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# The effect of calcium fluoride on the desulfurization of chromium steels by rare earth

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**Abstract -** Two series of experiments were carried out for studying desulfurization process of chromium steel, which contains 13% chromium, where the desulfurization was conducted in inert gas atmosphere, at temperature 1600$^{o}$C in a resistance furnace, by using flux mixtures of rare earth metals and oxides with calcium fluoride. The obtained results proofed that: the mathematical models for the process is reliable and effective for the process optimization. The maximum desulfurization degree obtained was 58.33% for mixture of rare earth oxide with fluorspar ratio 1:2 and 73.68% for mixture rare earth (mischmetal) with fluorspar at the same ratio.

**Key words -** Steel refining, desulphurization, calcium fluoride, mischmetal, rare earth metals

## 1. INTRODUCTION

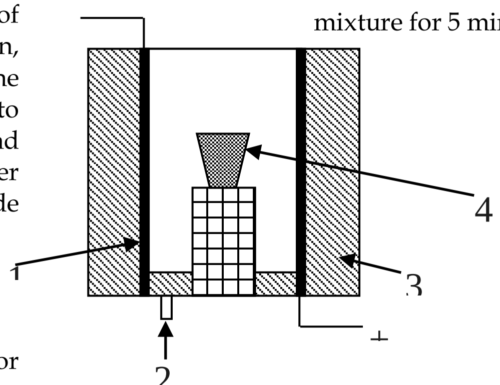
Steel desulfurization at the intermediate ladle treatment stage is one of the most important steel refining technological operations. The successful procedure of desulfurization process, provided by fire refining slag with a specific chemical composition, usually based on calcium oxide. The steel metal is mixing with the synthetic slag in inert gas to form the preprocessed refining slag, and then optimized the metal oxidation to provide the formation of iron oxide FeO in the produced slag to be less than 0.5 %.[1]

Using rare earth metals, for steel desulfurization is very promising. However, the number of practical and theoretical data on the use of rare earth metals for desulfurization is limited. Therefore, the work in this direction should be considered as highly effective refining Procedure. It is well known, that the percentage of basic oxides (CaO, $Ce_2O_3$) in the slag and the proportion of aluminum in the metal, which coordinates its oxidation, determine the refining ability of the flux. The process occurs, when oxides are decayed or dissociated into oxygen and metals, then it is free to react with sulfur and form sulfides. Although, the decomposition of $Ce_2O_3$ easier than CaO, and so the desulfurization with cerium oxide will be better than calcium oxide, but from the thermodynamic point of view; the desulfurization by using the calcium oxide is better than using the rare earth oxides.

Supplementary addition of fluorspar ($CaF_2$) for some slags can increase the solubility of CaO and thereby increase the desulfurization potentiality of the slag. Due to an increasing in the solubility of CaO, this led to increase the sulfide capacity in the slag, which increases the degree of desulfurization. However, the tiny addition of $CaF_2$ in the slag enhances only the lime flow and mobility to ensure saturation of the slag of the CaO, this lead to a critical drawback; representing on the deterioration of the wear resistance of the lining bricks, without any soundness increase in the degree of desulfurization, unfortunately, this often occurs in practice [12].

## 2. EXPERIMENTAL WORK

Two series of experiments were performed in a resistance vertical tube furnace (Taman furnace) for melting (Fig.1.) with inert volume 1.35 l. Argon gas was used for generating reduction atmosphere with flowrate 1.125 l/min. the study carried out on prepared steel alloy, which contains 13 % chromium table (1). After melting, pure aluminum was added for deoxidation, then synthetic slag mixture for 5 minutes.




1-Tube graphite, 2- Inlet gas, 3- Lining, 4- Crucible

Fig. 1: Taman furnace

Table (1) Chemical composition of prepared steel alloy for desulfurization

| C | Si | Mn | P | S | Cr | Al |
|---|---|---|---|---|---|---|
| 0.162 | 0.07 | 0.485 | 0.031 | 0.017 | 12.19 | 0.403 |

The first series of experiments, studied the removal of sulfur from metal by Synthetic slag mixtures, which consist of mixture of rare earth oxide with the fluorspar in powdered form. Eight experiments conducted with additive fluorspar from 0.5% to 4 %, and another four experiments in other varieties as shown in table (2).

Table (2): The composition of the added materials in percent by weight of the metal

| | RRE oxide | Al | $Al_2O_3$ | MgO | CaO | $CaF_2$ | $SiO_2$ |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 0 | 0 | 0 | 0 | 1 | 0 |
| 2 | 1 | 0 | 0 | 0 | 0 | 0.5 | 0 |
| 3 | 1 | 0 | 0 | 0 | 0 | 2 | 0 |
| 4 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 1 | 0 | 0 | 0 | 0 | 3 | 0 |
| 6 | 1 | 0 | 0 | 0 | 0 | 4 | 0 |
| 7 | 0 | 1 | 0 | 0 | 0 | 1 | 0 |
| 8 | 1 | 0 | 0 | 0 | 0 | 1 | 0 |
| 9 | 1 | 1 | 0 | 0 | 0 | 0 | 0 |
| 10 | 0.6 | 0 | 1 | 0.21 | 0.9 | 0.3 | 0 |
| 11 | 0.6 | 0.5 | 0 | 0.21 | 0.9 | 0.3 | 0 |
| 12 | 0.6 | 0 | 1 | 0.21 | 0.3 | 0 | 0.3 |

*Crucible damaged

In the second series of experiments Synthetic slag mixtures, which consist of mixtures of rare earth metals (mischmetal) in an amount of 1% of the processed metal in pieces form and consumption of powdered fluorspar changed from 1% to 4% by weight of the steel.

## 3. Results and discussion

The effective impact of addition a $CaF_2$ on steel refining by rare earth oxide explained by the equations (1-4), which describe the transition of cerium oxide to the sulfide and its thermodynamic characteristics. This leads to define the next conclusions

$$Ce_2O_3 + 3[S] + 2[Al] = Ce_2S_3 + Al_2O_3 \qquad (1)[2\text{-}8]$$

$\Delta G$o = -891718 + 354.46T J/Mole (2)

$$\lg K = \frac{a_{Ce_2S_3} * a_{Al_2O_3}}{a_{Ce_2O_3} * a^2_{[Al]} * a^3_{[S]}} = \frac{46572}{T} - 18.512 \qquad (3)$$

$$L_S = 32 * \sum n_{RO} * f_S * \sqrt[3]{K * [Al]^2 * f_{Al}^2} \qquad (4)$$

At T = 1873o K, K4 = 2.26* 106

$$a_{Ce_2S_3} = a_{Al_2O_3} = a_{Ce_2O_3} = 1$$

The activity coefficients of sulfur and aluminum will be calculated by using the interaction parameters (which equal to $f_S$ = 0.71, $f_{Al}$ = 1.13), we can estimate the degree of desulfurization of the investigated melt.

$$\eta_S = \frac{\Delta S}{[S]_i} * 100 = \frac{\lambda * L_S}{1 + \lambda * L_S} * 100 \qquad (5)[2]$$

Where, λ = slag ratio, $L_S$ = distribution coefficient of sulfur, ΔS = removed sulfur, $[S]_i$ = initial sulfur, $[S]_f$ = final sulfur, $\eta_S$ = desulfurization degree.

Equation (3) showed that, increasing the temperature offending and resisting the desulfurization process thermodynamically.

However, increasing temperatures theoretically should have a positive effect on the kinetics of the process, due to the reducing of metal and slag viscosities, which improves sulfides transition from metal to slag.

This article studied the influence of composition of synthetic slag mixture on the degree of desulphurization of the melt, where such group of experiments were conducted by slightly change of ratio between fluorspar addition and rare earth metal oxides. As shown by experimental data, the optimized degree of desulfurization has obtained when the ratio of rare earth oxide to the fluorspar as 1:2 was 58.33 %.

Any more increase in the ration of the processed fluorspar to the oxides of rare earth metals; leads to the crucible damage, due to the reaction occurs between the crucible material and fluorspar. It is highly recommended; that the balance of fluorspar to the oxide of rare earth metals in the mixture should not exceed the ratio of 2:1

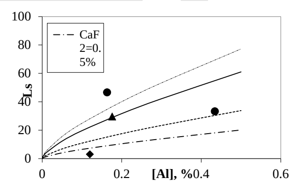



Fig. 2: The effect of Aluminum content at different amounts of $CaF_2$ on the coefficient of sulfur distribution ($L_S$) during desulfurization by rare earth oxide (lines = calculated, points = experimental)

As Shown in Fig.2. That the calculated and actual coefficient of sulfur distribution ($L_S$) of steel melt containing 13% chromium achieved when; adding various percentage of $CaF_2$ related to steel metal, and the activity of $Ce_2O_3$ and $Ce_2S_3$ shall equal unity. It was noted that that; with increasing amount of Al in the steel metal; leads to increase the reduction of rare earth oxide and so increases the distribution coefficient of sulfur ($L_S$). In

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addition, an increasing $CaF_2$ amount in the synthetic slag enhances the distribution coefficient of sulfur ($L_S$).

Experiments group from 10-12 studied the effect of changing the slag composition on the degree of desulfurization of steel metal. Basicity index equation (6) was used to calculate the basicity of synthetic slag and its effect on the coefficient of sulfur distribution ($L_S$)

$$B = \frac{x_{CaO} + x_{CaF_2} + x_{MgO} + x_{Ce_2O_3}}{x_{Al_2O_3} + x_{SiO_2}} \quad \text{---- (6)}$$

In experiments group from (10-12), (table 1) shows the amount weights of the synthetic slag components where increasing the amount of moles in the proportion of synthetic slag components (n), leads to an increase in distribution coefficient of sulfur ($L_S$) according to equation (4). The basicity of synthetic slag has direct proportional effect on the ($L_S$) to a limited value shown in fig (3). At low values of basicity of synthetic slag (B), we got low Ls. It is clear that; fluorspar has a positive effect on slag mixture and enhances desulfurization process.

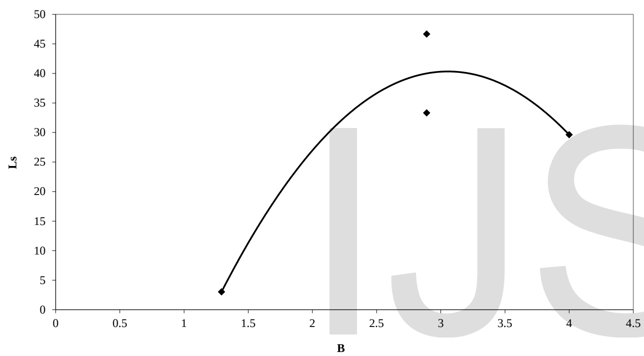


Fig 3: the effect of slag basicity on the coefficient of sulfur distribution ($L_S$)

As shown in Fig.3, that the influence of the basicity on the distribution coefficient of sulfur in metal, where the optimum coefficient of sulfur distribution ($L_S$) at the slag basicity of 2.8. It is close to the ordinary meaning of basicity of the slag at the desulfurization of steel.

On the second series of experiments, we studied the process of steel desulfurization by using rare earth metals in the mixture with fluorspar spar. The experiments performed at a flow rate of rare earth metals in an amount of 1% of the processed metal, and consumption of fluorspar changed from 1% to 4% by weight of the steel.

$$2[Ce] + 3[S] = Ce_2S_3 \quad \Delta G^o = -1014618 + 390.86T\ J \quad (7)$$

$$\lg K = \frac{a_{Ce_2S_3}}{a^2_{[Ce]} * a^3_{[S]}} = \frac{52991}{T} - 20.414 \quad (8)$$

$$L_S = 32 * \sum n_{RO} * f_S * \sqrt[3]{K * [Ce]^2 * f^2_{Ce}} \quad (9)$$

T = 1873o K, K = 7.55 * 107

$$\gamma_{CaF_2} = a_{CaS} = a_{CeF_3} = 1$$

and $f_S = 1.107$, $f_{Ce} = 1.129$

Analysis of equation (8) shows that; when temperature increases, leads to depression of the equilibrium constants as well as depression of the distribution coefficient of sulfur. Besides that, the viscosity of slag and metal decreases and hence improves the kinetics of the process.

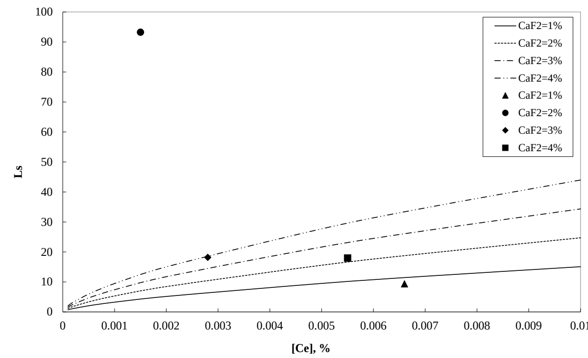


Fig. 4: Effect of cerium in metal on sulfur distribution at different presents of added $CaF_2$ (lines = calculated, points = actual)

Figure (4) shown, that the calculated and actual data of metal desulphurization using a mixture of Ce and $CaF_2$. Observed that the best distribution coefficient of sulfur in slag, containing 2% by weight of the metal $CaF_2$. This value is similar to which obtained in the first series of experiments.

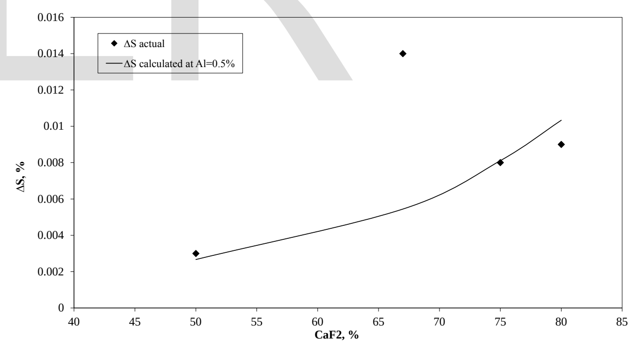


Fig. 5: The effect of $CaF_2$ on the degree of desulfurization (line = calculated, points = experimental)

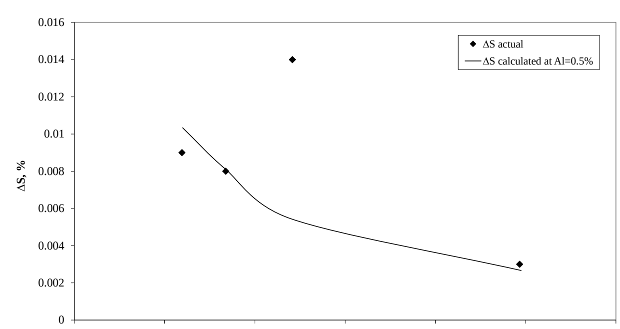

Fig. 6: The effect of ratio of RRE to $CaF_2$ on the removed sulfur (line = calculated, points = experimental)

In the experiments, due to increased proportion of $CaF_2$ from 1 to 4% by weight of the metal, the calcium content in the metal was increased from 0.0005 to 0.0009%. Fig.5. shows that, the solid line represent the results from calculation of mathematical model at [Al] = 0.5% and the points represent the results of experiments. The practical points proof the mathematical model of desulfurization by mixture of Mischmetal and feldspar and $CaF_2$ has a positive effect on enhancing desulfurization process. While figure (6) shows that, the solid line represent the results from calculation of mathematical model at [Al] = 0.5% and the points represent the results of experiments which proof that, with increasing the proportion of rare earth metal to fluorspar decreases desulphurization degree.

Although the removed sulfur by using fluorspar mixture with rare earth oxide was 58.33% and for mixture of fluorspar with mischmetal 73.68%. It is meaning that; mischmetal is better than rare earth oxide with 15% in desulfurization process, but for industrial applications, using rare earth oxide will be more economically than mischmetal for desulfurization process. Because the price of mischmetal is more doubled bulk rare earth oxide. However, for comparing between general refining and desulfurization, it will be different sight.

## 4. Conclusion

Thermodynamic model can expect the final sulfur in chromium steel after desulfurization by using flux mixtures with rare earth oxide. Fluorspar strongly improves desulfurization process by rare earth metals. Aluminum has a positive effect on enhancing desulfurization process. The basicity of synthetic slag has direct proportional effect on the ($L_S$) to a limited value. Using rare earth oxide is more economically than mischmetal for desulfurization process.

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