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EFFECTS OF BOTH FLUX COMPOSITIONS AND OXIDIZING CONDITIONS ON THE DEPHOSPHORIZATION OF HIGH-CHROMIUM HOT METAL

Yoshio Nakajima

Steel R&D Laboratories, Nisshin Steel Co.,Ltd.
11-1, Showa-cho, Kure-city, Hiroshima, 737 Japan

Synopsis: Based on the spread of using coke in the melting processes, such as scrap melting or smelting reduction of chromium ore in the stainless steel production, it is thought that the development of an inexpensive and effective method of dephosphorization of chromium-containing hot metal is a necessity. In this study, the dephosphorization was investigated by a method of injecting the powder mixture of lime and fluorspar with the carrier gas containing oxygen into the metal, in order to get the optimun mixing ratio of lime and fluorspa and oxidation condition. The results show clearly that even with about 30 mass pct of chromium, effective dephosphorization is possible, with a very small amount of chromium loss by oxidation. In addition, the oxygen potential of the dephosphorization was considered from a thermodynamic viewpoint.

Key words: dephosphorization,chromium,lime,fluorspa,hot metal,injection

1. Introduction

With the goals of reduction in electric energy use and less dependence upon electric energy in the melting processes of stainless steel production, a scrap metal melting process and a smelting reduction process of chromium ore, both of which use coke as a heat source and a reducing agent, have been developed$^{1)}$.

However, in these melting processes which utilize coke, almost all of the phosphorus is transferred into the metal. Thus, in order to keep the phosphorous content level of the product below a standard level, it may be necessary to subject the coke brands or other raw materials to some restrictions, or to dephosphorize the metal. It is therefore desired to develop a cost effective dephosphorization process of chromium-containing hot metal.

In the dephosphorization by oxidation of the molten metal containing chromium, though, chromium lower the activity of phosphorus, and for the preferential oxidation of chromium, it is difficult to raise the oxygen potential, and also the fluidity of the slag is lowered by the generated Cr_2O_3 in slag. Thus, the dephosphorization is generally said to be difficult. For this reason, other strong basic fluxes such as $Li_2CO_3$$^{2)}$ - and BaO$^{3)}$ -based fluxes have been studied.

On the other hand, in these melting processes using coke, the carbon concentration in metals usually increases. In cases where carbon concentration is high, it is reported that even with CaO-CaF_2 based fluxes, sufficient dephosphorization could be obtained$^{4)}$.However, appropriate study on the flux composition and oxidation condition has not yet been done. In this study, the author examined optimum flux composition and oxidation condition using CaO-CaF_2 based fluxes by injecting the fluxes directly into molten metal with a gas mixture of containing O_2. The result was that dephosphorization was effective for chromium content of up to about 30 mass pct. Additionally, the oxygen potential can be thought to be regulated by the formation reaction of $CaO \cdot Cr_2O_3$.

2. Experimental method

The injection experiments were carried out under atmospheric pressure using the test furnace shown in Figure 1. The weight of the molten metal was 300 kg, the bath depth was 480 mm, and the diameter of the furnace was 360 mm.The injection of the powder mixture with the gas mixture of $Ar+O_2$ was done by use of a Si_3N_4-SiC nozzle with an inner diameter of 5 mm. They were injected downward at an angle of 50 degrees from the horizontal at a position of 150 mm below the metal surface. The furnace used in the experiment is equipped with a high frequency induction coil with a maximum output of 400 kW(1kHz). During the injection, 100 ~ 300 kW of high frequency output were applied in order to keep the temperature in the range of 1480 ± 20 ℃. A 14%Graphite-MgO sleeve was employed as a furnace refractory.

Investigation was made into the following three points. The level of [%Cr] was varied at 8, 17 and 28 mass pct, in order to investigate the influence of chromium contents. The weight ratio of the lime to fluorspa, CaO/CaF_2, of the powder mixture was varied at 7/3, 6/4 , 5/5 and 4/6 in order to find the appropriate CaO/CaF_2 ratio. Finally, in order to investigate the effect of oxidation conditions, the gas flow rate of O_2 and the feeding rate of powder mixture were varied between 10 ~ 175 Nl/min, and 1.3 ~ 1.7 kg/min, respectively. Namely,the amount of O_2 per 1 kilogram of the flux, $O_2/(CaO+CaF_2)$ Nl/kg, was varied from 5.9 to 138.2 Nl/kg.The injection time was between 9~17 minutes, and the volume ratio of O_2/Ar was 2/1.

In addition, in order to maintain the handling temperature during the experiment, [%C] was set to ~6.0 mass pct for the case of [%Cr]=~28 ; to ~5.5 for [%Cr]=~17 and to ~5.0 for [%Cr] = ~8. [%Si] was held below 0.06 mass pct. The fluorspar used in the experiment was a refined product with a CaF_2 concentration of 98.6 mass pct, along with SiO_2 as an impurity with a concentration of 0.56 mass pct.

3. Experimental results

3.1. Effect of the CaO/CaF_2 ratio on the dephosphorization

Figure 2 shows the changes in dephosphorization behavior as the CaO/CaF_2 ratio was changed from 7/3 to 4/6. Figure 2 shows the results obtained with an almost fixed oxidation condition in which [%Cr] was set to ~28 mass pct, [%C] was set to ~6.0 mass pct, and the $O_2/(CaO+CaF_2)$ ratio was set to between 64 ~ 76 Nl/kg. As the CaO/CaF_2 ratio went from 7/3 to 6/4 to 5/5, dephosphorization behavior improved;however, at a ratio of 4/6, no further improvement was observed. In other words, the best dephosphorization behavior was obtained at a ratio of 5/5. At that time, a 69.5 kg/ton of the flux ($CaO+CaF_2$) was used, with a dephosphorization degree of 49 %.

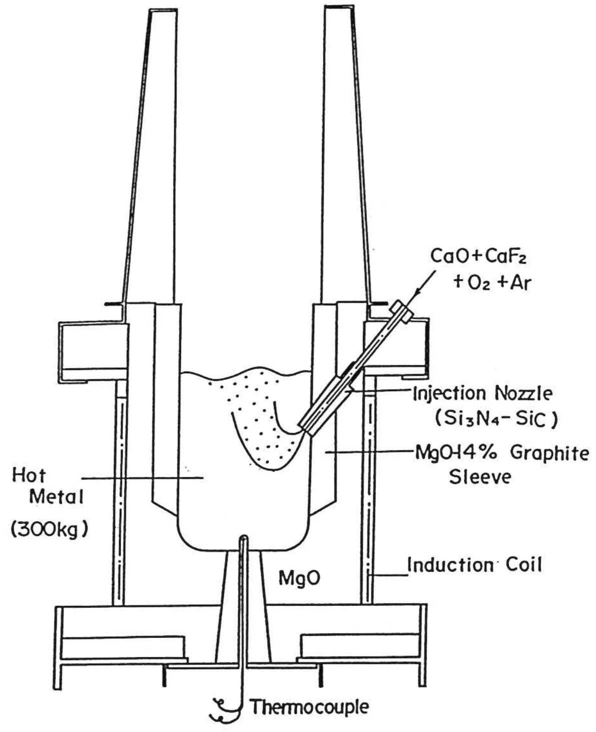

Fig.1 Experimental apparatus for oxygen-flux injection.

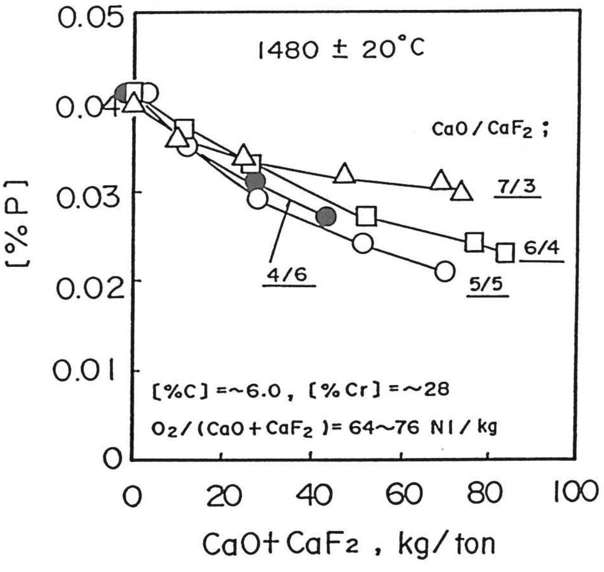

Fig.2 Effect of CaO/CaF_2 ratio on the dephosphorization.

3.2. Oxidation conditions

Figure 3 shows the relationship between $O_2/(CaO+CaF_2)$ ratio and dephosphorization degree, along with the Cr_2O_3 content in slag at the end of the injection; in this case, $CaO/CaF_2 = 5/5$, $[\%Cr]=28\sim29$ and $[\%C]=\sim6.0$. It can be seen that at $O_2/(CaO+CaF_2)= \sim40$ Nl/kg, the largest dephosphorization degree of 51% was obtained ($(CaO+CaF_2)=70$ kg/ ton), and also the Cr_2O_3 content in slag was at its lowest point, which was approximately 1 mass pct. However, as the $O_2/(CaO+CaF_2)$ ratio was increased past this point, the Cr_2O_3 content in slag increased, whereas the dephosphorization efficiency decreased. That is to say, there exists an optimum oxidation condition for the dephosphorization.

3.3. Influence of [%Cr]

Figure 4 shows the dephosphorization behavior when [%Cr] was varied at 8.1, 17.6 and 28.4 mass pct. The results in Figure 4 were obtained under an almost fixed oxidation condition of $O_2/(CaO+CaF_2) = 68\sim93$ Nl/kg, and $CaO/CaF_2 = 5/5$. As [%Cr] decreased, the behavior of dephosphorization improved ; the dephosphorization degree at 70 kg/ton of $(CaO+CaF_2)$ was 48.8 % at [%Cr]=28.4, 68.2 % at [%Cr]=17.6, and 79.2 % at [%Cr]=8.1.

4. Discussion of results

4.1. Optimum ratio of CaO/CaF_2 for dephosphorization

Figure 5 shows iso-thermal sections of the phase diagram of the system $CaO-CaF_2-Cr_2O_3$ at 1500 ℃[5]. This figure also shows the slag compositions given in this study([%Cr]=28~29), in which the CaO/CaF_2 ratio was varied from 7/3 to 4/6. As shown in Figure 5, in Region C, the following three phases coexist,i.e., CaO(s), $CaO\cdot Cr_2O_3$(s) and the liquid phase (a). Thus, in Region C, the activity of Cr_2O_3, a_{Cr2O3}, is constant, and $a_{CaO}= a_{CaO\ Cr2O3}=1$ at a given temperature. In this case, a_{Cr2O3} at 1500 ℃ is calculated to be 0.01 by equation (3).

$$CaO(s)+Cr_2O_3(s)=CaO\cdot Cr_2O_3(s) \tag{1}$$

$$\Delta G^{\circ}_{(1)}=-240{,}000+97T\ (J/mol)^{6)} \tag{2}$$

$$\log a_{Cr2O3}=-12{,}536/T+5.07\ (a_{CaO}=a_{CaO\ Cr2O3}=1) \tag{3}$$

That is to say, in Region C, the oxygen potential, P_{O_2}, is a fixed value based on [%Cr] and temperarure.

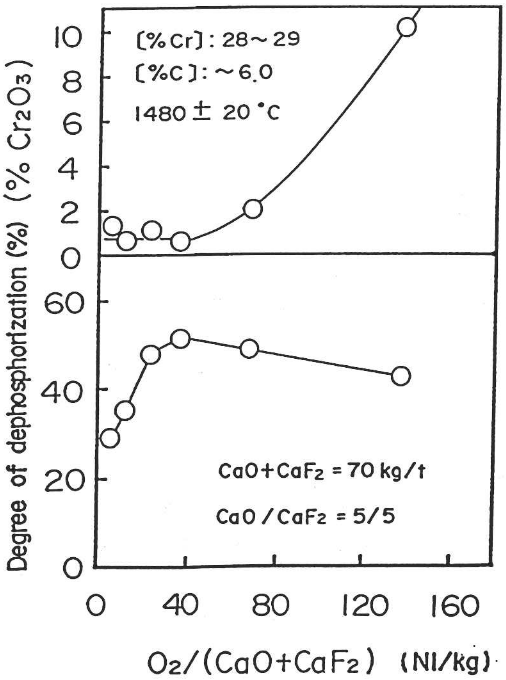

Fig.3 Degree of dephosphorization and $(\%Cr_2O_3)$ as a function of $O_2/(CaO+CaF_2)$ ratio.

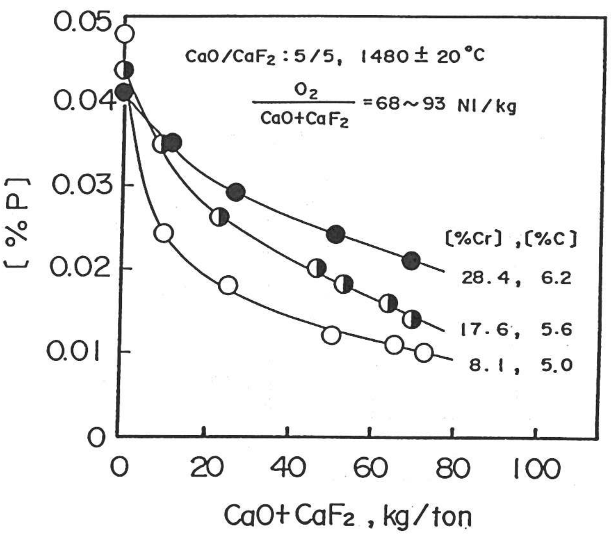

Fig.4 Changes in [%P] with $(CaO+CaF_2)$ for the different [%Cr] and [%C].

Region B is an area where $a_{Cr_2O_3}$ increases from 0.01 to 1 as (%CaF_2) increases,and where Po_2 becomes higher.However, in order to get a high Po_2 value in this region, (%Cr_2O_3) must be increased because of the relatively high solubility of Cr_2O_3 in the slag.In addition,in this region, phosphate capacity, $Cpo_4{}^{3-}$ 7), of the slag is thought to be decreased because the slag composition is away from the CaO-saturated region.

In region A, although the slag is a liquid, both a_{CaO} and $a_{Cr_2O_3}$ of the slag are low. Therefore, from the viewpoint of $Cpo_4{}^{3-}$ and Po_2, Region A is not thought to be a good region for dephosphorization.

Figure 6 shows the relationship between (%CaF_2) in slag and a phosphorus partition ratio, Lp = (%P)/[%P]. In Region C (noted by "○"), as (%CaF_2) increased (as the slag composition approaches the liquid phase (a)), Lp increased, with the result that it approached the calculated value of $Lp,_{cal.}$, which will be discussed later. On the other hand, Lp fell when Region B was entered (noted by ●). In other words, it can be said that the slag compositions in Region C which are close to the liquid phase (a) are favorable for dephosphorization.

4.2. Oxygen potential

As shown in Figure 3, there was an optimum oxidation condition, from which the oxidation power was further increased, the dephosphorization degree did not improve. This fact means that the oxygen potential may be determined by the formation reaction of $CaO \cdot Cr_2O_3$ shown by reaction (4).

$$2\underline{Cr}+CaO(s)+3/2O_2(g)=CaO\cdot Cr_2O_3(s) \tag{4}$$

$$\Delta G^{\circ}{}_{(4)}=-1,388,400+437.72T \ (J/mol) \tag{5}$$

$$\log Po_2=2/3[(\Delta G^{\circ}{}_{(7)}-\Delta G^{\circ}{}_{(9)})/(19.144T)-2\log a_{Cr})] \tag{6}$$

where,

$$2Cr(s)+CaO(s)+3/2O_2(g)=CaO\cdot Cr_2O_3(s) \tag{7}$$

$$\Delta G^{\circ}{}_{(7)}=-1,350,000+344T \ (J/mol)^{6)} \tag{8}$$

$$Cr(s)=\underline{Cr} \tag{9}$$

$$\Delta G^{\circ}{}_{(9)}=19,200-46.86T \ (J/mol)^{8)} \tag{10}$$

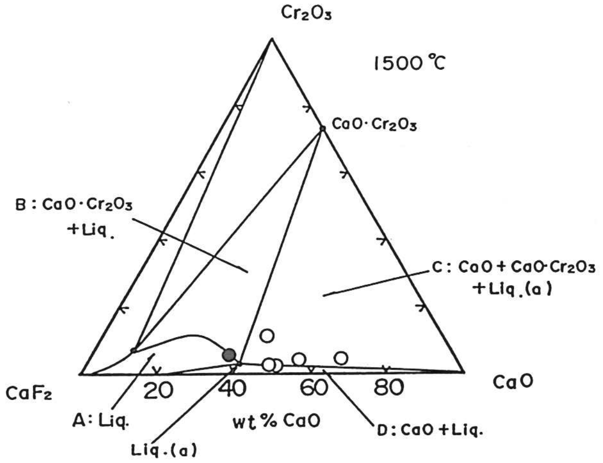

Fig.5 Iso-thermal sections of the phase diagram of the system $CaO-CaF_2-Cr_2O_3$ at 1500$^{5)}$.Plotted data show the slag compositions in this study.

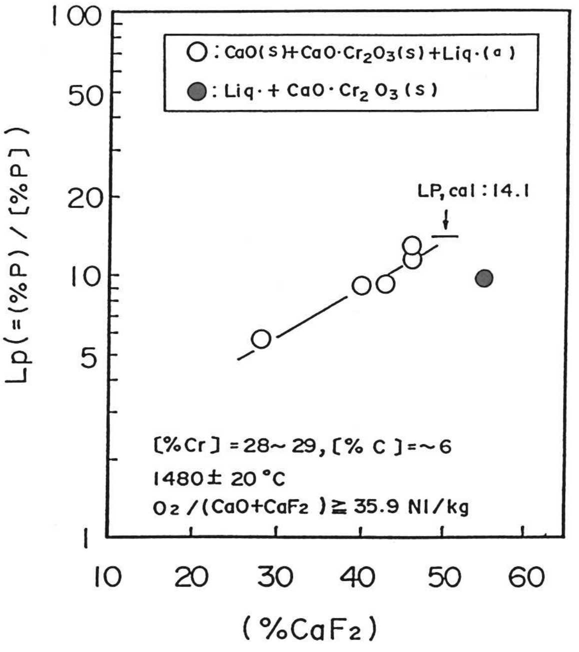

Fig.6 Relationship between (%CaF_2) and L_P.

From the definition of $C_{PO_4^{3-}}$, the equilibrium value of L_P is given by equation (11), using $C_{PO_4^{3-}}$ and P_{O_2}.

$$\log L_P = -0.486 + \log C_{PO_4^{3-}} + \Delta G^\circ_{(12)}/(19.144) + \log f_P + 5/4 \log P_{O_2} \quad (11)$$

Where,

$$1/2P_2 = \underline{P} \quad (12)$$

$$\Delta G^\circ_{(12)} = -157{,}700 + 5.4T \ (\mathrm{J/mol})^{9)} \quad (13)$$

f_P:the activity coefficient of phosphorus in metal

Figure 7 shows a comparison of $L_{P,cal.}$ and $L_{P,obs.}$. Here, $L_{P,cal.}$ is the calculated L_P by equation (11), using 10^{22} 10) as the value of $C_{PO_4^{3-}}$ and the P_{O_2} given by equation (6). Also, Figure 8 shows a comparison of $P_{O_2}(L_{P,obs.})$ which gave the observed L_P and $P_{O_2}(CaO \cdot Cr_2O_3)$ which is the calculated P_{O_2} by equation (6). As can be seen from Figure 7, in the cases of [%Cr] being 28~29 and ~17 mass pct, the observed and calculated values of L_P showed excellent agreement. Also, referring to Figure 4, in cases where $O_2/(CaO+CaF_2)$ was greater than 40 Nl/kg, it was mentioned that dephosphorization efficiency decreased. When the decarburization amount,i.e.,[%C] after the treatment, is took into consideration, the experimental and observed values of L_P are quite close, as shown by three plots with [%Cr] between 28~29 mass pct in Figure 7. It can be surmised, then ,that the fall in the dephosphorization efficiency in this case was due to the fall in [%C].

However, when [%Cr] was ~8 mass pct, the observed value of L_P was lower than the calculated one. The reason for this may be that,as shown in Figure 8, when [%Cr] was equal or greater than 17 mass pct, $P_{O_2}(L_{P,obs.})$ and $P_{O_2}(CaO \cdot Cr_2O_3)$ were in good agreement, but at [%Cr]=~8, P_{O_2} did not increase up to the levels of $P_{O_2}(CaO \cdot Cr_2O_3)$.

It is thought that the value of P_{O_2} in the molten metal in this study is close to the carbon-saturated value ($P_{O_2}=1.99 \times 10^{-16}$ atm, 1500℃) and is smaller than $P_{O_2}(CaO \cdot Cr_2O_3)$ by about three orders of magnitude. How much an interfacial P_{O_2} increases, when two phases having a large difference in P_{O_2} come into contact with each other, is thought to depend upon the treatment method. Under the experimental conditions in this study, the slag/metal interfacial P_{O_2} seems to have been limited to the level of $P_{O_2}=1.4 \times 10^{-13}$ atm($\log P_{O_2}=-12.85$).

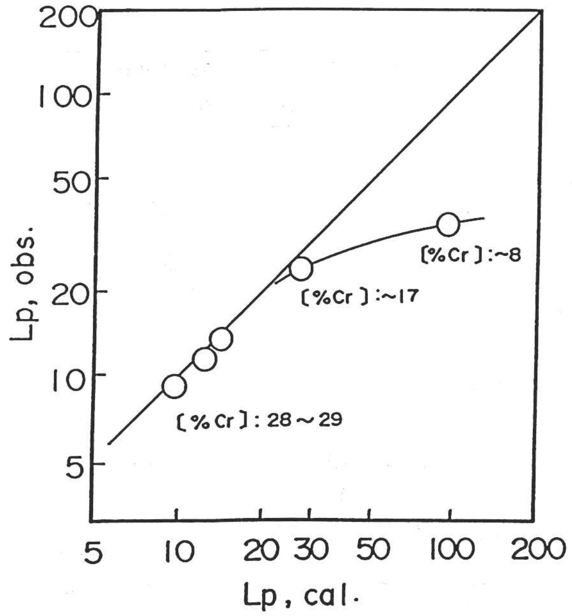

Fig.7 Comparison between the observed and calculated values of L_P.

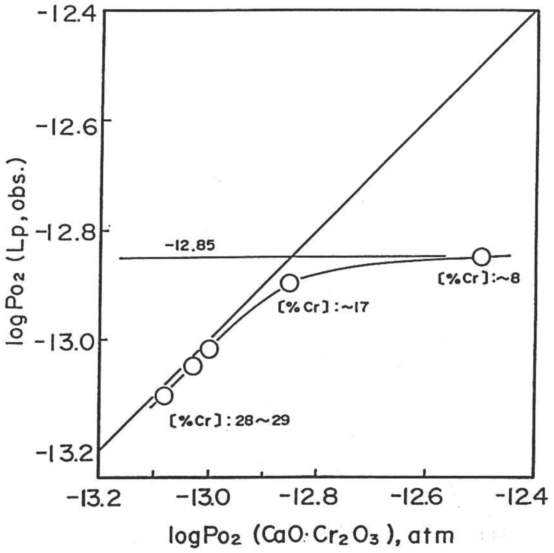

Fig.8 Comparison between $P_{O_2}(CaO \cdot Cr_2O_3)$ and $P_{O_2}(L_{P,obs.})$

5. Conclusion

By the method of injecting the powder mixtures of lime and fluorspa with the gas mixtures of O_2 and Ar into a 300 kg of chromium-containing hot metal($[\%Cr] \leqq 29$), the optimum lime to fluorspa ratio and oxidation conditions for dephosphorization have been studied. The results are as follows:

(1) Slags which are CaO-saturated and contain the liquid phase(a) as much as possible are best suited for dephosphorization. That is to say, the best ratio of lime to fluorspa is about 1/1. In this case, we obtained the dephosphorization degree of about 50 % using a flux consumption of 70 kg/ton with the metal composition of $[\%Cr]=28\sim29$ and $[\%C]=\sim6$ at the temperature of 1480 ± 20 ℃.

(2) Optimum oxidation conditions are obtained at an O_2/(lime+fluorspar) ratio of about 40 Nl/kg.In this case,the Cr_2O_3 content of slag was between 1~2 mass pct,and oxidation losses in chromium were kept between 0.05 ~ 0.1 mass pct($[\%Cr]=28\sim29$).

(3) In the high chromium content of $[\%Cr] \geqq 17$, the dephosphorization was well explained when the oxygen potential is considered to be regulated by the formation reaction of $CaO \cdot Cr_2O_3$.

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