

RECOVERY OF PURE $MnSO_4$ BY CRYSTALLIZATION AFTER SEPARATION OF Fe(III) AND Zn(II) FROM THE REDUCTIVE LEACHING SOLUTION OF MANGANESE DUST CONTAINING Mn_3O_4

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Abstract

Manganese dust generated during the production of ferroalloys contains iron and zinc oxides together with other minor oxides. Pure manganese compounds can be recovered from the leaching solution of the manganese dust by removing the impure ions. In this work, sulfuric acid and ferrous sulfate were employed as leaching and reducing agents for the manganese oxides in the dust. First, the leaching conditions for complete dissolution of the manganese oxides were investigated by varying the concentration of sulfuric acid and ferrous sulfate, and pulp density. Second, after oxidizing Fe(II) to Fe(III) by hydrogen peroxide, Fe(III) was removed from the solution by three stages of counter current extraction with D2EHPA. Third, Zn(II) was removed by two stages of cross current extraction with Cyanex 272. Stripping conditions for Fe(III) and Zn(II) were determined from the respective loaded organics. Fourth, $Mn(OH)_2$ was precipitated from the raffinate by adjusting the pH of the solution to 10 with NaOH solution. The $MnSO_4$ crystals with 99.5% purity were recovered by crystallization from the sulfuric acid solutions after the precipitates of $Mn(OH)_2$ were dissolved. A comparison of the cost of the chemicals used to recover MnO_2 and $MnSO_4$ indicated that the current process was much more economical.

Keywords: Manganese dust; Recovery; Hydrometallurgy; Crystallization; $MnSO_4$ crystal

1. Introduction

Manganese metal and compounds are used as raw materials in diverse fields such as battery, fertilizer, steel, and additive manufacturing [1]. Considering the increasing demand for manganese in modern industry, it is essential to effectively recover manganese from waste containing manganese. Manganese dust generated in smelters is considered harmful but is still an attractive secondary resource [2]. Manganese dust is mostly composed of high-valence manganese oxides such as Mn_3O_4 and MnO_2 , whose composition depends on the conditions used for the production of manganese alloys [3]. Many studies have been performed to recover manganese from manganese dust using hydrometallurgical processes, which are efficient for the recovery of valuable metals from secondary resources [4-6]. Since the manganese oxides in the Mn dust are difficult to dissolve by pure inorganic acid solutions, reducing agents are added to the inorganic acid solutions. In recent years, extensive work has been carried out on the reductive leaching of manganese oxides using various reducing agents, such as oxalic acid [1,4,7].

In general, the chemical composition of the manganese dust produced by the industry is quite complicated, due to the different manufacturing methods for the production of manganese alloys [8]. The leaching solution obtained from the dissolution of manganese dust often contains a certain amount of other metal ions such as iron and zinc, which impacts the purity of manganese ions [9,10]. Therefore, in order to produce metal compounds with high-purity, extensive solvent extraction, precipitation, and cementation have been carried out for the separation and purification of target metal ions [11-14].

We reported on a hydrometallurgical process to recover pure MnO_2 from Mn dust containing Mn_3O_4 . The mixture of H_2SO_4 and $H_2C_2O_4$ was employed as a leaching and a reducing agent to completely dissolve the Mn dust [3]. The drawbacks of this process are the slow leaching kinetics (reaction time > 4 h) and a low pulp density of 10 g/L owing to the solubility of the oxalates. Moreover, expensive NaClO was employed as an oxidizing agent during the oxidative precipitation of MnO_2 from pure Mn(II) solutions after the removal of impurity ions. These drawbacks would have a negative impact on the economic

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efficiency of the process of recovering of pure manganese compounds from Mn dust.

Therefore, the objective of this work was to circumvent the above-mentioned disadvantages of our previously reported method. For this purpose, FeSO_4 was selected as the reducing agent for the manganese oxides present in the Mn dust. To avoid using expensive NaClO during the recovery of MnO_2 from the solution, the Mn(II) present in the solution after the removal of impure ions was precipitated as Mn(OH)_2 and then pure MnSO_4 crystals were recovered from the solution after dissolving the precipitated Mn hydroxides. The MnSO_4 and MnO_2 are employed in various fields due to the differences in their water solubility and other properties. However, MnSO_4 is generally less expensive than the MnO_2 and can be transformed into MnO_2 by a straightforward chemical precipitation method [15]. In this study, the effect of some variables on the dissolution of Mn from the Mn dust was investigated. The major impure ions present in the leaching solution of Mn dust, iron and Zn(II) , were separated by solvent extraction. MnSO_4 crystals with a purity higher than 99.5% were recovered by the method reported in this work. A comparison of the operation costs for the recovery of one ton of MnO_2 and MnSO_4 from the dust was made.

2. Experimental

2.1. Reagents and Chemicals

Manganese dust provided by a company in Korea was used for this work. The characterization of the dust by X-ray diffraction (XRD, X'Pert-PRO, the Netherlands) and X-Ray fluorescence spectrometer (XRF, Hitachi, Tokyo, Japan) in our previous study indicated that the Mn in the dust was present as Mn_3O_4 and the weight percentages of Mn, Fe, and Zn oxides in the dust were 95.6 %, 2.46 %, and 0.55 %, respectively, as shown in Table 1 [3]. Although the manganese dust contained a small amount of other trace components, such as SiO_2 , CaO , MgO , and PbO_2 , the sum of the weight percentages of Mn, Fe, and Zn oxides was 98.57 %. Therefore, the behavior of these three components, Mn, Fe, and Zn was investigated to determine the optimum conditions for leaching and the separation step. Then the behavior of the three components together with the minor components was investigated in continuous experiments.

Table 1. XRF data on the components of manganese dust employed in this work [3]

Metal oxide	Mn_3O_4	Fe_2O_3	ZnO	Eu_2O_3	K_2O	SiO_2	CaO	MgO	PbO_2
Mass percentage, %	95.6	2.46	0.55	0.41	0.34	0.2	0.12	0.11	0.05
Oxide/ element	SO_3	Cl	P_2O_5	Al_2O_3	CuO	NiO	Cr_2O_3	CoO	-
Mass percentage, %	0.04	0.04	0.03	0.03	0.02	0.01	0.01	0.01	-

Sulfuric acid (Daejung Chemical & Metals Co., Korea, >95%) and FeSO_4 (Junsei Chemical Co., Ltd., Japan, >98.5%) were employed as the leaching agent and reducing agent, respectively, in leaching experiments. Hydrogen peroxide (Daejung Chemical & Metals Co., Korea, 30%) was employed as an oxidizing agent to oxidize Fe(II) to Fe(III) in the oxidation experiments. The pH of the solution was adjusted by adding NaOH (Daejung Chemical & Metals Co., Korea, >97%) and dilute H_2SO_4 solution. The concentration of ferrous ions in the solution was measured by titration using potassium permanganate (Junsei Chemical Co. Ltd., Japan, >99%) [16]. In addition, acetone (Daejung Chemical & Metals Co., Ltd, Korea, >99.8%) and deionized water were used to wash the precipitates obtained from precipitation and crystallization experiments.

In the solvent extraction of Fe(III) and Zn(II) , D2EHPA (di-2-ethylhexyl-phosphoric acid, Cytec Industries, Canada, 95%) and Cyanex 272 (Bis(2,4,4-trimethylpentyl) phosphinic acid, Cytec Industries, Canada, >85%) without any further purification were employed as extractants, which were diluted with commercial grade kerosene (Daejung Chemical & Metals Co., Ltd, Korea, >90%). Dilute H_2SO_4 and aqua regia solutions prepared by mixing HCl (Daejung Chemical & Metals Co., Korea, 35%) and HNO_3 (Daejung Chemical & Metals Co., Korea, 60%) were used as stripping agents for stripping Zn(II) and Fe(III) , respectively.

2.2. Procedure and analytical methods

Leaching, oxidation, precipitation, and crystallization experiments were performed in a 100-mL glass beaker. The mixtures in the respective experiments were stirred at a speed of 400 rpm using a magnetic stirrer (Daihan Scientific Co., Korea) capable of controlling temperature and time. The pH of the solutions was measured by a thermal scientific pH meter (Orion Star A211, China). Except for the crystallization experiments of MnSO_4 , all experiments were carried out at room temperature. After leaching, precipitation, and crystallization, the insoluble residues were separated from the solution using filter paper (ADVANTEC No. 2, 110 mm, Toyo Roshi Kaisha, Ltd). The MnSO_4 crystals obtained from the crystallization experiments were characterized by XRD and scanning electron microscope (SEM, Regulus 8230, HITACHI, Japan). The concentration



of the metal ions in the solution was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, optima 8300, Perkin Elmer). The leaching (%L), oxidation (%O), and precipitation (%P) percentages were calculated as:

$$\%L = \frac{m_{\text{solution}}}{m_{\text{sample}}} \times 100\% \quad (1)$$

$$\%O \text{ or } \%P = \frac{m_{\text{initial}} - m_{\text{filtrate}}}{m_{\text{initial}}} \times 100\% \quad (2)$$

where m_{solution} , m_{sample} , m_{initial} , and m_{filtrate} are the mass of the metals in pregnant leach solution (PLS), in the manganese dust, in the aqueous before oxidation and precipitation, and in the aqueous after oxidation and precipitation, respectively.

Solvent extraction experiments were carried out in 100 mL of plastic screw-cap bottles sealed with parafilm with an equal volume (20 mL) of aqueous and organic phases. The two phases were shaken for 30 min at room temperature using a Burrell wrist action shaker (Burrell model 75, USA). After the separation of the aqueous and organic phases using 100 mL of the separatory funnel, the concentration of the metal ions in the aqueous phase was measured by ICP-OES, while that of the metal ions in the organic phase was calculated by mass balance. The extraction (%E) and stripping (%S) percentages were calculated as:

$$\%E = \frac{m_{\text{initial}} - m_{\text{aq}}}{m_{\text{initial}}} \times 100\% \quad (3)$$

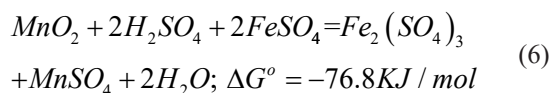
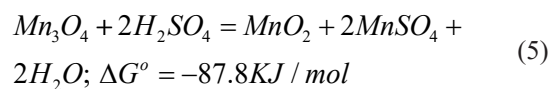
$$\%S = \frac{m_{\text{aq}}^*}{m_{\text{organic}}} \times 100\% \quad (4)$$

where m_{initial} , m_{aq} , m_{aq}^* , and m_{organic} are the mass of the metal ions in the aqueous phase before extraction, in the aqueous phase after extraction, in the aqueous phase after stripping, and in the organic phase before the stripping, respectively.

3. Results and discussion

3.1. Leaching of manganese dust using a mixture of FeSO_4 and H_2SO_4

Reducing agents are necessary to dissolve Mn_3O_4 . Since the dust contained Fe_2O_3 , FeSO_4 was added to sulfuric acid as a reducing agent and the mixture of sulfuric acid and FeSO_4 was employed in the leaching experiments. The leaching reaction of Mn_3O_4 by this mixture can be represented as [17,18]:



According to equations (5) and (6), MnO_2 which is formed in the disproportionation reaction of Mn_3O_4 can be reductively dissolved in the presence of FeSO_4 . The pulp density of the manganese dust in the leaching experiment is a critical factor. Therefore, the effect of pulp density on the leaching percentage was investigated by varying from 50 to 120 g/L. In these experiments, the concentration of H_2SO_4 and the molar ratio of FeSO_4 to Mn_3O_4 were fixed at 2 M and 2.2, respectively. Moreover, the stirring speed, reaction time, and reaction temperature were controlled at 400 rpm, 120 min, and 25°C, respectively. Fig. 1 shows that the percentage of leaching of Mn(II) decreased slightly from 100% to 91.8% and the pH increased from 0.32 to 0.93 as the pulp density of the manganese dust was increased from 50 g/L to 120 g/L. The increased pulp density has a negative impact on the leaching kinetics, causing the leaching percentage of metals to gradually decrease with increasing pulp density. In contrast, when the pulp density was less than 100 g/L, it did not affect the leaching percentage of Zn(II), which remained at approximately 100%. The leaching percentage of Zn(II) was then reduced to 96.7% as the pulp density rose to 120 g/L. Manganese oxide was completely dissolved by the mixture of FeSO_4 and H_2SO_4 at a pulp density of 50 g/L, which was selected as the most suitable condition.

The role of FeSO_4 as a reducing agent in dissolving Mn_3O_4 is important. The amount of FeSO_4 added to the sulfuric acid solution during leaching would affect the concentration of iron ions in the leaching solution. Therefore, the effect of the molar ratio of FeSO_4 to Mn_3O_4 on the leaching behavior of the dust was investigated. For this purpose, the

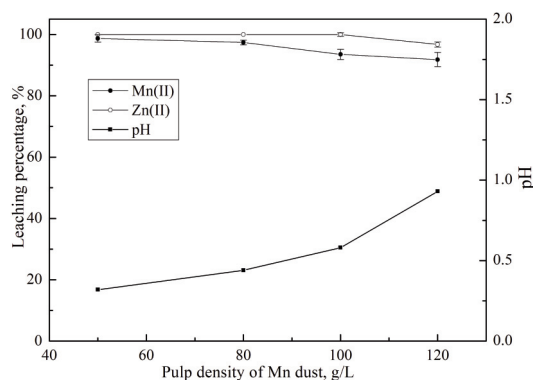


Figure 1. Effect of the pulp density on leaching percentage of Mn(II) and Zn(II) from the dust (2 M H_2SO_4 , 2.2 of molar ratio of FeSO_4 to Mn_3O_4 , 2 h, 400 rpm, 25°C)



leaching experiments were done by varying the molar ratio of FeSO_4 to Mn_3O_4 from 0.5 to 2.2. In these experiments, the concentration of H_2SO_4 and the pulp density were fixed at 2 M and 50 g/L, respectively. Stirring speed, reaction time, and temperature were the same as the conditions for Fig. 1. When the molar ratio of FeSO_4 to Mn_3O_4 was higher than 2.0, the Mn oxides were completely dissolved together with the Zn oxides (see Fig. 2). The stoichiometry of equations (5) and (6) indicates that two moles of FeSO_4 are necessary to dissolve one mole of MnO_2 . Therefore, our results are in good agreement with the proposed leaching equations for Mn_3O_4 . Moreover, the change in the molar ratio of FeSO_4 to Mn_3O_4 had an insignificant effect on the final pH of the solution. In

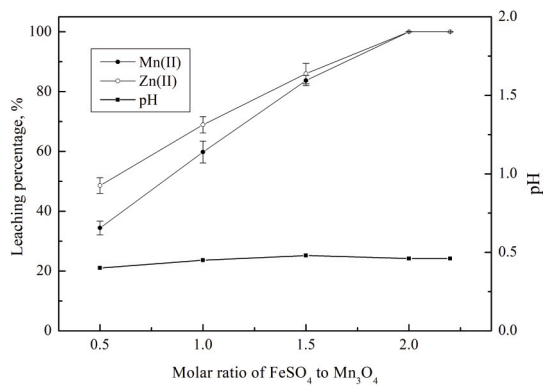


Figure 2. Effect of the molar ratio of FeSO_4 to Mn_3O_4 on leaching percentage of Mn(II) and Zn(II) from the dust. (2 M H_2SO_4 , 50 g/L of pulp density, 2 h, 400 rpm, 25°C)

order to investigate the effect of H_2SO_4 concentration, the H_2SO_4 concentration was varied from 0.5 to 2 M at a pulp density of 50 g/L. In these experiments, the molar ratio of FeSO_4 to Mn_3O_4 was fixed at 2 and stirring speed, reaction time, and temperature were the same as the previous experiments. Fig. 3 shows that Mn and Zn oxides were completely dissolved when the H_2SO_4 concentration was higher than 0.8 M, while the pH of the solution decreased steadily with increasing H_2SO_4 concentration. From these experiments, the following suitable conditions were found to completely dissolve Mn oxides from the dust: 0.8 M H_2SO_4 , the molar ratio of FeSO_4 to Mn_3O_4 of 2, pulp density of 50 g/L, 25°C, and 400 rpm.

Fig. 4 shows the effect of reaction time on the leaching of the dust under the above mentioned conditions. Manganese and zinc oxides were completely dissolved when the reaction time was longer than 15 min, indicating that the mixture of FeSO_4 and H_2SO_4 had faster reaction kinetics for the dissolution of Mn_3O_4 . The concentrations of Mn(II), iron, and Zn(II) in the leaching solution obtained under the appropriate conditions are represented in Table 2. The solution pH of the leaching solution was

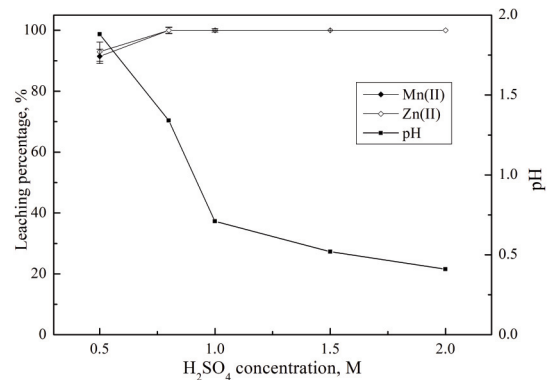


Figure 3. Effect of the molar ratio of FeSO_4 to Mn_3O_4 on leaching percentage of Mn(II) and Zn(II) from the dust. (2 M H_2SO_4 , 50 g/L of pulp density, 2 h, 400 rpm, 25°C)

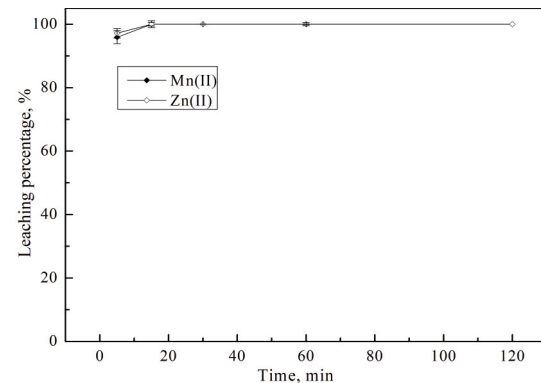


Figure 4. Effect of time on the leaching percentage of Mn(II) and Zn(II) from the dust (0.8 M H_2SO_4 , 50 g/L of pulp density, 2 of molar ratio of FeSO_4 to Mn_3O_4 , 400 rpm, 25°C)

Table 2. The concentration of metal ions in the leaching solution under the most suitable conditions

Metal ions	Mn(II)	Fe(III)	Zn(II)	Fe(II)
Concentration, ppm	34609	24475	226	893

* The pH of the leaching solution was 1.3

1.3. Table 2 shows that the concentrations of Fe(II) and Fe(III) are 893 and 24475 mg/L, respectively. According to the calculation between the pulp density of the manganese dust and the XRF data, the iron in the manganese dust was completely dissolved during the leaching. In addition, no insoluble residues were found during the filtering after the leaching experiments. Therefore, it can be said that all the iron oxides were completely dissolved in the manganese dust.

In conclusion, 50 g/L of pulp density, 0.8 M H_2SO_4 , 2 of molar ratio of FeSO_4 to Mn_3O_4 , 15 min of reaction time, 400 rpm, and 25°C were obtained as the optimal leaching conditions, and the metal composition of the PLS is shown in Table 2. The final pH of the leaching solution was 1.3 and actual leach



liquor was employed as the feed solution in the subsequent separation experiments.

3.2. Separation of Fe(III) by solvent extraction with D2EHPA

After performing the leaching experiments, the concentrations of Mn(II), Fe(III), Zn(II), and Fe(II) in the PLS were 34609, 24475, 226, and 893 mg/L, respectively. There is a large difference in the chemical properties between Fe(II) and Fe(III). Since the concentration of Fe(II) in the PLS was much lower than that of Fe(III), it is better to oxidize Fe(II) to Fe(III) for subsequent separation of iron from the PLS. For this purpose, H₂O₂ was employed as an oxidizing agent and added to the PLS at room temperature and stirred for 30 min. Fig. 5 shows the variation in the oxidation percentage of Fe(II) when the molar ratio of H₂O₂ to Fe(II) was varied from 0.5 to 2.0. When the molar ratio of H₂O₂ to Fe(II) was higher than 1.5, all the Fe(II) was oxidized to Fe(III).

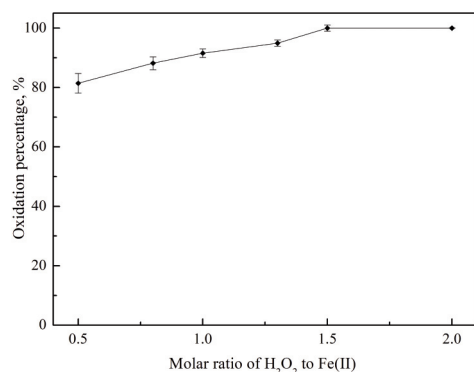
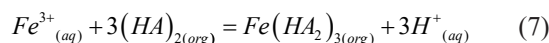


Figure 5. Effect of the molar ratio of H₂O₂ to Fe(II) in the solution on oxidation percentage of Fe(II) (30 min, 400 rpm, 25°C)

There was not much difference in the final pH after oxidation and the concentration of Fe(III) in the PLS was 24530 mg/L. The slight decrease in the concentration of metal ions in the PLS after the oxidation with H₂O₂ was ascribed to the increase in the volume of the solution due to the addition H₂O₂. Namely, the concentration of Mn(II) and Zn(II) was reduced to 33824 and 221 mg/L, respectively. Ferric hydroxides can be precipitated when solution pH is higher than 2. However, colloidal Fe(OH)₃ would be precipitated at room temperature, making it difficult to filter it out of the solution. Although some precipitation processes of Fe(III) at high temperatures such as the jarosite and goethite processes are operated in zinc smelters, these processes require high temperature. Many publications have reported that Fe(III) can be selectively extracted by D2EHPA from weak acidic solutions. Therefore, solvent extraction with D2EHPA was attempted to separate Fe(III) from

the PLS after the oxidation of Fe(II). Solvent extraction reaction of Fe(III) by D2EHPA can be represented as follows [19]:



where the (HA)₂(org) represents the D2EHPA.

Considering the concentration of Fe(III) in the PLS, solvent extraction experiments were performed by varying the D2EHPA concentration from 0.3 to 1.5 M. Fig. 6 shows that the extraction percentage of Fe(III) was gradually increased as D2EHPA concentration increased from 0.3 to 1.3 M, while a small amount of Mn(II) and Zn(II) was extracted together with Fe(III). In our extraction results, the extraction percentage of Mn(II) and Zn(II) was less than 4%. The co-extraction of Mn(II) and Zn(II) can be prevented by countercurrent extraction with lower concentration of the extractant (see Table 3). In

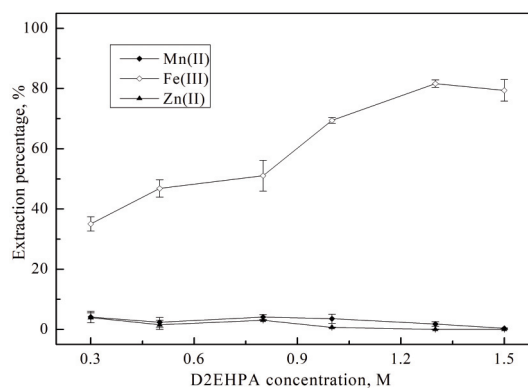


Figure 6. Effect of D2EHPA concentration on the extraction percentage of Fe(III) from the leaching solution after oxidation of Fe(II) (O/A = 1, 30 min, 400 rpm, 25°C)

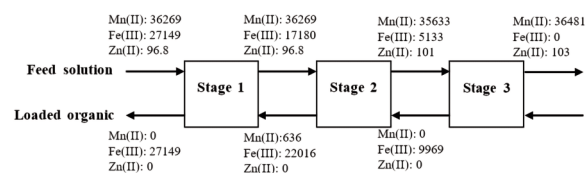


Figure 7. Batch simulation of three stages of countercurrent extraction of Fe(III) with 1.0 M D2EHPA from the real leaching solution

continuous extraction, the viscosity of the organic phase would affect the kinetics of the solvent extraction and the viscosity of the D2EHPA solution is proportional to its concentration. Therefore, 1 M D2EHPA was selected and three stages of countercurrent extraction were done by batch simulation methods. Table 3 and Fig. 7 show the concentration and extraction percentage of the metal ions together with the final pH of each stage.

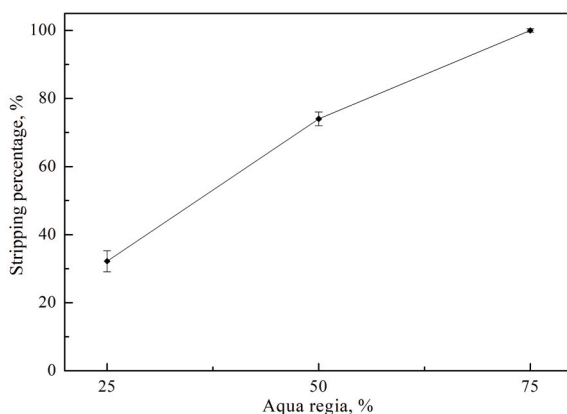


Table 3. Metal concentration, extraction percentage, and solution pH in each stage during 3 stages of counter current extraction of Fe(III) by D2EHPA

Metal ions		Mn(II)	Fe(III)	Zn(II)	pH
1 stage	Concentration, ppm	33824	15527	221	0.49
	Extraction, %	0	36.7	0	
2 stage	Concentration, ppm	33824	4636	221	0.41
	Extraction, %	1.8	81.1	0	
3 stage	Concentration, ppm	33824	0	221	0.41
	Extraction, %	0	100	0	

Although a small amount of Mn(II) was co-extracted in the second extraction stage, Fe(III) was completely and selectively extracted from the PLS after three stages of countercurrent extraction with 1 M D2EHPA.

Extensive research has been investigated on the stripping of Fe(III) from the loaded D2EHPA [20]. When the concentration of Fe(III) in the loaded D2EHPA is high, aqua regia is known to be the most effective stripping agent. The concentration of acids in the aqua regia was first diluted by adding distilled water and the resulting aqua regia solutions were employed as stripping agents. The concentration of the acids in aqua regia solutions was represented as the volume ratio of aqua regia to the solution in this work. Fig. 8 shows that the stripping percentage of Fe(III) was gradually increased as the volume ratio of aqua regia increased. Complete stripping of Fe(III) was possible by 75% (v/v) of aqua regia. The stripping solution consists of nitric acid, hydrochloric acid and Fe(III). In this work, a sulfuric acid solution was employed in the leaching of Mn dust. Therefore, it is necessary to first recover Fe(III) compounds from the stripping solution and then the solution can be further used as a stripping agent for Fe(III).

**Figure 8.** Effect of the aqua regia concentration on the stripping of Fe(III) from the loaded D2EHPA (O/A = 1, 30 min, 400 rpm, 25°C)

3.3. Separation of Zn(II) by solvent extraction with Cyanex 272

After three stages of countercurrent extraction of Fe(III), the concentrations of Mn(II) and Zn(II) in the raffinate were 33824 and 221 mg/L, respectively. Our previous work demonstrated that Zn(II) in solution could be selectively extracted with 0.4 M Cyanex 272 at pH 2.5, O/A of 1, room temperature, and reaction time of 30 min [3]. Therefore, in this study, Zn(II) was separated from the raffinate by two stages of cross current extraction under the above conditions. First, the initial pH of the raffinate was adjusted to 2.5 by adding concentrated NaOH solution, which led to a significant decrease in the metal concentration in the solution because of the addition of NaOH solution. Therefore, the concentrations of Mn(II) and Zn(II) were reduced to 26650 and 172 mg/L, respectively. Table 4 shows the change in the concentration and extraction percentage of the metal ions, and the final pH of the raffinate. Two stages of cross current extraction completely extracted Zn(II). The Zn(II) in the loaded Cyanex 272 was completely stripped by an H₂SO₄ solution of pH 1 at one stage. Therefore, Zn(II) was selectively and completely separated from the solution after the extraction of Fe(III).

3.4. Crystallization of MnSO₄ crystals from solution containing MnSO₄

3.4.1. Crystallization of MnSO₄ from raffinate

After two stages of cross current extraction of Zn(II) using Cyanex 272, the raffinate contained a large amount of Na(I) and Mn(II) together with a small amount of Si(IV), Ca(II), and K(I). The concentrations of Mn(II), Na(I), K(I), Si(IV) and Ca(II) in the solution were 26650, 13227, 70.27, 41.03 and 19.42 mg/L, respectively, and the final pH of the raffinate was 2.44. Considering the high concentration of MnSO₄ in the solution, crystallization experiments were carried out to recover MnSO₄ crystals from the raffinate. For this purpose, the temperature of the raffinate was kept at 85°C for 48 hours. The recovered crystals were



Table 4. Metal concentration, extraction percentage, and solution pH in each stage during 2 stages of cross current extraction of Zn(III) by Cyanex 272

Metal ions		Mn(II)	Zn(II)	pH
Feed after adjusting pH, ppm		26650	172	2.5
1 stage	Concentration, ppm	26650	32.1	2.48
	Extraction, %	0	81.34	
2 stage	Concentration, ppm	26650	0	2.44
	Extraction, %	0	100	

* Raffinate should be adjusted to pH 2.5

washed with acetone several times and their XRD and SEM images are represented in Fig. 9(left) and Fig. 10 (A1, A2). The left XRD image in Fig. 9 shows that the crystals formed from the raffinate contain MnSO_4 and Na_2SO_4 . The presence of Na_2SO_4 in the crystallized MnSO_4 is ascribed to the high concentration of Na(I) in the raffinate. The SEM images of A1 and A2 in Fig. 10 show that the crystal surface has a significant degree of roughness, while the difference in the particle size of the crystals is obvious and the shape is irregular. In order to determine the purity of MnSO_4 in the recovered crystals, the crystals were dissolved in a weakly acidic solution and the concentration of the metal ions was measured by ICP-OES. According to Table 5, the crystals contained significant amounts of Na(I), K(I), and Ca(II), and thus the purity of MnSO_4 was only 65.96%.

general, aqueous solutions contain dissolved oxygen, which can lead to oxidative precipitation of Mn(II) as MnO_2 [21]. Therefore, nitrogen gas was purged into the solution for 30 min to expel the dissolved oxygen from the solution. Then, 4 M NaOH solution was added dropwise to the solution for 30 min. In these experiments, the flow rate of N_2 gas, stirring speed, and temperature were controlled to 50 cc/min, 400 rpm, and 25°C, respectively. The pH of the solution was increased from 8 to 11 as NaOH solution was added. Manganese(II) was completely precipitated when solution pH was 10 (see Fig. 11). The purity of Mn(OH)_2 precipitates thus obtained was measured by dissolving in the aqua regia. Although the Mn(OH)_2 precipitates were washed several times with deionized water and acetone, the precipitates still contained a certain amount of Na(I), resulting in the Mn(II) purity

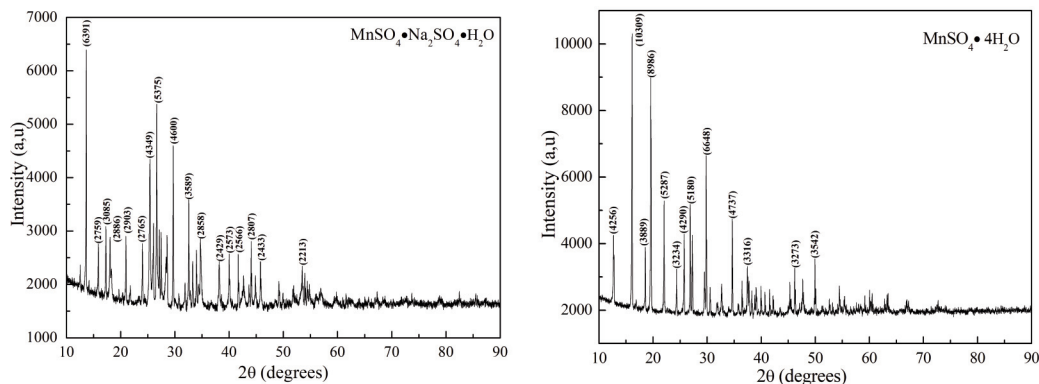


Figure 9. X-ray Diffraction of crystals (the left crystals were obtained from the raffinate after the separation of Fe(III) and Zn(II); the right crystals were obtained from the solution after the dissolving Mn(OH)_2)

3.4.2. Further purification of Mn(II) by precipitation and re-dissolution of Mn(OH)_2

The results on the purity of MnSO_4 recovered by crystallization from the raffinate indicated that it is necessary to remove Na(I), K(I), and Ca(II) from the solution in order to recover pure MnSO_4 . The precipitation pH of Mn(II) is much lower than Ca(II). Therefore, it is possible to selectively precipitate Mn(II) as hydroxides, which would make it possible to separate Mn(II) from Na(I), K(I), and Ca(II). In

of approximately 96.4% (see Table 5). The presence of Na(I) in the Mn(OH)_2 precipitates might be ascribed to adsorption.

In order to produce MnSO_4 with high purity, the Mn(OH)_2 precipitates were re-dissolved in the H_2SO_4 solution with pH 4 and crystallization experiments were carried out. In the crystallization experiments, a saturated MnSO_4 solution was generated by maintaining the temperature of the H_2SO_4 solution at 85°C for 48 h after Mn(OH)_2 was dissolved. The MnSO_4 crystals were then washed with acetone after

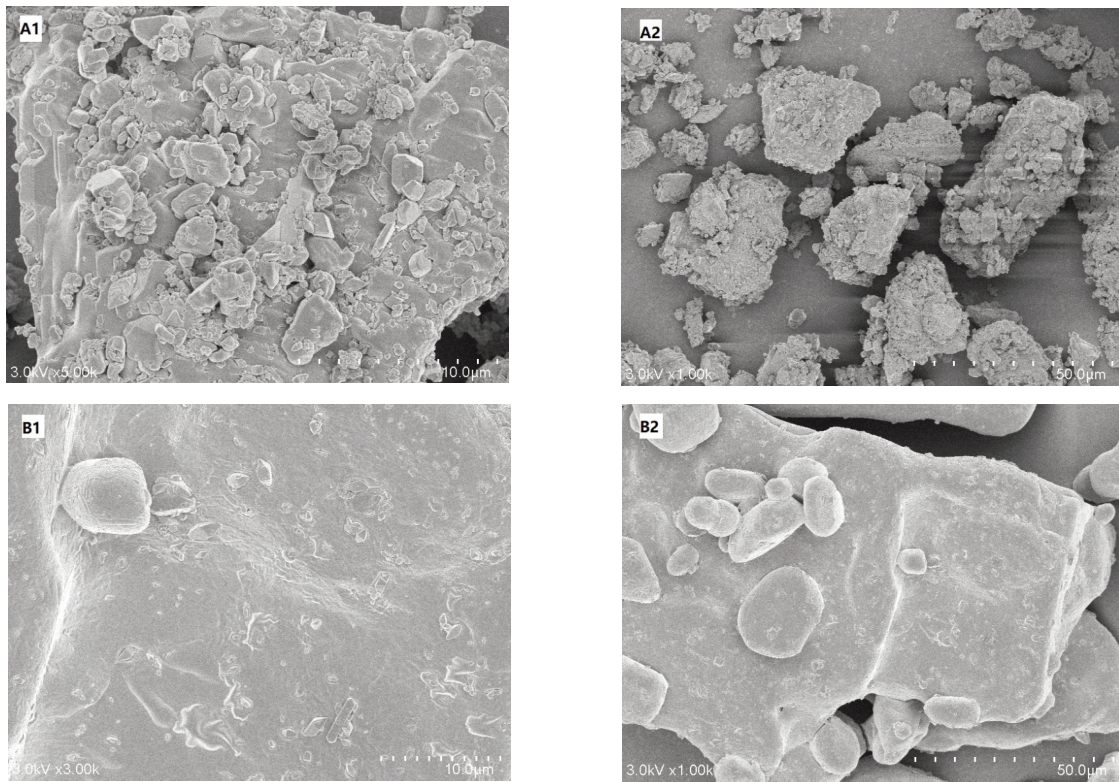


Figure 10. SEM images of crystals (crystals of A1 and A2 were obtained from raffinate; crystals of B1 and B2 were obtained from solution after the dissolution of $Mn(OH)_2$)

Table 5. The concentrations of the metal ions in the solutions obtained by dissolving manganese compounds to check their purities

Operations	Metal ions, ppm									Purity, %
	Mn(II)	Na(I)	K(I)	Ca(II)	Si(IV)	Fe(III)	Zn(II)	Mg(II)	Al(III)	
$MnSO_4$ Crystals (crystallization from raffinate ¹)	4266	2128	55.83	13.07	4.75	0	0	0	0	65.96
$Mn(OH)_2$ (precipitation from raffinate ¹)	6178	225.7	4.7	0	0	0	0	0	0	96.4
$MnSO_4$ Crystals (crystallization from solution ²)	4178	17.4	1.15	0	0	0	0	0	0	99.56

¹Raffinate was obtained after continuous solvent extraction of Fe(III) and Zn(II)

²Solution represents the sulfuric acid solution after dissolving the $Mn(OH)_2$

filtering. The characteristics and purity of the $MnSO_4$ crystals thus recovered were determined by XRD, SEM, and ICP-OES. Table 5 shows that the purity of the $MnSO_4$ crystals was higher than 99.5%, indicating that the precipitation of $Mn(OH)_2$ is effective in separating Na(I), K(I), and Ca(II). While $MnSO_4 \times Na_2SO_4 \times H_2O$ was detected in the $MnSO_4$ crystals from the raffinate, only $MnSO_4 \times 4H_2O$ was

detected from the crystals after precipitation of $Mn(OH)_2$ (see Fig. 9). Fig. 10 shows the difference between the surface characteristics of the two crystals. Although both types of crystals were adequately ground in the mortar, the high-purity $MnSO_4$ crystals showed smooth surfaces and larger particle sizes, while the mixed crystal of Na_2SO_4 and $MnSO_4$ had granular and rough surfaces.

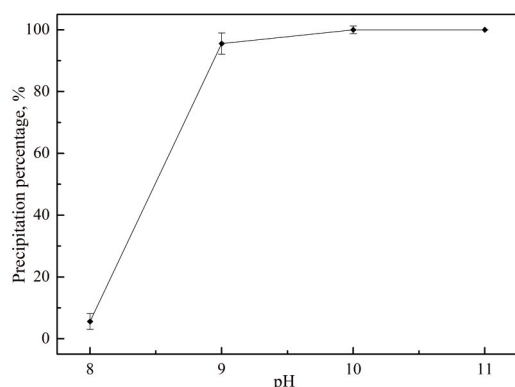


Figure 11. Effect of pH on the precipitation percentage of Mn(II) from raffinate obtained from solvent extraction of Zn(II) (30 min, 400 rpm, 25°C)

3.5. A proposed process for the recovery of pure MnSO₄ crystals from Mn dust and analysis of process economics

In this study, the mixture of H₂SO₄ and FeSO₄ was employed as a leaching agent and reducing agent, respectively, for the complete dissolution of Mn₃O₄, and the PLS mainly contained Mn(II), Fe(III), Fe(II), and Zn(II). In order to recover high-purity MnSO₄ crystals from the PLS, oxidation, solvent extraction, precipitation, and crystallization were carried out.

Namely, after oxidizing Fe(II) by H₂O₂, Fe(III) and Zn(II) were selectively extracted using D2EHPA and Cyanex 272, respectively. Then, Mn(OH)₂ was precipitated from the raffinate by adjusting solution pH. The precipitates Mn(OH)₂ were dissolved in sulfuric acid solution and MnSO₄ crystals were recovered by crystallization. In the above operations, the corresponding suitable conditions were obtained and our data show that the purity of MnSO₄ crystals and the recovery percentage of Mn were approximately 99% and 99.9%, respectively.

Table 6 shows the comparison of the operating conditions and costs for the production of MnO₂ and MnSO₄ from manganese dusts between this process and the previously reported process. In the previous process, H₂C₂O₄ was employed as a reducing agent and MnO₂ was recovered by oxidative precipitation, while in this work FeSO₄ was employed as a reducing agent and MnSO₄ was recovered by crystallization. Compared to the mixture of H₂SO₄ and H₂C₂O₄, employment of the mixture of H₂SO₄ and FeSO₄ as a leaching medium could completely dissolve the manganese oxides within 15 mins even though the pulp density was increased fivefold. This would have a favorable effect on the process economy for the treatment of managed dust. In both processes, solvent extraction was employed to separate Fe(III) and Zn(II) from the leaching solutions. Since ferrous ions are present in the leaching solution in this process,

Table 6. Comparison of the process details and the operation cost between the previous and current work for the production of 1 ton of manganese compounds from the dust

Processes		Previous	Current
Leaching		Pulp density= 10 g/L, H ₂ SO ₄ = 0.4 M, H ₂ C ₂ O ₄ = 0.04 M, Reaction time = 4 h	Pulp density= 50 g/L, H ₂ SO ₄ = 0.8 M, FeSO ₄ = 0.44 M, Reaction time = 15 min
Separation	Oxidation	-	H ₂ O ₂ = 0.027 M
	Fe(III) Extraction	D2EHPA = 0.5 M, 2 stages of cross current	D2EHPA = 1 M, 3 stages of counter current
	Zn(II) Extraction	Cyanex 272 = 0.4 M, 2 stages of cross current	Cyanex 272 = 0.4 M, 2 stages of cross current
Precipitation		NaClO = 0.38 M	Adjusting solution pH to 10 with 4 M NaOH
Crystallization		-	Heating H ₂ SO ₄ solution of pH 4 at 85 °C for 48 h
Product, g		MnO ₂ , 7.2	MnSO ₄ , 36.0
Purity, %		99.999	99.56
Recovery, %		~99.9	~99.9
Cost/ton, Dollar		46556	11200

* Chemical prices in this table were quoted from their corresponding companies



H₂O₂ was employed as an oxidizing agent before solvent extraction of Fe(III) by D2EHPA, which would increase the cost of the reagents. The purity of the recovered MnSO₄ was 99.56% due to the presence of a trace of sodium ions, which was slightly lower than that of the MnO₂ (99.999%) recovered in the previous work. The operating costs were calculated by considering the price of the required chemicals. First, the price of reagents needed for processing the products from one liter of leaching solution was calculated, and subsequently the total cost of the reagents required for manufacturing one ton of products was computed. Since the extractants in solvent extraction can be recycled after stripping, the cost of the extractants was not included in the operating cost. Table 6 shows that the price of the chemicals required for production of one ton of MnO₂ in the previous work is almost four times the price of producing one ton of MnSO₄ in the current study. Although the purity of MnO₂ was higher than that of MnSO₄ crystals, the current process might be attractive in recovering MnSO₄ crystals from the manganese dust on the basis of process economics and kinetics.

4. Conclusions

A process was developed to recover MnSO₄ crystals from manganese dust containing Mn₃O₄ together with minor metal oxides such as iron and zinc. In order to completely dissolve the manganese dust, FeSO₄ and H₂SO₄ were employed as reducing and leaching agents, respectively. Manganese oxides were completely dissolved when the pulp density, H₂SO₄ concentration and the molar ratio of FeSO₄ to Mn₃O₄ were 50 g/L, 0.8 M, and 2, respectively, while the stirring speed, reaction temperature, and time were 400 rpm, 25°C and 15 min, respectively. Subsequently, oxidation, solvent extraction, precipitation, and crystallization experiments were performed to separate Fe(III) and Zn(II), and to generate MnSO₄ crystals. For this purpose, D2EHPA was employed to selectively extract Fe(III) from the leaching solution with three stages of counter-current extraction and Zn(II) can be removed by Cyanex 272 with two stages of cross-current extraction. Aqua regia and H₂SO₄ solution were employed as stripping agents for the stripping of Fe(III) and Zn(II), respectively, from the loaded organic phases. To produce MnSO₄ crystals with high purity, Mn(OH)₂ was precipitated from the raffinate obtained from the continuous extraction of Fe(III) and Zn(II). After dissolving the precipitates of Mn(OH)₂ in sulfuric acid solution with pH 4, pure MnSO₄ crystals were recovered by crystallization. The XRD and SEM images of the crystals confirmed that the crystals consisted of MnSO₄·4H₂O. The purity of the MnSO₄

crystals thus recovered was 99.5%. The price of the chemicals required to recover MnSO₄ crystals from the dust would be much cheaper than that for the recovery of MnO₂.

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Author Contributions

Methodology and editing: Man Seung Lee; data support and writing-original draft preparation: Jiang Xian Wen and Thi Nhan Hau Nguyen. All authors have read and agreed to the published version of the manuscript.

Data availability

The data of this work could be obtained by contacting with the corresponding author by e-mail.

Declarations of competing interest

The authors declare no conflict of interest.

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DOBIJANJE ČISTOG MnSO_4 KRISTALIZACIJOM NAKON ODVAJANJA Fe(III) I Zn(II) IZ RASTVORA ZA REDUKTIVNO LUŽENJE PRAŠINE MANGANA KOJA SADRŽI Mn_3O_4

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Apstrakt

Prašina mangana nastala tokom proizvodnje ferolegura sadrži okside gvožđa i cinka zajedno sa drugim oksidima. Čista jedinjenja mangana mogu se dobiti iz rastvora za luženje manganove prašine uklanjanjem primesnih jona. U ovom radu korišćeni su sumporna kiselina i gvožđe sulfat kao sredstva za ispiranje i redukciju oksida mangana u prašini. Prvo ispitani su uslovi luženja za potpuno rastvaranje oksida mangana variranjem koncentracije sumporne kiseline i gvožđe sulfata, kao i gustine pulpe. Drugo, nakon oksidacije Fe(II) u Fe(III) vodonik-peroksidom, Fe(III) je uklonjen iz rastvora u tri faze protivstrujne ekstrakcije sa D2EHPA. Treće, Zn(II) je uklonjen u dve faze cirkulatorne ekstrakcije sa Cianek 272. Uslovi uklanjanja za Fe(III) i Zn(II) su određeni iz odgovarajuće organske materije. Četvrto, Mn(OH)_2 je istaložen iz rafinata podešavanjem pH rastvora na 10 sa rastvorom NaOH. Kristali MnSO_4 sa 99,5% čistoće su dobijeni kristalizacijom iz rastvora sumporne kiseline nakon što su precipitati Mn(OH)_2 rastvoreni. Poređenje troškova za hemikalije koje se koriste za dobijanje MnO_2 i MnSO_4 pokazalo je da je trenutni proces mnogo ekonomičniji.

Ključne reči: Prašina mangana; Dobijanje; Hidrometalurgija; Kristalizacija; Kristal MnSO_4

