





Transactions of Nonferrous Metals Society of China

www.tnmsc.cn



Trans. Nonferrous Met. Soc. China 25(2015) 1677–1684

Manganese extraction by reduction-acid leaching from low-grade manganese oxide ores using CaS as reductant

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Received 6 June 2014; accepted 25 September 2014

Abstract: The extraction of manganese from low-grade manganese oxide ores using CaS derived from CaSO₄ as reductant was investigated. The effects of mass ratio of CaS to ore, reduction temperature, reduction time, liquid to solid ratio (L/S ratio), stirring speed, leaching temperature, leaching time and H_2SO_4 concentration on the leaching rates of Mn and Fe during the reduction–acid leaching process were discussed. The leaching rates of 96.47% for Mn and 19.24% for Fe were obtained under the optimized conditions of mass ratio of CaS to manganese oxide ore 1:6.7, L/S ratio 5:1, stirring speed 300 r/min, reduction temperature of 95 °C for 2.0 h in the reduction process and leaching stirring speed of 200 r/min, H_2SO_4 concentration of 1.5 mol/L, leaching temperature of 80 °C for 5 min in the leaching process. In addition, this process can be employed in the recovery of manganese from various manganese oxide ores, and Mn leaching rate above 95% is obtained.

Key words: manganese; manganese oxide ore; calcium sulfide; reduction; leaching

1 Introduction

Manganese plays an important role in many fields, such as steel production, cell preparation of dietary additives, fertilizers and fine chemicals [1,2]. Among them, most of the manganese is consumed in steelmaking industry acted as an alloying element. However, the shortage and low grade of manganese carbonate ores have become the main problems that restrict the sustainable development of manganese industry. Therefore, it becomes a hot spot to develop an economic and efficient process to recover manganese from manganese oxide ores.

As the manganese oxide ores are stable in dilute sulfuric acid and alkaline media, the reducing condition is necessary to leach manganese from the ores. To date, various routes have been reported in the literature for the reduction leaching of low-grade manganese oxide ores [3,4]. Generally speaking, such ores can be treated either by reduction roasting followed by acid leaching or directly by reductive acid leaching using different reducing agents [5]. leaching include coal, graphite or sulfur [6,7], pyrite [8], and cornstalk [9]. However, the above methods often not only generate plenty of smoke dust, but also require a high reaction temperature. Therefore, those processes for exploiting manganese oxide ores are characterized by high production costs, energy consumption and serious environmental pollution. As for the directly reductive leaching methods, there are also some reduction methods such as pyrite reduction leaching [10,11], oxalic acid reduction leaching [1], methanol reduction leaching [12], sulfur dioxide reduction leaching [13], iron (II) sulphate reduction leaching [14], hydrogen peroxide reduction leaching [2,15], organic biomass reduction leaching [3,16], and biological bacteria reduction leaching [17]. The main problems with these hydrometallurgical processes are the purification of Mn from the leaching solution, high production cost, low leaching rate, etc.

Recently, our research group found that low-grade manganese dioxide ores can be reduced fully by CaS under mild conditions in aqueous solution. And manganese can be easily leached from the reduced product using sulfuric acid. Moreover, the results show that the use of CaS gives lower iron dissolution compared with previous study, which can reduce the cost

The reductants used for reduction roasting-acid

Foundation item: Project (21376273) supported by the National Natural Science Foundation of China; Project (2010FJ1011) supported by the Key Program of Science and Technology of Hunan Province, China

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for separating iron precipitate from leach liquor. In particular, as reported in literature, CaS can be prepared from the industrial byproducts such as phosphogypsum, flue gas desulfurization residues and waste gypsum boards [18,19]. Accordingly, making use of CaS to reduce manganese dioxide ores can not only reduce the cost, but also comply with the requirement of green economy.

In this work, an attempt was made to prepare CaS from $CaSO_4$ and to find out its potential use as reductant for the reduction leaching of manganese from manganese dioxide ores. Using the synthesized CaS and low-grade manganese oxide ore from Hunan, China, as raw material, the effects of reduction and leaching conditions on the leaching rate of manganese were investigated. For proving that this technology can be applied widely due to the nature of CaS rather than the particularity of Hunan manganese ore, experimental condition applicability of CaS as reductant to other types of manganese oxide ores was also researched.

2 Experimental

2.1 Materials

Low-grade manganese oxide ores used in this work were obtained from Hunan Province, China. The samples were crushed and then screened to provide the ore with particle size of less than 75 μ m in advance. The chemical composition of the ore material is given in Table 1, which shows that the manganese grade of the ore is 20.59%. The XRD pattern of the sample, presented in Fig. 1, indicates that manganese mainly exists in the form of MnO₂. CaSO₄ used in this work was analytically pure and bought from Aladdin Industrial Corporation (Shanghai, China). The coal used in the experiment was obtained from Gansu Province, China, and the chemical composition is presented in Table 2. The coal sample was ground and its size range was smaller than 0.147 mm.

2.2 Synthesis of CaS

In this work, the synthesis of CaS was conducted based on the previous study [19,20]. The main chemical reaction about CaS generation between $CaSO_4$ and coal during the roasting is shown in Eq. (1). And the synthesis

Table 1 Major chemical composition of manganese oxide orefrom Hunan Province, China (mass fraction, %)

| Mn | Fe | SiO ₂ | MgO | S |
|--------------------------------|-------|------------------|------|-------|
| 20.59 | 11.49 | 37.63 | 0.75 | 0.29 |
| Al ₂ O ₃ | CaO | | K | Ti |
| 8.31 | 0.70 | 0.89 | | 0.163 |



Fig. 1 XRD pattern of manganese oxide ore

 Table 2 Chemical composition of coal (mass fraction, %)

| С | S | Ash | Volatile matter |
|-------|------|-------|-----------------|
| 72.61 | 0.67 | 16.59 | 60.80 |

procedures are as follows: $CaSO_4$ and coal were firstly mixed at mole ratio of C to $CaSO_4$ being 3.0 in a 30 mL ceramic crucible. When the temperature in the muffle furnace increased from room temperature to 1273 K, the covered ceramic crucible was then placed in the middle of reactor for 2.0 h. After the experiments, the sample residue was collected for further analysis to determine the purity and yield of the CaS. And the purity and yield of the CaS were determined using methylene blue spectrophotometric method according to GB/T 16489– 1996. In addition, the obtained solid products were analyzed by XRD and SEM to investigate and confirm the crystalline phases and morphology of as-synthesized CaS.

$$CaSO_4 + 2C = CaS + 2CO_2 \uparrow \tag{1}$$

2.3 Leaching procedure

In this work, reduction leaching of manganese from low-grade manganese oxide ores was conducted in a two-step process. At first, the low-grade manganese dioxide ore and CaS were added to a 250 mL glass flask containing 50 mL deionized water. The obtained ore slurry was then agitated at the required temperature for certain period. After reaction, the slurry was filtered and the residue was washed with the distilled water. The filter residue was dried at 85 °C for 2 h, and subjected to leaching process described below.

After the reduction was completed, the filter residue was leached in a beaker containing certain H_2SO_4 solution, which was placed into a water bath with mechanical stirring. At the end of each leaching experiment, the leaching solutions were filtered. Manganese in filtrate was estimated by potassium

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periodate spectrophotometric method (GB 11906–1989). The spectrophotometric analysis of iron content was performed at 510 nm using *o*-phenanthroline as color developing agent (GB/T 3049–2006). The leaching rate was calculated by referring the amount of leached metal in the liquor to its original input quantity.

2.4 Characterization

The quantitative chemical composition was determined by X-ray fluorescence (Axios, PANalytical, Holland) on manganese oxide ore and coal used in the experiment. The crystalline phases were determined by XRD (D8 Discover, Bruker, Germany). The morphology and particle size of the crystals were observed by field emission scanning electron microscopy (FE–SEM, Mira3, Tescan, Czech Republic).

3 Results and discussion

3.1 Characterization of synthesized CaS

To further determine the composition of the solid products after the reduction of $CaSO_4$ by coal, the crystalline phases of the solid products were illustrated by XRD (see Fig. 2). It can be seen in Fig. 2 that the products are nearly pure CaS. Meanwhile, the obtained values of purity and yield of CaS are 94.93% and 95.01%, respectively. Therefore, both XRD test and purity data prove that $CaSO_4$ is completely decomposed to generate the target product of CaS.



Fig. 2 XRD pattern of synthesized CaS (Experimental conditions: mole ratio of C to $CaSO_4$ 3.0; reaction time 2.0 h; temperature 1273 K)

The morphology and particle size of the synthesized CaS were observed by FE–SEM. The results are shown in Fig. 3. It clearly shows that only leaf-shaped particles, which are highly dispersed small particles of micrometer scale, were observed for the synthesized CaS. Therefore, as far as could be determined by either X-ray diffraction (XRD) or scanning electron micrograph (SEM) analysis,

the only solid product formed during the induction period was CaS.



Fig. 3 FE–SEM images of synthesized CaS (Experimental conditions: mole ratio of C to CaSO₄ 3.0; reaction time 2.0 h; temperature 1273 K)

3.2 Reduction process

The effects of reduction temperature, mass ratio of CaS to manganese oxide ore, reduction time, liquid to solid ratio (L/S, mL/g) and stirring speed on the leaching rate of Mn were discussed under the following leaching conditions: H_2SO_4 concentration 3.0 mol/L; L/S ratio 5:1; leaching temperature 80 °C; leaching time 30 min and stirring speed 300 r/min.

3.2.1 Effect of reduction time

The effect of reduction time on the leaching of Mn was carried out within the period range from 0.5 to 2.5 h, while all other experimental parameters were kept constant (mass ratio of CaS to manganese oxide ore 1:6.7; L/S ratio 5:1; reduction temperature 95 °C; stirring speed 300 r/min). The data obtained are shown in Fig. 4, which shows that the reaction speed of manganese dioxide is rapid, resulting in an acid leaching rate of Mn of 70.15% after only 0.5 h. With the increase of reduction time, the leaching rates are improved, especially in the initial period of 0.5–2.0 h. At the reduction time of 2.0 h, the leaching rate of Mn reaches 96.47%. When the leaching time is above 2.0 h, there is

no significant difference on leaching rate of Mn. Hence, it can be recommended that the reduction time of 2.0 h would be adequate for the process.



Fig. 4 Effect of reduction time on leaching rate of Mn

As the phase is very complex in the manganese oxide ores as shown by XRD (see Fig. 1), electrolytic manganese dioxide (Guizhou Redstar Developing Co., was employed research the Ltd.) to phase transformation of manganese compounds during the reduction process. Figure 5 demonstrates the XRD patterns of reduced samples obtained at different reduction time of 0.5, 1.0, 1.5, 2.0 and 2.5 h. As displayed in Fig. 5, CaS in the reduced product disappears after the manganese dioxide is reduced with CaS for certain period in aqueous solution. And the disappearance of CaS in XRD pattern is probably due to the following reasons. At 95 °C, the oxidation-reduction reaction between manganese dioxide and CaS is a rapid process. In addition, CaS crystals begin to hydrolyze or dissolve with increasing temperature of aqueous solutions, particularly when the temperature is above 90 °C on the basis of our previous related studies. Therefore, the undesirable emission of H₂S can be avoided in the following acid leaching process. Meanwhile, some new-born compounds, including Mn₃O₄ and Ca(OH)₂, are generated. Mn₃O₄ exists at all reduction time; however, the diffraction peaks of Mn₃O₄ in the reduced samples at longer reduction time (>2.0 h) are stronger than those at shorter reduction time (<1.5 h). It is noteworthy to mention that MnO₂ always exists at 0.5-1.0 h but disappears after the reduction time reaches 1.5 h. The variation trend can be explained by the fact that when the reduction time is up to 1.5 h, MnO₂ can be fully reduced with CaS to form Mn₃O₄. According to the above analysis, the most likely chemical reaction in the reduction process can be represented as follows:

$$2CaS + 3MnO_2 + 2H_2O = Mn_3O_4 + 2Ca(OH)_2 + 2S \quad (2)$$

Meanwhile, based on thermodynamic calculation,

the standard Gibbs free energy ΔG^{Θ} is calculated to be -265 kJ/mol, implying a very strong tendency for this reaction to occur at 95 °C. However, no detectable peaks attributable to sulfur generated from Eq. (2) are observed in the XRD patterns (see Fig. 5). It is speculated that the obtained sulfur is either amorphous or too thin to possess the required long range order to show any crystalline form by X-ray diffraction.



Fig. 5 XRD patterns of manganese dioxide reduced by CaS at different reduction time

The major chemical reaction involved during the leaching process of manganese from the reduced product is as follows:

$$2Mn_3O_4 + 6H_2SO_4 = 6MnSO_4 + 6H_2O + O_2\uparrow$$
(3)

3.2.2 Effect of mass ratio of CaS to manganese oxide ore

Initial experiments were carried out by varying the mass ratio of CaS to manganese oxide ore. The amount of CaS was varied from 0.5 to 2.0 g while keeping the reduction condition as: manganese oxide ore 10 g, L/S ratio 5:1, reduction temperature 95 °C, stirring speed 300 r/min for 2.0 h. Varying the mass ratio of CaS to manganese oxide ore from 1:20 to 1:5, the effect of mass ratio on leaching rate of manganese is shown in Fig. 6.

The leaching rate of Mn increases rapidly with a increase in the mass ratio, but it becomes slow with further increase to 1:6.7 at which 96.47% leaching rate of Mn is obtained. This indicates that almost all of the MnO_2 minerals in the ore are reduced in the reduction process. Therefore, mass ratio of 1:6.7 was used in the subsequent tests.

3.2.3 Effect of L/S ratio

To optimize the effect of L/S ratio on the leaching rate of Mn, the reduction reaction process was conducted with L/S ratio between 3:1 and 12:1 by keeping other conditions constant (mass ratio of CaS to manganese oxide ore 1:6.7; reduction temperature 95 °C; stirring speed 300 r/min; reduction time 2.0 h). The data obtained are given in Fig. 7. Figure 7 shows that as the L/S ratio

increases from 3:1 to 5:1, the leaching rate of Mn increases from 82.16% to 96.47%, and reaches the plateau when the L/S ratio is 5:1. Afterwards, when the L/S ratio is higher than 5:1, the leaching rate of Mn slightly increases. Therefore, a L/S ratio of 5:1 is recommended in this study for the sake of a higher Mn leaching rate.



Fig. 6 Effect of mass ratio of CaS to manganese oxide ore on leaching rate of Mn



Fig. 7 Effect of L/S ratio on leaching rate of Mn

3.2.4 Effect of reduction temperature

In order to study the effect of temperature on the leaching process of Mn from manganese oxide ore, different experiments were carried out in the reduction temperature range of 75–95 °C by keeping other conditions constant (mass ratio of CaS to manganese oxide ore 1:6.7; L/S ratio 5:1; reduction time 2.0 h; stirring speed 300 r/min). The results obtained are illustrated in Fig. 8. As observed, the leaching rate of Mn increases from 45.87% to 96.47% as the reduction temperature increases from 75 °C to 95 °C. This behavior can be explained by the fact that high reduction temperature can accelerate reaction rate between MnO_2

and CaS. Therefore, the reduction temperature of 95 °C was chosen as the optimum condition in the next experiments.



Fig. 8 Effect of reduction temperature on leaching rate of Mn

3.2.5 Effect of stirring speed

Under the experimental conditions of mass ratio CaS to ore 1:6.7, reduction temperature 95 °C for 2.0 h, L/S ratio 5:1, the variation of leaching rate of Mn with the stirring speed is shown in Fig. 9. The results in Fig. 9 show that the leaching rate of Mn increases with the increase of the stirring speed. When stirring speed is below 250 r/min, the leaching rate of Mn increases proximately linearly as the stirring speed increases. The variation trend in the leaching rate of Mn following the increase of stirring speed from 100 r/min to 250 r/min can be explained by the fact that high speed stirring makes MnO₂ contact with CaS fully, as a result, the reduction reaction was accelerated. However, when stirring speed is over 250 r/min, the increase of leaching rate is slow. The leaching rate reaches 96.47% at stirring speed of 300 r/min. Therefore, the stirring speed of 300 r/min was chosen for the subsequent study.



Fig. 9 Effect of stirring speed on leaching rate of Mn

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3.3 Acid leaching process

The effects of H_2SO_4 concentration, stirring speed, leaching temperature and leaching time on the leaching rate of Mn were then investigated. And the L/S ratio used in the leaching process was kept at 5:1 by the consideration of the Mn concentration in the feed solution employed in the electrolytic manganese metal industry. The reduction conditions were as follows: reduction temperature 95 °C, mass ratio of CaS to manganese oxide ore 1:6.7, L/S ratio 5:1, reduction time 2.0 h and stirring speed 300 r/min. The leaching rate of Fe is also considered as it is the main impurity element, which will aggravate purification process subsequently. 3.3.1 Effect of leaching time

The measurement on the effect of leaching time on the leaching rates of Mn and Fe was carried out within the period range from 5 to 60 min, when the stirring speed, leaching temperature and H_2SO_4 concentration were set at 300 r/min, 80 °C and 3.0 mol/L, respectively. The results are plotted in Fig. 10. Figure 10 indicates that the leaching rate of Mn remains unchanged after 5 min, demonstrating that the leaching reaction is very rapid. The leaching rate of Fe increases obviously with the increase of leaching time. Considering the leaching cost in the leaching process, the suitable leaching time is set to be 5 min.



Fig. 10 Effect of leaching time on leaching rates of Mn and Fe

3.3.2 Effect of H₂SO₄ acid concentration

The effects of H_2SO_4 concentration on the leaching rates of Mn and Fe were examined by varying the H_2SO_4 concentration from 0.5 to 3.0 mol/L, when the stirring speed, leaching temperature and leaching time were set at 300 r/min, 80 °C and 5 min, respectively. The results are summarized in Fig. 11. The leaching rates of Mn and Fe in Fig. 11 are both enhanced fast with a increase in the H_2SO_4 concentration from 0.5 to 1.5 mol/L. However, the leaching rate of Mn is almost unchanged when the H_2SO_4 concentration is over 1.5 mol/L, indicating that leaching reaction nearly reaches equilibrium. A H_2SO_4 concentration of 1.5 mol/L corresponds to the maximal leaching rate of Mn being 96.47% and a leaching rate of Fe being only 19.24%. Thus, the most favorable H_2SO_4 concentration is 1.5 mol/L in this work.



Fig. 11 Effect of H_2SO_4 concentration on leaching rates of Mn and Fe

3.3.3 Effect of leaching temperature

Fixing the H₂SO₄ concentration 1.5 mol/L, leaching time 5 min and stirring speed 300 r/min, the influence of leaching temperature on the leaching rate was investigated and presented in Fig. 12. It is observed that as the temperature increases from 40 °C to 80 °C, the leaching rate of Mn increases dramatically from 41.50% to 96.47%. This behavior can be explained by the fact that with the rise of leaching temperature, the chemical reaction (Eq. (3)) is accelerated and the leaching rate is also improved. When the leaching temperature is above 80 °C, the leaching rate of Mn increases slightly, and its maximum nearly keeps constant. Meanwhile, when temperature increases from 40 °C to 95 °C, the leaching rate of Fe increases from 14.54% to 20.02%. Accordingly, considering the equipment and leaching cost, a leaching



Fig. 12 Effect of leaching temperature on leaching rates of Mn and Fe

temperature of 80 $^{\circ}\mathrm{C}$ is recommended for subsequent tests.

3.3.4 Effect of stirring speed

The test about the effect of stirring speed on leaching rates of Mn and Fe from the manganese ore was carried out in stirring speed range from 50 to 300 r/min at 1.5 mol/L H₂SO₄, leaching temperature 80 °C and leaching time 5 min. The results obtained in Fig. 13 show that the leaching rates of Mn and Fe increase with the increase of the stirring speed until it reaches 200 r/min. The leaching rates of Mn and Fe increase from 75.60% and 10.56% to 96.47% and 19.24%, respectively. However, when the stirring rate is above 200 r/min, there is no significant difference on leaching rates of Mn and Fe. Therefore, a stirring speed of 200 r/min is recommended in this work.



Fig. 13 Effect of stirring speed on leaching rates of Mn and Fe

3.4 Reduction-acid leaching manganese of other manganese oxide ore

In our research, the novel process was applied to other types of manganese oxide ores such as Guanxi ore (Guangxi, China) and manganese anode mud (Hunan, China). The reduction leaching of manganese oxide ores was carried out under conditions of 10 g ore, reduction temperature 95 °C, L/S ratio 5:1, reduction stirring speed 300 r/min for 2.0 h, leaching stirring speed 200 r/min for 5 min, H₂SO₄ concentration 1.5 mol/L, and leaching temperature 80 °C. The results are shown in Table 3. The amount of CaS for these materials varied to optimize the leaching rate. The amount of CaS corresponding to the maximum leaching rate shows that the amount of the required CaS is dependent on the manganese content of ore and decreases with the decrease in Mn content. As can be seen from Table 3, both leaching rates of Guanxi ore and manganese anode mud can reach above 95%. These results indicate that this process can be applied to the recovery of manganese from manganese ore, and is promising to be utilized widely in manganese industry.

Although more detailed works need to be done

before practical applications can be realized, we believe that this process would be a key technology that offers novel solutions to reduction leaching of manganese oxide ores in an economical and efficient process.

 Table 3 Reduction-acid leaching results of different manganese oxide ores

| Manganese ore | Mass ratio of CaS to manganese oxide ore | Leaching rate of Mn/% |
|--|--|--------------------------|
| Guangxi ore (26.24% Mn, mass fraction) | 0.18 | 95.68 |
| Manganese anode mud (49.39% Mn, mass fraction) | 0.32 | 98.62 |

4 Conclusions

1) Using coal as a reducer, $CaSO_4$ can be completely decomposed into the target product of CaS. And the purity and yield of CaS are up to 94.93% and 95.01%, respectively.

2) Manganese dioxide in the manganese oxide ores can be reduced fully by CaS, forming Mn_3O_4 , at only 95 °C. CaS cannot be detected in the reduced product, so, the harmful H₂S gas is avoidable in the following acid leaching process.

3) The optimal conditions for reduction–acid leaching low-grade manganese ores are determined as follows: the reduction temperature 95 °C for 2.0 h, mass ratio of CaS to manganese oxide ore 1:6.7, L/S ratio 5:1, stirring speed 300 r/min in the reduction reaction process and H_2SO_4 concentration 1.5 mol/L, leaching temperature of 80 °C for 5 min, stirring speed 200 r/min in the leaching process. The Mn and Fe leaching rates of 96.47% and 19.24%, respectively, are obtained under the above optimal conditions.

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以硫化钙为还原剂还原-酸浸提取 低品位氧化锰矿中的锰元素

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摘 要:以CaSO₄制备得到的CaS为还原剂,研究氧化锰矿的还原-酸浸过程,考察硫化钙与矿石的质量比、还原温度、还原时间、液固比、搅拌速率、浸出温度、浸出时间和H₂SO₄浓度对氧化锰矿中锰及铁浸出率的影响。 结果表明:优化的还原工艺条件为硫化钙与矿石质量比1:6.7、液固比5:1、搅拌速率300 r/min、还原温度95 ℃、 还原时间2.0 h;酸浸工艺条件为搅拌速率200 r/min、H₂SO₄浓度1.5 mol/L、浸出温度80 ℃、浸出时间5 min。 在此优化条件下,锰的浸出率达到96.47%,而铁的浸出率仅为19.24%。该工艺可以应用于不同类型氧化锰矿中 锰的提取,且锰的浸出率均高于95%。

关键词: 锰; 氧化锰矿; 硫化钙; 还原; 浸出

(Edited by Wei-ping CHEN)

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