

# pH 值对石灰(石灰石)湿法脱硫 反应机理的影响\*

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**摘要** 为了探讨 pH 值对石灰(石灰石)湿法脱硫反应机理的影响, 进行了用亚硫酸钙沉淀与水的混合液吸收  $\text{SO}_2$  的实验. 研究表明, 溶液中离子及化合物的型态与体系的 pH 值密切相关. 体系 pH 值小于 7 时, 硫阴离子主要以  $\text{HSO}_3^-$  型态存在, 脱硫反应以生成  $\text{Ca}(\text{HSO}_3)_2$  为主; 体系 pH 值大于 7 时, 硫阴离子主要以  $\text{SO}_3^{2-}$  型态存在, 脱硫反应以生成  $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  或  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  为主.

**关键词** pH 值, 石灰(石灰石)脱硫, 反应机理.

石灰(石灰石)脱硫是适合我国国情的烟气脱硫措施, 它具有处理费用低、效果好等优点. 近几年来, 笔者在进行“高效一体化脱硫除尘新设备与新工艺”实验研究与工业实践中发现, 湿式石灰(石灰石)脱硫(以下简称脱硫)反应机理因体系 pH 值不同而有不同. 因而, 通常存在的忽视 pH 值对脱硫反应机理的影响是欠妥的<sup>[1-10]</sup>.

## 1 实验设计及结果分析

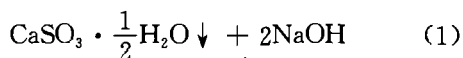
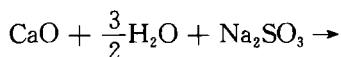
为了研究在某些 pH 值下, 石灰(石灰石)湿法脱硫过程并无结垢产生的现象, 设计了采用亚硫酸钙沉淀与水的混合液吸收  $\text{SO}_2$  的实验.

### 1.1 实验装置

实验装置及流程如图 1 所示. 其中吸收塔为  $\phi 39$  mm 有机玻璃筛板塔, 塔板数为 3.

### 1.2 实验及结果分析

由于缺少亚硫酸钙试剂, 用分析纯  $\text{CaO}$  及  $\text{Na}_2\text{SO}_3$  制备.



过滤, 多次洗涤以除去  $\text{NaOH}$  后, 用水配成含

5%、10%  $\text{CaSO}_3$  的混合液, 置于低位槽中, 按图 1 流程进行  $\text{SO}_2$  吸收试验, 结果如表 1 所示.

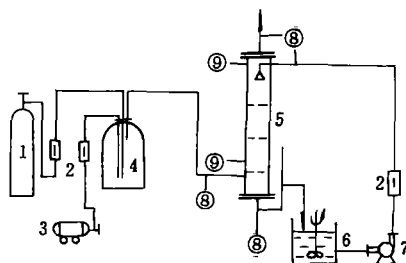
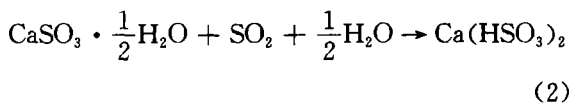


图 1 实验装置及流程

1.  $\text{SO}_2$  钢板 2. 流量计 3. 空气压缩机
4. 混合缓冲瓶 5. 筛板塔 6. 低位槽
7. 循环泵 8. 取样分析点 9. 压力测量点

1<sup>#</sup>、2<sup>#</sup>实验终止后, 发现低位槽中原有的亚硫酸钙沉淀物的体积已减少至起始体积的 1/4 左右, 说明亚硫酸钙与水的混合液在吸收  $\text{SO}_2$  后, 亚硫酸钙发生了变化<sup>[11]</sup>:



$\text{Ca}(\text{HSO}_3)_2$  溶解度很大, 因而吸收塔内无结垢

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发生。1<sup>#</sup>、2<sup>#</sup>实验的 pH 值<8。3<sup>#</sup>、4<sup>#</sup>实验则发生了严重的结垢现象,这是由于生成了亚硫酸钙或硫酸钙沉淀。该实验起始 pH>8。

可见,吸收液 pH 值不同,吸收 SO<sub>2</sub> 的反应机理亦不同。

1.3 溶液 pH 值与离子型态

取出 1<sup>#</sup>实验终止后的 pH=4.21 的清液,向其中投加 CaO,其设加的 CaO 量与溶液 pH 值变化关系示于图 2。

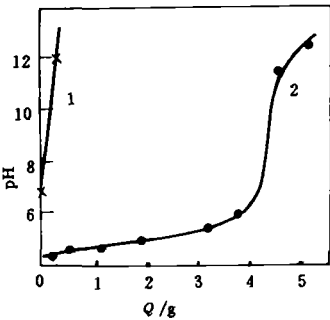


图2 投加CaO量与pH值变化  
1. 清水+CaO, 对照 2. 吸收液+CaO

由图 2 可见,清水内投加 CaO 后, pH 值与投加 CaO 量成直线关系,且投加量很少就使 pH 迅速升高,而 1<sup>#</sup>实验后清液内投加 CaO, pH 值与投加 CaO 量间呈曲线关系,且开始呈很平缓的上升趋势,至 pH=6 以后,曲线迅速上升。在 pH=4—6 间,溶液表现出一定的缓冲性能, pH>6 后缓冲性能丧失。在相同体积的清水和 1<sup>#</sup>实验后上清液中投加 CaO,欲使溶液 pH 值达到 12 左右,后者的投加量是前者的 16 倍左右。

笔者认为,在清水中投加少量 CaO 后,由于 Ca(OH)<sub>2</sub> 的离解,溶液中存在着 OH<sup>-</sup>、Ca<sup>2+</sup>、Ca(OH)<sub>2</sub> 等离子和化合物<sup>[1]</sup>, OH<sup>-</sup> 离子使溶液 pH 值迅速升高。图 2 中曲线 2 可用图 3 来解释。

图 3 是 SO<sub>2</sub> 溶于水后,溶液中硫阴离子的型态与溶液 pH 值的关系曲线<sup>[12]</sup>。

当 pH 值为 4—6 时,溶液中主要存在的硫阴离子为 HSO<sub>3</sub><sup>-</sup> (图 3),当投加 CaO 后,尽管离解出 Ca<sup>2+</sup> 及 OH<sup>-</sup>,但 OH<sup>-</sup> 与 HSO<sub>3</sub><sup>-</sup> 离解出的

H<sup>+</sup> 结合为 H<sub>2</sub>O 而使 HSO<sub>3</sub><sup>-</sup>→H<sup>+</sup>+SO<sub>3</sub><sup>2-</sup> 反应式平衡向右移动,从而显示出缓冲溶液的特性。但是,到 pH>6 以后,溶液中 HSO<sub>3</sub><sup>-</sup> 逐渐减少,甚至主要为 SO<sub>3</sub><sup>2-</sup> 形式,失去了缓冲特性,出现了图 2 曲线 2 中迅速上升的一段。

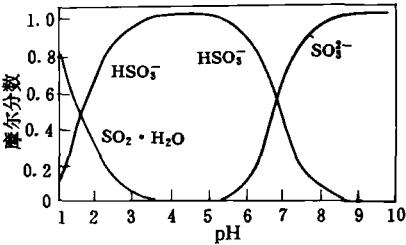


图3 溶液 pH 值与硫阴离子型态

因此,脱硫过程的循环吸收液中硫阴离子的型态与溶液的 pH 值密切相关。

图 4 为在 φ150 mm 吸收塔内,用石灰浆液循环吸收 SO<sub>2</sub> 过程中,浆液 pH 值随时间变化的关系。可以看出,在 pH>12 的 AB 段,由于浆液中有较多的 Ca(OH)<sub>2</sub>, pH 值变化缓慢,在 pH=12—6.8 的 BC 段,由于浆液中 Ca(OH)<sub>2</sub> 已将耗尽,由 Ca(OH)<sub>2</sub> 离解出的 OH<sup>-</sup> 迅速减少, pH 值迅速降低,在 pH=6.8—4 的 CD 段,由于浆液具有缓冲能力, pH 值变化平缓。

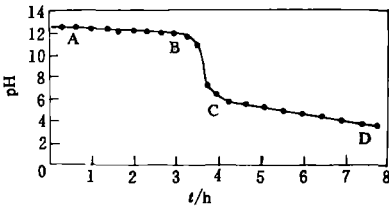


图4 石灰浆液脱硫过程 pH 值的变化

2 脱硫机理及 pH 控制

从上述实验及分析可知,脱硫机理(或主要反应)与吸收液中离子或化合物的形态密切相关,即与溶液的 pH 值密切相关。

笔者认为,石灰(石灰石)湿法脱硫的主要反应是: SO<sub>2</sub> + H<sub>2</sub>O→H<sub>2</sub>SO<sub>3</sub>, H<sub>2</sub>SO<sub>3</sub>→H<sup>+</sup> + HSO<sub>3</sub><sup>-</sup>, HSO<sub>3</sub><sup>-</sup>→H<sup>+</sup> + SO<sub>3</sub><sup>2-</sup> 和 HSO<sub>3</sub><sup>-</sup> + 1/2 O<sub>2</sub>→

表 1  $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  和  $\text{Ca}(\text{OH})_2$  吸收  $\text{SO}_2$  实验结果

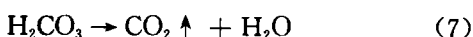
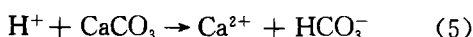
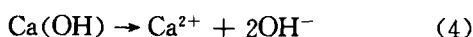
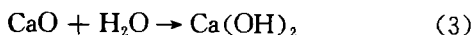
编号	吸收剂	pH 值		操 作 条 件			脱硫率 /%	结垢情况
		始	终	混合气量 / $\text{m}^3 \cdot \text{h}^{-1}$	$\text{SO}_2$ 流量 / $\text{ml} \cdot \text{h}^{-1}$	液气比 / $\text{L} \cdot \text{m}^{-3}$		
1 <sup>1)</sup>	5% $\text{CaSO}_3$	8	4.21	2.5	421	4	96.8	无结垢
2	10% $\text{CaSO}_3$	8	4.25	2.5	350	6	98.2	无结垢
3 <sup>1)</sup>	$\text{Na}_2\text{SO}_3 + \text{Ca}(\text{OH})_2$ (相当于 5% $\text{CaSO}_3$ )	>14	4.5	2.5	100	6	98.5	严重结垢
4	5% $\text{Ca}(\text{OH})_2$	>12	4.5	2.5	250	4	98.5	严重结垢

1) 3<sup>#</sup> 实验的吸收剂未滤去(1)式生成的 NaOH

$\text{SO}_4^{2-} + \text{H}^+$ , 后者易发生在 pH 值较低<sup>[10]</sup>时, 以及有  $\text{Fe}^{2+}$ 、 $\text{Mn}^{2+}$ 、 $\text{Cu}^{2+}$  等变价金属离子的催化氧化作用时。

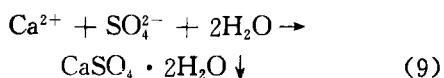
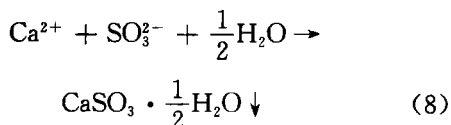
体系 pH 值 < 7 时,  $\text{HSO}_3^-$  为主要存在形式; pH 值 > 7 时, 以  $\text{SO}_3^{2-}$  为主。

石灰(石灰石)进入液相离解生成  $\text{Ca}^{2+}$ :



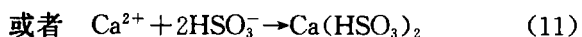
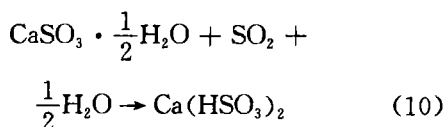
钙离子与硫阴离子结合

pH > 7—8:



由于亚硫酸钙及硫酸钙在水中溶解度甚小, 这是 pH 较高时易结垢的主要原因。

pH < 7—8 时:



亚硫酸氢钙溶解度较大, 这是体系 pH < 7—8 时不结垢的主要原因。

### 3 结论

(1) 石灰(石灰石)湿法脱硫机理与体系 pH

值、液相中离子及化合物的型态密切相关。

(2) 体系 pH < 7 时, 液相中硫阴离子主要以  $\text{HSO}_3^-$  形态存在, 体系具有缓冲能力, 脱硫过程中主要生成溶解度很大的  $\text{Ca}(\text{HSO}_3)_2$ , 此时无结垢发生。

(3) 体系 pH > 7—8 时, 液相中硫阴离子主要以  $\text{SO}_3^{2-}$  型态存在, 体系无缓冲能力, 脱硫过程中主要生成溶解度很小的  $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  或  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 此时易发生结垢现象。

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**Study on the Residual Dynamics of Cyhalothrin in Soybean and Soil.** Li Zhixiang et al. (Institute of Agro-environmental Protection, Tianjin, 300191); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 36—38

In order to make up the standards for safe use of cyhalothrin on soybean, a field experiment was conducted to study the residual dynamics of cyhalothrin in soil and leaves of soybean. The residues of cyhalothrin in green soybean, mature soybean and soil were determined by GLC. Results of two years' study showed that cyhalothrin dissipated rapidly from leaves and soil. Its half lives in leaves and soil were 6.6—7.1 and 6.7—11.6 days, respectively. The soybean field was sprayed twice with cyhalothrin at a rate of 15 g a.i./hm<sup>2</sup>. At harvest, the final residues of cyhalothrin in soil was 0.008 mg/kg, the residues of cyhalothrin in green and mature soybean were all below their detectable limits (0.004 mg/kg). Cyhalothrin is a pesticide of easy dissipation ( $T_{1/2} < 30$  d). It is safe if applied twice at a recommended rate (7.5 g a.i./hm<sup>2</sup>).

**Key words:** cyhalothrin, soybean, residue, GLC, soil.

**Application of Solvent Extraction for Treatment of Wastewater from Luminous Powder (ZnS) Manufacturing Process.** Zhu Wapeng and Yang Zhihua (Dept. of Environmental Engineering, Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 39—41

A solvent extraction process for zinc recovery from wastewater from luminous powder (ZnS) manufacturing process was studied. The optimum operation parameters of each unit were determined in laboratory. The zinc ion (I) in wastewater was extracted by D<sub>2</sub>EHPA (di-(2-ethyl-hexyl)-phosphoric acid) in the state of saponification-kerosene solution and extracted back by sulfuric acid solution. The zinc recovery rate was more than 95%, nickel in wastewater was not extracted and extraction rate of copper in wastewater was less than 7%. The concentrated zinc solution could be reused in luminous powder (ZnS) manufacturing process. Concentration of zinc, copper and nickel in effluent, after treated by using lime, are lower than the National Wastewater Discharge Standards.

**Key words:** solvent extraction, zinc, D<sub>2</sub>EHPA, di-(2-ethyl-hexyl)-phosphoric acid, luminous powder (ZnS).

**pH Value Effect on the Reaction Mechanism of Wet FGD with Lime/Limestone.** Chen Zhaoqiong et al. (Dept. of Chemical Eng., Xiangtan University, Xiangtan 411105); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 42—44

The reaction mechanism of wet FGD with Lime/Limestone was studied. The results showed that the species of ions and compounds in the solution effected significantly the reaction mechanism of wet FGD. While pH of the system < 7, main species of sulfur negative ions is HSO<sub>3</sub><sup>-</sup> and desulphudation are forming Ca(HSO<sub>3</sub>)<sub>2</sub> mainly. pH of the system > 7, then main species of sulfur negative ions is SO<sub>3</sub><sup>2-</sup> and desulphudation are forming CaSO<sub>3</sub> · 1/

2H<sub>2</sub>O or CaSO<sub>4</sub> · 2H<sub>2</sub>O mainly.

**Key words:** pH value, FGD with lime/limestone, mechanism.

**Designing and Implementation of Acidic Deposition Management Information System in Liuzhou.** Guo Jinghai and He Kebin. (Dept. of Environ. Eng. Tsinghua University Beijing, 100084); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 45—47

According to analysis on environmental information regulator regime and combined with the feature of acidic deposition in Liuzhou, the structure and function of management information system of acidic deposition were analyzed systematically, system analysis, requirement analysis and software design were made in detail, on which the overall frame of system were established and five subsystem including database operating, chart, picture, database repairment and model were designed.

**Key words:** acid rain, acidic deposition, management information system.

**Environmental Decision Support System.** Peng Zhiliang et al. (South China Institute of Environmental Sciences, NEPA, Nanjing 510655); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 48—52

In this paper a new structure map for decision support systems (DSS) was presented and the concept, content and design guidelines of environmental decision support systems (EDSS) were discussed. An example based on the design guidelines above mentioned was given to illustrate the application of EDSS to regional water quality management.

**Key words:** environmental management, decision support system, environmental decision support system.

**Determination of Nitrite and Nitrate in Water by Capillary Electrophoresis.** Ren Hongxing et al. (Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, National Analytical Research Center of Electrochemistry and Spectroscopy, Changchun, 130022); *Chin. J. Environ. Sci.*, 17(5), 1996, pp. 53—55

Nitrite and nitrate in mineral water and well water have been determined by capillary electrophoresis with internal standard method at 211 nm in pH 8.2 borate buffer. Cetyltrimethylammonium bromide (CTAB) was used as electroosmotic flow modified (EOF) reagent, and the reproductivity RSDs of migration time for nitrite and nitrate anions were less than 1.5%. Dimethyl sulfoxide (0.05%) was applied as the internal standard in this detection, and the RSDs of peak high ratio of anions to dimethyl sulfoxide were around 20% for the concentration at µg/g level. Detection limits for nitrite were  $2.5 \times 10^{-11}$  mol, and  $1.8 \times 10^{-11}$  mol, respectively. The results were good agree with the results of ion chromatography.

**Key words:** nitrite, nitrate, internal standard method, capillary electrophoresis.

**The petroleum Hydrocarbons in Economical Shellfish along the Coast of Huanghai and Bohai Seas.** Shang