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Novel Process of Reduction Roasting Manganese Ore with Sulfur Waste and Extraction of Mn by Acid Leaching

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Abstract: Manganese dioxide is typically reduced to a bivalent state before being extracted; here, sulfur is considered an efficient reductant and sulfur-based reduction has been industrialized in China. In this study, the reaction mechanism between MnO_2 and gaseous sulfur was investigated. Thermodynamically, the reduction of MnO_2 by gaseous sulfur is feasible. The predominant phase diagram as functions of temperature and input $\text{S}_2(\text{g})$ fraction in the S_2 – MnO_2 system was calculated. Experimental validation showed that MnO_2 was reduced stepwise to low-valence manganese oxides and manganese sulfate. The phase composition of the roasted products was complex, and MnS was inevitably formed. The valence state as well as microstructure of manganese dioxide during reduction roasting were also investigated by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy–energy-dispersive spectroscopy (SEM–EDS). The reaction process could be described by an unreacted nuclear model. Manganese was extracted by sulfuric acid solution after reduction by sulfur waste. In sulfuric acid, 95.2 wt% Mn extraction was achieved, using a roasting temperature of 450 °C, roasting time of 30 min, and S_2/MnO_2 molar ratio of 0.40. With the same conditions, low Fe extraction was achieved. On the other hand, in deionized water, 24.3 wt% Mn extraction was achieved, confirming the formation of MnSO_4 .

Keywords: manganese dioxide; sulfur; reduction roasting; acid leaching; reaction mechanism

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1. Introduction

Manganese is the fourth most widely used metal after iron, aluminum, and copper. It is used in numerous fields, such as ferrous and non-ferrous metallurgy, batteries, the chemical industry, agriculture, and animal husbandry [1–3]. Manganese carbonate and oxide ores are two primary resources for extracting Mn. Manganese carbonate ore is valuable because Mn(II) is soluble in acid solutions, making the extraction process extremely simple. However, globally, its availability is limited. Manganese oxide ores are extensively employed for manganese production [4–6]. Mn is always present in minerals as a high-valence oxide, such as pyrolusite (MnO_2), which constitutes 60% of the global manganese reserve. As MnO_2 is stable under direct acidic and alkaline conditions, it is necessary to convert the insoluble Mn(IV) into soluble Mn(II) before leaching Mn from oxide ore [7].

The reduction of Mn(IV) from oxide ores can proceed via routes such as pyrometallurgy, hydrometallurgy, and bio-hydrometallurgy. The type of a reducing agent is key for Mn extraction. Thus far, many reductants have been explored for reducing Mn(IV) , such as carbon-based, sulfur-based, hydrogen-based [8,9], metal-based, and miscellaneous reductants. Carbon-based reductants include coal [10], graphite, and CO, while sulfur-based reductants include elemental sulfur [11], SO_2 [12], Na_2SO_3 , $(\text{NH}_4)_2\text{SO}_3$ [13], H_2SO_4 , CaS and $\text{Na}_2\text{S}_2\text{O}_3$. Iron powder [14], ferrous sulfate, and other iron salts can be used as metal-based reductants. Pyrite (FeS_2) [15], CH_4 , organics compounds [16], and biomass [17] are

classified as miscellaneous reductants, as they comprise two reducing elements. Hydrogen peroxide has also been employed as a reductant on the laboratory scale [18].

In the process of desulfurization of oil, natural gas, and coal gas, a considerable amount of low-quality sulfur sludge, sulfur mud, and sulfur slurry is produced as hazardous waste [19,20]. Not only that, the hydrometallurgical recovery of metals from sulfide concentrates, such as chalcopyrite, enargite, and sphalerite, typically generates elemental sulfur in the oxidative leaching processes [21]. The elemental sulfur content of direct leaching residue can exceed 70%. Due to the existence of active elemental sulfur, conventional means, such as incineration or landfill, are incapable of handling the sulfur-bearing hazardous wastes. Considering the growing number of environmental problems, the ways of waste re-use in production and new material installation are expanding [22,23]. The waste can be re-consumed for production of construction material such as asphalt, concrete or applied in the development of new products, such as copolymers, lithium–sulfur batteries, etc. Despite the broad range of recycling techniques available, a big share of byproducts consisting of sulfur compounds is still stored in a form of stable sulfate rocks such as gypsum or anhydrite.

In recent years, sulfur-based reduction or sulfidation using elemental sulfur as a reductant has gained considerable research attention, because sulfur (pure sulfur can be replaced by sulfur waste) is a high-efficiency reductant. An alternative process, viz., the reduction roasting of manganese oxide ore with elemental sulfur prior to acid leaching, has been successfully developed [11,24,25]. Sulfur-based reduction has also been industrialized in China, using a fluid-bed furnace (ebullated furnace) as the main roasting device [26]. Therein, sulfur was sublimated or gasified in the ebullated furnace because of the low boiling point of elemental sulfur. This implies that gaseous sulfur was the main reducing agent during reduction. The SO_2 gas generated during reduction roasting can be absorbed to prepare sulfuric acid and then used for acid leaching. Hence, in this study, to explore the reduction mechanism of manganese dioxide (MnO_2) using a gaseous reducing agent, the phase transformation, valence state changes, and microstructure were investigated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy–energy-dispersive spectroscopy (SEM–EDS). The mechanism of reduction roasting was investigated via thermodynamic analysis and experimentation. Reduction roasting followed by acid leaching was also conducted to extract Mn from a manganese oxide ore.

2. Experimental

2.1. Materials

2.1.1. Sulfur Waste

Solid sulfur (powder) with a purity greater than 99.99 wt% was used as a reducing agent for investigating the reaction mechanism of manganese dioxide. Sulfur waste, obtained from an oxygen pressure leaching sphalerite process, was used for extraction of Mn from low-grade Mn ore. The purity of S in the sulfur waste was 85.51 wt%. The XRD results in Figure 1 indicate that the main phases in sulfur waste were elemental sulfur (S) and residual sphalerite (ZnS). The morphology of sulfur waste in Figure 2 reveal that its particle size was almost uniform. The particle size of sulfur waste is not critical because it will be sublimated for reduction.

Figure 1. XRD patterns of the sulfur waste and manganese oxide ore.

Figure 2. The morphology of sulfur waste.

2.1.2. Mn-Bearing Materials

The manganese oxide ore used in this study was obtained from Xiatian mine located in Xiangzhou County, Guangxi Province, China. The main chemical composition of the raw material, obtained by chemical analysis, is shown in Table 1. The S content was measured by Nacho carbon and sulfur analyzer (CS-3000, NCS Testing Technology CO., Ltd., Beijing, China). The total Mn and Fe contents (TMn, TFe) were 21.97 wt% and 28.70 wt%, corresponding to 34.75 wt% MnO₂ and 41.00 wt% Fe₂O₃, respectively. The gangue composition contained 8.32 wt% SiO₂ and 5.15 wt% Al₂O₃. The XRD analysis of the raw material in Figure 1 indicates that the manganese ore is primarily composed of pyrolusite (MnO₂) and quartz (SiO₂). The Mn-bearing mineral also contains todorokite

($\text{Ca}_{0.8}\text{Mn}_4\text{O}_8(\text{H}_2\text{O})_2$). The size of raw material was ground to approximately 80 wt% passing through 0.074 mm before its use in reduction roasting. In addition, chemically pure MnO_2 was used to investigate the reaction mechanism.

Table 1. Main chemical composition of the manganese ore, wt%.

Material	MnO ₂	Fe ₂ O ₃	SiO ₂	CaO	MgO	Al ₂ O ₃	P	S	LOI
Manganese ore	34.75	41.00	8.32	0.36	0.29	5.15	0.16	0.10	11.41

LOI: Loss on ignition.

2.2. Experimental Procedure

A sealable stainless-steel reactor was used for reduction roasting. The reduction experiments were conducted in a muffle furnace (Hefei Kejing Material Technology Co., Ltd., Hefei, China), as shown in Figure 3. Before reduction roasting, the raw Mn material and elemental sulfur (S_2/MnO_2 ranges from 0.25 to 0.50) were loaded into the reactor separately, to prevent the Mn material being reduced directly by elemental sulfur. Next, the container carrying the sample was introduced into the hot zone of the muffle furnace, which was preheated to the desired temperature (350–550 °C). Upon heating, solid sulfur melted/gasified or sublimated, then contacted with the Mn-bearing sample. The sample was reduced at a given temperature for a certain period (10–50 min), during which time the furnace was aerated with N_2 gas flowing at a rate of 3 L/min. Subsequently, the container was taken out and cooled naturally to room temperature. Finally, the reduced sample was collected and prepared for analysis and leaching tests.

Figure 3. The schematic of roasting apparatus.

2.3. Analytical Methods

After reduction, the roasted samples were examined by X-ray powder diffraction (Rigaku D/max 2500, Rigaku, Tokyo, Japan) using $\text{Cu K}\alpha$ radiation, a tube current of 250 mA, voltage of 40 kV, 2θ scanning range of $10\text{--}80^\circ$, 2θ step size of 0.02° , and scanning speed of $8^\circ/\text{min}$. SEM (JSM-7800F, Rigaku, Tokyo, Japan) was performed to investigate the morphology of the powder, which was equipped with an EDAX energy dispersive X-ray spectroscopy (EDS) detector. SEM images were recorded in backscatter electron modes operating in low vacuum mode at 0.5 Torr and 20 keV. By the powder tableting method, the valence of different elements in the obtained powder was detected by XPS (ESCALAB250Xi, Thermo Fisher Scientific, Shanghai, China) under a vacuum of 10^{-10} mbar at room temperature. High-resolution spectra were recorded with an analyzer (Thermo

Fisher Scientific, Shanghai, China) pass energy of 30 eV, and the binding energy (BE) of the obtained spectra was calibrated against the C 1 s photoelectron peak at 284.6 eV.

Thermodynamic analysis was conducted using the pure substances database of FactSage 8.0 (Montreal, Canada and Aachen, Germany). The Mn content in the roasted products and residue was determined by chemical analysis. The detailed chemical analysis procedure has been described in the reference of [24].

The extraction ratio of Mn was calculated using the following equation:

$$\gamma = \left(1 - \frac{m_1 \times \beta}{m_0 \times \alpha}\right) \times 100\% \quad (1)$$

where γ is the extraction ratio (wt%), m_0 is the weight of the reduced product (g), α is the Mn content of the reduced product (wt%), m_1 is the weight of the leached residue (g), and β is the Mn content of the leached residue (wt%).

3. Thermodynamic Analysis of Gaseous Sulfur-Based Reduction

The equilibrium phase composition of the MnO_2 –S system can be calculated using FactSage 8.0. In this study, solid sulfur was used as the reducing agent for the reduction of MnO_2 . To determine the actual reaction agents that came in contact with MnO_2 , the behavior of solid sulfur was investigated. Figure 4 shows the phase composition for 1 mol solid sulfur in the temperature range of 400 °C to 600 °C at 1 atm. According to the figure, solid sulfur first melted into the liquid form, because its melting point is only 119 °C. Liquid sulfur was the sole phase in the temperature range of 400–470 °C. By increasing temperature, liquid sulfur gasified to sulfur vapors with different sulfur atoms. The gaseous phases formed during heating were extremely complex. The phases, including S_8 , S_7 , and S_6 , were the main gaseous species, whose contents increased first and then decreased gradually with increasing temperature. Meanwhile, the $\text{S}_2(\text{g})$ content increased steadily as the temperature increased, which indicated that the complex gaseous sulfur molecule decomposed to a simple sulfur molecule. Hence, $\text{S}_2(\text{g})$ was determined as the main phase at high temperatures, and considered for the subsequent thermodynamic analysis.

Figure 4. Phase composition as a function of temperature based on 1 mole solid sulfur.

The main reactions occurring in the MnO_2 – $\text{S}_2(\text{g})$ system and their Gibbs energies are compared in Table 2. Most reactions occurred spontaneously or at low temperatures, which implies that the reduction of MnO_2 by $\text{S}_2(\text{g})$ was feasible. The equilibrium phase composition, as a function of the S_2/MnO_2 molar ratio and temperature, was also calculated, and the results are plotted in Figure 5. MnO_2 was reduced stepwise to form low-valence manganese oxides and MnSO_4 (or SO_2). Comparison of reactions 2 and 3 revealed that

Mn_2O_3 and MnSO_4 were formed more easily than SO_2 from the view of thermodynamics. The theoretical S_2/MnO_2 molar ratio was 0.10 (Table 2, Equation (5)); accordingly, the residual MnO_2 decomposed when the molar ratio was less than 0.10 and the temperature was greater than 782 K. Consequently, an area composed of Mn_2O_3 , MnSO_4 , and gas (O_2) is seen in Figure 5. Since MnO_2 was completely reduced, the reduction of Mn_2O_3 proceeded. The results in Table 2 and Figure 5 show that Mn_3O_4 and MnSO_4 were preferentially generated (Equations (6) and (7)) in the calculated temperature range. Subsequently, Mn_3O_4 was reduced to form MnO and MnSO_4 because the Gibbs energy of Equation (9) was the lowest (among Equations (8)–(11)). According to previous studies, MnO is acid-soluble, whereas MnSO_4 is water-soluble. Thermodynamic calculation indicated that a S_2/MnO_2 molar ratio of 1/6 was sufficient for properly converting MnO_2 to MnO and MnSO_4 . Hence, Mn was leached during the subsequent acid leaching after roasting with a S_2/MnO_2 molar ratio of 1/6.

In addition, both MnO and MnSO_4 can react further with sulfur to form different products; this largely depends on the roasting temperature and S_2/MnO_2 molar ratio. The reaction order and predominant field of various products are shown in Table 2 (Equations (12)–(15)) and Figure 5, respectively.

Table 2. Main reactions and their Gibbs energies as a function of temperature.

Equations	Main Reactions	$\Delta_r G^\ominus - T/\text{kJ/mol}$	Spontaneous Reaction T/K
(3)	$4\text{MnO}_2 = 2\text{Mn}_2\text{O}_3 + \text{O}_2(\text{g})$	$166.568 - 0.213 T$	$T > 782 \text{ K}$
(4)	$\text{S}_2(\text{g}) + 8\text{MnO}_2 = 4\text{Mn}_2\text{O}_3 + 2\text{SO}_2(\text{g})$	$-390.985 - 0.279 T$	Spontaneous
(5)	$\text{S}_2(\text{g}) + 10\text{MnO}_2 = 4\text{Mn}_2\text{O}_3 + 2\text{MnSO}_4$	$-872.778 + 0.070 T$	Spontaneous
(6)	$\text{S}_2(\text{g}) + 12\text{Mn}_2\text{O}_3 = 8\text{Mn}_3\text{O}_4 + 2\text{SO}_2(\text{g})$	$-339.479 - 0.165 T$	Spontaneous
(7)	$\text{S}_2(\text{g}) + 16\text{Mn}_2\text{O}_3 = 10\text{Mn}_3\text{O}_4 + 2\text{MnSO}_4$	$-808.395 + 0.213 T$	$T < 3795$
(8)	$\text{S}_2(\text{g}) + 4\text{Mn}_3\text{O}_4 = 12\text{MnO} + 2\text{SO}_2(\text{g})$	$199.734 - 0.360 T$	$T > 555$
(9)	$\text{S}_2(\text{g}) + 6\text{Mn}_3\text{O}_4 = 16\text{MnO} + 2\text{MnSO}_4$	$-89.445 - 0.047 T$	Spontaneous
(10)	$\text{S}_2(\text{g}) + 2/5\text{Mn}_3\text{O}_4 = 6/5\text{MnS} + 4/5\text{SO}_2(\text{g})$	$-68.194 - 0.004 T$	Spontaneous
(11)	$\text{S}_2(\text{g}) + 2/3\text{Mn}_3\text{O}_4 = 4/3\text{MnS} + 2/3\text{MnSO}_4$	$-194.357 + 0.140 T$	$T < 1192$
(12)	$\text{S}_2(\text{g}) + 2\text{MnO} = 3/2\text{MnS} + 1/2\text{MnSO}_4$	$-207.471 + 0.163 T$	$T < 1273$
(13)	$\text{S}_2(\text{g}) + 4/3\text{MnO} = 4/3\text{MnS} + 2/3\text{SO}_2(\text{g})$	$-97.964 + 0.036 T$	$T < 2721$
(14)	$\text{S}_2(\text{g}) + \text{MnSO}_4 = \text{MnS} + 2\text{SO}_2(\text{g})$	$121.050 - 0.220 T$	$T > 550$
(15)	$\text{S}_2(\text{g}) + 4\text{MnSO}_4 = 4\text{MnO} + 6\text{SO}_2(\text{g})$	$778.091 - 0.986 T$	$T > 789$

Figure 5. Predominant phase diagram as functions of temperature and input $\text{S}_2(\text{g})$ fraction in the S_2 – MnO_2 system.

4. Results and Discussion

4.1. Reaction Mechanism of Manganese Dioxide with Gaseous Sulfur

4.1.1. Phase Transformation during Reduction Roasting

Chemically pure MnO_2 was used to investigate phase transformation. The phase composition of the roasted samples under different conditions is plotted in Figure 6. MnO_2 was absent in all the XRD patterns. Instead, manganese oxides (Mn_2O_3 , Mn_3O_4 , or MnO), manganese sulfate (MnSO_4), and manganese sulfide (MnS) were observed. Nevertheless, the difference between these XRD patterns was distinct. At a fixed roasting temperature of 450°C and S_2/MnO_2 molar ratio of 0.17, the phases in the roasted samples contained Mn_2O_3 , Mn_3O_4 , and MnSO_4 . This implies that MnO_2 was reduced stepwise to form low-valence oxides and MnSO_4 , which is consistent with the results in Table 2 (Equations (4)–(7)). As the S_2/MnO_2 molar ratio increased to 0.25, the peak intensities of Mn_2O_3 and Mn_3O_4 decreased, but MnS was observed distinctly. According to the thermodynamic analysis (Equations (8)–(11)), Mn_3O_4 was preferentially reduced to MnO and MnSO_4 (Equation (9)). This phenomenon is different from the reaction between Mn_3O_4 and solid/liquid sulfur, where MnS was more easily formed [24,25]. The formation of MnS may be attributed to the reaction between MnO and gaseous sulfur (Equations (12) and (13)), and requires further investigation. With an increase in the S_2/MnO_2 molar ratio to 0.50, the formation of MnS intensified. However, the peaks of Mn_3O_4 were still observed in the XRD patterns. The phase composition of the samples roasted at 400°C and 450°C was similar. However, a small amount of MnO was observed in the XRD pattern for roasting at 500°C . An increase in the roasting temperature contributed to the formation of MnO , which is consistent with the results in Table 2. Compared with the thermodynamic analysis, the difference in the phase composition observed experimentally may also be affected by kinetic factors, which were not investigated in this study. Although the boiling point of sulfur was approximately 470°C , sulfur can also sublime below its boiling point. Consequently, the manganese oxides were already reduced at temperatures below 470°C .

Figure 6. XRD patterns of roasted products as functions of roasting temperature and S_2/MnO_2 molar ratio (roasting time: 30 min).

4.1.2. XPS Analysis

XPS was conducted to investigate the electronic structure of the main elements on the surface of the roasted samples. XPS fitting parameters for Mn 2p and S 2p were listed in Table 3. Figure 7 shows the XPS profiles (Mn 2p and S 2p) of the samples obtained at various temperatures. The Mn 2p_{3/2} spectra arise from three valence states, Mn²⁺ (640.4–641.7 eV), Mn³⁺ (641.7–641.9 eV), and Mn⁴⁺ (641.9–642.6 eV) [27,28], which indicates that the manganese oxides were not completely reduced to Mn²⁺. Mn³⁺ and Mn⁴⁺ mainly combined with oxygen to form a Mn–O bond, whereas Mn²⁺ may have combined with oxygen (Mn–O) or sulfur (Mn–S). The XPS results were in line with the XRD results except for the presence of Mn⁴⁺. This difference between the XPS and XRD results may be attributed to the fact that XPS is a surface-sensitive analysis; alternatively, the low content of Mn⁴⁺ may not have been detected by XRD. Furthermore, the effect of roasting temperature on the XPS results for Mn was not significant. This is because XPS is a surface analysis technique. The S 2p profiles of the products contained two types of S species, SO₄^{2−} (168.1–169.6 eV) and S^{2−} (161.4–163.5 eV) [28,29], which indicated the presence of MnSO₄ and MnS. However, S^{2−} was not apparent at temperatures above 500 °C. The results were partly consistent with the XRD patterns and thermodynamic analysis. As discussed before, an increase in the roasting temperature contributed to the formation of MnO.

Table 3. XPS fitting parameters for Mn 2p and S 2p.

Temperature/°C	Type	FWHM/ev	Atomic/%
400	Mn ²⁺	2.00	48.65
	Mn ³⁺	1.98	7.56
	Mn ⁴⁺	1.96	19.51
	SO ₄ ^{2−}	1.32	18.25
	S ^{2−}	1.48	6.03
450	Mn ²⁺	2.00	39.33
	Mn ³⁺	1.98	9.16
	Mn ⁴⁺	1.75	12.59
	SO ₄ ^{2−}	1.18	34.22
	S ^{2−}	1.39	4.70
500	Mn ²⁺	2.00	36.06
	Mn ³⁺	1.98	7.61
	Mn ⁴⁺	1.82	13.89
	SO ₄ ^{2−}	1.16	42.44
550	Mn ²⁺	2.00	39.94
	Mn ³⁺	1.98	5.81
	Mn ⁴⁺	1.98	16.16
	SO ₄ ^{2−}	1.13	38.09

Figure 7. XPS analysis of roasted products as functions of roasting temperature and S_2/MnO_2 molar ratio (roasting time: 30 min).

4.1.3. Morphological Analysis of the Reduced Products

SEM and EDS were used to characterize the microstructure and elemental distribution of the roasted products, respectively. Figure 8 shows the SEM images of the samples roasted under different conditions. Three main phases can be observed, according to the morphology of these samples. The flaky structure belongs to MnO or MnS, because both have similar crystal textures. The larger columnar granule is $MnSO_4$, and the sporadically distributed particles are low-valence manganese oxides. By increasing the roasting temperature, the crystal sizes increased gradually. As the S_2/MnO_2 molar ratio increased, the proportion of the flaky structure increased. This implies that an increase in the amount of sulfur contributed to the formation of MnS. With increasing roasting temperature, the grain size correspondingly increased. Figure 9 shows the EDS profiles of the samples roasted at 450 °C for 30 min with a S_2/MnO_2 molar ratio of 0.25. It was difficult to distinguish the different phases based on the EDS results, as Mn, S, and O were present in all phases. The contents of Mn, S, and O varied widely. Spots 1 and 4 exhibited higher S content, while spots 2 and 3 exhibited lower O content.

Figure 8. SEM images of samples roasted under different conditions.

Figure 9. EDS results of the samples roasted at 450 °C ($S_2/MnO_2 = 0.25$, 30 min).

4.1.4. Discussion of Reaction Mechanism

Based on the thermodynamic calculation and experimental results, the reaction mechanism of MnO_2 with gaseous sulfur is illustrated in Figure 10. The reaction is a typical gas–solid chemical reaction, which can be described by an unreacted nuclear model. During reduction, the gaseous reactant diffused continuously to the surface of the particles, the unreacted core gradually shrank and was wrapped by solid products, and the gaseous products reached the main gas stream through the solid product layer. In general, heating did not destroy the structure of the raw material. Upon heating and reduction, solid sulfur (S_8) sublimated and decomposed to gaseous sulfur with small molecules (S_7 , S_6 ... S_2 , S). MnO_2 was then reduced stepwise to form products in the following order: $Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO \rightarrow MnS$. This reduction was accompanied by the formation of $MnSO_4$. Theoretically, MnO was more easily formed than MnS under the current experimental conditions. However, MnS was inevitably generated as the reductant established contact with MnO . Gaseous sulfur must diffuse through the product layers to react with the unreacted nuclei. Thus, MnS was formed, and could not be reduced further. Reduction was inhibited as the product layer thickened, which hindered the diffusion of gaseous sulfur. In addition, $MnSO_4$ reacted with gaseous sulfur to form MnS/MnO and SO_2 in cases where the reductant was in excess.

Figure 10. Schematic diagram of the reaction mechanism between manganese dioxide and gaseous sulfur.

4.2. Extraction of Mn from Mn Ore

4.2.1. Effect of Roasting Temperature

MnO_2 is insoluble in an acidic environment. Therefore, to extract Mn from manganese oxide ore, MnO_2 must be reduced to a bivalent state. MnO and MnS are acid-soluble and MnSO_4 can be leached by water. Leaching experiments were conducted to evaluate the conversion of MnO_2 to low-valence compounds during roasting. Manganese oxide ore was used as the raw material in the leaching experiments. The roasted products were leached by 1 M H_2SO_4 as well as deionized water. The leaching conditions were fixed according to the literature [24] as follows: a leaching temperature of 25 °C, leaching time of 10 min, liquid/solid ratio of 5, and rotating speed of 200 rpm.

The effect of the roasting temperature on Mn extraction was investigated by maintaining a roasting time of 30 min and S_2/MnO_2 molar ratio of 0.50. The results in Figure 11 indicate that more than 95.0 wt% Mn was leached by acid at temperatures above 400 °C; the leached amount subsequently remained almost constant. When the roasting temperature was increased to 550 °C, the amount of Mn extracted by water leaching increased continuously from 17.5 to 35.9 wt%, indicating that increasing temperature contributed to the formation of MnSO_4 . According to the thermodynamic analysis in Figure 5, for a fixed S_2/MnO_2 molar ratio of 0.50, the solid products were MnS and MnSO_4 , derived from the reaction between $\text{S}_2(\text{g})$ and MnO . Hence, the enhanced Mn extraction by water leaching may be due to kinetic factors arising with increasing roasting temperature.

Figure 11. Effect of roasting temperature on the leaching ratio of Mn (30 min, S_2/MnO_2 : 0.5).

4.2.2. Effect of Roasting Time

The amount of Mn extracted as a function of roasting time is plotted in Figure 12. Reduction roasting was carried out at 450 °C with a S_2/MnO_2 molar ratio of 0.5. The amount of Mn extracted by acid leaching increased from 71.6 to 95.2 wt% as the roasting time increased from 10 to 30 min, and remained almost unchanged after 30 min. Nevertheless, the amount of Mn extracted by water leaching increased continuously to approximately 28 wt% with an increase in roasting time, indicating that more $MnSO_4$ was generated. This may be attributed to the fact that MnO reacted further with $S_2(g)$ to form MnS and $MnSO_4$. The results were in good agreement with the thermodynamic analysis. A roasting time of 30 min was sufficient for the acid leaching of Mn.

Figure 12. Effect of roasting time on the leaching ratio of Mn (450 °C, S_2/MnO_2 : 0.5).

4.2.3. Effect of S_2/MnO_2 Molar Ratio

The effect of the S_2/MnO_2 molar ratio on Mn extraction was investigated by varying the molar ratio from 0.25 to 0.50. Several experiments were conducted at 450 °C for 30 min.

The results in Figure 13 indicate that as the S_2/MnO_2 molar ratio increased from 0.25 to 0.40, the amount of Mn leached by acid increased distinctly from 51.6 to 94.5 wt%. Furthermore, the amount of Mn extracted by water leaching increased from 18.5 to 23.3 wt%. According to our previous studies, even if the manganese oxides were not reduced to Mn^{2+} -bearing compounds, the intermediate oxides (such as Mn_3O_4) would also be dissolved in the acid solution by the following reaction. Thus, a further increase in the amount of sulfur would mildly affect Mn extraction via acid leaching and water leaching.

The chemical composition of the leached residue obtained by acid leaching is plotted in Table 4. The content of MnO_2 was low, at 3.35 wt%, while other components were enriched. Only 3.5 wt% of Fe was extracted, resulting in the enrichment of Fe in the residue and part of Fe_2O_3 has been reduced to Fe_3O_4 . The leached residue can be used as a raw material in ironmaking.

Figure 13. Effect of S_2/MnO_2 molar ratio on the leaching ratio of Mn (450 °C, 30 min).

Table 4. Main chemical composition of the leached residue, wt%.

Composition	MnO_2	Fe_2O_3	Fe_3O_4	SiO_2	CaO	MgO	Al_2O_3
Content	3.35	25.26	45.47	15.02	0.65	0.57	9.78

5. Conclusions

In this study, the reaction mechanism between MnO_2 and gaseous sulfur was investigated in detail. The following conclusions can be drawn:

- (1). Thermodynamically, the reduction of MnO_2 by gaseous sulfur was feasible and easy. Solid sulfur sublimated and decomposed to form small molecules of sulfur gases. The phase composition depended on the temperature and input mole fraction of sulfur.
- (2). MnO_2 was reduced stepwise to low-valence manganese oxides, and manganese sulfate was generated simultaneously. The reaction process could be described by an unreacted nuclear model. The phase composition of the roasted products was complicated and MnS was inevitably formed, although the formation of MnO was thermodynamically easier than that of MnS .
- (3). Mn was extracted by H_2SO_4 solution from manganese oxide ore after reduction by gaseous sulfur. A Mn extraction of 95.2 wt% was achieved in H_2SO_4 solution with a

roasting temperature of 450 °C, roasting time of 30 min, and S₂/MnO₂ molar ratio of 0.40. The Mn extraction in deionized water was 24.3 wt%, while Fe was extracted in traces.

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