

A pilot-scale jet bubbling reactor for wet flue gas desulfurization with pyrolusite

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Abstract: MnO_2 in pyrolusite can react with SO_2 in flue gas and obtain by-product $\text{MnSO}_4 \cdot \text{H}_2\text{O}$. A pilot scale jet bubbling reactor was applied in this work. Different factors affecting both SO_2 absorption efficiency and Mn^{2+} extraction rate have been investigated, these factors include temperature of inlet gas flue, ration of liquid/solid mass flow rate (L/S), pyrolusite grade, and SO_2 concentration in the inlet flue gas. In the meantime, the procedure of purification of absorption liquid was also discussed. Experiment results indicated that the increase of temperature from 30 to 70 K caused the increase of SO_2 absorption efficiency from 81.4% to 91.2%. And when SO_2 concentration in the inlet flue gas increased from 500 to 3000 ppm, SO_2 absorption efficiency and Mn^{2+} extraction rate decreased from 98.1% to 82.2% and from 82.8% to 61.7%, respectively. The content of MnO_2 in pyrolusite had a neglectable effect on SO_2 absorption efficiency. Low L/S was good for both removal of SO_2 and Mn^{2+} extraction. The absorption liquid was filtrated and purified to remove Si, Mg, Ca, Fe, Al and heavy metals, last product $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was obtained which quality could reach China GB1622-86, the industry grade standards.

Keywords: wet FGD; jet bubbling reactor; SO_2 ; pyrolusite; manganese sulfate

Introduction

It is a main issue for the environmental protection to reduce SO_2 emission from power plants in China. In the past 10 years, many flue gas desulfurization (FGD) processes were available for the reduction of SO_2 emission. The wet FGD processes, especially the calcium sorbent desulfurization process, have the advantages of lower capital cost and are commonly adopted in power plants in Europe, America and Japan, where the by-product is high-quality gypsum, which can be used for wallboard manufacture (Krasnopoler, 1991; Soud, 2000). However, the gypsum after desulfurization in China had to be deposited leading to secondary pollution because there are abundant nature high-quality gypsum resource (Xu, 2000). Thus, it has been an important subject to find other effective absorbent and the corresponding byproduct in China. On the other hand, in the traditional production process of manganese sulfate, two minerals, pyrites and pyrolusite, were used, ripened by concentrated sulfate acid, which had produced an amount of waste acid and waste gas causing serious pollution. To combine the process of wet FGD with the production process of manganese sulfate, SO_2 in flue gas dissolved in pyrolusite slurry can react with MnO_2 in pyrolusite and create manganese sulfate. Thus, flue gas desulfurization with pyrolusite is a low investment technique for wet FGD process and a profitable substitute technique for traditional manganese sulfate production process. It has a good potential in applications. Especially, it is suitable for retrofitting of existing small or middle scale power plants.

There are four main types of wet scrubbers used in the process of flue gas desulfurization with pyrolusite, the spray scrubber (Liang, 1994), the packed tower (Hu, 2004), the jet bubbling reactor (JBR) (Zhu, 2002; 2003), and the orifice column (Wang, 1999). The JBR reactor does not need large recycle pumps and spray heads, making desulfurization system less complex than other conventional spray tower

systems. The investigations showed that previous studies on JBR used in wet FGD process mainly focus on limestone process (Zheng, 2003). Application of JBR with pyrolusite for wet FGD has not been investigated. In this work, pyrolusite based wet FGD pilot plant, downscaled from a full-scale JBR plant has been constructed and tested under different experiment conditions, including temperature of inlet gas flue, ration of liquid/solid mass flow rate (L/S), pyrolusite grade and SO_2 concentration in the inlet flue gas. In the meantime, the procedure of purification of absorption liquid was also discussed.

A schematic drawing of a full-scale JBR is shown in Fig. 1. The flue gas entered the JBR and was then distributed through a large number of gas sparging tubes, which were immersed below the surface of the pyrolusite slurry. This jet of gas in the slurry created a froth layer, which provided a very high gas-liquid interfacial area for SO_2 mass transfer to the slurry and promoted absorption of SO_2 from the flue gas. The bubbles in the froth zone were continuously collapsing and reforming. As a result, keeping a fresh interfacial area and the transport of reaction, products can entered rapidly from the froth zone to the bulk slurry solution.

Although the reaction among SO_2 in flue gas and pyrolusite may be complex, our research (Zhu, 2002) showed the overall reaction in the system could be represented as follows,



1 Materials and methods

1.1 Materials

Typical experimental flue gas of 10000 Nm^3/h was introduced from a coal-fired power plant of 75 t/h, flue gas flow rate at about $1 \times 10^4 \text{ Nm}^3/\text{h}$, which lies in Mianyang City, Sichuan Province, China. Two kinds of pyrolusite were from Qinchuan County, Hanyuan County of Sichuan Province, China, respectively. The compositions of pyrolusite are showed in Table 1. The feed slurry was

prepared by mixing tap water with a required amount of commercial pyrolusite.

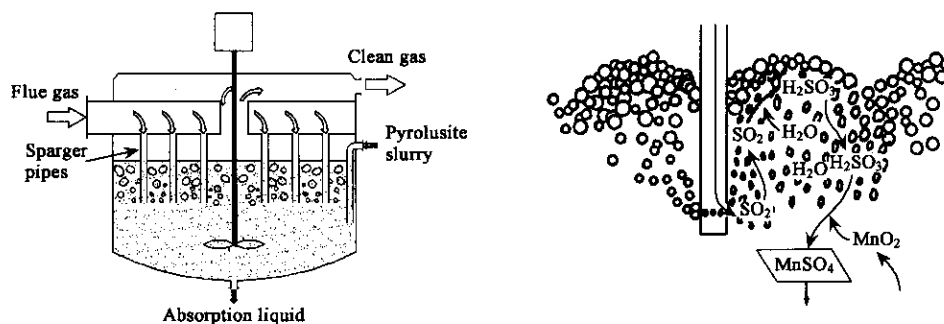


Fig. 1 Schematic illustration of a jet bubbling reactor and the chemical reaction

Table 1 The compositions of pyrolusite (wt%)

Pyrolusite	MnO ₂	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Others
Qingchuan	22.5	42.8	1.75	22.9	5.09	2.8	0.23	0.52	41
Hanyuan	50.5	28.2	0.77	13.8	3.62	1.4	0.1	0.39	22

1.2 Main equipments

The main equipments are JBR, the absorption slurry filtrator, the feed, and product tanks. JBR reactor is a cylinder with an inner diameter of the 1.5 m and a height of 3.0 m, fitted with four vertical baffles, sampling pulp at different height and a floating contact system for slurry level control. An axial four-blade stirrer with fixed speed of 150 r/min, creates a high degree of mixing in the liquid phase. All pipes and vessels are made of steel coated with acid proof material to avoid corrosion.

1.3 JBR wet FGD pilot plant

A schematic illustration of the pilot plant is shown in

Fig. 2. Firstly, flue gas moved through a venture section, and then went through the water-film dust collector from the bottom and flows out. Meanwhile, it was cooled and saturated with water in it, then flue gas entered JBR reactor and was distributed through gas sparger tubes and jetted into the slurry, SO₂ in flue gas reacted with pyrolusite. As a result, SO₂ was absorbed, the purified flue gas finally flowed into the stack and went into atmosphere. The addition of fresh pyrolusite slurry was controlled by maintaining the holding tank pH at a constant value (typically 3.0—3.5). The changing weight of the feed tank over time was recorded and allowed the feed consumption rate to be calculated.

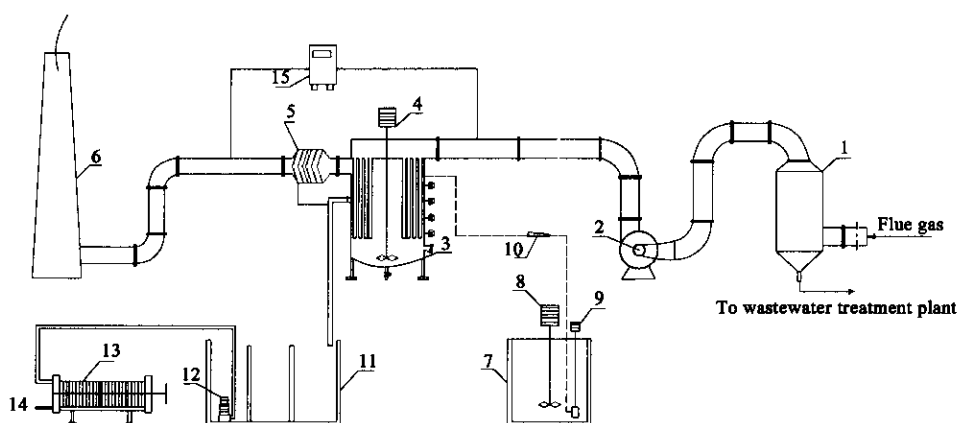


Fig. 2 Schematic illustration of the experimental pilot-scale JBR apparatus

1. water-film dust collector; 2. fan; 3. jet bubbling reactor; 4. agitator; 5. mist collector; 6. stack; 7. pyrolusite slurry feeder; 8. slurry agitator; 9. pyrolusite slurry pump; 10. pyrolusite slurry volume meter; 11. absorption slurry settler; 12. absorption liquid pump; 13. filter; 14. mother liquid of manganese sulfate; 15. online gas analyzer

1.4 Analysis

Content of SO₂ in inlet and outlet of flue gas was detected by a set of on-line gas analyzer (SIMENS Ultramat-23). Concentration of metal ions in both liquid samples and residual of pyrolusite were determined by atomic absorption spectrometer (AA7000 Institute of Eastwest Electronic Technology of Beijing, China). The composition of the MnSO₄ · H₂O by-product was determined by China GB1622-86 method.

2 Results and discussion

Four experimental series were examined in the pilot plant. Experimental parameters for a selected base case are presented in Table 2.

The other experiments involved perturbations from the base case with respect to SO₂ concentration in inlet flue gas, MnO₂ content of the pyrolusite, temperature of inlet flue gas and ratio of liquid/solid mass flow rate. For a wet FGD plant

Table 2 Experimental parameters of the base case

Parameter	Value	Value [*]
Flow rate of flue gas, Nm ³ /h	10000	/
SO ₂ concentration in inlet flue gas, ppm	~ 2000	500—3000
Temperature of flue gas, °C	~ 80	30—100
Pressure of flue gas, Pa	1.35 atm	/
Ratio of liquid /solid, mass flow rate, kg/kg	3:1	2:1—4:1
MnO ₂ content of pyrolusite, wt%	50.6	24.3, 50.6
Slurry pH in reactor	3.5	/
Pyrolusite type	Hanyuan	Qingchuan and Hanyuan

Notes: * While the parameter being set as effect factor, chemical analysis of Qingchuan and Hanyuan pyrolusite was provided in Zhu *et al.* (Zhu, 2002)

the rate of SO₂ removal is a key parameter, however, for plants employing the pyrolusite as absorbent, another key parameter which should be considered is the extraction rate of manganese. There are two reasons for this: (1) good utilization of pyrolusite and (2) a relatively high productivity and a saleable MnSO₄·H₂O product (i.e. China GB1622-86 industry grade standards). Consequently, the degree of desulfurization and the extraction rate of manganese were

analyzed for each experiment: $\eta = \left(\frac{C_{SO_2, out}}{C_{SO_2, in}} \right) \times 100\%$,

where, η is SO₂ absorption efficiency, %; $C_{SO_2, out}$ is the concentration of SO₂ in outlet flue gas, ppm; $C_{SO_2, in}$ is the concentration of SO₂ in inlet flue gas, ppm.

Equation for expressing extraction rate of manganese is as follows:

$$X_B = \left(1 - \frac{C_{Mn, out}}{C_{Mn, in}} \right) \times 100\%$$

where, X_B is extraction rate of manganese, %; $C_{Mn, out}$ is the net mass of Mn²⁺ of liquid in JBR, kg; $C_{Mn, in}$ is the net mass of Mn of pyrolusite, kg.

2.1 Effect of temperature of inlet flue gas

Temperature of flue gas was changed from about 30°C to 100°C by mixing with cool air. The effect of temperature of flue gas on SO₂ absorption efficiency and Mn extraction rate is showed in Fig.3.

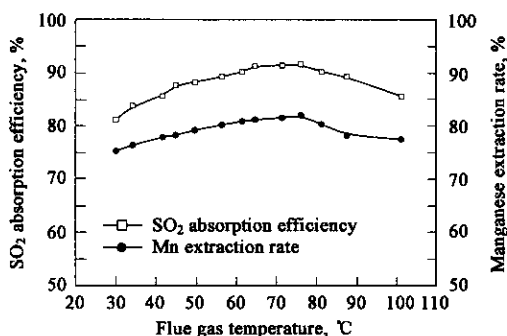


Fig.3 Effect of flue gas temperature on desulfurization efficiency and manganese extraction rate

Experimental results show that the SO₂ absorption efficiency and Mn extraction rate improved with the increase of inlet flue gas temperature from 30°C to 75°C, but decreased when the flue gas temperature exceeded 75°C. Temperature of inlet flue gas may affect SO₂ absorption efficiency in three ways positively or negatively. Firstly, the increase of the temperature can enhance mass transfer

coefficient of SO₂. Secondly, the reaction rate of Eq. (1) will be promoted by increase of temperature (Zhu, 2002). However the solubility of SO₂ in aqueous would decrease when increasing temperature. Therefore, within a range of temperatures of 30—75°C, the positive effect of temperature had superiority over the negative effect, and contrarily, it is negative effect when the flue gas temperature exceeded 75°C. Temperature effect on Mn extraction rate was similar to that of SO₂ absorption efficiency because SO₂ reacted with MnO₂ stoichiometrically as Eq. (1). Practically, as regards to a industry application, the temperature of flue gas was usually lower than 80°C if a water-film dust collector used, which meant the process of FGD with pyrolusite slurry could combine with the exiting wet dust collector to retrofit existing power plants.

2.2 Effect of ratio of L/S(liquid/solid mass flow rate)

Ratio of liquid /solid mass flow rate changed from 4:1 kg/kg to 2:1 kg/kg while molar of MnO₂ contained in slurry was kept stoichiometric ratio with molar of SO₂ in inlet flue gas by adjusting flow rate of slurry. The experimental results are showed in Fig. 4, which indicated that desulfurization efficiency and Mn extraction rate both increased with ratio of L/S decreasing. Jetted into pyrolusite slurry, flue gas collided with pyrolusite particles and was distributed into more fine gas bubble with ratio of L/S decreasing, which promoted the turbulent and enhanced the mass transfer between gas and liquid. On the other hand, the mean residence time of pyrolusite particles in liquid phase increased with ratio of L/S decreasing, which accelerated the reaction between SO₂ dissolved in liquid and pyrolusite particles and thus promoted the extraction rate of Mn. In addition, a higher extraction rate of Mn could be obtained under lower ratio of L/S, which could increase the output rate of the by-product manganese sulfate. Therefore, it is necessary to keep lower ratio of L/S in JBR.

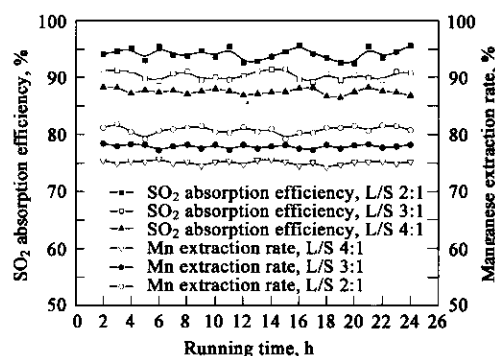


Fig.4 Effect of ratio of liquid/solid mass flow rate on desulfurization efficiency and manganese extraction rate

2.3 Effect of pyrolusite grade

Pyrolusite from Qingchuan with a mean content of MnO₂ 22.5 wt% and pyrolusite from Hanyuan with a mean content of MnO₂ 50.5 wt% was used to investigate the effect of pyrolusite grade, while molar of MnO₂ contained in slurry was kept stoichiometric ratio with molar of SO₂ in inlet flue gas by adjusting flow rate of slurry. The experimental results are showed in Fig.5.

Experimental results show that the effect of pyrolusite grade on the SO₂ absorption efficiency was neglectable. This

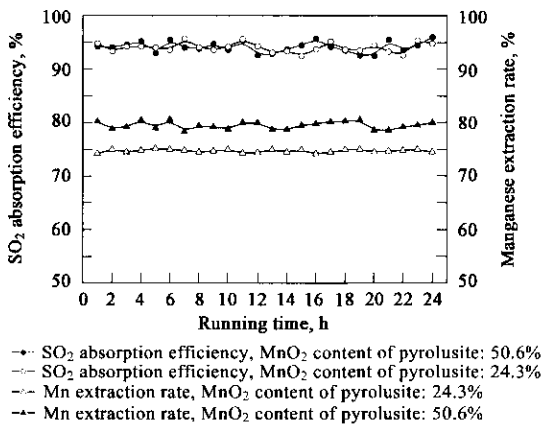


Fig.5 Effect of pyrolusite grade on desulfurization efficiency and manganese extraction rate

effect attributed to that the reaction between SO₂ (aq) and MnO₂ is a instantaneous and irreversible (Zhu, 2002), which rate is independent of content of MnO₂ in pyrolusite if molar ratio of MnO₂ and SO₂ was kept stoichiometric ratio. However, extraction rate of Mn increased as regards to high pyrolusite grade. This is due to that when the amount of SO₂ in flue gas was low, less pyrolusite was needed to maintain the same desulfurization efficiency, and the feed rate of pyrolusite slurry tended to decrease, resulting in an increase of solids residence time in JBR and thus leading to an increase of extraction rate of Mn. Furthermore, the results suggested that different grade pyrolusite could be used directly in the FGD with pyrolusite system. However, the use of high grade pyrolusite was better than that of lower grade pyrolusite because higher concentration of Mn²⁺ in absorption leachate could be obtained, which could increase the output rate of the by-product manganese sulfate, and decreased amount of solid wastes. Therefore, if available, high grade pyrolusite is a proposed selection in an industry.

2.4 Effect of SO₂ concentration in inlet flue gas

Fig.6 shows the effect of SO₂ concentration in inlet flue gas on degree of desulfurization and extraction rate of Mn.

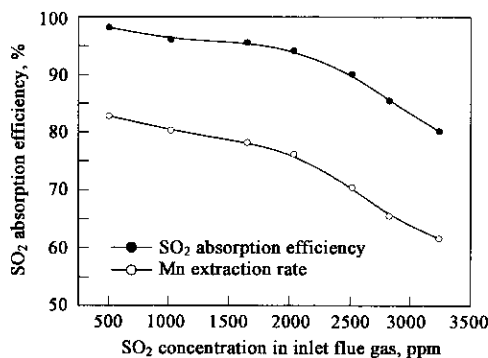


Fig.6 Effect of SO₂ concentration in inlet flue gas on desulfurization efficiency and manganese extraction rate

The effect of inlet SO₂ concentration on SO₂ removal efficiency was quite significant. An increase in inlet SO₂ concentration led to a decrease of both SO₂ removal efficiency and extraction rate of Mn under the experimental conditions given. The drop in SO₂ removal efficiency was a result of the

lower enhancement factor for mass transfer of SO₂. But the utilisation of pyrolusite increased with a decrease in inlet SO₂ concentration. This can be explained that at a lower SO₂ concentration, less pyrolusite was needed to maintain the same pH of the holding tank, and rate of the pyrolusite slurry feed decreased, resulting in an increase in JBR solids residence time, and leading to an increase of extraction rate of Mn. The experimental results also indicated that when SO₂ concentration in inlet flue gas was relatively high, such as above 3000 ppm, two or more JBRs could be used in application to ensure high desulfurization rate and extraction rate of Mn at the same time.

2.5 Purification of the by-product manganese sulfate

2.5.1 Components in filtrate of absorption liquid and residual pyrolusite

During absorption, other components such as Si, Al, Fe, Ca, Mg, K, Na, Co, Ni contained in pyrolusite were also extracted at the same time. At a given set of JBR operating conditions, the components of filtrate of absorption liquid and residual pyrolusite were analysed and the results are shown in Table 3 and Table 4.

Table 3 Components in filtrate of absorption liquid (wt%)

Pyrolusite	Mn	Si	Al	Fe	MnSO ₄	Ca	Mg	K	Na
Qingchuan	8.5	4.6	0.0025	0.018	23.6	0.015	0.57	0.022	0.013
Hanyuan	16.3	5.6	0.0019	0.038	44.4	0.042	0.11	0.550	0.330

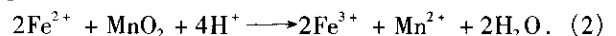
Table 4 Components in residual pyrolusite (wt%)

Pyrolusite	Mn	Si	Al	Fe	Ca	Mg	K	Na
Qingchuan	1.3	10.8	12.5	6.9	1.09	0.051	0.067	0.043
Hanyuan	1.8	13.2	0.77	7.6	0.015	0.34	0.006	0.0075

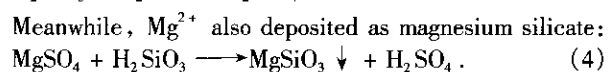
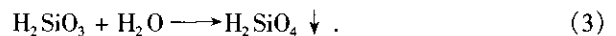
Table 3 shows that the filtrate of absorption liquid must be purified to remove the Si, Al, Fe, Ca, Mg, Co and Ni to ensure the quality of by-product sulfate manganese. Table 4 indicated that the residual pyrolusite could be used as roadbed materials or cement additive after Mn and Fe were removed.

2.5.2 Filtrate refinement

The refining process of filtrate is illustrated in Fig.7. Firstly, Fe²⁺ in filtrate solution was oxidized to Fe³⁺ by MnO₂ added as oxidant.



Then, pH value of the filtrate solution was adjusted to 5.5 by adding amount of lime, which can lead to about 99% of Fe³⁺ and Al³⁺ removed by hydroxylation. Thirdly, heavy metals, including Cu²⁺, Pb²⁺, Co²⁺, Ni²⁺ could be removed by adding MnS in solution, according to the differences of solubility product of different metal sulfides. In addition, the filtrate contained silicic acid, which would converge to multimolecule silicic acid gradually and finally formed silica gel that affected the quality of sulfate manganese. Silicic acid could be removed by heating filtrate to a certain extent that silicic acid converged to silica gel and deposited.



Ca²⁺ was removed as CaSO₄·2H₂O by evaporating and condensing the filtrate solution until the concentration of

Mn^{2+} reached 1.3 g/ml, and then kept for 48 h.

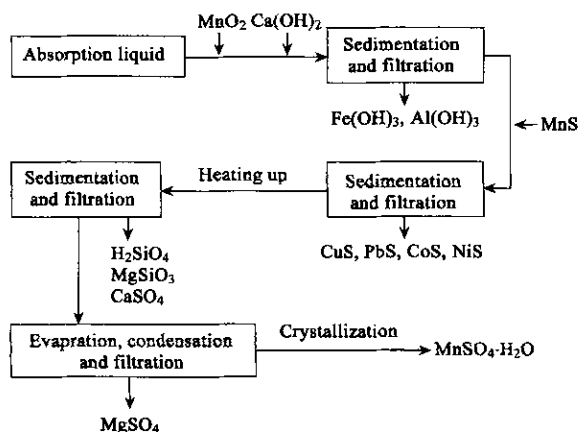


Fig.7 Schematic illustration of the filtrate refinement process

After all the refinery procedures above have been finished, the mother solution of $MnSO_4$ was evaporated and condensed to saturation level. Then, $MgSO_4$ was removed by filtrating the hot mother solution. After crystallization, the by-product $MnSO_4 \cdot H_2O$ was obtained.

The quality analysis result is shown in Table 5, which indicated that the quality of by-product $MnSO_4 \cdot H_2O$ could meet the national industry grade standard.

Table 5 Quality of by-product $MnSO_4 \cdot H_2O$ (wt%)

	$MnSO_4 \cdot H_2O$	Fe	Cl	pH	Insoluble components
GB1622-86(China)	≥ 98.0	≤ 0.004	≤ 0.004	5-7	≤ 0.05
Product in this experiment	98.1	0.004	0.002	5-7	0.03

3 Conclusions

With a pilot-scale jet bubbling reactor for wet flue gas desulfurization with pyrolusite, the different factors affecting both absorption efficiency of SO_2 in flue gas and rate of extraction Mn in pyrolusite have been investigated. Both parameters improved with the increase of inlet flue gas temperature from 30°C to 75°C, but decreased when the flue gas temperature exceeded 75°C. Besides, both absorption

efficiency of SO_2 and rate of extraction Mn increased with ratio of L/S decreasing. The effect of pyrolusite grade on the SO_2 absorption efficiency was almost neglectable. An increase in inlet SO_2 concentration led to a decrease of both SO_2 removal efficiency and extraction rate of Mn.

After the absorption liquid was filtrated, and impurities in the liquid were removed, and then the filtrate solution was evaporated, concentrated and crystallized, $MnSO_4 \cdot H_2O$ was obtained which quality could reach China GB1622-86, the industry grade standards. There existed, however, a trade-off among the pyrolusite utilization, sulfate manganese production and the rate of SO_2 removal. In future work, experiments with different depth of gas distribute pipe and various additives (such as rhodochrosite) should be further examined.

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