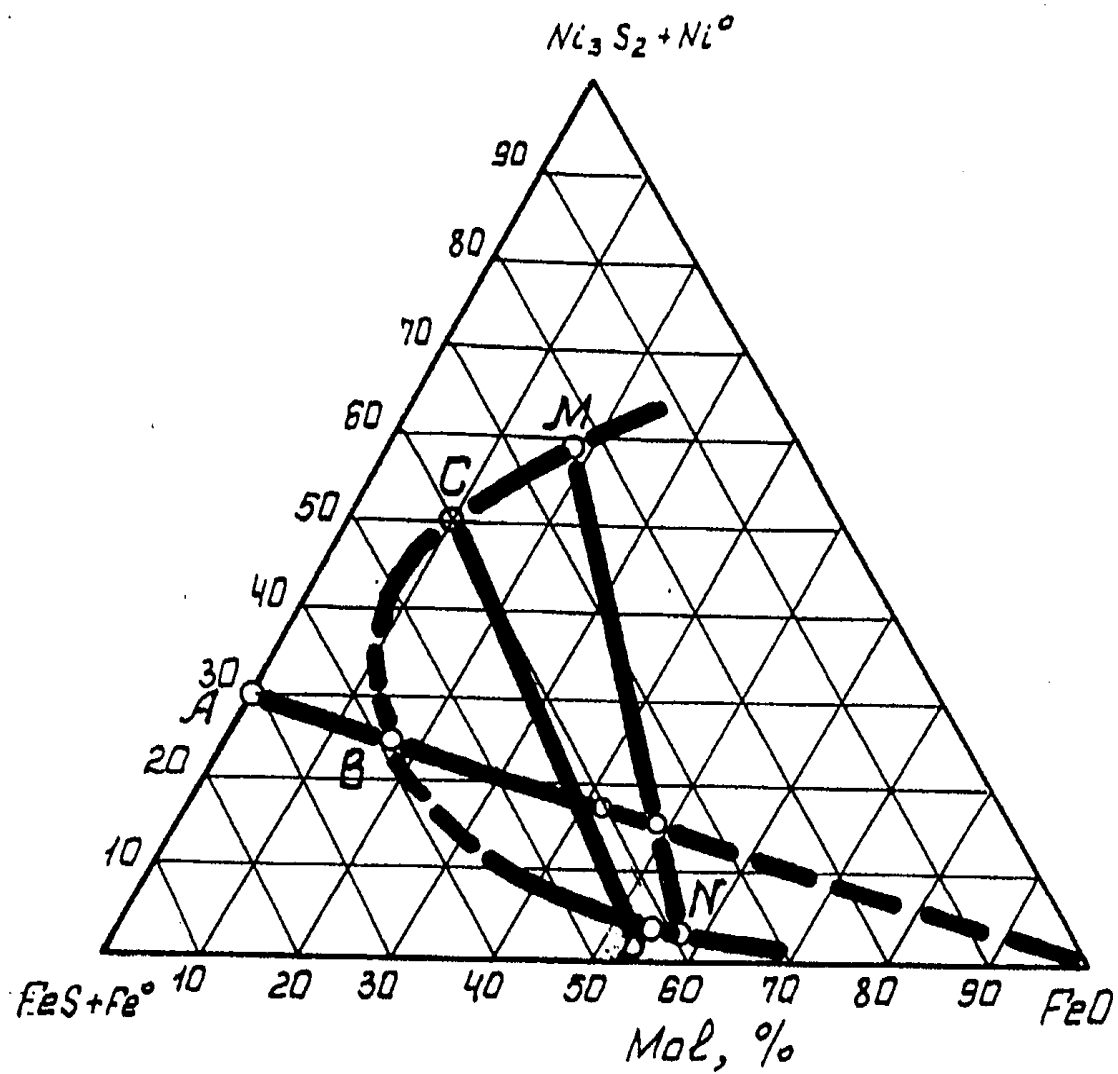


Figure 5 - Separation regions in the FeO-(FeS+Fe $^{\circ}$ )-(Ni $_3$ S $_2$ +Ni $^{\circ}$ ) system at 1250°C.

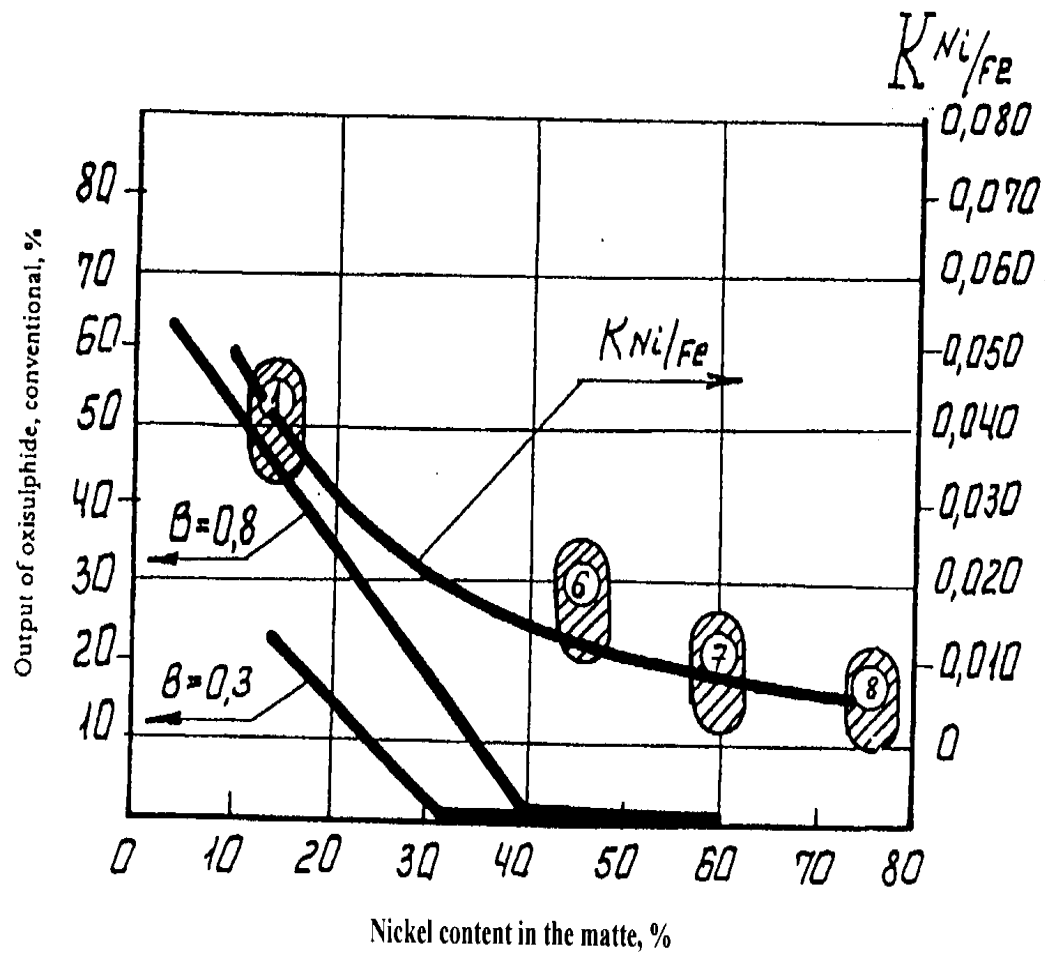


Figure 6 - The relationship of the conventional equilibrium constant  $K_{Ni/Fe}$  and output of the oxisulphide alloy.

