9-27-2021

ANALYSIS OF THE POSSIBILITY OF INCREASING THE DEGREE OF ZINC WAELZ AND REDUCING METAL LOSSES DURING WAELZ

Bakhriddin Tilovkabulovich Berdiyarov Dr.
Tashkent state technical university, mr.berdiyarov@gmail.com

[12] Sultanov I.A. Gazootdacha – odin iz osnovnix pokazateley effektivnosti razrabotki mestorojdeniy// Jurnal «Neftyanoye xozyaystvo», №1, 2001g.

[13] Tarasenko I.K., Chusev V.N. Problema nedovibora gaza iz produktivnix terrigennix kollektorov // Sbornik statey. Obzor zarubejnogo opita, Xarkov, KGU, 2005.

[14] Khalismatov I.Kh., Burltskaya I.P., Sagaidachnaya O.S. Analiz geologo-geofizicheskix materialov i rezultatov razrabotki mestorojdeniy Ustyurtskogo neftegazonosnogo regiona s selyu utochneniya konechnoy gazootdachi. Mejdunarodnaya nauchno-prakticheskiye konferensiya "Teoreticheskiye i prakticheskiye aspekti neftegazovoy geologii Sentralnoy Azii i puti resheniya sovremennix problem otrasli" Tashkent-2009 st. 122-124.

[15] Khalismatov I.Kh., Abidov A.A., Babadzhanov T.L. et al. Metodicheskiye rekomendatsii po otsenke konechnoy gazootdachi slojno postroyennix produktivnix terrigennix kollektorov. Tashkent NXK«Uzbeknefgaz» 2009 g.

[16] Khalismatov I.Kh., Burlutskaya I.P., Gom S.Yu. Opredeleniye koeffitsiyent gazootdachi terrigennix kollektorov no stadii poiskovix rabot. //Nauchno-texnicheskiy jurnal «Problemi energo- i resursosberejeniya» 2009 g. №3-4 str. 80-83.

[17] Khalismatov I.Kh., Burlutskaya I.P., Gom S.Yu. Botirova N. Opredelenie koefficient gazootdachi terrigennih kollektorov no stadii razvedki mestorojdeniya i proektirovaniy razrabotki. // Uzbekskiy jurnal Nefti i gaza 2010 g. №1 str. 76-81.

[18] Khalismatov I. et al. Uchet koeffitsenta izvlecheniya gaza pri podscheta zapasov na gazovih i gazokondensatnih mestorojdeniya. // Uzbekskiy jurnal Nefti i gaza 2016 g. №4.

[19] Khalismatov I., Zakirov R.T., Agzamov Zh.Sh., Saakova Yu. Otsenka konechnoy gazootdachi terrigennix produktivnix i sostav pri ispolzovaniy veroyatno po statisticheskix metodov International scientific and Practical Conference "WORD Science expo 2020 Methodology of Modern Research" 28-29 Mart 2016 Dubai UAE .

[20] M. R. Juraev, G.A. Bimurzaev, B. H. Razykov, and B. Kh. Khaidarov Conditions of formation of sulfide waters in paragenesis with evaporite and oil and gas-based formations in the artesian pools of the republic of uzbekistan // Technical science and innovation 2020 vol. 3. https://uzjournals.edu.uz/btstu/vol2020/iss3/16

ANALYSIS OF THE POSSIBILITY OF INCREASING THE DEGREE OF ZINC WAELZ AND REDUCING METAL LOSSES DURING WAELZ

B.T. Berdiyarov

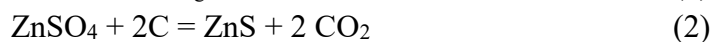*Tashkent State Technical University 100095, Tashkent, Uzbekistan*

Abstract: *The article examines the flow process of zinc cakes, which is formed during the selective melting of zinc burns, and the factors influencing it. The effects of silica and calcium oxide on the combustion of coke added to the Welting process were analyzed. When the kinetic kinetics of zinc ferrites and silicates present in zinc cakes are studied, the addition of lime to the strategy promotes the thermodynamic recovery of zinc and reduces graphite consumption. The article also examines the temperature dependence of the rate of reduction reactions of zinc silicate and zinc oxides. Studies of the kinetics of coal-thermal reduction of zinc ferrite have shown that the average rate of metal stripping is eight times higher than when removing pure zinc oxide at 1100 ° C. The addition of 5% $CaCO_3$ increases the rate of zinc stripping by 1.26*

times at 1050 °C, and by 1.13 times at 1100 ° C. In the presence of CaCO₃, the degree of sintering of the reduced ferrite decreases, which is partially associated with a reduction in the reduction of iron to metal. With the thermal contraction of zinc ferrite without the addition of CaCO₃ at 1050 ° C for 5 min, the degree of iron reduction to the metallic phase was 28.9%, at 1100 ° C in 5 min 42.8%, and with the addition of CaCO₃ 20.9 and 38.2%, respectively. The addition of calcium oxide to the shaft during the welting process leads to the destruction of zinc silicate bonds. This, in turn, increases the concentration of zinc in the weight.

Keywords: waelz, zinc, ferrite, silicate, vital, oxidation, thermodynamics, beneficiation, roasting, graphite, charge, Gibbs energy, free energy, hydrogen.

INTRODUCTION. Welting or wealz - the process is carried out in a rotary tube furnace in the temperature range of 1000-1200 ºC. The high value of temperature is limited by the solubility of the slag, which must be in a solid-state throughout the whole process [1-5].

The regenerating substance is coke. In the first minutes of the process, the following reactions occur.

$$ZnO + C = Zn_{gas} + CO \qquad (1)$$
$$ZnSO_4 + 2C = ZnS + 2\ CO_2 \qquad (2)$$
$$ZnO + Fe_2O_3 + FeO = ZnO + FeO \cdot Fe_2O_3 \qquad (3)$$
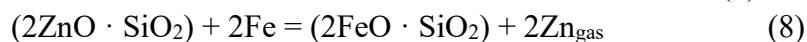$$2CO + O_2 = 2CO_2 + Q \qquad (4)$$
$$CO_2 + C = 2CO \qquad (5)$$

Reactions 1 and 3 occur due to the zinc compounds in the shaft reacting with the carbon in the coke. Reactions 4 and 5 take place in the gaseous phase of the furnace. Oxidation of CO in the gas phase helps to maintain the high temperature in the furnace, while zinc vapors are oxidized in the gaseous phase [3]:

$$Zn + 0,5O_2 = ZnO + Q \qquad (6)$$

The resulting zinc oxide is discharged into the dust collection system by the gas flow.

In the middle of the furnace, zinc oxide interacts with two silicon oxides to form silicates.

Iron, zinc, and lead are present in the cake in ferrite, magnetite, and hematite. The iron compounds in the vapor are actively reduced in the second half of the furnace from oxides and sulfides to a metallic state. As a result, the zinc in the compound is released from difficult-to-recover substances:

$$ZnS + Fe = FeS + Zn \qquad (7)$$
$$(2ZnO \cdot SiO_2) + 2Fe = (2FeO \cdot SiO_2) + 2Zn_{gas} \qquad (8)$$
$$ZnO + Fe = FeO + Zn_{gas} \qquad (9)$$

MATERIAL AND METHODS. Thus, at the end of the Welting process, compounds in the form of zinc oxide, sulfide, and silicate are reduced in the reaction mass of the furnace. The remaining amount of zinc in clinker is 0.1-1.0%. Zinc is found in clinker in the following forms, sulfide 45; silicate 17; aluminate-ferrite 20; oxide 18.

Various chemical compounds are included in the composition of the Waelz materials, which influence each other. To understand the physical and chemical processes occurring in Waelz furnaces, following the kinetics of gasification, reduction, etc., is necessary. And pure compounds in the presence of various mineral impurities [6-10].

To study the effect of mineral additives on the combustion rate of coke, experiments were carried out on its oxidation with additions of SiO_2.

RESULTS. The study results (Figure 1) showed that the coke combustion rate and the energy characteristic of the speed (apparent activation energy) depend little on the coke fraction in the mixture with SiO_2 in the range of 600-1100 °C.
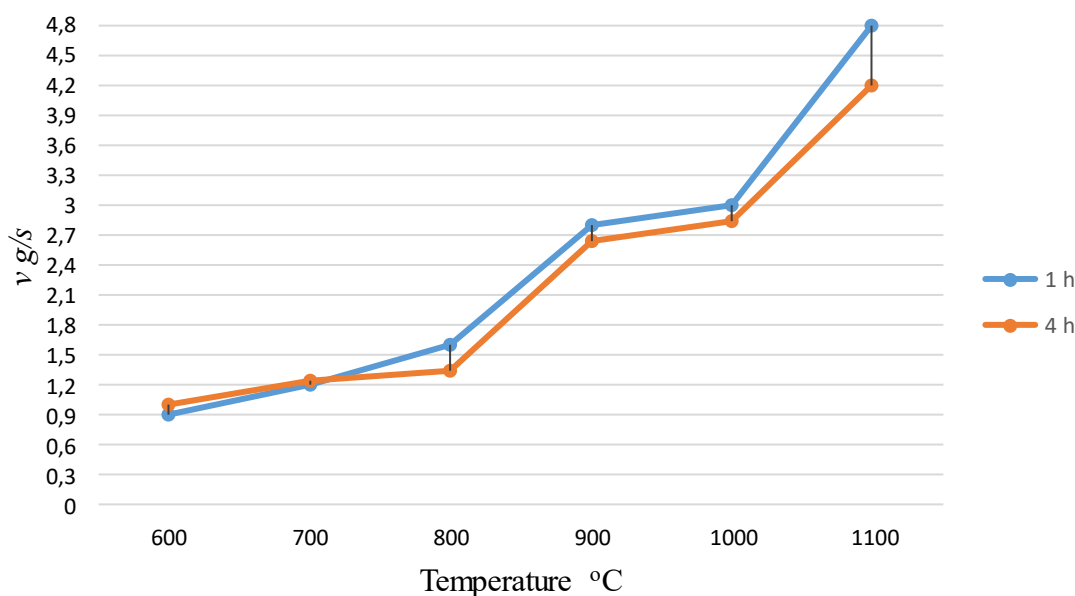

Figure 1. Dependence of the coke combustion rate v on temperature with the addition of one h (1) and four h (2) quartz sand. Totalweight 5 g.

Therefore, it can be assumed that in the initial stage of Waelz, in the zone of drying, decomposition of sulfates and carbonates, the heating rate of the charge will depend little on the fraction of coke breeze in it. As a result, when washing the furnace from the crust, the temperature in the drying zone of the furnace is raised using a mixture of coke with a rich zinc material, for example, with zinc ash, in the load. The dosage of zinc ash does not reduce the burning rate of solid fuel; at the same time, when it is heated above 1000 °C, an intense sublimation of zinc occurs, followed by its exothermic oxidation in the gas phase.

The influence of CaO additions on the ignition temperatures and achieving the maximum burning rate of graphite was studied by recording the heating curves on a Rigaku Denki thermal analyzer. The study results showed that the ignition temperatures decreased with an activating additive to the graphite of 3 - 8% (mol.) CaO [11]. So, the temperature of the beginning of the combustion of graphite without the addition of CaO was 640 - 660 °C, and with the addition of 618 - 622 °C. The temperature of the maximum burning rate is 865 -886 °C and with the addition of CaO 810 - 834 °C. At higher temperatures (above 1100 °C), the effect of mineral impurities on the combustion rate and carbon gasification is not affected [12].

In zinc cakes, most of the zinc is in the form of ferrites (40-50%) and sulfates (30-35%), as well as in the form of sulfides (6-7%) and silicates (3-5%).

Isobaric potential of coal-thermal reduction of zinc ferrite, according to the reference literature, for the reaction [9]:

$$ZnO \cdot Fe_2O_3 + 2C = Zn_{(g)} + 2FeO + 2CO(CO_2) \qquad (10)$$

has the following meanings:

$\Delta Z_{(10)} = - 614\ 600 - 190.5T$ J/mol; $\Delta H_{(10)} = - 614.6$ kJ/mol. Below are the ΔZ values determined by reaction (10):

T, °C	1000	1100	1200	1300
$\Delta Z_{(10)}$**,kJ/mol**	**-857,1**	**-876,2**	**-895,2**	**-914,3**

The isobaric potential of reaction (10) $\Delta Z_{(10)}$ was calculated using an approximate formula without considering the temperature dependence of the heat capacity. The inaccurate data shows that the equilibrium constant of reaction (10) is almost 30 - 35 orders of magnitude higher. This fact indicates that the reduction of zinc from ferrite according to reaction (10) proceeds more favorably than zinc oxide.

Studies of the kinetics of coal-thermal reduction of zinc ferrite have shown [11-16] that the average rate of metal stripping is eight times higher than when removing pure zinc oxide at 1100 ° C. The addition of 5% $CaCO_3$ increases the rate of zinc stripping by 1.26 times at 1050 °C (Figure 2) and by 1.13 times at 1100 ° C. In the presence of $CaCO_3$, the degree of sintering of the reduced ferrite decreases, which is partially associated with a reduction in the reduction of iron to metal. With the thermal contraction of zinc ferrite without the addition of $CaCO_3$ (molar ratio $ZnO \cdot Fe_2O_3$: C = 1: 2) at 1050 ° C for 5 min, the degree of iron reduction to the metallic phase was 28.9%, at 1100 ° C in 5 min 42.8%, and with the addition of $CaCO_3$ 20.9 and 38.2%, respectively. These results can be explained from the thermodynamic point of view: in the process of carbon-thermal reduction of zinc ferrite in the presence of calcium carbonates, compounds of the type of dicalcium ferrite are formed, which is more difficult to reduce than Fe_2O_3.
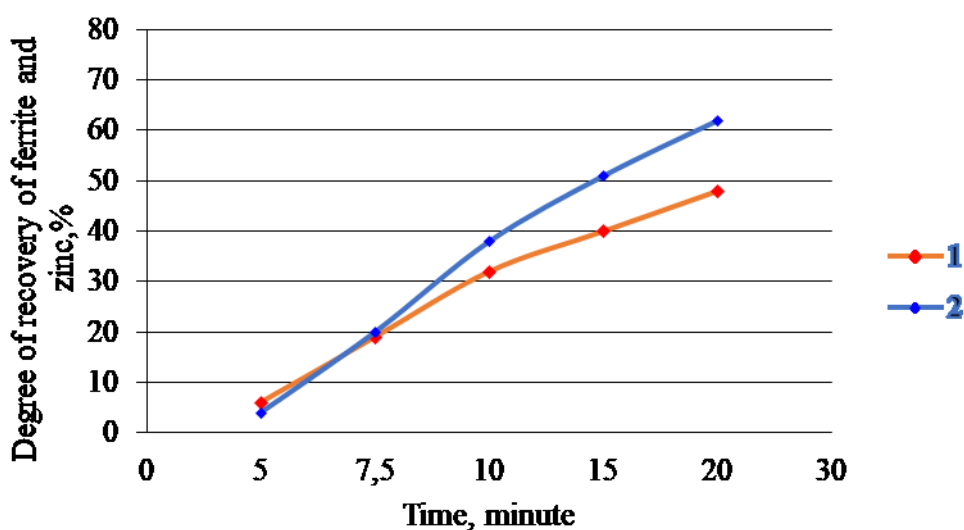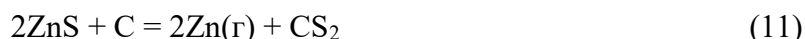

Figure 2. Reduction of zinc ferrite with graphite at 1050 °C without additive (1) and with the addition of 5% $CaCO_3$ (2)

ZnS interacts with carbon at 1200-1300 °C and above according to the reaction

$$2ZnS + C = 2Zn(г) + CS_2 \qquad (11)$$

The temperature of the onset of the reaction (11) is 1300 °C, the Prost is 1450 °C, and the Johnson starts at 1200 °C, and the reaction proceeds noticeably at 1300 °C. $\Delta H_{(11)} = 517.3$ kJ / mol.

The isobaric potential of reaction (11) has the following temperature dependence: $\Delta H_{(11)} = 517\,300 - 199.9T - T\,(-21.4M_0 + 12.1/W_1)$ (M_0 and M_1 are the coefficients according to Temkin - Schwarzman)

Below are the ΔZ values determined by reaction (11):

T, °C	1000	1100	1200	1300
$\Delta Z_{(11)}$,**kJ/mol**	275,8	257,8	239,9	221,8

It should be noted that zinc sulfide is thermodynamically more easily reduced by carbon monoxide:

$$ZnS + CO = Zn(г) + COS \quad (12)$$
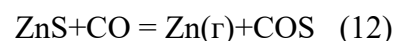
$\Delta Z_{(12)} = 301\,906 + 14{,}98\,T\lg T + 2{,}72 \cdot 10^{-3}T^2 + 3{,}49 \cdot 10^5 T - 178{,}99T$

$\Delta Z_{1100\,°C} = 132\,041$ kJ/mol

and hydrogen

$$ZnS + H_2 = Zn\,(г) + H_2S \qquad (13)$$

$\Delta Z_{(13)} = 95\,162$ kJ/mol at T = 1100 °C

Zinc silicate $2ZnO \cdot SiO_2$ belongs to difficult-to-recover compounds. Comparing the thermodynamic characteristics of the reaction

$$2ZnO \cdot SiO_2 + 2C = 2Zn(г) + 2CO + SiO_2 \qquad (14)$$
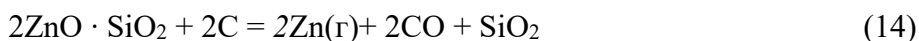
$\Delta Z_{(13)} = 263\,600 - 189{,}5T$ kJ/mol

$\Delta Z_{(13)} = -263/6$ kJ/mol

and reaction (10), it can be seen that the equilibrium constants of reaction (14) are 2 orders of magnitude less than reaction (10) of the reduction of pure zinc oxide.

Below are the ΔZ values determined by reaction (14):

T, °C	1000	1100	1200	1300
$\Delta Z_{(14)}$,**kJ/mol**	22,4	3,4	-15,5	-34,5

The recovery of silicate at a noticeable rate [3% (w / h)] begins at 1000 ° C. An increase in temperature dramatically speeds up healing. So, at 1200 ° C, 16.5% of zinc silicate is restored per hour, while the apparent activation energy of the reduction is 129.7 kJ/mol. The introduction of potassium and sodium carbonate additives changes the kinetic character of the reduction curves and increases the reduction rate of $2ZnO \cdot SiO_2$; the apparent activation energy decreases to 71.14 kJ / mol.

1) ZnO+ H$_2$ = Zn + H$_2$O; 2)ZnO + CO = ZnO + CO;
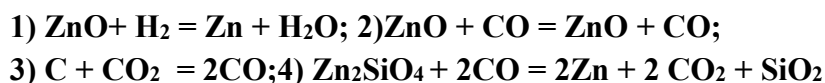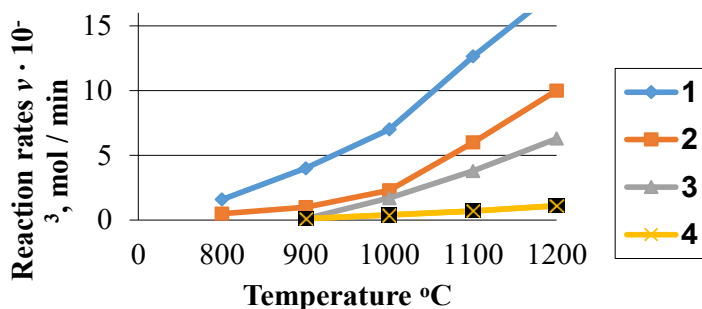**3) C + CO$_2$ = 2CO;4) Zn$_2$SiO$_4$ + 2CO = 2Zn + 2 CO$_2$ + SiO$_2$**

Figure 3. Dependence of the reaction rate of zinc silicate and zinc oxide reduction on temperature

It was shown in [11] that at 900-1200 ° C,the interaction of zinc silicate 2ZnO · SiO$_2$ with carbon monoxide proceeds more slowly than the interaction of ZnO with hydrogen, carbon monoxide, and the reaction of carbon gasification (Figure 3).

From this, it can be concluded that the addition of CaO to the waelz mixture leads to the destruction of the zinc silicate compound, which, in turn, contributes to an increase in the extraction of zinc into sublimates.

CONCLUSION. To reduce the loss of zinc with clinker, it is necessary to shift the sublimation zone to the feed end during the cold course of the waelz process. The following methods can achieve this:

- reducing the furnace load;
- increasing the vacuum in the dust chamber with the simultaneous supply of secondary fuel;
- a gradual increase in the supply of secondary air;
- a decrease in the moisture content of the charge;
- an increase in the loading of the content of lead and sulfur;
- a decrease in the rotational speed of the furnace.

Reference

[1] Constantinian J.P. Demonstration of the conditions conducive to agglomeration of zinc calcines in fluidized bed roasters. / J.P. Constantinean [идр.]. // Miner.Eng, 2011. – № 13. – P. 1409 – 1420.

[2] Nyberg J. Characterization and control of zinc roasting process. / J. Nyberg // Finland: Oulu, 2004. – 114 p.

[3] Chen T.T. Mineralogical changes occur during the fluid-bed roasting if zinc sulfide concentrates. / T.T. Chen, J.E. Dutrizac. // Metals and Mater. Soc. 2004. – №12. – P. 46 – 51.

[4] Piere J. Agglomeration zinc calcine during the fluid-bed roasting.. / J. Piere, S.C. Bouffard, J.R. Orace. // Mineral Engineering. 2011. – № 24. - P. 1409 – 1420.

[5] Svens K., Kerstiens B., Runkel M. Recent experiences with modern zinc processing technology. / K. Svens, B. Kerstiens, M. Runkel. //«Erzmetall». – 2003. – №2. – P. 94 – 103.

[6] Matkarimov S.T., Nosirkhujayev S.K., Berdiyarov B.T., Ochildiyev K.T., Marjorie B.I. Processing of slags of copper manufacturing with the use of ideal mixing equipment. Technical science and innovation, №2/2020 y. 227-234 p.

[7] KhojievSh.T., Berdiyarov B.T., Kadirov N.A., Obidov B.M. and Turan M.D. (2021) Utilization of household waste-based solid fuel // Technical science and innovation: Vol. 2021: Iss.1. P. 168-176.

[8] Samadov A.U., Berdiyarov B.T. Rux xomashyosini velslash jarayonida "nastil" hosil bo'lish sabablarining tahlili va oldini olish choralari. / O'zbekiston konchilik xabarnomasi jurnali-Navoiy, 2019. - № 1. - S. 70-71.

[9] Xasanov A.S., Xudoyarov S.R., Berdiyarov B.T., Tolibov B.I. Izucheniye vozmojnosti predotvrasheniya obrazovaniya trudnorastvorimix soyedineniy sinka pri dobavke v shixtu objiga razlichnix komponentov. // Vestnik TashGTU, 2019. - № 1, - S. 197-204.

[10] Khasonov A.S. Berdiyarov B.T. Research of education and prevention of ferrite and silicates of zinc when roasting sulphidic zinc concentrates in furnaces of the boiling layer. Austria. European science Review, 2018. - № 11-12.- P. 62-66.

[11] Yusupxodjayev A.A., Xasanov A.S., Berdiyarov B.T. Innovatsionnie texnologii objiga sulfidnix sinkovix konsentratov. "Monografiya" Toshkent: TKTI 2019 sh.b.t. 9 S.144.

[12] Berdiyarov B.T., Matkarimov S.T., Vliyaniye oksida kalsiya na ferritizatsiyu sinka. // Mejdunarodnaya nauchno-texnicheskaya konferensiya «Innovatsiya-2016», - Tashkent, 2016. - S. 84-86.

[13] Valiyev X.R., Berdiyarov B.T., Xudoyarov S.R., Yusupxodjayev A.A. Issledovaniye vliyaniya SaO na stepen vosstanovleniya sinka pri velsevanii sinkovix kekov. / Materiali nauchno-prakticheskoy konferensii "Innovatsionnie texnologii gorno-metallurgicheskoy otrasli" Navoiy, 21 oktabrya 2011. - S. 122-124.

[14] Yusupxodjayev A.A., Valiyev X.R., Xudoyarov S.R.,Berdiyarov B.T. Velsevlash jarayoniga suv bug'ining ta'siri. / Materiali nauchno-prakticheskoy konferensii "Innovatsionnie texnologii gorno-metallurgicheskoy otrasli" Navoi, 21 oktabrya 2011. -S. 121-122.

[15] Berdiyarov B.T., Xudoyarov S.R., Matkarimov S.T., Axmadjonov A., Alimov U. Termodinamicheskoye obosnovaniye objiga sinkovogo konsentrata pri dobavke v shixtu CaCO3. Proceedings of the III International Scientific and Practical Conference "Scientific and Practical Results in 2016. Prospects for Their Development" (December 27-28, 2016, Dubai, UAE)№ 1(17), Vol.1, January, 2017. -S. 34-35.

[16] Berdiyarov B.T., Xudoyarov S.R., Yusupxodjayev A.A., Valiyev X.R. Samadov A.U. Issledovaniye ferrita sinka pri velsevanii sinkovix kekov: Sbornik nauchnix statey Respublikanskoy nauchno-prakticheskoy konferensii "Sovremennie problemi ratsionalnogo nedropolzovaniya". – Tashkent, 2013. - S. 224-225.