

The Leaching and Kinetics of Magnesium in Phosphate Ore Slurry during FGD Process

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Summary: The phosphate ore reserves in China are very large, but the overall quality is poor, and the magnesium impurity in phosphate ore is not conducive to the production of phosphorus chemical products. Recovery of sulfur dioxide from exhaust gas by phosphate slurry is a new desulfurization technology developed in recent years. During SO₂ removal from flue gas by phosphate ore slurry, in phosphate ore magnesium can be simultaneously reduced. The magnesium leaching process could be described by the reaction-controlled shrinking core model. The leaching process of magnesium from phosphate ore slurry in FGD process includes 5 steps and 10 steps, which describes a gas-liquid-solid three-phase complete reaction process of removing magnesium from industrial flue gas desulfurization of phosphate slurry. In this study, a three-phase mass transfer kinetics model was established to find the controlling factors of the desulfurization reaction rate of the magnesium removal system of phosphate ore slurry in the FGD Process, and the research showed that the gas film resistance was the key control step, the solid film resistance was negligible. The reaction relation of desulfurization and removal of magnesium from phosphate slurry was obtained as $k=3.766 \times e^{-10318.39/RT}$.

Keywords: Phosphate ore, magnesium, flue gas desulfurization, reaction-controlled shrinking core model, reaction kinetics

Introduction

China is one of the world's major consumers of coal resources. A large amount of sulfur dioxide is released during the combustion of coal, triggering a series of environmental and safety problems [1]. Therefore, more and more attention has been paid to the control of sulfur dioxide. Phosphorus slurry removal of SO₂ from small and medium-sized coal-fired boilers, especially phosphorus chemical enterprises, is a promising desulfurization technology [2]. Appropriate impurity content in phosphate rock is conducive to the decomposition of phosphate rock, phosphate rock contains metal oxides such as CaO, MgO, Al₂O₃, etc., and these oxides are often used as additives for wet flue gas desulfurization [3]. Yu [4] studied that MgO can significantly improve the total mass transfer coefficient and desulfurization rate of gas phase. Sun [5] also proved that Mg ion has the ability to promote SO₂ absorption. In the previous study, our research group found that the use of phosphate ore slurry as a

desulfurizer had excellent desulfurization ability. The pilot test results in a phosphorus factory also showed that the phosphate ore slurry could absorb and purify the tail gas of sulfuric acid, maintained the SO₂ removal rate $\geq 80\%$ for more than 10 h [6]. The active component of this desulfurization is mainly Fe₂O₃, and the presence of impurities such as MgO and Al₂O₃ in minerals is also beneficial to the desulfurization process [9]. However, the previous studies only focused on the desulfurization efficiency, and the purification effect of impurities (such as Al, Mg, Ca, etc.) in the phosphate ore, that is, the improvement of the grade of the phosphate ore has not been comprehensively studied. Moreover, the mechanism of desulfurization reaction in phosphate ore slurry is extremely complex, involving the mutual mass transfer between gas, liquid, and solid phases, the chemical reactions in the liquid phase, and the chemical reactions on the liquid-solid two-phase surface [10]. In addition, from the reaction type point of view, the reaction of SO₂ with phosphate

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slurry includes a series of processes such as the neutralization of acid and basic oxides, the redox reaction of SO_2 , and the catalytic oxidation of transition metal ions. Therefore, the process of phosphate ore desulfurization is a complex and influential process. It is of great theoretical and practical significance to investigate its mechanism deeply. The establishment of the model is helpful to find out the controlling factors in the reaction process, and has a reference and guidance function for the subsequent research work. 11.

In this work, based on the double film theory and the morphology and reaction behavior of each substance in phosphate slurry, a three-way mass transfer kinetic model was established to analyze the controlling factors controlling the reaction rate of phosphate slurry desulphurization and magnesium removal system, and the macroscopic kinetic equation of reaction was derived.

Experimental Apparatus and Methods

The experimental flow chart for the experimental research on the removal of magnesium in phosphate ore slurry by industrial smoke SO_2 is as follows Fig 1.

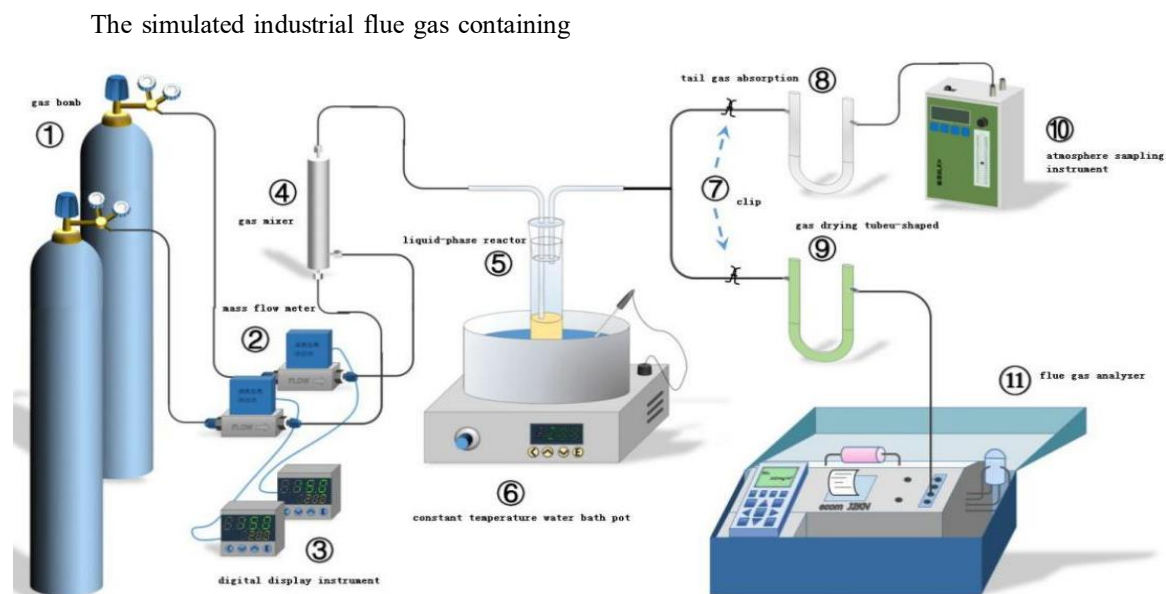


Fig. 1: Process flow chart of magnesium in the industrial gas SO_2 removal phosphate slurry.

Table 1 Chemical composition of phosphate ore.

Chemical Composition	Al_2O_3	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	SiO_2	Fe_2O_3	MgCO_3	CaCO_3	others
Content%	0.77	66.60	1.91	0.56	12.67	11.83	5.66

low concentrations of sulfur dioxide was prepared by the dynamic gas distribution method of the cylinder. The SO_2 gas in the cylinder and the H_2O -free air are measured by a mass flow meter in a corresponding ratio, and mixed in a gas mixer to obtain a specific concentration of sulfur dioxide-simulated industrial flue gas for the experiment. This method avoids the local gas mixing unevenness in the static gas distribution of the air bag, and the slow oxidation reaction of SO_2 and O_2 in the flue gas in the air bag.

The ore used in the experiment was from the phosphate rock mined in the Jinning area of Yunnan Province, milled to 100 mesh (0.15 mm) accounted for more than 90%. The phosphate slurry was mixed with water to prepare a certain concentration of phosphate slurry for reaction absorbent. The chemical compositions of phosphate ore was determined by X-ray fluorescence (XRF) method, as shown in Table 1.

X-ray diffraction (XRD) was used to analyze the phase composition of phosphate rock. The XRD data of the scanning range of 10° - 80° and a scanning rate of $2^\circ/\text{min}$. As shown in Fig 3, the main components of phosphate rock are $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (PDF 99-0050), $\text{CaMg}(\text{CO}_3)_2$ (PDF 71-1662) and SiO_2 (PDF 85-0865) 2.

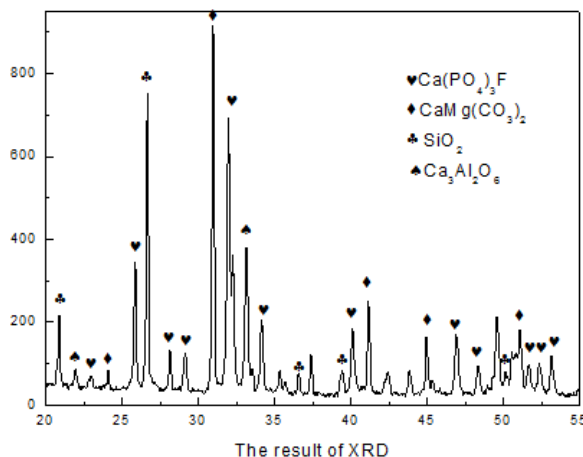


Fig. 2: Test results for original phosphate XRD.

The mass flow meter measures the simulated flue gas into the reactor and is absorbed after reacting with 20 ml phosphate ore slurry. Ensure that the bubbles in the simulated flue gas are in full contact with the pulp slurry at a sufficient height and time in the reactor. The reaction process needs to maintain a certain reaction temperature and stirring rate. After the reacted flue gas enters the U-type exhaust gas absorption tube of the reaction gas path, it is finally discharged by the atmospheric sampler. When the exhaust gas concentration is measured, it is adjusted to measure the gas path. After the exhaust gas is dried, it enters the flue gas analyzer for measurement. The method for detecting magnesium in the phosphate ore slurry after the reaction is determined by flame atomic absorption spectroscopy with AA320N atomic absorption spectrophotometer.

The test conditions are as follows: the concentration of slurry absorption liquid is 10% (solid-liquid ratio 1:10), the simulated flue gas SO_2 concentration is 1500mg/m^3 , the reaction temperature of slurry absorption liquid is 35°C , the flue gas flow rate is 300ml/min , and the pH of slurry absorption liquid is 6.

Results and Discussion

Three-phase mass transfer process

According to the reaction of phosphorus slurry and gas sulfur dioxide, a three-phase mass transfer diagram of the reaction process is drawn 15, as shown in Fig 3.

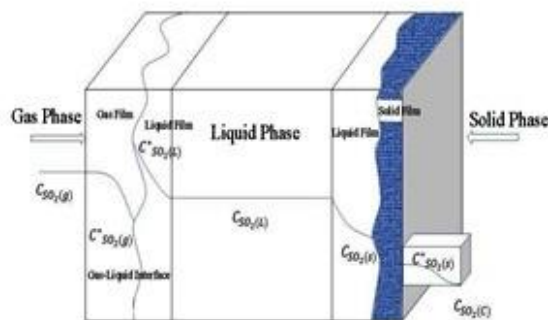


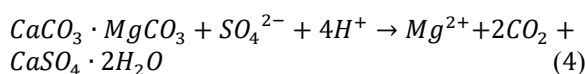
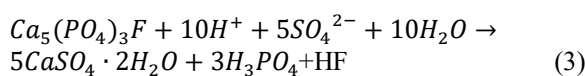
Fig. 3: Phosphorus slurry desulfurization and magnesium removal three-phase mass transfer schematic.

This Fig shows the gas-liquid-solid three-phase mass transfer process and constraining conditions in the process of removing magnesium from flue gas desulfurization in the phosphate slurry industry. The main steps of magnesium removal from flue gas desulfurization in the phosphate slurry industry may be:

1. The sulfur dioxide (SO_2) in the flue gas passes through the gas film and enters the gas-liquid two-phase interface from the gas phase. During the diffusion process, the concentration of sulfur dioxide rapidly decreases from $C_{\text{SO}_2}(\text{g})$ to $C^*\text{SO}_2(\text{g})$, and sulfur dioxide (SO_2) reaches gas-liquid equilibrium when it reaches the gas-liquid interface.
2. Sulfur dioxide (SO_2) in the flue gas passes through the liquid-phase interface and diffuses through the liquid film to the main liquid phase. The concentration of sulfur dioxide (SO_2) rapidly decreases from $C^*\text{SO}_2(\text{L})$ to $C_{\text{SO}_2}(\text{L})$.
3. When the sulfur dioxide (SO_2) in the flue gas diffuses into the liquid film or the liquid phase, sulfur dioxide (SO_2) will meet with H_2O in the liquid phase and a combined reaction occurs to generate sulfurous acid H_2SO_3 .

$$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \quad (1)$$
4. The primary product of sulfur dioxide (SO_2) and H_2O , H_2SO_3 , diffuses from the liquid phase to the liquid film on the solid surface. The content of sulfur dioxide (SO_2) in the flue gas also decreases rapidly from $C_{\text{SO}_2}(\text{L})$ to $C_{\text{SO}_2}(\text{s})$.
5. The primary product H_2SO_3 , sulfur dioxide (SO_2) and H_2O reaches the liquid film on the solid surface, it diffuses to the solid film on the outer surface of the solid, and the content of sulfur dioxide in the flue gas decreases from $C_{\text{SO}_2}(\text{s})$ to

- $C^*SO_2(s)$.
- Sulfur dioxide (SO_2) and primary product H_2SO_3 reaches the solid film on the outer surface of solid, they diffuse through the solid pores to the reaction interface, and the sulfur dioxide content in the flue gas also rapidly decreases from $C^*SO_2(s)$ to $CSO_2(c)$.
 - H_2SO_3 etc. and Fe^{3+} in phosphate ore slurry catalyze the formation of sulfuric acid H_2SO_4 with sulfurous acid H_2SO_3 , Calcium fluorophosphate ($Ca_5(PO_4)_3F$) undergoes an oxidation-reduction reaction at the interface of the reaction, generating calcium sulfate hydrate ($CaSO_4 \cdot 2H_2O$), HF, and phosphoric acid H_3PO_4 . The reaction with dolomite ($CaCO_3 \cdot MgCO_3$) leaches the magnesium ion Mg^{2+} in the phosphate ore. This can be illustrated by reaction (2)-(4).



- The reaction product calcium sulfate hydrate ($CaSO_4 \cdot 2H_2O$), HF, and phosphoric acid H_3PO_4 and magnesium ion Mg^{2+} diffused into the solid film on the outer surface of the solid particle through the solid-phase micropores.
- The reaction product calcium sulphate hydrate ($CaSO_4 \cdot 2H_2O$), HF, and phosphoric acid H_3PO_4 and magnesium ion Mg^{2+} diffuse from the solid film on the outer surface of the solid particle to the liquid film on the solid surface.
- The reaction product calcium sulphate hydrate ($CaSO_4 \cdot 2H_2O$), HF, and phosphoric acid H_3PO_4 and magnesium ion Mg^{2+} diffused to the liquid phase through the liquid film on the solid surface.

The above 10 steps constitute the complete gas-liquid-solid three-phase mass transfer in the process of magnesium removal from flue gas desulfurization in the phosphate ore slurry industry. The general desulfurization and magnesium removal from the phosphate ore slurry industry can be divided into five processes by induction. Here are:

- Gas-phase diffusion process, there is gas film resistance to the process of sulfur dioxide.
- Liquid phase diffusion process, which has liquid film resistance to primary product such as H_2SO_3 .
- The primary product such as H_2SO_3 reaches the

liquid film on the solid surface, it will diffuse to the solid film on the outer surface of the solid particle, and there will be solid film resistance in this process.

- The primary product such as H_2SO_3 reaches the solid film on the outer surface of the solid particle, it diffuses to the reaction interface through the solid-phase micropores. This process has an internal diffusion.
- The primary products such as H_2SO_3 and Fe^{3+} in the phosphate slurry catalyze the formation of H_2SO_4 with H_2SO_3 , and reaction occurs with the calcium fluorophosphate ($Ca_5(PO_4)_3F$) at the interface of the reaction phase to form calcium sulfate hydrate ($CaSO_4 \cdot 2H_2O$) HF and phosphoric acid H_3PO_4 react with dolomite ($CaCO_3 \cdot MgCO_3$) to leaching Mg^{2+} in the phosphate ore. This process has chemical resistance.

Diffusion Resistance

Fig 4 shows the particle size distribution of phosphorus tailings. In this particle size analysis, Malvern 2000 laser particle size analyzer was used to analyze the particle size of phosphorus tailings. The results showed that the particle size of mineral powder in the reaction system is more than 90% greater than or equal to 100 mesh (0.15mm), The diffusion resistance caused by the particle size of the small reactants has little influence on the reaction system, so the influence of the diffusion resistance on the whole reaction system of desulfurization and magnesium removal from the phosphate slurry industry is not considered 19.

Gas film resistance

According to Fick's law of diffusion 44120, sulfur dioxide diffuses from the gas phase through the gas film into the liquid film as

$$\frac{dn_{SO_2(g)}}{dt} = A(g) \frac{D_{SO_2(g)}}{\delta_{SO_2(g)}} (C_{SO_2(g)} - C_{SO_2(g)}^*) \quad (5)$$

$SO_2(g)$ is the main concentration of SO_2 in gas phase, $kmol/m^3$, $C^*SO_2(g)$ is SO_2 concentration at gas-liquid interface, $kmol/m^3$.

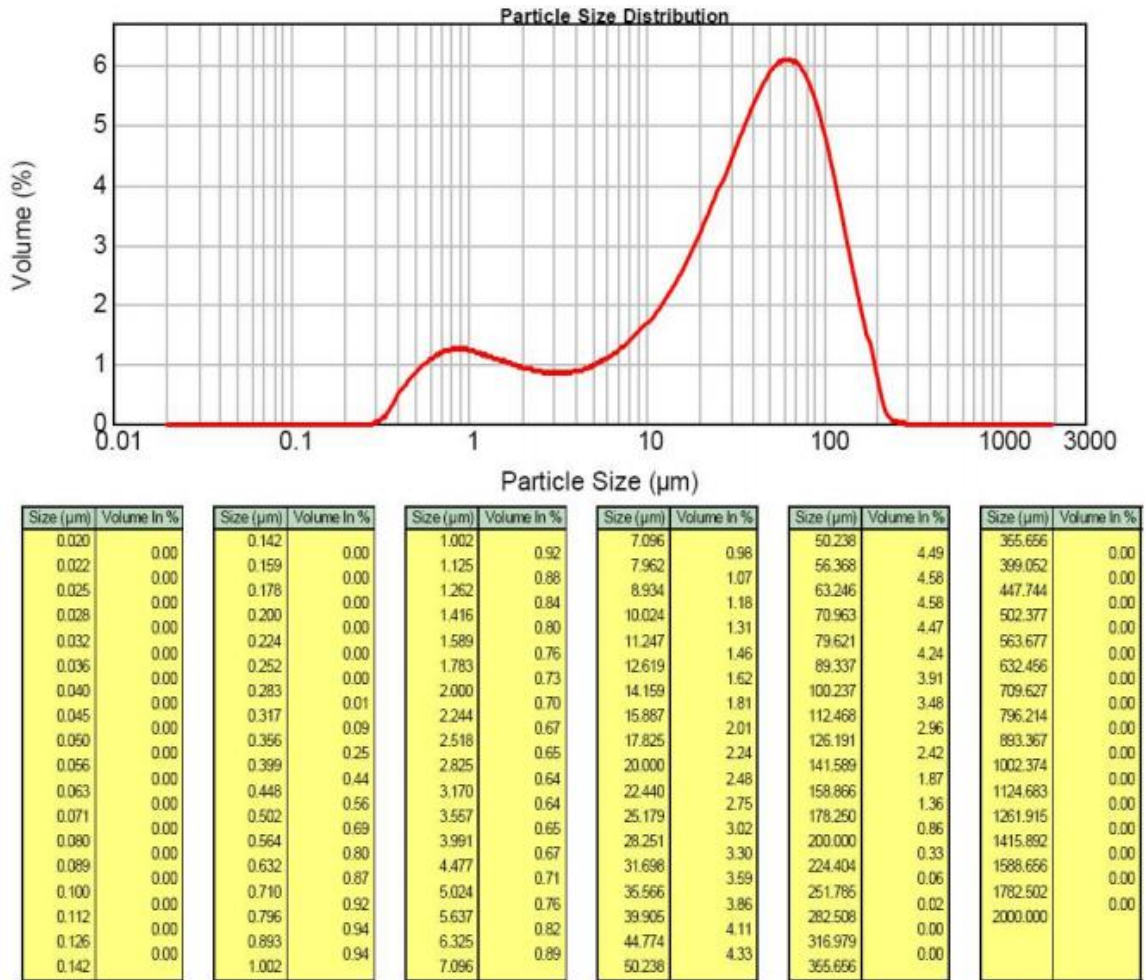


Fig 4. Particle size distribution of phosphate ore.

The mass transfer reaction rate is proportional to the gas-liquid contact area, so the film resistance is the control step for desulfurization and magnesium removal from the phosphate slurry industry.

Solid film resistance

Phosphorus slurry industrial flue gas desulphurization magnesium removal system in the phosphate rock particles do not participate in the chemical reaction of insoluble inert material adsorption on the surface of the phosphate rock formation material solid film resistance layer. The structure of the denser solids in the phosphate rock has been studied in the “reduced-core model of the particle size” 19. It is determined that the resistance of the solid film is negligible, so no consideration is needed

Interface chemical reaction control

In the particle size-reduced particle reaction, at the reaction interface, the amount of SO₂ that is consumed after reacting with MgO in the phosphate rock per unit of time is the reference (magnitude of the reference is magnesium), calculated on a per particle basis (assuming that the reaction particles are spherical Granules)21.

$$-\frac{dn_{SO_2}}{dt} = 4\pi R_i^2 k C_{SO_2(t)}^n \tag{6}$$

Where $\frac{dn_{SO_2}}{dt}$ is the rate of consumption of the reactant SO₂, mol/s; $C_{SO_2(t)}$ is the SO₂ concentration of the reactant in the liquid phase at the reaction interface, mol/m³.

The reaction rate of the reactant MgO in a

single particle at a single time²¹ is

$$\frac{dn_{MgO}}{dt} = \frac{4\pi R_c^2 \rho_{MgO} X_{MgO}}{M_{MgO}} \times \frac{dRc}{dt} \quad (6)$$

where ρ_{MgO} is the density of the reactant MgO, Kg/m³; X_{MgO} is the MgO content in phosphate slurry, %; M_{MgO} is the molecular weight of the reactant.

Obtained by (2) and (3)

$$\frac{dRc}{dt} = -\frac{M_{MgO}k}{\rho_{MgO}X_{MgO}} C_{SO_2(t)}^n \quad (7)$$

Assuming that the reaction is surface chemical reaction control, the concentration of reactant SO₂ at the reaction interface is equal to the concentration of its gas phase body, ie, $C_{SO_2(g)}=C_{SO_2(t)}$.

$$\frac{dRc}{dt} = -\frac{M_{MgO}k}{\rho_{MgO}X_{MgO}} C_{SO_2(g)}^n \quad (8)$$

Finally get

$$\frac{M_{MgO}kt}{\rho_{MgO}X_{MgO}Ro} C_{SO_2(g)}^n = 1 - (1 - X_{Mg})^{\frac{1}{3}} \quad (9)$$

$$\frac{M_{MgO}kt}{\rho_{MgO}X_{MgO}Ro} C_{SO_2(g)}^n = K \quad (10)$$

$$1 - (1 - X_{Mg})^{1/3} = Kt \quad (11)$$

The chemical reaction rate equation indicates that if the reaction process is controlled by chemical reactions, under certain conditions, $1 - (1 - X_{Mg})^{1/3}$ with time is linear relationship²². The experimental data are substituted into equation (12) for verification, and the results are shown in Fig 5.

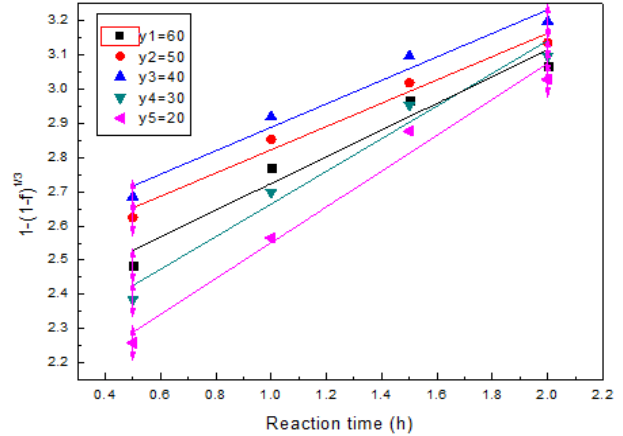


Fig 5: Linear relationship between $1 - (1 - X_{Mg})^{1/3}$ and time under different temperature conditions

According to the experimental data, $1 - (1 - X_{Mg})^{1/3}$ has a linear relationship with time under different temperature conditions, which indicates that the process is controlled by chemical reaction.

According to Fig 6, $Lgk_0=1.32611$, and then $k_0=e^{1.32611}=3.766$.

$$Ea=K \times 1000 \times 2.303 \times R = 0.5389 \times 1000 \times 2.303 \times 8.314 = 10318.39 \text{ J/mol} = 10.318 \text{ kJ/mol}$$

$$\text{So } k = 3.766 \times e^{-10318.39/RT}$$

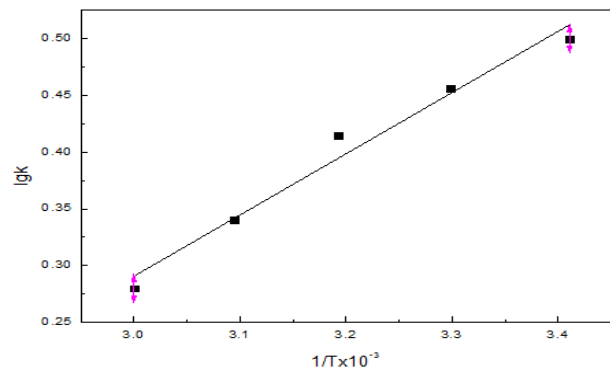


Fig 6: Linear relationship between slope and lgk .

Conclusion

1. Based on the results above, the leaching process of magnesium in the FGD Process using phosphate ore slurry included 5 processes and 10 steps, and the kinetic equation of magnesium could be obtained as below:

$$k=3.766 \times e^{-10318.39/RT}$$

2. The leaching process was controlled by interface chemical reaction. It is determined that the resistance of the solid film is negligible. The gas-liquid film resistance is the control step for desulfurization and magnesium removal from the phosphate slurry industry. And the influence of the diffusion resistance on the whole reaction system of desulfurization and magnesium removal from the phosphate slurry industry is not considered.

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