

HEAT TREATMENT PROCESSES OF STEEL-SMELTING SLAGS IN THE RECOVERY ENVIRONMENT

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Abstract

In article questions of development, low-waste technologies of processing of steel-smelting slag are considered, gland allowing by extraction and its connections from steel-smelting slag to receive additional raw materials for production became, and the remains to use in building industry. Complex processing of steel-smelting slags as the main way of engineering-ecological development of society was offered in the mid-sixties the past century, generally by scientists from the CIS countries. Based on their application, it was supposed not only it is most useful to use the consumed raw material resources, but also to try to process formed entirely waste. Thus present at a firm oxidizer iron assimilates with metal and promotes degree increase complex raw materials use. In this case, as firm oxidizers can be used, oxides the connections of iron taken from utilized slags of joint-stock company "Uzbeksteel."

Keywords: Slag, metallurgical dust, fusion mixture, melting, production efficiency

1. MAIN TEXT

The main problem of modern steel-smelting production in the world is the complex processing of slag, utilization of valuable components, and increase in complexity of the use of raw materials. Over time the given problem will increase since every possible exhaustion of the rich and easily opened ore fields, increase in requirements to environmental protection, growth of needs for ferrous metals is observed. Production of ferrous metals is followed by the formation of slag and other types of technogenic waste. Their quantity, in connection with the rapid growth of the smelting of cast iron and steel, continuously increases and now is hundreds of millions of tons. It is easy to present what huge areas can be busy with slag dumps. And it when the deficiency of the fertile land plots occupied by the industrial enterprises sharply increases and becomes aggravated situation with the protection of natural resources. But it is only one side of the problem, and the second consists of potential opportunities for the use of slag in the national economy [1].

One of the main problems of the ferrous metallurgy of Uzbekistan is the chronic deficiency of feedstock. For a variety of reasons available in the republic, iron ore fields aren't involved in an industrial turn. JSC "Uzbeksteel" is forced to work for scrap metal, which amount in the region continuously decreases almost wholly. The central part of hot – the bracketed iron is imported from foreign countries. These difficulties at conducted to the fact that only a small part of a necessary product is satisfied at the expense of original production. In this regard, involvement in the production of sources. Gland being in secondary technogenic formations of the local industrial enterprises is "relevant."

At the department of "Metallurgy," TashSTU researches on additional extraction of iron and its oxides from wastage of metallurgical production are conducted.

The slags which are formed during the smelting of steel in JSC "Uzbeksteel" contain in the structure, pure iron of 10 – 12 %, and concentration of its oxides reaches several tens percent. In-plant these slags subject dry

magnetite enrichment and add the emitted material to proceeding fusion mixture. Tails of magnetite enrichment are a production wastage and are stored in particular dumps.

The analysis which is carried out by us showed that this wastage contains first a large amount of iron and its oxides. So, the mean value of the content of metal iron made 3.8 %, and its oxidic content of 16.8 %. These concentrations quite compared with poor iron oxides and can be used in metallurgical production. Now in plant saved up more than 1.5 million tons. This wastage and 60-70 thousand tons are annually formed follow-up. The same picture is also observed at other enterprises of ferrous metallurgy [2].

The technology of receiving crude ore and coal pellets from the thin-milling of the materials supporting not less than 70-90 % of fraction of 0.074 mm practically remains the same, as well as for ore granules, and can be realized on the granulators used now that will be coordinated with results of work [7]. Because of the high capillary moisture capacity of thin-milling fuel in comparison with a concentrate, the humidity of furnace charge for receiving the ore-fuel of granules needs to be maintained 2-4 % above, then by production the ore-fuel of pellets. Crude the ore-fuel pellets from 20 % of fuel (powder of the Angren coal) with a diameter of 10 mm maintained before the destruction of loading 0.8 kg, and after drying of 1.0-1.2 kg / a pellet.

We conducted researches on the definition of influence of temperature of roasting on some technological indicators of the process of enrichment of iron ore pellets. The results of the researches are given in **Figures 1-3**. Experiments were done under the following conditions: roasting time – 60 minutes, diameter of a pellet – 10 mm, the composition of furnace charge of 80 % poor ore, and 20 % of fuel.

In **Figure 1** changes in the content of iron in concentrate depending on roasting temperature are presented.

From **Figure 1** it is visible that an increase in temperature of roasting iron content grows in a concentrate. This phenomenon can be explained as follows. For the course of chemical or structural changes in a stationary phase, there has to be a movement of atoms. Various mechanisms of this phenomenon are possible. The transition of atoms from regular knots of a lattice in a nearby vacancy [3] can be one of them. Vacancies exist in each crystal at all temperatures other than absolute zero. The speed with which diffusion of atoms in this case proceeds depends on the ease of movement of atoms from the regular knot in vacant and on the concentration of vacancies. Movement of atoms in any direction is equivalent to the wandering of vacancies in the opposite direction. Therefore in a similar case, it is possible to speak about the diffusion of vacancies.

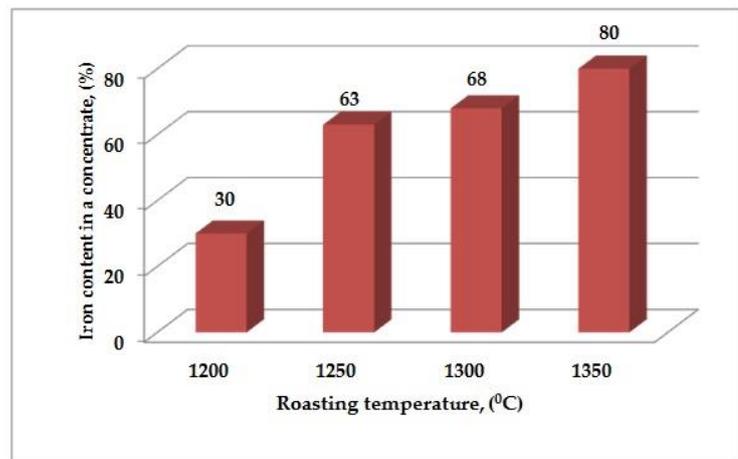


Figure 1 Influence of temperature of roasting on the iron content in a concentrate

One of the options of this process is the so-called "relay" mechanism at which the atom which is in an interstice passes into a regular knot, pushing out the atom which was earlier there is a new interstice.

The valid mechanism of the process in this system is defined by the relative size of the energy, which is required for the course of this process. Diffusive processes, as a rule, in many respects, determine the speed of chemical reactions and agglomeration.

The size of energy necessary for this purpose is called the energy of activation of process, and the expression can present the temperature dependence:

$$D = D_0 \exp(-E/RT) \quad (1)$$

where E is the seeming energy of activation of diffusion.

The size of the coefficient of diffusion and its change with the growth of temperature increases also that most reactions of restoration of oxides of iron accelerate.

Process of restoration of iron of oxides, according to Baykov's principle about the sequence of transformations, proceeds in steps by the transition from the highest oxides to the lowest in schemes



or



At the same time, according to the chart Fe – O in a system arise not only with the lowest oxides and metal but also solid solutions.

Restoration of oxides of iron solid carbon perhaps on the following reactions:

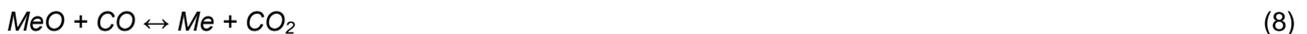


For the last reaction:

$$\lg K_p = -7,730/T + 7.84 \quad (7)$$

Total negative thermal effect 4,240 kJ/kg of iron.

Carbon oxide reversible reaction is the cornerstone of processes of restoration of oxides of metals:



This reaction proceeds from left to right when ΔG reactions – size negative, i.e., when the thermodynamic potential of a system decreases upon transition from an initial state to equilibrium.

If to express a constant of balance through partial pressure of gases and vapors of participants of reaction:

$$K_p = \frac{P_{me} \cdot P_{CO_2}}{P_{meo} \cdot P_{CO}} \quad (9)$$

where to P_{me} , P_{meo} , P_{CO} , – vapor pressure and gases of participants of reaction at balance and to express an initial state through

$$K_p^1 = \frac{P_{me}^1 \cdot P_{CO_2}^1}{P_{meo}^1 \cdot P_{CO}^1} \quad (10)$$

That $\Delta G = RT \ln K_p^1 - RT \ln K_p$ or $\Delta G = RT \ln \frac{P_{me} \cdot P_{CO_2}}{P_{meo} \cdot P_{CO}}$ (11)

The reaction goes from left to right when $K_p^1 < K_p$, and ΔG reactions – size negative. The size of a constant of balance can be determined on the equation:

$$\ln K_p = -\frac{\Delta G}{RT} \text{ or } K_p = -\frac{\Delta G^0}{4.57T} \quad (12)$$

where ΔG^0 – standard izobarno – the isothermal potential of the reaction determined by a difference:

$$\Delta G^0 = \Delta G_{CO_2}^0 - \Delta G_{CO}^0 - \Delta G_{MeO}^0 \quad (13)$$

from sizes of standard thermodynamic potentials of formation of the CO₂, CO, and MeO connections from elements.

Values $\Delta G^0_{CO_2}$, ΔG^0_{CO} and ΔG^0_{MeO} it is possible to find in reference books and also according to charts of dependence ΔG^0_{MeO} from temperature (the chart of the energy of Gibbs).

In some cases, MeO and Me are in the condensed firm or liquid phases, then $P_m = const$ and $P_{meo} = const$,

$$K_p = \frac{P_{CO_2}}{P_{CO}} \quad (14)$$

The thermal effect of reaction (18) can be calculated on warmth of education of participants of reaction from elements:

$$Q = (Q_{CO_2} - Q_{CO}) - Q_{MeO} \quad (15)$$

At 298 To $Q_{CO_2} = 94.05$ kilocalories (398.13 KJ)

$Q_{CO} = 26.5$ kilocalories (110.77 KJ)

then $Q_{298} = 67.65$ (282.78) - Q_{MeO}

Reactions of restoration of oxides of metals carbon oxide can be exothermic or endothermic depending on the warmth of the formation of oxide from elements [4]. Thermal effects of the reaction of restoration of some oxides by carbon oxide, kilocalories are given below (*4.18 KJ):

Cu ₂ O + CO = 2Cu + CO ₂	27.8
PbO + CO = Pb + CO ₂	16.6
NiO + CO = Ni + CO ₂	10.0
½ Ge ₂ + CO = ½ G+ CO ₂	61.1
FeO + CO = Fe + CO ₂	3.2
ZnO + CO = Zn + CO ₂	-15.0
½ SiO ₂ + CO = ½ Si + CO ₂	-37.2
NbO+ CO = Nb + CO ₂	-29.0
UO ₂ + CO = ½ U + CO ₂	-61.1
MgO + CO = Mg + CO ₂	-75.5
½ TiO ₂ + CO = ½ Ti + CO ₂	-59.7

If > 67.6 kilocalories (282.78 KJ), then the thermal effect of reaction of restoration - the negative size that is observed at metals with considerable affinity to oxygen (Zn, Ti, Nb, V, and others).

If > 67.6 kilocalories (282.78 KJ), then the thermal effect of reaction of restoration of oxide of metal - the particular size, and the reaction is followed by allocation of heat. Thus, then the affinity of metal to oxygen is more, especially the thermal effect of reaction of restoration of its oxide is negative [5].

It is possible to calculate a constant of the balance of restoration of oxides of metals carbon oxide and to graphically represent the dependence of a logarithm of constant equilibrium reactions of restoration from temperature (**Figure 2**).

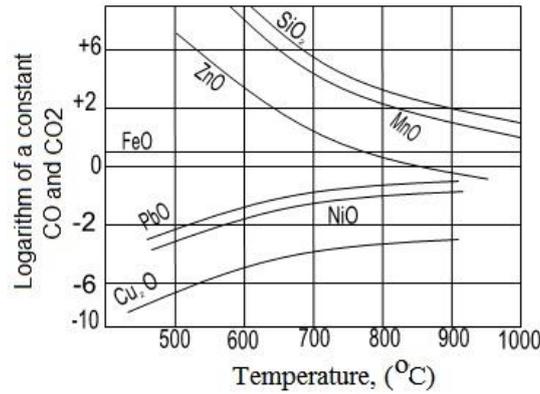


Figure 2 Dependence of a logarithm of a constant of a balance of reactions of restoration of various oxides carbon oxide from temperature

Knowing a balance constant at this temperature, it is possible to calculate it on equilibrium structure of a gas phase for reaction under conditions

$$\frac{1}{Kp} = \frac{P_{CO}}{P_{CO_2}}; P_{CO} + P_{CO_2} = P; \% CO + \% CO_2 = 100 \%$$

$$\text{Then } P_{CO} = \frac{\% CO \cdot P}{100}; P_{CO_2} = \frac{\% CO_2 \cdot P}{100} = \frac{(100 - \% CO)P}{100} \quad (16)$$

$$\frac{1}{Kp} = \frac{P_{CO}}{P_{CO_2}} = \frac{\% CO}{\% CO_2} = \frac{\% CO}{100 - \% CO} \quad (17)$$

$$\text{From where } CO_2 = \frac{Kp \cdot 100}{1 + Kp} \% \text{ and } CO = \frac{100}{1 + Kp} \% \quad (18)$$

In **Figure 3**, equilibrium structures of a gas phase for reactions of restoration of oxides of metals independence – from temperature are represented.

In the lower part of this chart, the metals with a small affinity to oxygen (Cu, Pb, Ni) demanding for the restoration of insignificant concentration CO in a gas phase with the size $Kp > 1$ are located. In the top part of the chart, metals with considerable affinity to oxygen (Zn, Si, Mn) are located for which $Kp < 1$ demanding for recovery of the considerable contents CO in a gas phase.

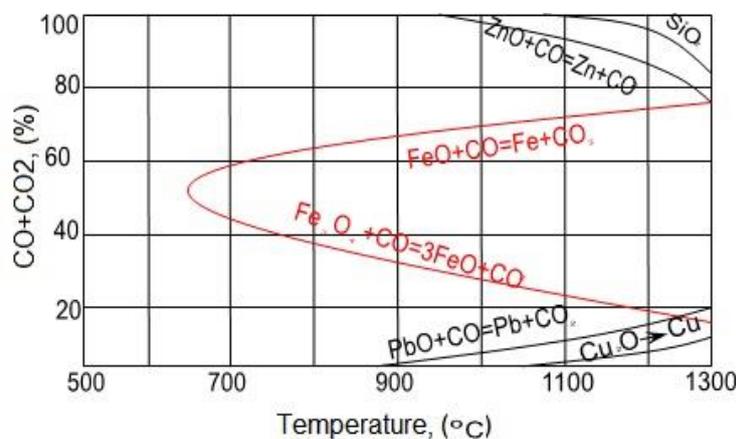
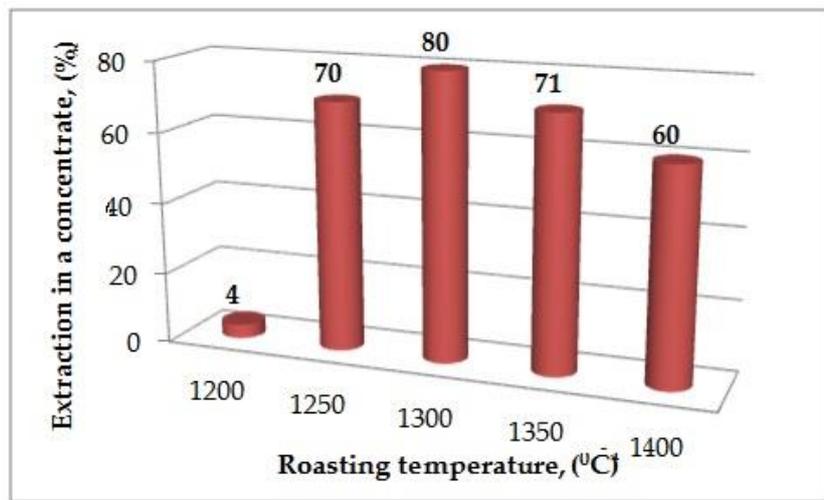


Figure 3 Dependence of equilibrium concentration CO in the mix with CO₂ for reactions of restoration of oxides of metals carbon oxide from temperature

From charts (**Figures 2 and 3**), it is visible that constants of the balance of reaction of restoration of oxides for from them metals with temperature increase (FeO, Cu₂O, NiO) for others decrease (ZnO, SiO₂, Fe₃O₄).

At the negative thermal effect of chemical reaction, according to Le-Chatelie's principle, an increase in temperature shifts balance of reaction of restoration of iron from left to right, i.e., towards the formation of metal.

An essential indicator of the concentrating process is the extraction of a valuable component in a concentrate. In **Figure 4** results of researches on the definition of this indicator depending on roasting temperature are presented.



Roasting time – 15 min. in air current; d pellets = 10 mm; structure of 80 % ore, 20 % coke.

Figure 4 Influence of temperature of roasting on the extraction of iron in a concentrate

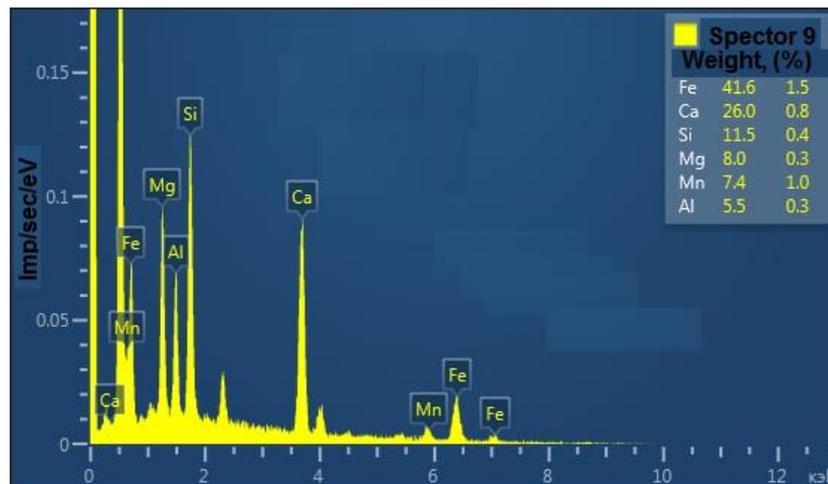


Figure 5 The electronic and microscopic picture of concentrate after recovery

From data in **Figures 4 and 5** it is visible that with temperature increase, the extent of extraction of iron in a concentrate increase. It is a consequence of the fact that at high temperatures, recovery processes proceed more intensively. However, the extent of extraction remains quite low, and it leads to the fact that at heat treatment of the crushed iron ore materials, the agglomeration phenomenon is observed. It especially becomes more active if the porous pressed body is exposed to processing. Thus, agglomeration is shown at heat treatment as separate dispersion particles (for example, at recovery or roasting of concentrates in the boiling layer), and granules (crude pellets, briquettes) [6].

The first porous body is the system remote from a status of thermodynamic equilibrium at the same time in many parameters. It is caused by a big free surface of separate particles, the existence of micro distortions of type of shift of atoms from regular provisions in a grid, nonequilibrium defects of type of dislocations, excess vacancies, etc. At complexity of the structure of dispersion medium non-equilibrium of a system is also caused by a field of a gradient of concentration. At agglomeration, reduction of the surface energy of particles, and "curing" of separate defects, alignment of concentration [7] happens the being irreversible process, both.

Solid-phase agglomeration influences the process of recovery when processing ore and coal pellets. At recovery them in the mine furnace, this process is of great importance because the upper limit of temperatures of recovery is limited to temperature of agglomeration of pellets in clusters with violation of the modes of process.

Processing of iron ore materials during thermal recovery has, in comparison with the clean phenomenon, some features from which first of all it is necessary to select:

- a) existence of a large number of components (oxides of iron, silicon, aluminum, calcium, magnesium and so forth);
- b) noticeable amount of the gases which are formed during the process;
- c) course of oxidation-reduction processes;
- d) course of solid-phase reactions (between magnetite and silicon dioxide, lime and hematite and other);
- e) possibility of formation of a quantity of a liquid phase of variable structure and properties.

These features do not give the chance to use without changes of a pattern of agglomeration, found mainly for metal powders. For example, iron ore material is the system remote from thermodynamic potential in many parameters. As chemical reactions follow recovery processing, reduction of free energy of a system as a result of course of reactions can be characterized by more powerful flows of substance, than other processes. In other words, the approach of a system to balance in one parameter can be energetically justified in that case when it is followed by temporary removal from the balance in other parameters. Practically it can be expressed in another process of change of porosity of granules, the size of grains, etc.

Generally, the pellet can be considered as a porous polycrystal with an extensive network of interparticle borders. The more the area the interparticle of borders, the is more dense and stronger a pellet. Proceeding from it, an objective criterion of the behavior of iron ore particles when heating is the total area of interparticle contacts or an inverse value – the total area of contacts of a particle – a time which is expressed by a total or specific surface of time.

We conducted researches on the determination of strength properties in a cold condition of pellets from a specific surface of time. The specific surface of time was determined by a popular bottle method. The results of the researches are presented in **Figure 6**.

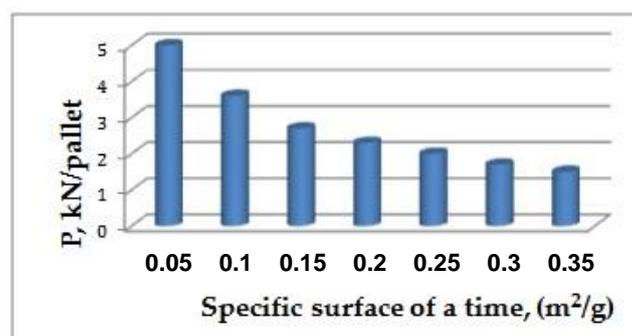


Figure 6 Dependence of cold durability on a specific surface of time in pellets

From data in **Figure 6** it is visible that with an increase in a specific surface of time durability of pellets significantly falls. Especially it is essential to consider it when loading material in the mine furnace since, at the same time, pellets can collapse that reduces gas permeability of furnace charge, increases dust remove, and the recoverability of oxides owing to change of aerodynamic conditions in the furnace decreases.

Also, furnace charge agglomeration since will significantly be at a loss recoverability owing to a decrease in a reactionary surface, and the formation of hardly reparable connections has an adverse effect.

Based on the analysis of possible ways of involvement in the ore-fuel of pellets in the industry, it is possible to conclude that such basic opportunity is available. The choice of an optimal variant will depend on technological and technical and economic indicators by the preparation of raw materials for metallurgical conversion.

By results of the conducted researches, it is possible to conclude:

- it is defined that when using as coal reducer, the content of metal iron in pellets is lower than when using oil coke. Proceeding from the received results and also considering the cost of the oil coke (about 4.4 million bags for ton) exceeding coal cost (about 0.5 million bags for ton) and the high content of the sulfur in coke which is harmful impurity for steel the decision as a reducer to use brown Angren coal was made;
- the optimum amount of the coal added to furnace charge of the roasting making 20 % of the mass of a gravitational concentrate is defined;
- it is established that the optimum temperature of recovery roasting is 1100 °C;
- it is defined that the process of restoration of iron of oxides proceeds in steps according to the following scheme: at temperatures above 560 °C of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$, below 560 °C magnetite is restored to metal iron, passing wustite $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$.

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