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A PROCESS OPTIMIZATION ON HIGH TEMPERATURE ELECTROLYTIC DESULFURIZATION IN HOT METAL PRETREATMENT USING MAGNESIT-BASED DESULFURIZER

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A magnesite-based desulfurizer was used for removing sulfur from hot metal by means of high temperature electrolysis technique. Through carrying out orthogonal factorial experiments it was found that the effect of the electric current on desulfurization is more significant than that of temperature. Results of single-tailed test show that when the temperature is constant, the desulfurization rate first increases with the increase of the current to a maximum value, and then, after dropping to the lowest level, gradually increases again as the current further increases. Finally, an optimum experimental condition is obtained as temperature of 1 400 °C and current of 1 A, achieving a desulfurization rate of 47,6 wt./% /min, which corresponds to a desulfurization efficiency of 62,6 %.

Key words: desulfurization, electrolysis, hot metal, pretreatment-temperature, current

INTRODUCTION

In traditional hot metal desulfurization processes [1], desulfurization operation is mainly carried out by adding a desulfurizer. In the process of desulfurization by wire-feeding, it is necessary to manufacture the wire into which desulfurization agent is added, all of which consume energy and undoubtedly make the process more complicated [2]. In terms of desulfurization efficiency, the desulfurizer can't play its role effectively. Besides, along with the progress of the reaction, the basicity and viscosity of the desulfurizer and temperature all will be changed, which further affects the desulfurization efficiency [3]. On the device side, the higher the reaction temperature and basicity and the longer the reaction time, the stricter requirement for the desulfurization equipment and hence the higher production cost [4-5]. In the present work, desulfurization experiments using a magnesite-based desulfurization agent constituted of [MgF_2,63 wt./%] [CaF_2, 12 wt./%] [NaF 18 wt./%] and [MgO 7 wt./%] were carried out so as to find out an optimum condition for high temperature electrolytic desulfurization in hot metal pretreatment.

Theoretical basis of desulfurization reaction based on magnesite

In the process of magnesium fluoride bearing melt electrolysis, the following reactions occur:

$$2MgF_2(s) = MgF_4^{2-}(diss) + Mg^{2+}(diss) \quad (1)$$

$$MgF_4^{2-}(diss) + MgO(s) = Mg_2OF_4^{2-}(diss) \quad (2)$$

$$Mg_2OF_4^{2-}(diss) + 0.5C(s) = 2MgF_2(diss) + 0.5CO_2 + 2e^- \quad (3)$$

The melting point of magnesium fluoride in magnesite-based desulfurizer is 1,261 °C and it is melted firstly at the hot metal temperature, forming $MgF_4^{2-}(diss)$ and $Mg^{2+}(diss)$. $MgF_4^{2-}(diss)$ further reacts with magnesium oxide to form $Mg_2OF_4^{2-}(diss)$ and then $Mg_2OF_4^{2-}(diss)$ reacts with carbon anode to form magnesium fluoride and carbon dioxide [6]. This series of reactions illustrated that $Mg_2OF_4^{2-}(diss)$ makes the melting point of magnesium oxide decrease so that the magnesite-based desulfurizer can be melted at the hot metal temperature.

The total electrolytic reaction is shown by formula (4), and the partial reactions are shown by formulae (5), (6) and (7), respectively.

Total reaction:

$$Mg^{2+}(diss) + 2e^- \rightarrow Mg\ (g) \quad (4)$$

Partial reactions:

$Mg^{2+}(diss) + e^- \rightarrow Mg^+$ rate limiting (5)

$Mg^+ + e^- \rightarrow Mg(1)$ very fast (6)

$Mg(1) \rightarrow Mg(g)$ very fast (7)

From the partial reactions it can be seen that the process of getting an electron is a limiting step, and the total rate of generating Magnesium depends on the diffusion coefficient of Mg^{2+}(diss). Mg^{2+}(diss) diffusion coefficient can be calculated using the Sand Equation[7] as below

$$\frac{nFD_{Mg^{2+}}^{1/2}\pi^{1/2}C_0^B}{2} = j\tau^{1/2} \quad (8)$$

where,

$D_{Mg^{2+}}^{1/2}$ – Diffusion coefficient of Mg^{2+} (diss);

τ – Transition time/ s;

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n – Electron number;
F – Faraday constant/ C/mol
C_0^B– Initial solute concentration/ mol/l;
j – Correction factor.

Therefore, the greater the current, the longer it will take to recover from the original steady state to a new steady state when the system is disturbed. From the equation (8) it can be seen that $D_{Mg^{2+}}^{1/2}$ increases with the increase of current. In the expression of diffusion coefficient, there is no temperature factor, so the effect of temperature can be ignored. In addition, according to the Sand Equation [7], the diffusion coefficient of $Mg_2OF_4^{2-}(diss)$ is calculated using equation (9).

$$i_p = 0,4958 \frac{F^{2/3}}{(RT)^{1/2}} \alpha^{1/2} A C_R^B D_R^{1/2} v^{1/2} \qquad (9)$$

where,
D_R – Diffusion coefficient of complex ions;
i_p– current density/ A/cm²;
R – Gas constant;
α – Phase change index;
A – Electrode surface area/ cm²;
C_R^B – Initial solute concentration/ mol/l;
v – Voltage scan speed/ V/min.

In the same reaction system, the electrode is the same and thus its surface area is constant. Because $i_p = \frac{I}{A_{(\text{Electrode surface area})}}$, when keeping the temperature constant and increasing the current, D_R increases. When keeping the current constant and increasing the temperature, D_R increases.

Through literature review [8], it is known that when the current density is low, the nucleation rate of magnesium on the cathode is low. The single-phase reaction of dissolved magnesium plays a major role in desulfurization, and multiphase reaction of magnesium vapor plays a secondary role in desulfurization.

EXPERIMENTAL

Experimental reagents and equipment

In order to ensure the accuracy of the experimental results, all reagents used in this study are analytic reagents. The experimental reagents are listed in Table 1.

The experimental equipment consists of a heating system, an electrolytic system and a supporting system as shown in Figure 1. The maximum temperature of the heating furnace is 1 400 °C, providing heat for the electrolytic reaction.

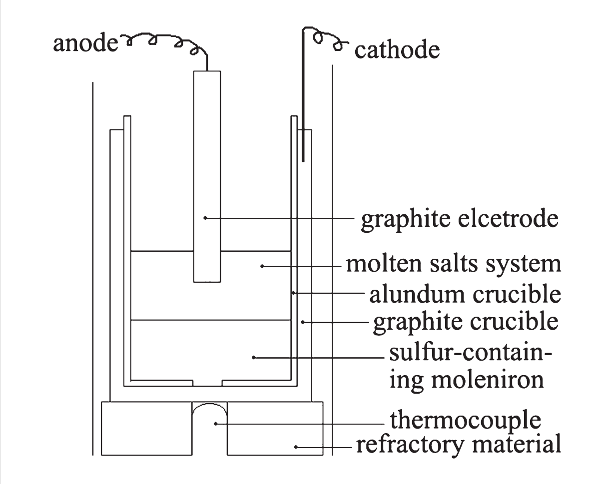

Figure 1 Schematic diagram of experimental equipment

Table 1 **Experimental reagents**

Material name	Specifications	Manufacturer
MgO	Analytic Reagents	Disney's Aladdin
MgF2	Analytic Reagents	Mclean
CaF2	Analytic Reagents	Chinese Medicine Reagent
NaF	Analytic Reagents	Chinese Medicine Reagent

Scheme of electrolysis experiment for magnesite-based desulfurizer

1) Orthogonal test scheme for desulfurization reaction

80 g magnesite-based desulfurizer was thoroughly mixed with 100 g pig iron containing 3 wt./% sulfur and the furnace was heated to 1 300 °C and electrolysis the sample. The final desulphurization reaction products were analyzed by using X-ray diffraction.(XRD)

2) Single-tailed test scheme of current factor

Use the above sample and the furnace was heated to 1 400 °C and electrolysis the sample. The current was adjusted from 0,5 A to 2,5 A with the step of 0,5 A.

3) Single-tailed test scheme of temperature factor

Use the above sample and the furnace was heated to 1 300 °C and electrolysis the sample.

RESULTS AND DISCUSSION

Results of orthogonal experiment

According to the sulfur content of the product obtained from the orthogonal experiment, the desulfurization efficiency and desulfurization rate were calculated, and the effects of temperature and current on the desulfurization rate and desulfurization efficiency were studied. The results are listed in Table 2 and the variance analysis of desulphurization efficiency is given in Table 3.

In this experiment, the overall desulfurization reaction was divided into two parts. One was electrolytic reaction of magnesium oxide in which magnesium was generated. The other was the desulfurization reaction of the generated Magnesium with sulfur in the hot metal. When comparing the F ratio of temperature with that of current, it is seen that the effect of the current on the desulfurization rate was more significant than that of the temperature. In the reaction of magnesium precipitation, magnesium ions got the electrons to form Mg. In the desulfurization reaction, the rate of Mg and sulfur combination is quick. The diffusion coefficient of magnesium ions was mainly affected by the current but that of Mg was mainly affected by temperature. Thus, the effect of current on the desulfurization rate was more significant than temperature.

Table 2 **Result of desulfurization rate in Orthogonal test**

Run No.	Tempera-ture /°C	I /A	Desulphurization Rate/ wt.%/min
1	1 300	1	33,8
2	1 300	1,5	36,5
3	1 300	2,5	13,0
4	1 350	1	33,6
5	1 350	1,5	33,3
6	1 350	2,5	33,2
7	1 400	1	47,6
8	1 400	1,5	17,6
9	1 400	2,5	26,8
Mean Value1	27,767	38,333	
Mean Value2	30,667	29,133	
Mean Value3	33,367	24,333	
Range	5,600	14,000	

Table 3 **Variance analysis of desulfurization rate in orthogonal test**

Factor	Sum of Squares	Degree of Freedom	F Ratio	F Critical Value
Temperature	47,060	2	0,188	4,320
Current	303,680	2	1,216	4,320
Error	499,56	4		

Similarly, the effects of temperature and current on desulfurization efficiency are shown in Table 5. The variance analysis of desulfurization efficiency is shown in Table 4. From Table 4, it can be seen that the effects of temperature and current on desulfurization efficiency were not significant. Therefore, we can directly use the data in Table 2 to combine the levels of A_3 and B_1 to form the optimum condition as A_3B_1. Comparing the F ratio of temperature with current shows that the effect of the current on desulfurization efficiency was relatively and more significant.

Table 4 **Variance analysis of desulfurization efficiency in Orthogonal test**

Factor	Sum of Squares	Degree of Freedom	F ratio	F Critical Value
Temperature	221,402	2	0,644	4,320
Current	1351,696	2	3,931	4,320
Error	687,74	4		

Table 5 **Result of desulfurization efficiency in Orthogonal test**

Run No.	Tempera-ture /°C	I /A	Desulfurization Efficiency/%
1	1 300	1	56,4
2	1 300	1,5	25,5
3	1 300	2,5	21,7
4	1 350	1	56,0
5	1 350	1,5	55,5
6	1 350	2,5	22,0
7	1 400	1	62,6
8	1 400	1,5	29,3
9	1 400	2,5	44,7
Mean Value1	34,533	58,333	
Mean Value2	44,500	36,767	
Mean Value3	45,533	29,467	
Range	11,000	28,866	

Results of single-tailed test

a) Effect of current on desulfurization rate and desulfurization efficiency

According to the single-tailed test scheme, the results of the desulfurization rate are given in Table 6 and the effect of current on the desulfurization rate is shown in Figure 2. It can be seen from this figure that when the current was in the range between 0,5 A and 1 A, the desulfurization rate increased with the increase of the current and peaked at 1 A before it dropped to the lowest level at 1,5 A. Then, when the current was in the range between 1,5 A and 2,5 A, the desulfurization rate gradually increased with the increase of the current again, but the value was markedly under the peak.

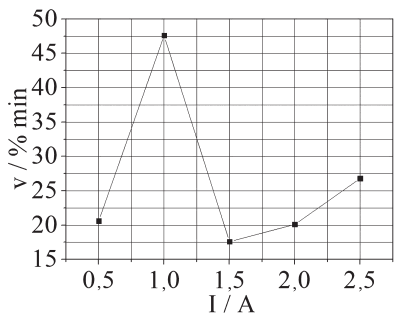

Figure 2 Effect of current on desulfurization rate at temperature of 1 400 °C

Magnesium production rate increased with the increase of current. When the current was in the range from 0,5 A to 1 A, with magnesium bubbles generated constantly, the dominance of desulfurization reaction changed from single-phase reaction to multiphase reaction. Because the temperature was constant, the mass transfer of sulfur in hot metal was essentially constant, and the multiphase desulfurization reaction rate was higher than the single-phase desulfurization reaction rate. Thus, the increase of the desulfurization rate was obviously observed in this stage. As the reaction proceeds, the multiphase desulfurization reaction became dominant and the size of the magnesium bubbles followed normal distribution.

Table 6 **Results of desulfurization rate and efficiency in single-tailed test**

I / A	0,5	1	2	2,5
Desulphurization Rate /wt.%/min	20,60	47,6	20,1	26,8
Desulfurization Efficiency / %	34,4	62,6	33,5	44,7

b) Effect of temperature on desulfurization rate and desulfurization efficiency

According to the single-tailed test scheme, the results are shown in Table 7 and the data are plotted in Figure 3. This figure shows that the desulfurization rate increased with the increase of temperature. When the temperature was changed, the diffusion coefficient of magnesium ions did not change. In the case of the same

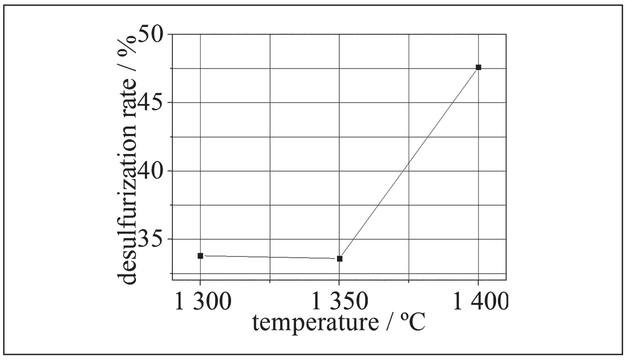

Figure 3 Effect of temperature on desulfurization rate at current of 1 A

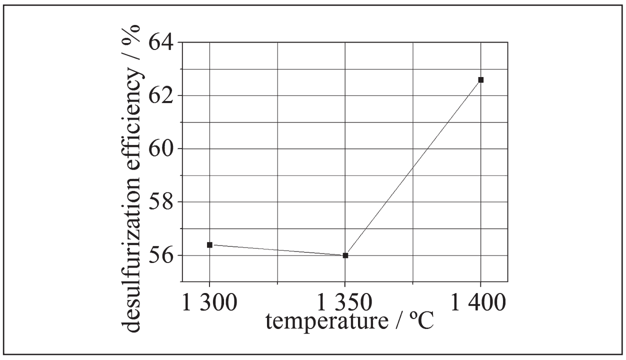

Figure 4 Effect of temperature on desulfurization efficiency at current of 1 A

current, the generation rate of magnesium was the same. In the single-phase desulfurization reaction, when the temperature was increased, the mass transfer coefficient of (S) to magnesium sulfide increase, the speed of single-phase desulfurization reaction increased. Under the condition of high temperature and a standard atmospheric pressure, the solubility of magnesium decreased with the increase of temperature. In the multiphase desulfurization reaction, the mass transfer of sulfur to magnesium bubble surface played a major role, and the size of the bubbles varies with the generation rate of magnesium in the process of magnesium bubble rising. The change of magnesium bubble's size can be ignored.

Table 7 **Effect of temperature on desulfurization rate**

Temperature / °	1 300	1 350	1 400
Desulphurization Rate /wt.%/min	33,8	33,6	47,6

Table 8 **Effect of temperature on desulfurization efficiency**

Temperature / °C	1 300	1 350	1 400
Desulfurization Efficiency / %	56,4	56,0	62,6

Therefore, when the temperature was raised, both the mass transfer rate of sulfur to magnesium bubble surface and the multiphase reaction rate increase. In conclusion, in the process of electrolytic reaction, when the temperature was raised, the desulfurization rate increased and a maximum value was obtained at 1 400 °C.

CONCLUSIONS

The effects of temperature and electric current on electrolytic desulfurization of hot metal using magnesite-based desulfurizer were experimentally investigated in the present work. From analyzing the experimental results, the following conclusions can be drawn:

(1) The results of orthogonal experiments demonstrate that the effect of the current on desulfurization is more significant than that of temperature; and the optimum condition for desulfurization is found to be 1, 400 °C and 1 A, achieving desulfurization rate of 47,6 wt.% / min corresponding to desulfurization efficiency of 62.6%.

(2) The results of single-tailed tests show that the desulfurization rate and the desulfurization efficiency all increase with the increase of the current in the range from 0,5 A to 1 A (reaching a peak level), but decrease with further increase of the current between 1 A and 1,5 A; When the current is in the interval between 1,5 A and 2,5 A, the desulfurization rate and desulfurization efficiency gradually increase with the increase of current again, but the value is lower than the peak level.

(3) The results of single-tailed tests also indicate that, when the current is held at 1 A, the desulfurization rate and desulfurization efficiency increase with the increase of temperature.

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Note: Liwen Zhou is the responsible translator and the corresponding author, Anshan, LiaoNing, China.