abstract: production experience shows that use of many types of secondary mineral resources is technically feasible and efficient. one of the resource in the production of non-ferrous metals is use of waste of iron and steel industry, in which the content of non-ferrous metals up to industrial conditions. thus, in dusts of gas purification of some plants of ferrous metallurgy the zinc content reaches 15 %.

key words: zinc, charge, oxidized zinc ore, gas purification dust of blast furnace smelting, binding agent, carbothermic reduction

introduction. the annual volume of world production of zinc exceeds 10 million tones. half of this volume is used to protect steel against rust. environmentally attractive fact in favor of use of zinc is that 80 % of it is used again, and it does not lose its physical and chemical properties. protecting steel against corrosion, zinc helps to preserve natural resources, such as iron ore and energy. extending the service life of steel, zinc increases the life cycle of goods and capital investments, i.e. buildings, bridges, power and water distribution, telecommunications, thus protecting investment and helping to reduce repair and maintenance costs [1]. it is known [2], that 85 % of the total world production of zinc is obtained from concentrates, and the rest of sub-standard and secondary raw materials and wastes of chemical and metallurgical industries.
Increased release of zinc through the processing of substandard raw materials is an important economic and environmental objective.

The main zinc-containing waste from metallurgical industries are blast and steel smelting dusts (Table 1).

<table>
<thead>
<tr>
<th>Company</th>
<th>Product</th>
<th>Zn</th>
<th>Pb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karaganda Metallurgical Plant (Kazakhstan)</td>
<td>Blast-furnace dust</td>
<td>1.1-1.4</td>
<td>0.19</td>
<td>44.9-47.8</td>
</tr>
<tr>
<td></td>
<td>Converter slag</td>
<td>0.9-1.1</td>
<td>0.4-0.5</td>
<td>58.6-60.8</td>
</tr>
<tr>
<td>West-Siberian Metallurgical Plant (Russian Federation)</td>
<td>Blast-furnace dust</td>
<td>12.3-15.0</td>
<td>0.2-0.8</td>
<td>38.5-40.1</td>
</tr>
<tr>
<td>Severstal (Russian Federation)</td>
<td>Dust of electric steel furnaces (ESF shop)</td>
<td>9.9-17.4</td>
<td>0.7-1.8</td>
<td>17.6-39.9</td>
</tr>
</tbody>
</table>

Analysis of scientific, technical and patent literature has shown the possibility of processing zinc-containing waste from iron and steel production. Difference of pyrometallurgical methods of extraction of zinc is in the parameters of technological mode, types of fuel and reducing agent used and the constructive design of systems. [3]

Industrial pyrometallurgical processing of dust and sludge of gas purification systems of blast furnaces and converter shops have been mastered by Germany company named AG Krupp, recycling dust and sludge of steel production in rotary tube furnaces [4].

Information on the joint recycling of oxidized zinc ore with zinc-containing waste from ferrous metallurgy is not available in the literature. At the same time, during the recycling of oxidized zinc ore with a low iron content it is necessary to introduce an iron product in the charge, promoting zinc stripping. Dust of ferrous metallurgy retaining high profitability of Waclz process, may be used as the flux instead of the ballast iron concentrate. In addition, the high zinc content in the blast furnace sludge will significantly extend the life of the deposit of oxidized zinc ore. Such type of deposit is Shaimerden deposit.

Application of charge briquetting in the reduction roast is one of the cost-effective processing methods [5-8]. High reactivity of charge is necessary for the process without slag with the recovery rate of oxides exceeding the speed of their melting. Use of active carbonaceous reducing agent, fine grinding of materials their careful hashing will meet this requirement. As a result of the production practice it is confirmed that joint briquetting of the crushed raw materials and a reducing agent is the best way of preparation of charge [9]. Addition of binders into the charge is intended to increase the strength of the briquettes. [10]

The objective of this work is to study the effect of the binder during the charge briquetting, the amount of the carbonaceous reducing agent, the type of reducing agent, the particle size of charge on the indices of high temperature reduction roasting of briquetted charge consisting of oxidized zinc ore, dust of gas purification of blast furnace smelting and solid reducing agent.

Experimental Part. Methods of analysis. X-ray fluorescence analysis was performed with the help of a wave dispersion spectrometer Venus 200 PANalytical B.V. (PANalytical B.V., Holland).

The chemical analysis of samples was performed with the help of an optical emission spectrometer with inductively coupled plasma Optima 2000 DV (PerkinElmer, USA).

Materials and Instruments. Materials for the study were the stale dust of gas purification of blast furnace smelting from the sludge of the storage area in the West Siberian Metallurgical Plant (Novokuznetsk, Russian Federation), containing, wt. %: Zn 12.3; Fe 40.1; Ca 3.4; Si 4.3; Mg 0.7; Mn 0.2; Al 1.6; Ti 0.3; Pb 0.8; S 1.0; ore of the Shaimerden deposit provided by “Kazzinc” Ridder Metallurgical Complex, containing weight %: Zn 21.4; Fe 2.6; Si 11.4; Al 5.0; Ca 6.7; Mn 0.8; Ti 0.2; Pb 0.5; Mg 0.3; F 0.2; Cu 0.01; As 0.02.

Studies on the effect of reducing agent on the high-temperature reduction process is conducted using carbonaceous materials available and used in the industry (Table 2).

Shubarkol deposit refers to low-ash gas coals. The special coke received by thermal-oxidative coking of Shubarkol deposit coal represents a solid carbonaceous reducing agent with grain size of 5-25 mm, possesses the developed steam structure formed as large pores, 150-300 microns in size, and less – 0.5-1.0 microns. [11].

Bentonite, hydrated lime and treacle were tested as a binding agent during the briquetting of the charge.

<table>
<thead>
<tr>
<th>Indices</th>
<th>Anthracite coal</th>
<th>Metallurgical coke</th>
<th>Special coke</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical Analysis, wt. %:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A') (ash content)</td>
<td>3.73</td>
<td>16.30</td>
<td>2.41</td>
</tr>
<tr>
<td>(W) (humidity)</td>
<td>2.31</td>
<td>1.05</td>
<td>3.19</td>
</tr>
<tr>
<td>(V_{av}) (volatile matter)</td>
<td>5.10</td>
<td>2.67</td>
<td>24.91</td>
</tr>
<tr>
<td>Carbon content, wt. %</td>
<td>90.20</td>
<td>79.7</td>
<td>69.20</td>
</tr>
<tr>
<td>Sulfur content, wt. %</td>
<td>0.18</td>
<td>0.96</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Great demands along with giving high mechanical strength to briquettes are placed on binders, they should not bring harmful or ballast impurity [12], and the value of binders should be comparable with the value of raw material agglomerates, otherwise the value of a binder will make briquetting as a noncompetitive method. Hydrated lime is one of binders having high bind and flux possibility as well as cheap and abundant. The main disadvantage of hydrated lime is that at temperature is above 570 °C, it decomposes and loses its strength.

The bentonite is the most widely used binder in the ferrous metallurgy, because it has a great capacity to absorb water and consists of layers of aluminum silicates.

The feed treacle is an advanced binder. This type of treacle is a waste from sugar-beet production, syrupy liquid of dark brown color with a water content of 22.7 % and carbohydrates of 58-60 %, mainly sugar, easily soluble in any proportion of cold and hot water and with a low value. Treacle is non-toxic, i.e. an environmentally friendly industrial product.

The high temperature roasting was performed at a temperature of 1250 °C in a horizontal furnace Nabertherm - 1300 (Germany) with automatic temperature control. The accuracy of temperature measurement was 5 °C.

Experimental Method. Due to the fact that the consumption of the solid reducing agent which provides maximum extraction of zinc fumes in each case varies depending on the kind of raw material, we selected the consumption of a solid reducing agent as obviously providing fullness of zinc sublimation.

Briquetting was performed on a laboratory press. The charge for pressing was mixed in a mixing cup with a binder, then the sample was maintained under the charge compression within 1-2 min after that briquettes were extracted from a forming block by means of extrusion. Briquettes have a cubic shape with an edge size of 19 mm.

The briquettes volume of 6.86 cm³ was selected based on the results of thermophysical calculations of heating and reducing in a horizontal tube furnace. Drying of briquettes was performed at 130 °C.

The quality of finished briquettes was evaluated for mechanical strength with the help of stroke method, with repeated dropping on a concrete slab from a height of 1 m to the briquette split.

The briquetted charge was placed in an alundum crucible which was moved into a working zone of a furnace. The furnace heating was stopped after reaching a temperature of 1250 °C. The crucibles were covered by an alundum cover. The formed fumes were collected on the inner surface of the cover. Determination of mass of a crucible containing calcine and fumes, was performed after cooling the furnace to room temperature.

Results and Discussion. During experiments on study of the effect of a carbonaceous reducing agent type on high-temperature zinc reduction, calculation of the amount of solid reducing agent necessary for reduction of oxides under the equal conditions, was performed with regard to the carbon content in the material. The ratio in the charge before briquetting was:

ore : dust : special coke : treacle = 1 : 0.5 : 0.39 : 0.1;
ore : dust : anthracite : treacle = 1 : 0.5 : 0.35 : 0.1;
ore : dust : metallurgical coke : treacle = 1 : 0.5 : 0.4 : 0.1.

Effect of the binder on the indices of high temperature reductive roasting. Correctly chosen method of preparation of the charge is an initial prerequisite for the achieving of high indices of zinc extraction. One of the components constituting the charge is a binder used during briquetting.

Results of the reduction roasting of charge briquettes with various binders are given in Table 3.

<table>
<thead>
<tr>
<th>Charge Components</th>
<th>Number of strokes of the briquette</th>
<th>Calcine efficiency, %</th>
<th>Zink content in calcine, wt. %</th>
<th>Degree of metallization Fe, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore</td>
<td>50.5</td>
<td>6.0</td>
<td>52.2</td>
<td>0.50</td>
</tr>
<tr>
<td>Dust</td>
<td>25.3</td>
<td>19.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reducing agent*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The binder is treacle of 4.7 wt. %

| Ore               | 52.2                             | 7.0                  | 53.0                          | 0.79                          | 20.3                          |
| Dust              | 26.2                             | 20.3                 |                               |                               |
| Reducing agent*   |                                  |                      |                               |                               |

The binder is bentonite of 1.4 wt. %

| Ore               | 52.2                             | 9.0                  | 53.3                          | 0.90                          | 18.5                          |
| Dust              | 26.2                             | 20.3                 |                               |                               |
| Reducing agent*   |                                  |                      |                               |                               |

The binder is hydrated lime of 1.3 wt. %

*The content of carbon in the charge taking into account carbon in dust is 25.0 %

The data in Table 3 shows that the mechanical strength of the briquettes increases in the row: treacle < bentonite < hydrated lime and the residual content of zinc in a cinder submits to this regularity. Such behavior of the studied binders is caused by the fact that binding agents in the form of solutions, in comparison with powder, are more evenly distributed in volume of the briquetted material and have high reactivity [13].
The highest degree of metallization of iron during high-temperature roasting of briquetted charge is achieved using bentonite as a binder - 20.3%, and the lowest when using the hydrated lime - 18.5%.

Effect of the binder on the reduction of zinc and iron to metal during the roasting of the briquetted charge is determined by the briquette permeability, the denser briquette, the greater difficulty during the reduction reactions.

Results of roasting of briquettes of charge with treacle showed that the reduction reaction of zinc to gaseous state proceeds with greater speed, than iron metallization reaction in the received briquettes.

Effect of the type of the carbonaceous reducing agent on the residual zinc content in the product of roasting. Studies have shown that the reactivity of the subjects of the carbonaceous reducing agents have a significant effect on the zinc sublimation (Figure 1).

Shubarkol special coke was the most active reducing agent. The residual content of zinc in the calcine after reduction roasting of charge with this type of coke is 0.49 wt. %. Metallurgical coke has a much lower activity. The residual content of zinc in the calcine is 1.61 wt. %. The activity of anthracite has intermediate value. The residual content of zinc in the calcine is 0.93 wt. %.

The difference in the effect of the test carbonaceous reducing agents at the zinc sublimation due to the fact that according to [11], the reactivity of the special coke is 5.2 ml/g∙s, and, for example, metallurgical coke is 0.62 ml/g∙s only. Furthermore, the reactivity of special coke is 3.82 ml/m²∙s, and the reactivity of metallurgical coke is 0.05 ml/m²∙s.

Effect of the amount of solid reducing agent in a charge on the of high temperature roasting process.

The carbon content in the charge has a great effect on the process of high-temperature reduction of oxidized metals. The amount of reducing agent should be determined as the need to ensure the required concentration and getting loose, crumbling cinder.

Studies on the effect of the solid reducing agent as part of the charge was performed using special coke derived from the coal of Shubarkol deposit.

It is known [11] that, the share of costs for coking of coal in the structure of value is 85-90 %, and the share of the value of coke in the production value of the most non-blast furnace users as high as 40 - 50 % [1]. Therefore, it is necessary to attract non-deficient and cheap coal for the increasing of the efficiency of production that use the coke. For example, brown, long-flaming, gas, petrographically homogeneous, fortified coal of Shubarkol deposit. The coke cost received from such coals, is below the coke cost, received from hard coals.

Calculation of an expense of a solid reducing agent was performed in relation to amount of the oxidized zinc ore in charge. Results of experiments are given in Table 4.

Table 4 - Results of the reducing roasting of briquettes of charge with various quantity of a solid reducing agent

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity, wt. %</th>
<th>Special coke amount, wt. %</th>
<th>Calcine efficiency, %</th>
<th>Zinc content in calcine, wt. %</th>
<th>Degree of metallization Fe, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore</td>
<td>50.5</td>
<td>45.3</td>
<td>53.1</td>
<td>0.66</td>
<td>28.4</td>
</tr>
<tr>
<td>Dust</td>
<td>25.3</td>
<td>38.7</td>
<td>52.2</td>
<td>0.50</td>
<td>19.7</td>
</tr>
<tr>
<td>Treadle</td>
<td>4.70</td>
<td>32.0</td>
<td>53.7</td>
<td>0.79</td>
<td>16.2</td>
</tr>
<tr>
<td></td>
<td>25.3</td>
<td>25.3</td>
<td>55.3</td>
<td>0.92</td>
<td>14.9</td>
</tr>
</tbody>
</table>
The data in Table 4 shows that the residual zinc content in the calcine is reduced with increasing expense of a special coke from 25.3 to 38.7 %. A further increase in the expense of solid reducing agent increases the degree of metallization and residual zinc content in the calcine.

It should be noted that in case of special coke expense of 25.3 % the melting briquettes was observed, at an expense of 32 % the degree of fusion is less, but calcine is dense and difficult to destroy. In case of special coke expense of 38.7 % and above, calcines are loose, friable.

Effect of charge particle size on the residual content of zinc in the calcine. The effect of material size was studied in order to study the effect of variables of process parameters on the residual zinc content in the calcine. Because the size of the material largely effects on the efficiency of the recovery process. The finer the material and the lower the porosity, worse conditions for heat transfer and the probability of a material baking is higher.

In the study of the effect of particle size of charge on the high-temperature zinc reduction, all components of the charge were crushed to a uniform particle size. Content of the test charge, weight. %: oxidized zinc ore is 50.5; dust of gas purification of blast furnace smelting is 25.3; special coke is 19.5; treacle is 4.7.

Figure 2 shows the effect of charge particle size on the residual content of zinc in the calcine.

From this dependence curve, it follows that reducing of the charge particle size up to $P + 0.071 -0.04$ mm reduces the volatility of zinc, as evidenced by the high content of residual zinc calcine equal to 1.02 wt. %. Increasing of the charge particle size up to the 0.315-micron class led to a sharp reduction in the residual content of zinc in the calcine up to 0.02 wt. %. With further increase in particle size up to class 1.0 mm, the residual zinc content in the cinder was increased to 0.48 wt. %.

Conclusions. The treacle in an amount of 4.5-5.0 wt. % is the best binder during the briquetting of charge consisting of oxidized zinc ore, dust of gas purification of blast furnace smelting and solid reducing agent. %.

It is found that the solid reducing agent expense of 38-39 % of the oxidized zinc ore amount in the charge is optimal.

Studies of the effect of charge particle size have shown that the presence of dust reduces the gas permeability of charge, increases the probability of sintering of material, which has a negative impact on the performance of high temperature zinc reduction and necessitates briquetting.

Study of zinc reduction from various types of reducing agents showed prospects of special coke derived from brown coal of Shubarkol deposit for the high reduction of zinc oxide ore from the charge and dust of blast gas purification of furnace smelting gas.

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ТУЙІНДЕМЕ
Кептеме еңіншілік ресурстарды техникалық іс жасауға болатындығы және тұымдылғың жұмысқа қатысқаның тәжірбесін ұсындайды. Туынды тұымдылдардың әсері, құрылысқа қатысқан өндірістік қасиеттерін қамтамасыз етеді.

Одним из направлений ресурсосбережения при производстве цветных металлов является использование отходов чёрной металлургии, в которых содержание цветных металлов достигает промышленных кондиций. Так, в пылях газоочистки некоторых заводов черной металлургии содержание цинка достигает 15 %. В работе представлены результаты исследования влияния связующего при брикетировании шихты, вида углеродистого восстановителя, расхода восстановителя, тонины помола компонентов шихты на процесс карботермического восстановления цинка из окисленной цинковой руды с добавкой лежалой пыли газоочистки доменной плавки. В качестве связующего при брикетировании шихты испытывали бентонит, гашеную известь и патоку. Установлено, что оптимальным связующим является патока в количестве 4,5-5,0 мас. % от массы руды. Показано, что остаточное содержание цинка в продукте восстановительного обжига при использовании спецкокса, полученного из угля месторождения Шубарколь в 1,9 раз меньше, чем при использовании антрацита и 3,3 раза, чем при использовании металлургического кокса, т.е. спецкокс является наиболее активным восстановителем. Расход углерода при карботермическом восстановлении цинка из окисленной руды с добавкой пыли на 22-24 % ниже, чем при восстановлении цинка только из руды. Установлено, что измельчение шихты до класса +0,071-0,04 мкм снижает степень возгонки цинка. При размере шихты +1,0 мкм остаточное содержание цинка в огарке повышено. Высокая эффективность восстановления достигается при следующем составе шихты, мас. %: окисленная цинковая руда 53,8; пыль газоочистки доменной плавки 26,9; спец кокс 21,0; патока 5,3.

Ключевые слова: цинк, шихта, окисленная цинковая руда, пыль газоочистки доменной плавки, связующее, карботермическое восстановление

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