

Article

# Removal of Phosphorus from High-Phosphorus Manganese Ores by Ammonia-Ammonium Carbonate Leaching Method

Zhongbing Tu, Xiaoping Liang \*, Yu Wang and Chengbo Wu

College of Materials Science and Engineering, Chongqing University, Chongqing 400030, China; tu.zhongbing@163.com (Z.T.); wangyu@cqu.edu.cn (Y.W.); wuchengbo@cqu.edu.cn (C.W.)

\* Correspondence: xpliang@cqu.edu.cn; Tel.: +86-023-65127306

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**Abstract:** High-phosphorus manganese ores provide an important source of manganese, which is regarded as an irreplaceable material in the steel industry. The ammonia-ammonium carbonate leaching method was proposed for the removal of phosphorus and extracting manganese from high-phosphorus manganese ore, both effectively and environmentally. To explore the dissolution behavior of phosphorus and manganese in the ammonia-ammonium carbonate solution, the effect of the ammonia-to-ammonium carbonate concentration ratio, the leaching temperature, and the liquid-to-solid ratio on manganese extraction and dephosphorization rate were investigated. In addition, the composition of precipitated manganiferous sample, which was obtained from high-phosphorus manganese ores by ammonia-ammonium carbonate leaching process, was also studied. The results indicated that more than 99.2% phosphorus was removed and more than 83.5% of manganese was extracted by ammonia-ammonium carbonate leaching under the following conditions: ammonia to ammonium carbonate concentrations: 14:2 mol/L; liquid/solid ratio: 5:1 mL/g; leaching temperature: 25 °C; The precipitated manganiferous sample has little impurities, Mn% is 44.12%, P% is 0.02%, P/Mn = 0.00045.

**Keywords:** manganese; leaching; ammonia; ammonium carbonate

## 1. Introduction

Phosphorus is a harmful element for most types of steel, and its presence in iron sharply deteriorates the plasticity, toughness, and weldability of steel [1–3]. Steelmaking process has strict requirements on the phosphorus content of raw materials. As the main raw material for smelting, ferro-manganese alloy manganese ore is massively used as a deoxidizer and alloy additive in steelmaking. High phosphorus content of manganese ore will lead to the quality of ferro-manganese alloy cannot meet the specification for steelmaking. Large quantities of high-phosphorus manganese ores have been treated as waste. These high-phosphorus manganese ores not only occupy a large amount of land, but also pollute the soil and water due to the infiltration of harmful elements in the minerals [4,5]. Therefore, finding out an effective method of making use of these high-phosphorus manganese ore is meaningful for resource utilization and environmental protection.

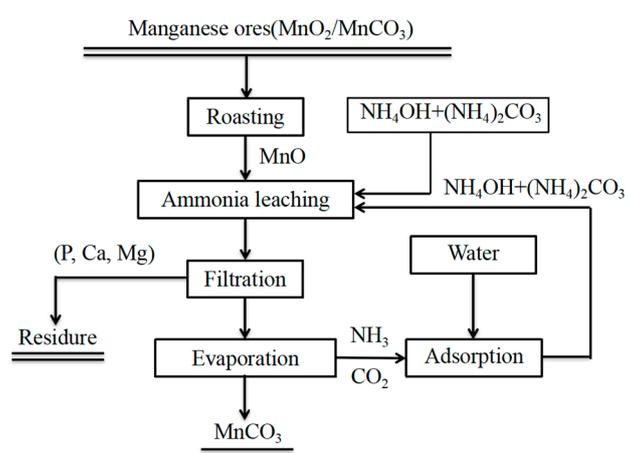
Removal of phosphorus is the key factor in treating these high-phosphorus manganese ore resources. Several methods have been developed for phosphorus removal, such as magnetic separation, acid leaching, ammonia-ammonium carbonate leaching, etc.

Magnetic separation is a method to remove phosphorus and improve manganese grade of high-phosphorus manganese ore, and it relies on a differences in magnetic susceptibility of manganese and phosphorus [6]. Hu studied the high gradient magnetic separation technology for treatment

with high phosphorus manganese ores from Huayuan, manganese ore grade improved from 23.60% to 27.50%, while the phosphorus content reduced from 0.17% to 0.14% [7]. Su studied magnetic separation–flotation method to separate manganese from high phosphorus manganese ores from Hubei, where manganese ore grade improved from 19.08% to 30.04%, while the phosphorus content reduced from 2.48% to 0.12% [8]. A portion of phosphorus can be removed by magnetic separation, but this method cannot remove phosphorus completely. Because the phosphorus-bearing minerals were intimately intermixed in the fine size in high-phosphorus manganese ores, it was hard to separate manganese oxides and phosphorus-containing phase by magnetic separation.

Acid leaching is a method to remove phosphorus and improve manganese grade of high-phosphorus manganese ore, and it relies on a difference in acid solubility of manganese and phosphorus. Phosphorus in manganese ore occurs as apatite, which is soluble in acid solution, while manganese oxides are insoluble, so that phosphorus can be removed from high-phosphorus manganese ore by acid leaching. S. B. Kanungo investigated acid leaching high-phosphorus braunite ores (mainly of  $\text{Mn}_2\text{O}_3$ ) and found their phosphorus content reduced to 70% to 90% [9,10]. Zhang studied magnetic separation-acid leaching of high-phosphorus rhodochrosite ores (mainly of  $\text{MnCO}_3$ ), manganese ore grade improved from 19.83% to 40.15%, while the phosphorus content reduced from 0.31% to 0.15% [11]. However, there are some problems with the acid leaching method. In addition to phosphorus, many other acid soluble substances, such as  $\text{CaCO}_3$  and  $\text{MgCO}_3$  are dissolved in acid solution, and the complex composition of waste liquid makes it difficult to dispose. The discharge of phosphorus-containing wastewater may cause environmental problems [12].

Ammonia-ammonium carbonate leaching is another method to remove phosphorus and improve the manganese grade of high-phosphorus manganese ore. In ammonia-ammonium carbonate leaching process, manganese and manganese monoxide can be dissolved as manganese amine complexes, but phosphorus and other impurities are insoluble in ammonia-ammonium carbonate solution, thus, phosphorus and other impurities can be separated with manganese. The flow sheet of ammonia-ammonium carbonate leaching process is shown in Figure 1. Manganese ores were roasted for converting  $\text{MnO}_2$  and  $\text{MnCO}_3$  into  $\text{MnO}$ ,  $\text{MnO}$  was then leached in the ammonia-ammonium carbonate solution as manganese amine complexes. By evaporating the leachate, the carbamate complexes were decomposed into  $\text{MnCO}_3$  and  $\text{NH}_3$ . The  $\text{MnCO}_3$  is precipitated from the leachate and  $\text{NH}_3$  is completely absorbed by water. Leaching agent can be recycled and barely wastewater is generated making this process environmentally.



**Figure 1.** Flow sheet of ammonia-ammonium carbonate leaching process.

In recent years, due to its lower toxicity, easier recovery and better selectivity, ammonia-ammonium carbonate leaching has been looked upon as a possible option for extracting manganese by researchers [13]. The literature review of ammonia-ammonium carbonate leaching is present in Table 1.

**Table 1.** The research status of ammonia-ammonium carbonate leaching of manganese.

Researchers	Year	Object	Results	Reference
Heindl; Ruppert; Skow; Conley	1955	Open-hearth slag	Ferromanganese product suitable for use as blast furnace feed was produced.	[14]
Mcintosh; Baglin	1992	BOF slag	About 80% of the manganese could be extracted.	[15]
Chen	1994	High-iron manganese ore	Manganese extraction reaches 59.9% to 64.8%.	[16]
Chen; Yi	2004	Low-grade manganese ore	Manganese extraction reaches 81.5% to 91.2%.	[17]

The ammonia-ammonium carbonate leaching was studied for steel slags to extract manganese. The U.S. Bureau of Mines investigated ammonia-ammonium carbonate leaching method to recover manganese from open-hearth slag, and manganese was dissolved as its amine complexes. By distilling the ammonia out of the solution, the manganese amine complexes were precipitated from the ammoniacal solution as insoluble manganese carbonate salts [14]. McIntosh and Baglin investigated the ammonia leaching method to recover manganese from several BOF (basic oxygen furnace) slags, the investigation showed that about 80% of the manganese could be extracted [15]. The ammonia-ammonium carbonate leaching was also studied for high-phosphorus manganese ores to extract manganese. Chen investigated ammonia-ammonium carbonate leaching of high-iron manganese ore to extract manganese, and manganese extraction reached 59.9% to 64.8% [16]. Chen and Yi studied the ammonia-ammonium carbonate leaching of low-grade manganese ore to extract manganese, and the results indicated that ammonia to ammonium carbonate concentration ratio, leaching temperature, liquid to solid ratio and leaching time had a significant influence on manganese extraction [17]. As mentioned above, the research focuses on the extraction of manganese from steel slags, high-iron manganese ores, or low-grade manganese ores. However, little study has been reported for ammonia-ammonium carbonate leaching of high-phosphorus manganese ores. Especially, the separation effect of phosphorus and manganese is not clear about the treatment in high-phosphorus manganese ores by ammonia-ammonium carbonate leaching method.

To explore the dissolution behavior of phosphorus and manganese from high-phosphorus manganese ore by the ammonia-ammonium carbonate leaching, in this paper, we studied the phosphorus and manganese leaching efficiency in ammonia-ammonium carbonate solution. The effect of ammonia to ammonium carbonate concentration ratio, leaching temperature and the liquid to solid ratio on manganese leaching efficiency and phosphorus leaching efficiency were discussed. In addition, the composition of precipitated manganiferous sample, which is obtained by ammonia-ammonium carbonate leaching was detected.

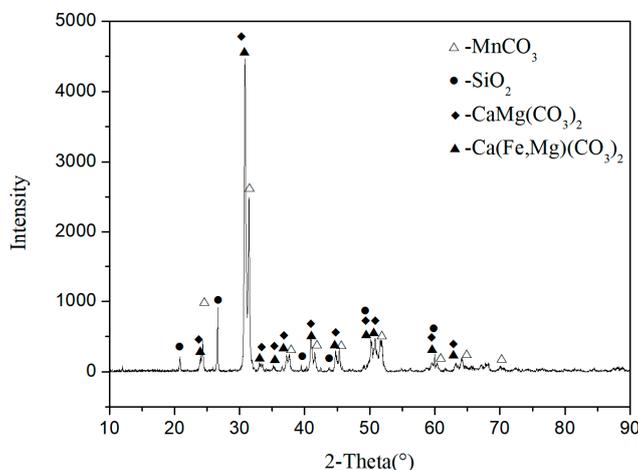
## 2. Material and Experimental Procedure

### 2.1. Materials

The manganese ore sample used in this study was obtained from Sichuan Province, China. The chemical composition was determined by X-ray fluorescence (XRF) analysis (Shimazu XRF-1800, Kyoto, Japan). The chemical analysis of manganese ore sample is listed in Table 2. The mass fraction of manganese and phosphorus is 17.83%, and 0.4%, respectively, P/Mn = 0.224, the result reveals the material is a typical high-phosphorus manganese ore. The phase analysis of high-phosphorus manganese ore was characterized via X-ray diffraction (XRD) (Shimazu XRD-6000, Japan). The XRD pattern was shown in Figure 2. The XRD pattern shows the ore is mainly composed by rhodochrosite, dolomite, ankerite and a small quantity of quartz.

**Table 2.** Chemical compositions of high-phosphorus manganese ore (mass fraction, %).

Element	Mn	Ca	Si	Mg	Fe	S	Al	P
Content	17.83	12.60	3.05	4.25	1.24	0.51	1.30	0.40

**Figure 2.** X-ray diffraction (XRD) pattern of high-phosphorus manganese ore.

## 2.2. Experimental

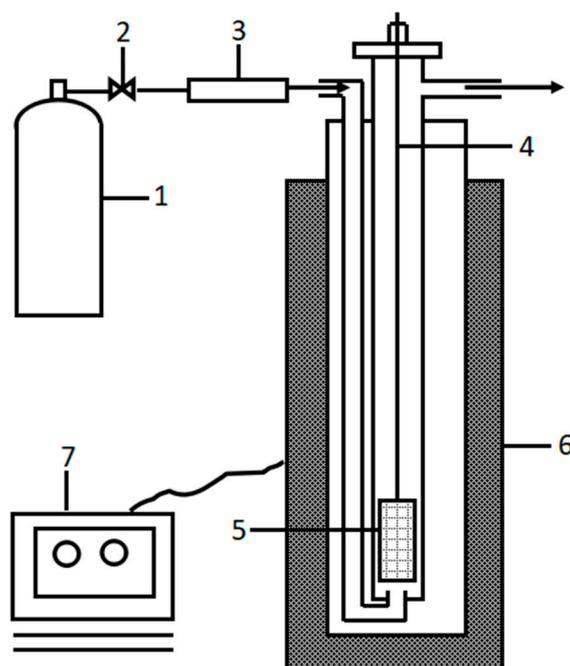
As shown in Figure 1, the ammonia-ammonium carbonate leaching process mainly include roasting, ammonia-ammonium carbonate leaching and evaporation. In order to investigate the separation effect of manganese and phosphorus in ammonia-ammonium carbonate leaching process, the experiments of roasting, ammonia-ammonium carbonate leaching, and evaporation were conducted.

### 2.2.1. Roasting Procedure

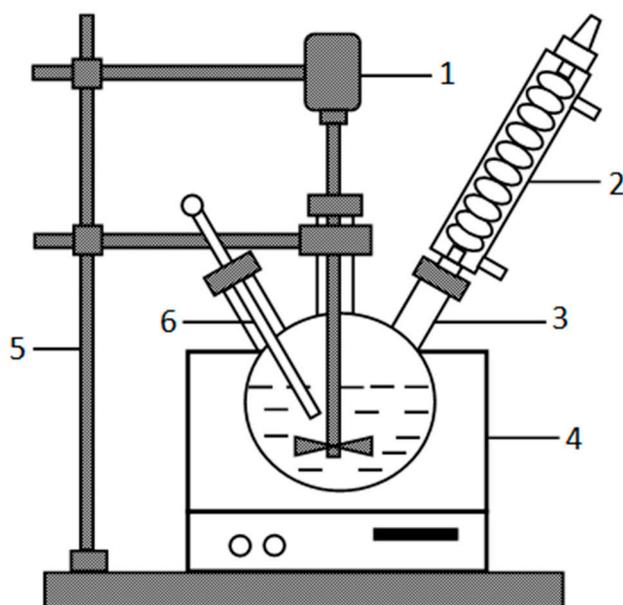
Roasting of the high-phosphorus manganese ore sample was carried out in a tube type resistance furnace. In each test, 100 g high-phosphorus manganese ore sample was put in an alundum crucible and the alundum crucible was heated at 650 °C for 1 h under a flow of nitrogen. The sketch of tube type resistance furnace is shown as Figure 3. To prevent manganese monoxide from being oxidized, the nitrogen gas was passed into the furnace as the heating process began. Cooling was also conducted under a nitrogen gas flow.

### 2.2.2. Leaching Procedure

A sum of 50 g roasted sample was leached in a three-neck spherical glass reactor at atmospheric pressure. The three-neck spherical glass reactor equipped with a mechanical stirrer, a temperature control unit and a cooler, the reactor is shown in Figure 4. Specific concentration of ammonia-ammonium carbonate solution was placed into the three-neck spherical glass reactor. When the desired stirring speed and reaction temperature were attained, 50 g roasted product was added to the ammonia-ammonium carbonate solution. After leaching for a certain time, the mixture is filtered. Manganese and phosphorus in residue was detected by perchloric acid ammonium ferrous sulfate titration and bismuth-phosphomolybdenum blue spectrophotometric method, respectively [18].



**Figure 3.** Sketch of tube furnace: 1—gas bottle; 2—reducing valve; 3—flowmeter; 4—thermocouple; 5—crucible; 6—vertical electro-thermal furnace; 7—temperature controller.



**Figure 4.** Sketch of leaching reactor: 1—mechanical stirrer, 2—cooler, 3—three-neck spherical glass reactor, 4—temperature control unit, 5—iron shelf, 6—thermometer.

This paper focuses on exploring the behavior of P and Mn in ammonia-ammonium carbonate leaching process. Ammonia to ammonium concentration, leaching temperature and liquid to solid ratio were employed as the variables in this leaching experiment. Because ammonia to ammonium concentration, leaching temperature, and the liquid to solid ratio have a significant influence on metal extraction [17,19–21]. Table 3 listed the experimental conditions to examine the effect of ammonia to ammonium concentration (14:0 to 14:3), leaching temperature (15 °C to 55 °C), and liquid to solid ratio (3:1 to 8:1) on the extraction of manganese and phosphorus. The leaching of manganese and phosphorus are primary indicators to evaluate the separation effect of manganese and phosphorus.

**Table 3.** Design of experimental condition in this study.

Number	Ammonia to Ammonium Concentration Ratio	Leaching Temperature (°C)	Solid to Liquid Ratio
1	14:0	25	5:1
2	14:0.5	25	5:1
3	14:1	25	5:1
4	14:1.5	25	5:1
5	14:2	25	5:1
6	14:2.5	25	5:1
7	14:3	25	5:1
8	14:2	15	5:1
9	14:2	25	5:1
10	14:2	35	5:1
11	14:2	45	5:1
12	14:2	55	5:1
13	14:2	25	3:1
14	14:2	25	4:1
15	14:2	25	5:1
16	14:2	25	6:1
17	14:2	25	7:1
18	14:2	25	8:1

The leaching efficiency of Mn was calculated by the follow formula:

$$\phi = \left(1 - \frac{\omega \times m_1}{17.83 \times m_2}\right) \times 100\% \quad (1)$$

$\phi$ —manganese efficiency, %;  $\omega$ —manganese mass fraction in residue, %;  $m_1$ —mass of residue, g;  $m_2$ —mass of raw material, g.

The leaching efficiency of P was calculated by the follow formula:

$$\eta = \left(1 - \frac{\omega \times m_1}{0.4 \times m_2}\right) \times 100\% \quad (2)$$

$\eta$ —phosphorus efficiency, %;  $\omega$ —phosphorus mass fraction in residue, %;  $m_1$ —mass of residue, g;  $m_2$ —mass of raw material, g.

The dephosphorization rate was calculated by the follow formula:

$$\mu = 100\% - \eta \quad (3)$$

$\mu$ —dephosphorization rate, %;  $\eta$ —phosphorus recovery, %.

### 2.2.3. Evaporation Procedure

The separation effect of P and Mn can also be evaluated according to the chemical composition of precipitated manganiferous sample obtained by evaporation. After leaching for a certain time, the mixture is filtered. The leachate was heat by magnetic stirrer with a temperature controller at 90 °C in 30 min. The magnetic stirrer is shown as Figure 5. The main reaction during evaporation is shown as Equation (4). The composition of the precipitated manganiferous sample was detected by XRF and

XRD analysis. It should be noted that the precipitated manganese sample is the final product of the ammonia-ammonium carbonate leaching process.

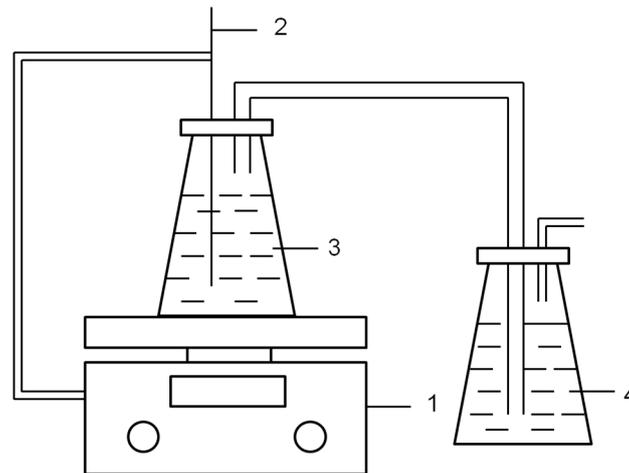
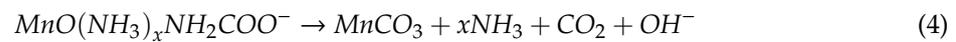


Figure 5. Sketch of evaporation reactor: 1—magnetic stirrer, 2—thermocouple, 3—leachate, 4—water.

### 3. Results and Discussion

#### 3.1. The Phases of Roasted Sample

The X-ray diffraction (XRD) patterns of roasted product are shown in Figure 6. Compared with Figure 2, it revealed manganese carbonate was converted into manganese monoxide by roasting. Dolomite, ankerite and quartz remain as impurities in roasted sample. The main reaction in roasting process can be expressed as Equation (5). The phase analysis indicated the roasted sample can be used in the following leaching process.

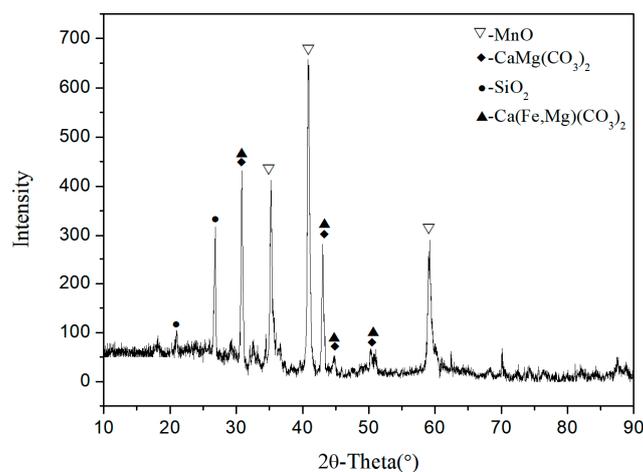
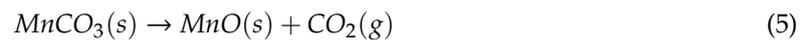


Figure 6. XRD pattern of roasted product.

### 3.2. Effect of the Ammonia to Ammonium Carbonate Concentration Ratio on Mn and P Leaching Efficiency

The effect of ammonia to ammonium carbonate concentration ratio on Mn leaching efficiency is shown in Figure 7. Mn extraction is only 4.8% and 5.3% in 14 mol/L pure ammonia solution and in 3 mol/L pure ammonium carbonate solution, respectively. Keeping the concentration of ammonia of 14 mol/L, and increasing ammonium carbonate concentration from 0 to 2.5 mol/L, Mn extraction increases quickly from 4.8% to 82.2%. The results indicated that Mn leaching efficiency was greatly affected by ammonia to ammonium carbonate concentration ratio. The MnO was difficult to dissolve in pure ammonia or pure ammonium carbonate solution, while it dissolved easily in ammonia-ammonium carbonate solution. This result is consistent with McIntosh [15] and Bingöl [21].

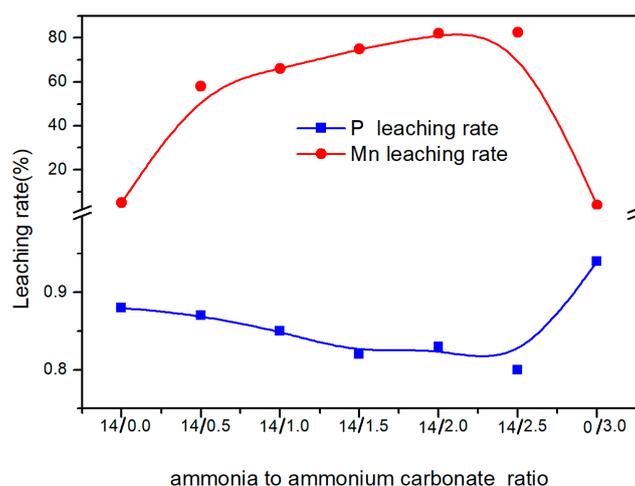


Figure 7. Effect of ammonia/ammonium carbonate on Mn and P leaching rate.

The effect of ammonia to ammonium carbonate concentration ratio on pH of solution is shown in Figure 8a. 14 mol/L pure ammonia solution and 3 mol/L pure ammonium carbonate solution has a pH of 12.6 and 9.2, respectively. Keeping the solution at an ammonia concentration of 14 mol/L, increasing ammonium carbonate concentration from 0.5 mol/L to 2.5 mol/L, the pH of the solution slightly changed from 10.5 to 10.3. This is because the mixture of ammonia and ammonium carbonate formed a buffer solution, and the pH of buffer solution changes slowly during leaching ( $\pm 0.5$ ) [22,23]. Yu studied the Eh-pH of Mn-NH<sub>3</sub>-H<sub>2</sub>O, and he found the manganese amine complexes were stable when the pH of solution in the range of 8.2 to 10.8 [24]. The Eh-pH of Mn-NH<sub>3</sub>-H<sub>2</sub>O is shown in Figure 8b. The pH of ammonia-ammonium carbonate solution in the experiment was in the range of 10.3 to 10.5, this was the reason why MnO can be easily dissolved in ammonia-ammonium carbonate solution.

As shown in Figure 7, the P extraction was less than 1% under all experimental conditions. The results indicated that P was hardly to be dissolved in ammonia-ammonium carbonate solution. The P in the high-phosphorus existed in the form of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. During ammonia-ammonium carbonate leaching, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> cannot react with NH<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub> to produce soluble ammonium phosphate. Due to the fact that the solubility product constant ( $K_{sp}$ ) of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> ( $2.07 \times 10^{-29}$ , at 25 °C) is much smaller than  $K_{sp}$  of CaCO<sub>3</sub> ( $2.8 \times 10^{-9}$ , at 25 °C) [25]. Therefore, the solubility of P is quite low in ammonia-ammonium carbonate solution.

In a word, the Mn extraction is much higher than P extraction under all experimental conditions so that it is feasible to separate Mn with P by ammonia-ammonium carbonate leaching. It seems the solution with ammonia to ammonium carbonate concentration ratio as 14:2 is suitable for extracting Mn and removing P.

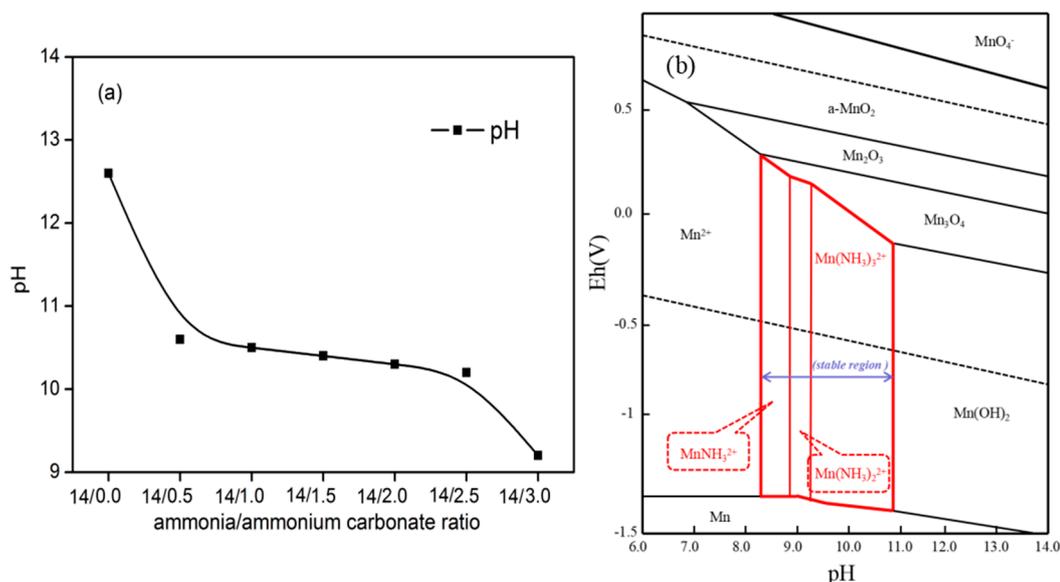


Figure 8. (a) Effect of ammonia/ammonium carbonate on pH. (b) The Eh-pH of Mn-NH<sub>3</sub>-H<sub>2</sub>O.

### 3.3. Effect of Leaching Temperature on Mn and P Leaching Efficiency

Leaching temperature has important effect on Mn and P leaching rate as shown in Figure 9. Mn extraction increases from 78.5% to 83.5% when leaching temperature rises from 15 °C to 25 °C. When leaching temperature is more than 25 °C, Mn extraction obviously decreases.

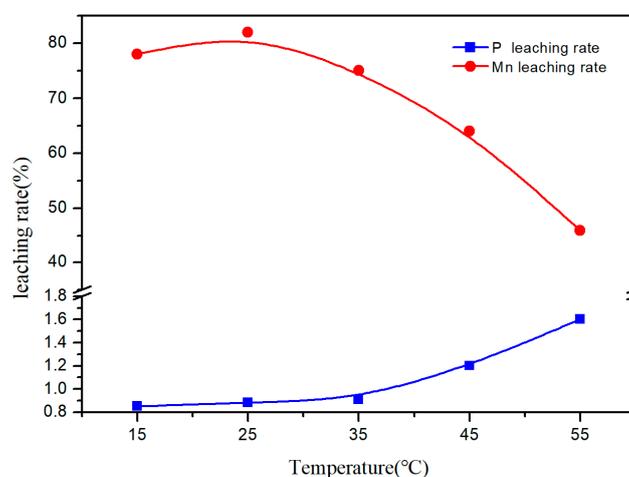


Figure 9. Effect of leaching temperature on Mn and P extraction.

The leaching reaction is shown as Equation (6). The leaching reaction is exothermic, increasing temperature is not conducive to the leaching reaction [26]. In addition, the volatility of NH<sub>3</sub> increases with temperature increasing. The small amount loss of NH<sub>3</sub> decreased the stability of manganese amine complexes so that manganese carbonate was precipitated out of the solution [27]. The precipitated manganese carbonate entered the residue resulted in lowering the Mn extraction. Leaching temperature over 25 °C is unfavorable to extract Mn.



The P extraction increases with leaching temperature increases. When leaching temperature increases from 15 °C to 35 °C, P extraction slightly increases from 0.83% to 0.92%. When leaching temperature above 35 °C, P extraction increases significantly from 0.92% to 1.61%. Devuyt studied

the solubility of phosphate in the ammonia-ammonium carbonate solution, and he found solubility of phosphate was very low below 35 °C, while, phosphate solubility increased rapidly with increasing temperature [27]. The results indicated that the increasing of the leaching temperature will lead to more phosphorus entering the solution, resulting in incomplete separation of phosphorus and manganese. Elevating the leaching temperature over 25 °C is unfavorable to extract Mn and remove P, ammonia-ammonium carbonate leaching process can be conducted at 25 °C.

#### 3.4. Effect of Liquid to Solid Ratio on Mn and P Leaching Efficiency

The effect of liquid to solid ratio on the Mn extraction was investigated in the range of 3:1~8:1. Kept the amount of solid constant, and liquid volume was changed to obtain the desired liquid to solid ratio during the experiments.

The results are presented in Figure 10. The Mn extraction increases from 56.2% to 81.3% with liquid/solid ratio increases from 3:1 to 5:1. Continue to increase the liquid-solid ratio from 5:1 to 8:1, Mn extraction almost unchanged.

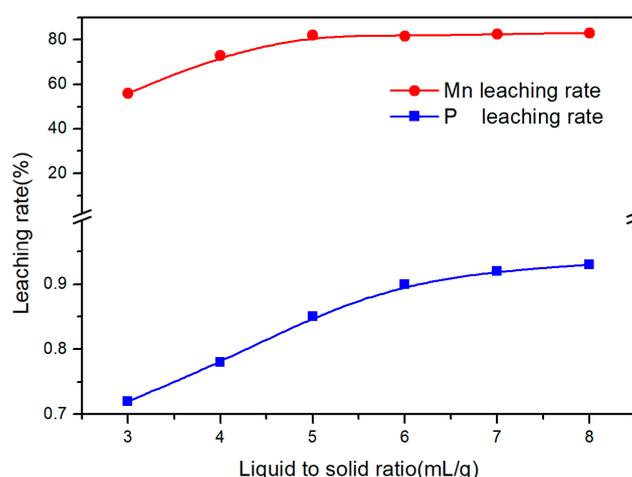


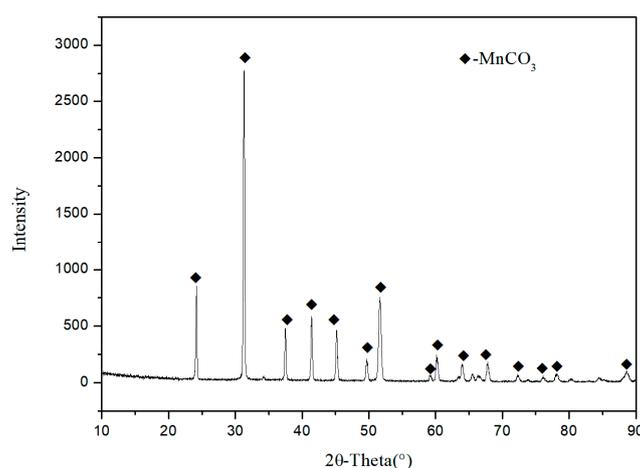
Figure 10. Effect of liquid to solid ratio on Mn and P extraction.

Under the condition of a fixed ammonia and ammonia carbonate concentration, the increases of liquid to solid ratio means more ammonia and ammonium ions in the solution, resulting in increasing the probability of leaching reaction. However, too much liquid will lower the manganese concentration in the solution, which is detrimental to the precipitation of manganese carbonate in the subsequent evaporation procedure [28]. The P extraction increases with liquid to solid ratio increases from 3:1 to 8:1. Increases liquid to solid ratio lead to more P enters the ammonia-ammonium carbonate solution. To maximize the recovery of Mn and reduce the dissolution of P, the suitable liquid to solid ratio is selected to be 5:1.

#### 3.5. The Composition of Precipitated Manganiferous Sample

The separation effect of P and Mn can be evaluated according to the chemical composition of precipitated manganiferous sample obtained by evaporation. The phase and chemical composition of the precipitated manganiferous sample is shown in Figure 11, and Table 4, respectively.

The precipitated manganiferous sample is the final product of ammonia-ammonium carbonate leaching, and it is mainly composed of  $\text{MnCO}_3$  ( $\text{MnCO}_3\%$  is 92.25%, Mn% is 44.12%). There is little impurities in the precipitated manganiferous sample (P% is 0.02%, P/Mn = 0.00045). A very small fraction of the P had gone into manganese product, the vast majority of P (more than 99.2%) had been removed. The results indicated that ammonia-ammonium carbonate leaching has good separation effect of phosphorus and manganese.



**Figure 11.** The XRD pattern of manganese product.

**Table 4.** The Chemical compositions of manganese product (mass fraction, %).

Component	Mn	MnCO <sub>3</sub>	Fe	P	CaCO <sub>3</sub>	MgCO <sub>3</sub>	Si
Content	44.12	92.25	-	0.02	3.42	1.85	-

#### 4. Conclusions

The ammonia-ammonium carbonate leaching method was investigated to remove phosphorus from high-phosphorus manganese ores. The dissolution behavior of phosphorus and manganese in the ammonia-ammonium carbonate solution was explored. The effects of ammonia to ammonium carbonate concentration ratio, leaching temperature and the liquid to solid ratio on manganese extraction and dephosphorization rate were discussed. Moreover, the composition of precipitated manganese sample obtained by evaporation was detected. Based on the lab-scale experimental study, the following conclusions can be arrived at:

(1) The ammonia-ammonium carbonate leaching method is an effective way to remove phosphorus and extract manganese for high-phosphorus manganese ores. More than 83.5% of manganese could be extracted and more than 99.2% of phosphorus could be removed from high-phosphorus manganese ores by ammonia-ammonium carbonate leaching.

(2) The ammonia to ammonium carbonate concentration ratio, liquid to solid ratio and leaching temperature appear to be critical process parameters when ammonia-ammonium carbonate leaching method was used to remove phosphorus from high-phosphorus manganese ores. The appropriate leaching conditions is ammonia to ammonium carbonate concentrations ratio: 14:2; liquid to solid ratio: 5:1 mL/g; leaching temperature: 25 °C.

(3) Manganese product achieved by ammonia-ammonium carbonate leaching has little impurity, its main component is MnCO<sub>3</sub>, MnCO<sub>3</sub>% is 92.25%, Mn% is 44.12%, P% is 0.02%, P/Mn = 0.00045.

This work has laid the foundation for the industrial application of ammonia-ammonium carbonate leaching and provided new insight in to treat with high-phosphorus manganese ores. The NH<sub>3</sub> can be recycled into leaching process and barely wastewater is generated making ammonia-ammonium carbonate leaching method environment-friendly. The future research will focus on carrying out larger scale experiments on ammonia-ammonium carbonate leaching.

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**Conflicts of Interest:** The authors declare they have no conflict of interest.

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