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INVESTİGATİON OF THE EFFECT OF ACİDİTY AND ALKALİNİTY OF THE ASH ON THE CORROSİON OF THE REFRACTORY PART OF THE FURNACE

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ABSTRACT

The acid open-hearth process allows steel to be produced with a lower gas content compared to the basic process. However, depending on the melting process factors and the type of process used (active or silicon-reducing), the hydrogen content in the resulting steel fluctuates from 2.5 to 6.5 sm^3 /100 g, and nitrogen – from 0.006%. This was the reason for a lengthy discussion between [1] and [4] about the behavior of gases in the bath of an acid open-hearth furnace. For a long time, it was believed that the main reason determining the behavior of gases in the metal of an acid open-hearth furnace was the rate of silicon reduction from high-silica materials into metal. [2] was the first to draw attention to the significant influence of the gas-protective properties of the slag cover. However, in the study [5], based on several melts with one acid slag, carried out in an induction furnace, the opinion was expressed that acid slags are impermeable to hydrogen and reliably isolate the molten metal from the water vapor of the open-hearth furnace atmosphere.

Introduction

Hydrogen permeability of acid steelmaking rust. The process of hydrogen transfer from the furnace atmosphere through acid slag into metal includes the stage of dissolution of water vapor in the rust melt without considering in detail the data available in the literature on the solubility of water vapor in the rust melt, it can be noted that they were first obtained in a study the results of which have recently been mainly confirmed by the work of American and Japanese scientists. The degree of acidity of the slag melt can be described by the equations of hydrogen mass transfer through the rust melt layer to the rust and metal interphase surface and the transition of hydrogen from the rust to the metal.

$$H_2O_{г} + 0^{2-}_{ru.} = 20H^{-}_{ru.}; \qquad (1)$$

$$H_2O_г + 2SiO^{4-}_{4ru.} = 2OH^{-}_{d.} + Si_2\,O^{2-}_{7ru.} \qquad (2)$$

$$H_2O_г + Si_2\,O^{6-}_{7} = 2OH^{-}_{ru.} + 2SiO^{2-}_{3ru.} \qquad (3)$$

The last stage, depending on the process conditions and the degree of oxidation of the metal, can proceed in different ways. For example, the decomposition of hydroxyl into oxygen and hydrogen can proceed with the participation of iron atoms of the surface layer of the metal or without the participation of iron atoms.

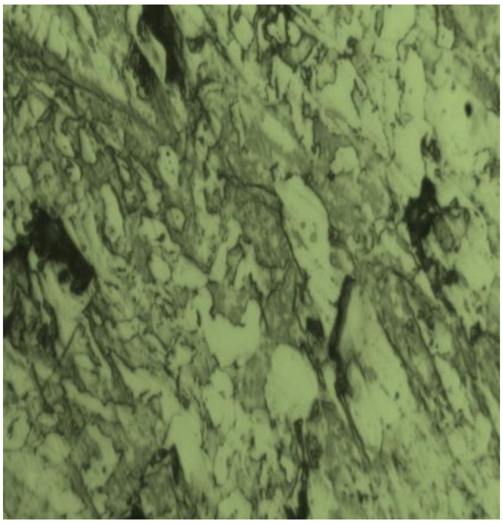

Fig. 1. Inclusions in steel 30KhGSNA. X500: a, b, aluminum additive after alloying steel with silicon; c-aluminum additive before alloying steel with silicon

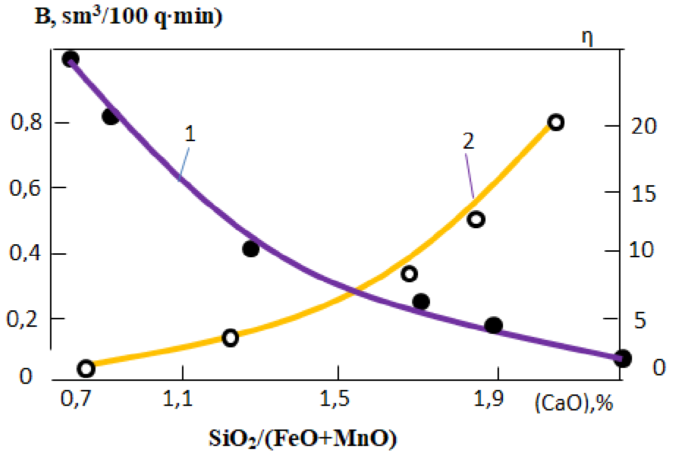

Fig. 2. The effect of the Si_2O /(FeO + MnO) ratio on the hydrogen permeability (1) and viscosity (2) of acidic open-hearth rust at 1650 ⁰C and p_(H_2O)= 150 mm Hg.

THEORETİCAL PART

In the conditions of experiments on studying the hydrogen permeability of slag melts, all the above-mentioned stages of hydrogen movement took place. Some researchers claimed that with an increase in the basicity of the slag, the hydrogen content in the steel increases, while others reported a decrease in the hydrogen concentration in the metal with an increase in the basicity of the rust melt [6]

Therefore, in the first series of experimental melts, the effect of the basicity (CaO/SiO_2) of electric steel-making rust on their hydrogen permeability was studied. The technique was similar to that previously described in as applied to the main electric steel-making rust. With the method used for supplying the steam-nitrogen mixture (see Fig. 1), which primarily washes the crucible with molten metal and rust, the gas permeability of the crucible could greatly affect the results obtained.

$$I = SAT^2e^{-\varepsilon f/\kappa T,} \qquad (5)$$

where I - is the emission current;

S - is the cathode area;

A - is a constant;

ε - is the electron charge.

Accordingly, the activation energy of the process of hydrogen transition from the gas phase to the slag increases. Comparison of hydrogen permeability of basic and acid steel-making slags shows that the hydrogen permeability of the latter is four to five times lower than that of the basic rust.

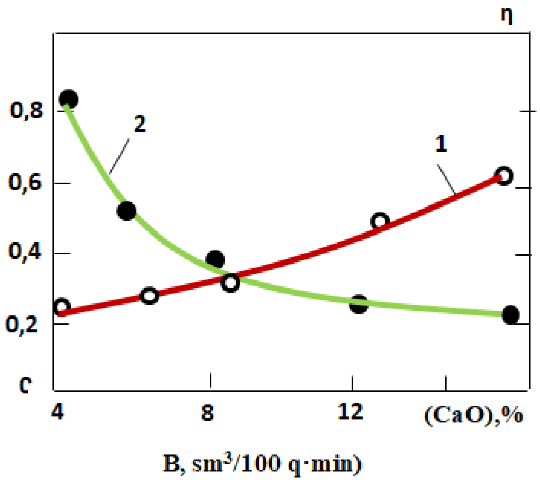

Fig. 3. Effect of CaO on hydrogen permeability (1) and viscosity (2) of acidic open-hearth

Slags of the silicon-reducing process contain up to 4.0% calcium oxide, and in the active process the concentration of this component reaches 15.0%. In this regard, it is extremely important to know the effect of calcium oxide on the hydrogen permeability of acid steel-making rust [7], The chemical composition of the melts studied for this purpose is given in Table 1 (Group II rust). The results obtained are presented in Fig. 4, from which it is evident that an increase in the calcium oxide content in the acid rust is accompanied by a significant increase in its hydrogen permeability. Such an effect of calcium oxide on the hydrogen permeability of acid rust is explained by the strong thinning effect of this component under these conditions and a decrease in the viscosity of the melt (see Fig. 3). In addition, with an increase in the calcium oxide content in silicate melts, the activity of oxygen anions increases, which promotes the dissolution of water vapor in the rust.

The effect of alumina content in acid slags on their hydrogen permeability is shown in Fig. 4. Alumina present in the acid slag increases its hydrogen permeability not only due to a decrease in the viscosity of the melt, but also due to an increase in the solubility of water vapor in the rust, since one weight unit of alumina binds a smaller amount of oxygen anions compared to silica.

$$SiO_2 + 2O^{2-} \rightarrow SiO_4^{4-};\ Al_2O_3 + O^{2-} \rightarrow 2AlO_2^{-}. \qquad (6)$$

Depending on the fuel used (blast furnace, generator, natural gas or fuel oil) and its humidity, the amount of water vapor in the atmosphere of the open-hearth furnace varies widely.

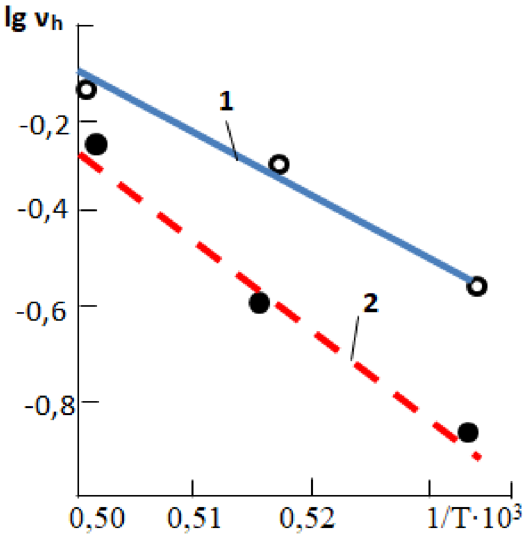

Fig. 4. Influence of temperature on hydrogen permeability of acidic rust 1 – 49,0% SiO_2; 2- 54,2% SiO_2

To do this, we represent the equation ($\upsilon_H = \beta_H S(C_1 - C_2)$) in the following form:

$$\upsilon_H = AB_0\, e^{-E/RT}(C_1 - C_2) \qquad (7)$$

$$lg = \upsilon_H = A_0 - B_0/T \qquad (8)$$

Where,

$$A_0 = lg\ AB_0 \qquad (9)$$

$$B_0 = E/R\ lg\ e = E/4,575 \qquad (10)$$

Table 2. Chemical composition of synthetic slags and their hydrogen permeability

Rust	**Contents of components, %**				**SiO2/FeO+MnO**	**Hydrogen permeability, sm³ /100 q-min at 1650 ⁰ C and different values of p_{H_2O}= 150 mm Hg.**			
	SiO_2	FeO	MnO	Al_2O_3		55	100	170	260
1	62,12	7,64	18,73	10,60	2,36	-	-	0,18	-
2	57,20	7,40	21,30	13,40	2,00	-	-	0,30	-
3	50,60	22,10	15.25	12,70	1.36	-	0,37	0,43	0,52
4	45,60	11,90	29,10	13,50	1,11	-	0,43	0,54	0,63
5	44,00	36,80	9,20	12,00	0,95	0,36	0,55	0,74	0,90
6	46,40	27,75	14,00	13,60	1,12	0,30	0,37	0,42	0,51
7	46,00	19,82	21,56	13,55	1,11	-	0,38	0,45	0,55
8	46,00	14,30	26,20	13,50	1,13	0,32	0,40	0,50	0,58

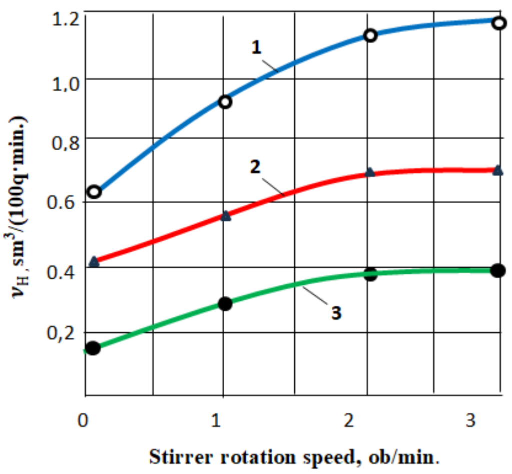

Fig. 5. Effect of mixing intensity on hydrogen permeability of rust with different compositions:

1 - 52,2% SiO_2 ; 14,6 % CaO; 11,6 % FeO; 16,8 % MnO; 2 – 49,0 % SiO2; 4,9 % CaO; 22,2 % FeO; 15,6 % MnO; 3 – 59,4 % SiO_2 ; 4,3 % CaO; 1,1-2,0 % FeO; 19,6 % MnO

In this case, the tangent of the angle of inclination of the straight line to the abscissa axis (Fig. 4) will characterize the apparent activation energy of the slag hydrogen permeability process. For the rust containing 49.0% silica, this value was equal to 56.8 kcal/mol, and for the melt with 54.20% silica, 74.6 kcal/mol [8],

Thus, the study of the hydrogen permeability of unstirred slags showed that the limiting link in the process is the mass transfer of hydrogen in the slag layer, determined mainly by the viscosity of the latter.

$$\upsilon_H = K_{OH^-}(OH^-) = K_{OH^-}\sqrt{K_{H_2O}(O^{2-})P_{H_2O}} = K_H\sqrt{P_{H_2O}} \qquad (10)$$

The next series of experimental smeltings was carried out to study the effect of rust mixing intensity on its hydrogen permeability. The slag was stirred with a special molybdenum mixer connected to an electric motor. It was noted (Fig. 6) that with an increase in the slag mixing intensity, the hydrogen mass transfer rate increases only to a certain limit and then remains unchanged at a certain level, depending only on the slag composition (for given values of p_{H_2O} in the gas phase and slag temperature) [9]. The rate of hydrogen transition from the gas phase through the slag to the metal is expressed as the rate of the first-order reaction and is proportional to the square root of the partial pressure of water vapor in the furnace atmosphere:

The activation energy of the process of hydrogen transfer from slag to metal was found to be equal to 70.0% kcal/mol for slag containing 49.0% silica and 97.0 kcal/mol for melt containing 59.4% silica.

The kinetic mode of hydrogen transfer through intensively stirred slags to metal is also confirmed by the peculiar influence of the MnO/FeO ratio in slags on their hydrogen permeability. This part of the study was carried out by us on synthetic rust melted from chemically pure reagents (Table 2).

The first series of experiments was carried out with unstirred slags. From the obtained data (Fig. 7, curve 1) it follows that with an increase in the MnO/FeO ratio from 0.50 to 2.42, the hydrogen permeability of rust increases from 0.42 to 0.54 **sm**^{3}/(100 q·min). Under conditions of mixed slags [10], the MnO/FeO ratio has a dual effect on the rate of hydrogen transfer from the slag to the metal (Fig. 7, curve 2).

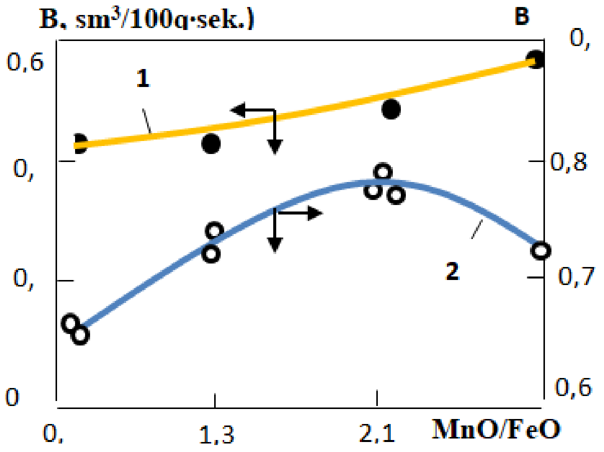

Fig. 6. Effect of the MnO/FeO ratio in slags on their hydrogen permeability at 1650 ^{0} C 1 – unstirred slags; 2 – intensively stirred slags;

using the "narrowing" method when processing experimental data on the hydrogen content in the slag and metal, he determined the equilibrium constants of the latter reactions (12) and (13). The values of the changes in the isobaric potential under standard conditions for these reactions are expressed respectively

$$\Delta G = 118000 - 61{,}5T \qquad (14)$$

$$\Delta G = 192800 - 91{,}0\ T \qquad (15)$$

These equations allow us to conclude that the reactions of hydrogen transfer from slag to metal are sharply endothermic, and the reaction involving iron cations is of greatest importance in the process of hydrogen transfer from slag to metal, because it requires less energy. It is evident from this that at a high value of the MnO/FeO ratio (from 1.85 and above), hydrogen transfer from slag to metal occurs mainly due to manganese cations. This process requires a large energy expenditure, therefore, the hydrogen permeability of slags, starting from the MnO/FeO ratio of 1.85, decreases. After laboratory studies, the effect of the slag regime on the behavior of hydrogen in the metal of acid open-hearth and electric steelmaking furnaces under industrial conditions was studied. The smelting was carried out using an active and silicon-reducing process. The open-hearth furnaces at both plants (Baku Steel Company) had the same capacity (90 t) with a hearth area of 30.0 and 28.0 m2 and were heated with fuel oil. The electric furnace had a capacity of 5 t.

Table 3. Hydrogen behavior in metal during melting carried out by silicon-reducing and active processes using recycled slag.

Melt number	**Sample number**	**[C], %**	**[Mn], %**	**Rust composition, %**						**(H), sm³/100q**	**υ, sm³/ (100 г·с)**
				SiO_2	Al_2O_3	FeO	CaO	MgO	MnO		
1	1	0,94	0,14	56,30	5,34	15,67	3,56	0,17	16,77	2,60	0,18
	2	0,46	0,25	57,54	4,54	12,48	3,73	0,14	19,47	2,48	
	3	0,33	0,25	58,80	4,32	10,94	4,14	0,15	19,42	2,70	
	4	0,36	0,35	60,56	4,08	9,86	3,77	0,16	19,44	3,90	
2	1	1,04	0,12	50,93	5,50	21,18	4,41	0,12	13,67	4,63	0,14
	2	0,44	0,31	57,37	3,92	12,48	4,36	0,13	18,91	4,18	
	3	0,36	0,27	61,34	3,44	10,15	3,40	0,13	18,91	3,09	
	4	0,36	0,45	61,46	3,04	9,72	4,02	0,14	17,84	4,54	
3	1	0,90	0,28	55,96	4,13	13,78	7,36	0,12	15,75	3,91	0.19
	2	0,36	0,30	59,41	3,10	10,59	4,64	0,13	18,62	3,26	
	3	0,25	0,27	61,74	3,32	10,61	4,13	0,13	15,24	2,84	
	4	0,27	0,27	60,80	3,76	10,01	4,30	0,14	18,46	4,40	
4	1	0,96	0,07	50,82	4,32	19,81	5,02	0,13	17,84	5,02	0,11
	2	0,45	0,16	57,52	4,40	13,54	5,18	0,15	17,91	2,90	
	3	0,35	0,23	60,02	4,30	12,33	4,70	0,13	17,52	2,70	
	4	0,38	0,50	59,92	4,24	12,19	4,58	0,14	18,11	4,30	
5	1	1,01	0,10	54,20	5,82	16,68	7,41	0,15	13,37	3,50	0,15
	2	0,47	0,29	56.08	4,18	13,06	5,83	0,14	19,03	2,81	
	3	0,32	0,20	58,32	4,46	10,83	5,65	0,14	19,61	2,80	
	4	0,33	0,31	58,48	4,48	10,60	5,77	0,13	19,59	4,06	

Samples were taken: 1 - after melting; 2 - at the end of ore boiling; 3 - at the end of clean boiling; 4 - before tapping.

Silicon reduction smelts were carried out by a duplex process (the main one was acid open-hearth furnaces). The data on these smelts are given in Table 3 (the first six smelts). The last four smelts (see Table 3) were carried out by an active process on a solid charge using 3.5% recycled slag and 0.5% iron ore. The smelts presented were carried out by an active process on a solid charge without the use of recycled rust.

In view of this, the issue of rust formation in an acid steel-making furnace, which has been discussed in detail in various works, is of extreme importance. Early slag formation in an acid steel-making furnace also plays a positive role in preserving the furnace bottoms and slopes from corrosion by rust rich in iron and manganese acids.

Comparison of the hydrogen content in the metal of the studied melts (Table 3). It can be noted that when using recycled slag in the charge, the average hydrogen content in the metal after melting and during the melting process is lower than in the metal of melts carried out without using recycled rust.

To obtain a lower hydrogen content in the metal after melting, it is necessary to have a rust in this period with a SiO_2 (FeO + MnO) ratio of 1.07 - 1.20 (Fig. 10). For melts carried out by the silicon-reducing process, this ratio can have a higher value

During the period of ore and pure boiling, the hydrogen content in the metal decreases and the more so, the higher the value of the ratio in the rust SiO_2 /(FeO + MnO + CaO) (Table 3). When the billet is transferred from the main furnace to the acid furnace in a liquid state, when using recycled rust in the charge, the average hydrogen content in the steel during the entire smelting is lower than in smelts on a solid charge and without recycled slag additives (Fig. 7). Additions of manganese ore instead of ferromanganese to the metal bath give a lower hydrogen content in the steel (melts 1-5 in Table 3). This is explained by the rapid increase in the silica content in the ruls due to the interaction of manganese ore with the lining of the slopes.

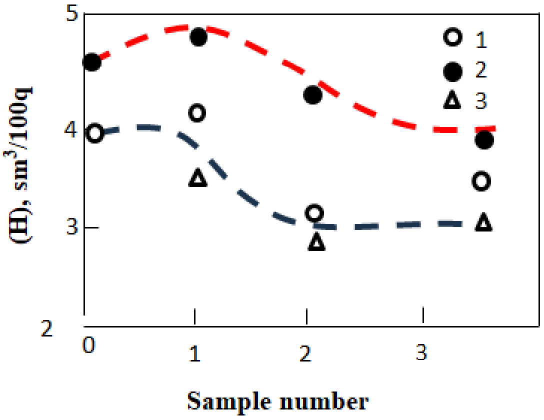

Fig. 7. Behavior of hydrogen in metal the course of acid open-hearth smelting (zero) sample - 1 hour before ore boiling, numbers - number of heats 1 - active process with additives turnover- a lot of rust; 2- without slag additives; 3- cream- recovery process

In an acid electric furnace, due to the lower content of water vapor in the gas phase, the concentration of hydrogen in the metal is significantly lower than in open-hearth steel. But even under these conditions, the rust is not a complete insulator of the metal from the hydrogen-containing atmosphere. Based on our data on the study of the behavior of hydrogen in the metal bath during 60 melts in an acid electric furnace, 14 of which are described in detail, the following pattern was revealed for the melting periods As a result of this study, it was established that in order to obtain a low hydrogen content in acid electric steel upon melting and throughout the entire melting process, it is necessary to obtain a silica content in the slag upon melting of at least 45–48%, for which it is advisable to add calcined sand or recycled rust.

Melting period	Hydrogen content in steel, sm³/100 q
Half an hour before melting	2,10 – 3,50
By melting	2,54 – 5,40
By melting	1,40 – 1,93
Before release	1,96 -2,94

Conclusions

1. By reducing the acidity of the slag, the service life of refractory materials with basic properties was increased

2. By creating a basic slag, the service life of furnaces built from basic refractory materials increased from approximately 1 to 3-3.5 times

3. It was found that the quality of the produced steel also depends on the nature of the slag created.

4. The chemical composition of the steel obtained during the smelting process also has a significant effect

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